Investigation of the Relation Between Structure and Melting Conditions of TeO_2 and Bi_2O_3 containing Photonic Glasses

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Acknowledgement

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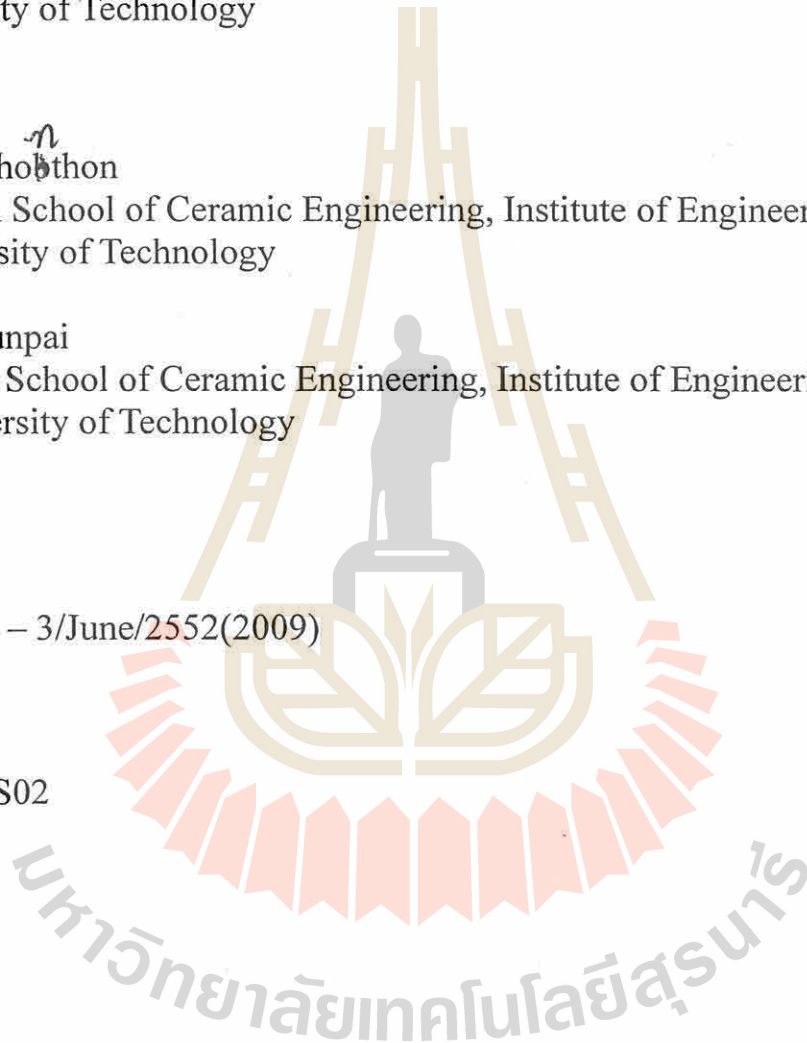
Abstract

The color center, near-infrared (NIR) luminescent characteristics of Te- and Bi-containing glasses were investigated based on redox equilibrium. Particularly, the factors affecting the redox equilibrium, melting temperature, glass compositions and addition of reducing agent (carbon), were investigated in detail in Te- and Bi- containing borate and borosilicate glasses. And the structure and properties of Te and Bi-containing glasses were also investigated.

It was found that the formation of color center and NIR luminescence characteristics of Te- and Bi-containing glasses and glass-ceramics were strongly affected by redox equilibrium. In oxidized side, color center and NIR luminescent center were not formed, and hence the NIR luminescence could not be detected. On the contrary, the darkening effect due to the formation process of Te and Bi metallic colloids, took place in strong reduced side, and also no NIR luminescence was observed. Therefore, the color center and NIR luminescent center can be formed mild to medium reducing condition and the NIR luminescence centered at 1100 ~ 1300 nm can be detected. It is suggested that the color center and NIR luminescent center in Te- and Bi-containing glasses is likely to be caused by Te-and Bi-clusters, electron trapped Te- and Bi-clusters and Bi^+, such as, Te_2, Te_2^-, Bi_2, Bi_3, Bi_2^-,etc.

New type NIR luminescent materials of Te-doped glasses and glass-ceramics which exhibit broad NIR luminescence were discovered for the first time to our knowledge.

The glass transition temperature (Tg) decreased monotonically with an increase in TeO_2 and Bi_2O_3 contents. The density also increases linearly with increasing amount of TeO_2 in TeO_2 containing glasss. On the contrary, the molar volume of Bi-containing glasses showed the minimum at about Bi_2O_3=10 mol%, indicating boron anomaly. XANES spectra indicate that TeO_4 trigonal bipyramids structural units are present uniformly in these glasses and this structural unit shares edges with BO_3 and BO_4 structural units. And BiO_6 octahedral structural units are present in Bi-containing glasses and this structural unit shares corners with BO_3 and BO_4 structural units. Thus, it is confirmed that TeO_2 acts as glass former, but Bi_2O_3 acts as modifier.

Contents

I. Introduction

In recent years, the demand to increase the transmission capacity of wavelength division multiplexing (WDM) system is indispensable due to rapid development of the telecommunication. Many attempts have been made on broadening and flattening of gain spectra of optical fiber amplifiers such as Er-doped fiber amplifiers (EDFAs) [1], tellurite based EDFA [2], Tm-doped fiber amplifiers (TDFAs) [3], fiber Raman amplifiers (FRAs) [4]. Broadband tunable lasers such as $Ti^{3+}:Al_2O_3$(Sapphire) [5] (VIS-NIR), $Cr^{4+}:Y_3Al_5O_{12}$ (YAG) [6] (NIR region), $Cr^{3+}:LiCaAlF_6$ (LiCAF) [7] (NIR region) were realized by using transition meatl ions as active ions. Ni^{2+} ion-doped spinel transparent glass-ceramics and crystal are also promising materials as broad band near infrared (NIR) tunable lasers [8].

Fujimoto et al. [9] discovered a new infrared (NIR) luminescence from a Bi-doped silica glass with long life time. The spectroscopic properties of this new Bi-doped silica glass are different from previous Bi-luminescent materials [10], and 1250 nm wide band luminescence is useful for optical amplifier of telecommunication with optical fiber. They proposed that this luminescence comes from Bi^{5+} ions, on the contrary, Peng et al. [11,12] estimated to be due to BiO or Bi cluster (molecule). The origin of NIR luminescence from Bi-doped glass and glass-ceramics is still unknown. Generally, the luminescence is the phenomenon in which the materials absorb the energy and emit UV-VIS and NIR light subsequently. In this process, the absorption center (color center) is regarded also as luminescent center.

Heavy metal oxide (HMO) glasses containing PbO, Bi_2O_3, Ga_2O_3, TeO_2, etc., have been found to have many unique properties and functions. The potential applications of these HMO glasses, knowledge of their various properties are considerable value. Many researches on the relation between their structures and properties of these HMO glasses have been carried out [13-15]. However, these glasses are often encountered by serious problems during preparation, such as crucible problems [13], coloration problems [14,15]. This indicates that these glasses are quite corrosive against crucible materials, and the valence state changes easily with preparation conditions.

Thus, despite the glasses containing heavy metal oxide are promising materials for the future telecommunication system, the properties of these glasses, especially, the relationship between the change in valence state and accompanying optical properties such as the formation of color center and luminescent center is still unknown. Here, the purpose of this research is to investigate the relationship between the change in valence state and accompanying optical properties such as the formation of color center and luminescent center of heavy metal oxide (TeO_2 and Bi_2O_3) containing glasses based on redox reaction in glasses.

The structures and properties of TeO_2 and Bi_2O_3 glasses were also investigated.

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II. Confirmation and determination of near-infrared luminescence from Te- and Bi-doped glasses and glass-ceramics

Abstract

The luminescence characteristics of Te- and Bi-doped glasses and glass-ceramics were investigated and the origin of coloration and near infrared luminescence was discussed. The colorations of these glasses and glass-ceramics might be due to the elemental clustering, such as Te_2/Te_2^- and Bi_2/Bi_2^-. The broad near infrared (NIR) luminescence can be detected in Te- and Bi-doped glasses and glass-ceramics. The electron spin resonance (ESR) signal at $g \approx 2.0$ was observed in Te- and Bi-doped glasses and glass-ceramics which exhibit NIR luminescence, and therefore this ESR signal is strongly related to the NIR luminescence. The ESR signal at $g \approx 2.0$ might be derived from molecular ions of Te and Bi, Te_2^- and Bi_2^-. Consequently it is suggested that the broad NIR luminescence of Te- and Bi-doped glass and glass-ceramics are most likely to be caused by elemental clustering, such as Te_2/Te_2^- and Bi_2/Bi_2^-.

1. Introduction

The demand to increase the transmission capacity of wavelength division multiplexing (WDM) system is indispensable due to rapid development of the telecommunication. Many attempts have been made on broadening and flattening of gain spectra of optical fiber amplifiers such as Er-doped fiber amplifiers (EDFAs) [1], tellurite-base Er-doped fiber amplifier (EDFA)[2], Tm-doped fiber amplifiers [TDFAs][3], fiber Raman amplifiers (FRAs)[4]. Broadband tunable lasers such as Ti^{3+}: Al_2O_3 (Sapphire)[5], Cr^{4+}: $Y_3Al_5O_{12}$ (YAG)[6], Cr^{3+}: $LiCaAlF_6$ (LiCAF)[7] were realized by using transition metals as active ions.

Recently Fujimoto et al.[8] discovered a new infrared luminescence from a Bi-doped silica glass with long life time. The glass has three excitation/absorption bands at 500 nm, 700 nm and 800 nm. These excitation bands are intrinsic for luminescent bands at 750, 1120 and 1250 nm, respectively[8]. These spectroscopic properties are different from previous Bi-luminescent materials, and 1250 nm wide band luminescence is useful for optical amplifier of telecommunication with optical fiber. Fujimoto et al. [8,9] proposed that this near infrared (NIR) luminescence comes from Bi^{5+} ion. On the other hand, Peng et al.[10,11] estimated to be due to BiO or Bi metal.

The color generation of glasses in visible region is basically caused by impurities, such as transition metal ions, rare earth ions, metallic and semiconductor particles, etc. There are numerous other sources of visible coloration in glasses which are of interest. Included in this group are blue-sulfur, pink-selenium, and purple-tellurium glasses whose colors are associated with elemental

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clustering[12]. Many researches on the luminescence properties of Te-doped crystals have been done[13-16]. The research on the luminescence properties of elemental clustering must be of interest.

The luminescent properties of Te- and Bi-doped glasses and transparent glass-ceramics were investigated and the origin of coloration and NIR luminescence was discussed in this paper.

2. Experimental

2. 1. Sample preparation

The compositions (wt%) of glasses studied are shown in Table 1. High purity silica sand, alumina and reagent grade chemicals of Li_2CO_3, Na_2CO_3, K_2CO_3, $CaCO_3$, H_3PO_4, H_3BO_3, MgO, ZnO, TiO_2, ZrO_2, TeO_2, Bi_2O_3 and carbon were used as raw materials. The addition of a slight amount of carbon produces a mild reducing condition. Batches corresponding to 25 g of glass were mixed thoroughly and melted in a 50 cc Pt/Rh10 or alumina crucibles under appropriate condition in an electric furnace in air. The melting conditions of glasses are shown in Table 2. After melting they were poured onto iron plate and pressed by another iron plate. Glasses were heat treated for nucleation and crystallization.

Table 1. Glass composition (wt%) studied.

Name	SiO$_2$	Al$_2$O$_3$	ZnO	MgO	CaO	Na$_2$O	K$_2$O	TeO$_2$	Bi$_2$O$_3$*	Carbon*
Te-Sp	46.9	26.54	10.59	5.25	TiO$_2$:1.75, ZrO$_2$:8.93			0.2*	–	–
Te-SL	72	2	–	4	8	13	1	1.6*	–	0.08
Te-ZTP		P$_2$O$_5$: 50.06, ZnO: 35.87						14.07	–	–
Bi-L·2S	80	4	–	P$_2$O$_5$: 3, Li$_2$O: 13.0				–	6.0	–
Bi-AlPO$_4$	28.07	23.82	P$_2$O$_5$: 33.17, B$_2$O$_3$: 4.07 , Li$_2$O: 13.0					–	6.0	–
Bi-Sp	46.9	26.54	10.59	5.25	TiO$_2$:1.75, ZrO$_2$:8.93			–	6.0	–

*: excess wt%

The glasses and glass-ceramics were cut and polished optically into about 1 mm in thickness for optical measurement.

2.2. XRD, SEM and ESR

X-ray diffraction (XRD) analysis was performed routinely to determine crystalline phases, percent crystallinity and crystal size[17,18] using Bruker AXS Model D5005. The fractured surface of glasses and glass-ceramics was observed by scanning electron microscope (SEM) (JEOL, JSM 6400). The electron spin resonance (ESR) spectra were measured using JEOL JES RE-2X at room temperature.

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2. 3. Absorption and emission measurements

The absorption spectra were measured with Cary 1E ultraviolet-visible (UV-VIS) spectrometer in the range of 300 nm to 800 nm at room temperature. The emission spectra in NIR region (1000 nm to 1700 nm) were measured under the excitation of 974 nm laser diode at room temperature. Emission from the sample was dispersed by a single monochromator (blaze, 1.0 μm; grating, 600 grooves/mm; resolution, 3 nm) and detected by an InGaAs photodiode.

3. Results

Some glasses are able to convert to transparent glass-ceramics based on lithium disilicate ($Li_2O \cdot 2SiO_2$) for L-2S, $AlPO_4$ (tridymite type) for $AlPO_4$ and spinel [$(Mg,Zn)Al_2O_4$] crystals for Sp. The crystalline phases, crystal size and percent crystallinity are summarized in Table 2. The percent crystallinity and crystal size are ranging 45~70±5% and 15~25±5 nm, respectively. All glass-ceramics are highly transparent.

Table 2. Melting condition, Heat treatment condition for crystallization, appearance and some properties of glasss-ceramics

Name	Melting condition °C-h	Heat treatment °C-h	Appearance*	Crystal		
				Phases	Percent (%)	Size (nm)
Te-Sp	1600-1 Pt/Rh10	800-10, 1000-5	Pale brown Brown-pink	Spinel	45±5	15±5
Te-SL	1450-1 Pt/Rh10	–	Pale green	–	–	–
Te-ZTP	1200-1 alumina	–	Brilliant pink	–	–	–
Bi-L-2S	1450-1 Pt/Rh10	500-10, 650-5	Pale yellow Pale brown	Lithium disilicate	70±5	25±5
Bi-AlPO₄	1600-1 Pt/Rh10	510-10, 600-5	Brown Brown black	AlPO₄	50±5	20±5
Bi-Sp	1600-1 Pt/Rh10	800-10, 1000-5	Pale pink Pink	Spinel	45±5	15±5

*: upper=glass, lower=glass-ceramics

3. 1. Absorption spectra

Fig. 1. Absorption spectra of Te- and Bi-doped glass and glass-ceramics. (a). Te-doped glasses and glass-ceramics, (b). Bi-doped glasses and glass-ceramics.

(a)Te: ZTP Glass

(a)Te: Spinel Glass-ceramics
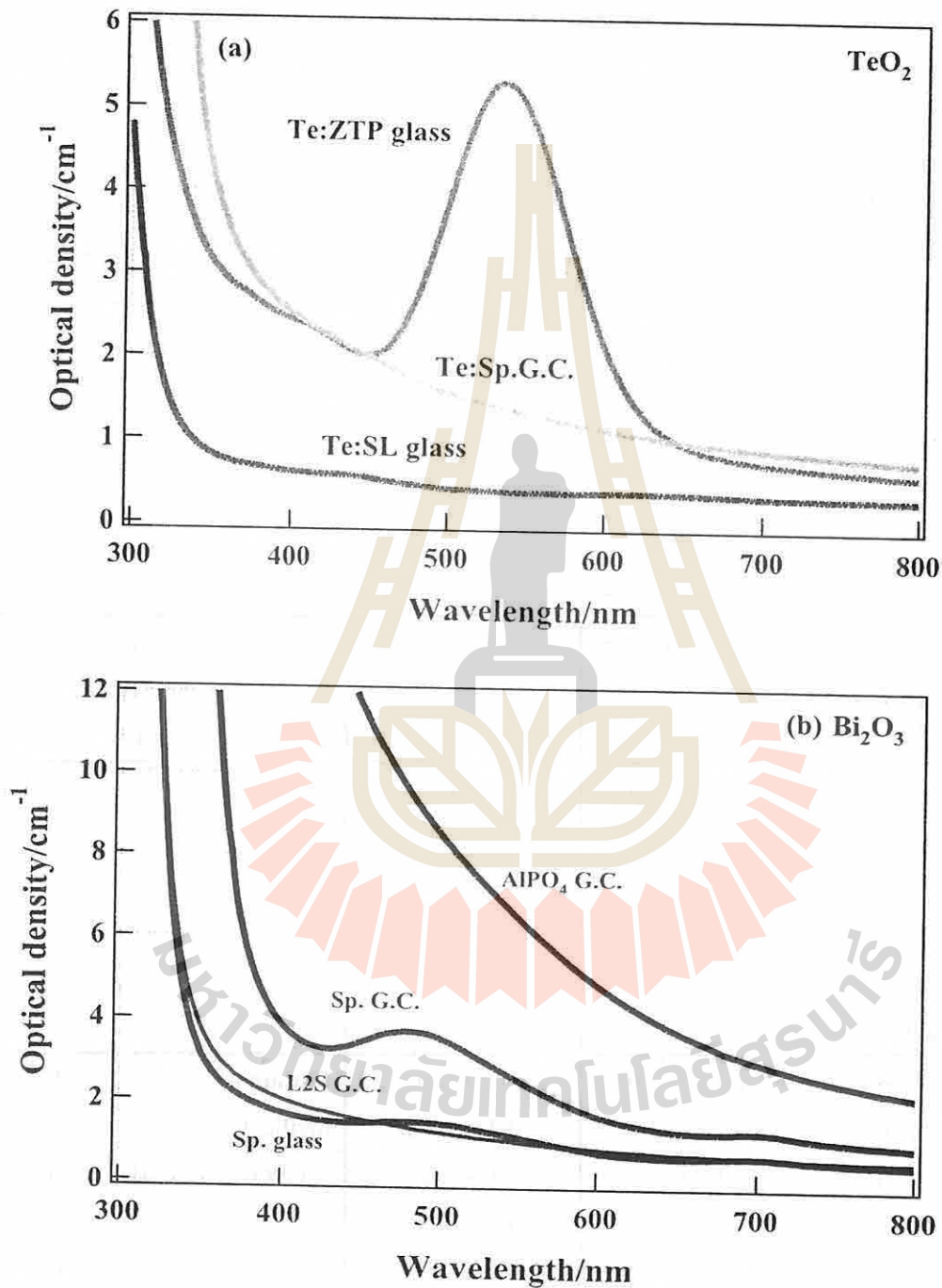
(b).Bi: AlPO$_4$ Glass-ceramics
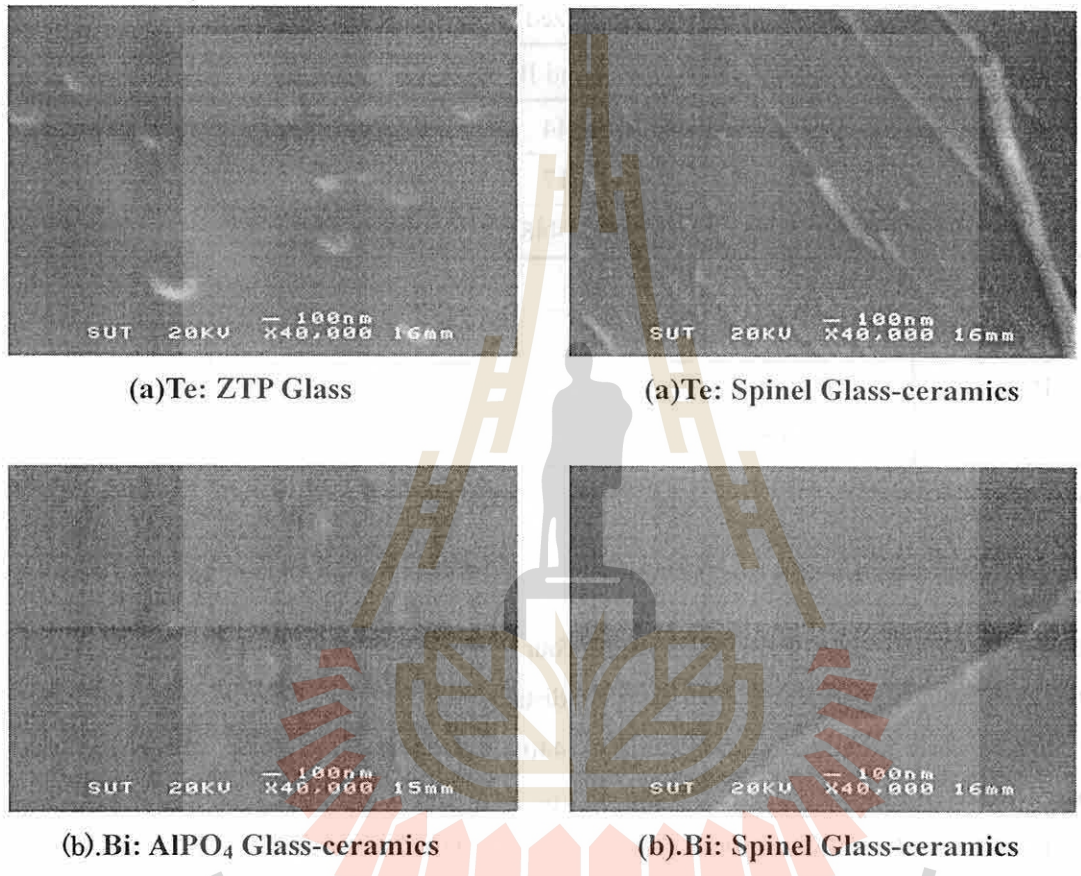
(b).Bi: Spinel Glass-ceramics

Fig. 2. SEM photos of Te- and Bi-doped glass and glass-ceramics. (a). Te-doped glasses and glass-ceramics, (b). Bi-doped glasses and glass-ceramics.

(a). Te-doped glasses and glass-ceramics

Appearance of samples are pale green for Te-SL, brilliant purple for Te-ZTP and brown-pink for Te-Sp. glass-ceramics, and absorption spectra are shown in Figure 1(a). Three absorption bands are observed at around 377, 444 and 625 nm for green Te-SL glass. For Te-ZTP glass, the strong absorption band at 537 nm with a shoulder at around 420 nm appears. On the contrary, the shoulder at around 420 nm is observed in Sp.

Table 3. Absorption bands analyzed by Gaussian distribution.

Name	Band I	Band II	Band III	Band IV
Te-Sp	377	444	(526)*	625
Te-SL	375	417	537	(600)*
Te-ZTP	–	420, (448)*	(556)*	(599)*
Bi-L·2S	–		–	–
Bi-AlPO$_4$	–		–	–
Bi-Sp	(370)*	480	–	700
Bi-Sp. G.C.	(370)*	480	–	700

*: very weak

glass-ceramics.

The absorption bands may be classified into four bands, and they are summarized in Table 3. The absorption spectra were analyzed with Gaussian distribution.

For green Te-SL glass, the absorption band at 440 nm is ascribed to $^3\Sigma_g \rightarrow {}^3\Sigma_u$ transition of Te$_2$ color center and the absorption band at 625 nm can be assigned to $^2\pi_g \rightarrow {}^2\pi_u$ transition of Te$_2^-$ color center[14]. The 377 nm band may relate to exciton transition[14]. The strong absorption band at 537 nm of Te-ZTP glass seems to be due to colloidal metallic Te[19]. Actually, many particle of about 200 nm in diameter are actually observed in Te-ZTP glass, and a small particle was also detected in Te-Sp. glass-ceramics as shown in Figure 2(a). This indicates that TeO$_2$ was reduced to metallic Te. This pink coloration might be due to the surface plasmon resonance absorption of Te colloids.

(b). Bi-doped glasses and glass-ceramics

Appearances of samples are yellow-brown for Bi-L·2S glass-ceramics, deep brown for Bi-AlPO$_4$ glass-ceramics and pale pink to pink for Bi-Sp. glass and glass-ceramics, and their absorption spectra are shown in Figure 1(b). Two absorption bands at around 480 nm and 700 nm appear in pink Sp. glass and glass-ceramics. This spectral pattern is the same as those reported previously[8-11]. On the contrary, no specific absorption band can be detected in Bi-L·2S and Bi-AlPO$_4$ glass-ceramics. Figure

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2(b) shows that particles of 100~200 nm in diameter precipitated in Bi-AlPO$_4$ glass-ceramics, while no particles can be detected in Bi-Sp. glass-ceramics. These particles may be colloidal metallic Bi[20]. This indicates that Bi$_2$O$_3$ was reduced to metallic Bi in Bi-AlPO$_4$ glass-ceramics.

3. 2. Luminescence in NIR region

Figure 3 shows the NIR luminescence spectra of Te- and Bi-doped glasses and glass-ceramics under the excitation of 974 nm laser diode at room temperature. A broad NIR luminescence at around 1200 nm can be observed in all Te-doped glasses and glass-ceramics. It should be noted that a weak and rather sharp luminescence can also be detected at around 1020 nm in Te-Sp. glass-ceramics.

On the other hand, pink colored Bi-Sp. glass and glass-ceramics exhibit NIR luminescence at around 1100 nm with a shoulder at around 1450 nm. However, no NIR luminescence can be observed in other two Bi-doped glass-ceramics (L·2S and AlPO$_4$ glass-ceramics).

3.3. ESR spectra

In order to determine the luminescent center of Te- and Bi-doped glasses and glass-ceramics, the ESR spectra were measured. The ESR spectra are shown in Figure 4. Two ESR signals were detected, g≈4.7 and g≈2.0 for both Te- and Bi-doped glasses and glass-ceramics. The ESR signals at g≈4.7 may be derived from impurities, such as Fe^{3+} ion in the sample.

It is noteworthy that ESR spectrum of Bi-doped Sp. glass and glass-ceramics is identical with that of Te-doped Sp. glass-ceramics. The ESR signal at g≈2.0 can also be observed in Bi-Sp. glass and Sp. glass-ceramics which exhibit NIR luminescence. However, the ESR signals at g≈2.0 can not be detected in Bi-AlPO$_4$ G.C. and Bi-L2S G.C. which do not exhibit NIR luminescence, and hence this ESR signal is strongly related to NIR luminescence.

4. Discussion

4. 1. Te-doped glasses and glass-ceramics

It was found that colorations of Te-doped glasses and glass-ceramics might be due to elemental clustering of Te, such as Te$_2$ and Te$_2^-$. The dimer of Te cluster is believed to be stable species[21,22]. In glasses and glass-ceramics, it is clear that TeO$_2$ was reduced to elemental Te during melting, and they aggregated to colloidal size. This colloidal metallic Te results in the pink coloration of ZTP glass. However, the NIR luminescence does not seem to be due to colloidal Te because the NIR luminescence is not proportional to the amount of colloidal Te.

In ESR spectra shown in Figure 4(a), two ESR signals were detected, g≈4.7 and g≈2.0. The ESR signals at g≈4.7 may be derived from impurities, such as Fe^{3+} ion in the sample. The ESR signals at g≈2.0 of SL and Sp. glass-ceramics have fine structure. This signal often appears in halide crystals and it is assigned to self-trapped hole or V$_k$ center[23,24]. This means that ESR signal at g≈2.0 is derived
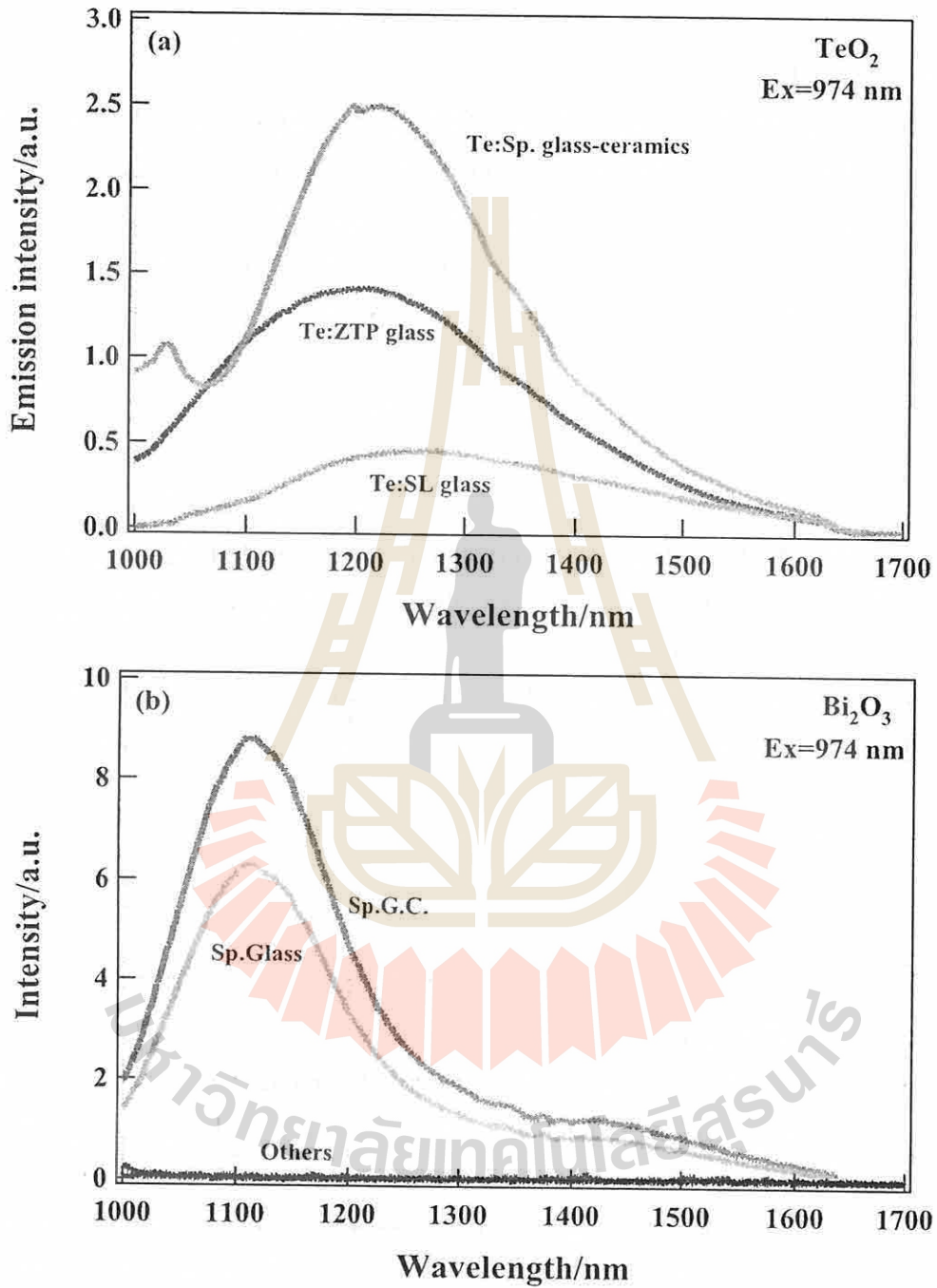
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Fig. 3. NIR luminescence spectra of Te- and Bi-doped glass and glass-ceramics. (a).
Te-doped glasses and glass-ceramics, (b). Bi-doped glasses and glass-ceramics.
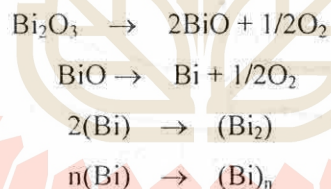
from halogen molecular ion, X_2^-. The similar ESR spectrum was obtained in Se-doped borosilicate glass and it is believed to be due to Se_2^- ions[25]. Since Te clustering such as Te_2^-/Te_2 exists in Te-doped glasses as mentioned previously, ESR signals at $g\approx2.0$ can be assigned to Te_2^- ions. The NIR luminescent intensity seems to be proportional to the intensity of $g\approx2.0$ signals of ESR spectra.

4. 2. Bi-doped glasses and glass-ceramics

The origin of the pink coloration and NIR luminescence of Bi-doped glasses and glass-ceramics are not clear yet. Here, the origin of the coloration and NIR luminescence of Bi-doped glasses and glass-ceramics will be discussed.

It is well known that the blue luminescence of Bi-containing glass is derived from Bi^{3+} ions in materials[26], therefore a large amount of Bi^{3+} ions present in Bi-L2S glass-ceramics and Bi-Sp. glass. On the contrary, Bi^{3+} ion scarcely exists in Bi-AlPO$_4$ glass-ceramics and Bi-Sp. glass-ceramics. This indicates that Bi^{3+} ion was reduced to lower valence state by further heat treatment for crystallization in Bi-AlPO$_4$ glass-ceramics and Bi-Sp. glass-ceramics.

The darkening effect of high Bi_2O_3-containing glasses was reported [20]. When glasses containing a large amount of Bi_2O_3 were melted at higher temperature, brown-black glasses could be obtained, and nano-scale Bi particles were detected by transmission electron microscope (TEM) observation[20]. The nano-scale Bi particles can also be detected in this study (Figure 2(b)). This darkening effect was related to a redox process partially reducing Bi^{3+} ions to a lower valence state, and hence the next process may be given:

$$Bi_2O_3 \rightarrow 2BiO + 1/2O_2$$
$$BiO \rightarrow Bi + 1/2O_2$$
$$2(Bi) \rightarrow (Bi_2)$$
$$n(Bi) \rightarrow (Bi)_n$$

Here, (Bi) indicates elemental Bi, (Bi_2) the molecular Bi and $(Bi)_n$ the metallic colloidal Bi. Above reactions go to right side at higher temperature and reducing condition.

From the result mentioned previously, it is clear that Bi^{3+} ions (L·2S glass-ceramics) and colloidal metallic Bi (AlPO$_4$ glass-ceramics) are not responsible for pink coloration and NIR luminescence. The NIR luminescence can be observed only for pink Sp. glass and glass-ceramics.

It is should be noted that ESR spectrum of Bi-doped Sp. glass-ceramics is identical with that of Te-doped Sp. glass-ceramics. The ESR signal at $g\approx2.0$ can also be observed in Bi-Sp. glass and Bi-Sp. glass-ceramics which exhibit NIR luminescence. This ESR signal can not be detected in AlPO$_4$ and L·2S glass-ceramics which did not exhibit NIR luminescence. Therefore, it seems that the ESR signal
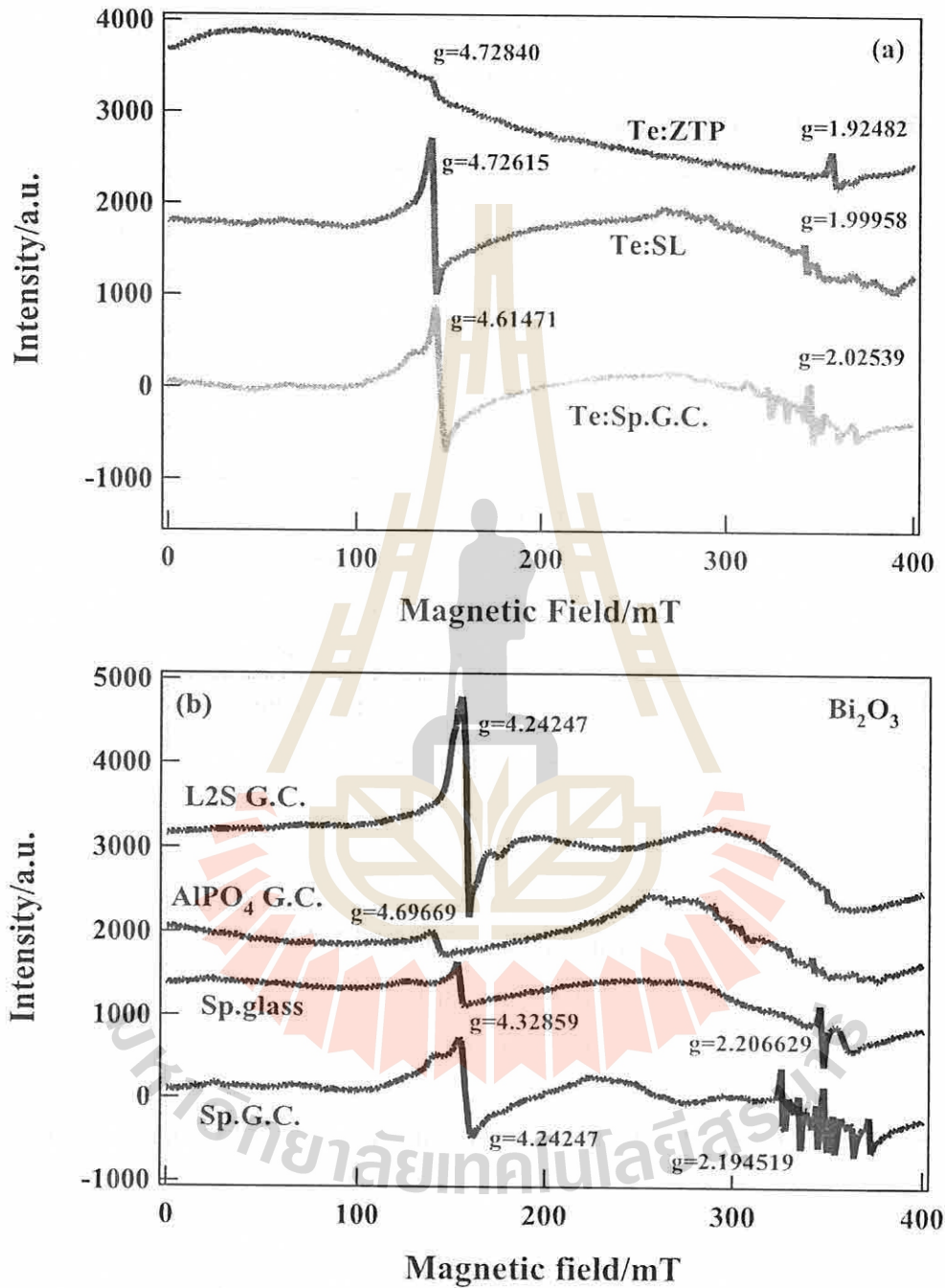
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Fig. 4. ESR spectra of Te- and Bi-doped glass and glass-ceramics. (a). Te-doped glasses and glass-ceramics, (b). Bi-doped glasses and glass-ceramics.

at $g \approx 2.0$ is strongly related to NIR luminescence and pink coloration. In analogy with Te-doped Sp. glass and Sp. glass-ceramics, this ESR signal may come from Bi molecular ions, Bi_2^-.

In Se-pink glasses, the analytical concentration of Se is usually few hundreds ppm, and the Se molecule or molecular ions contributing the color generation is believed to be few % of total Se presented in glasses[27]. Therefore, the concentration of Te and Bi molecular ions in glasses and glass-ceramics may be very low, ≈ 10-30 ppm.

5. Conclusion

The luminescence characteristics of Te- and Bi-doped glasses and glass-ceramics were investigated and the origin of coloration and near infrared luminescence was discussed. The colorations of these glasses and glass-ceramics might be due to the elemental clustering such as Te_2/Te_2^- and Bi_2/Bi_2^-. The broad NIR luminescence can be detected in Te- and Bi-doped glasses and glass-ceramics. The ESR signal at $g \approx 2.0$ can be observed in Te- and Bi-doped glasses and glass-ceramics which exhibit NIR luminescence, and therefore this ESR signal is strongly related to the NIR luminescence. The ESR signal at $g \approx 2.0$ might be derived from molecular ions of Te and Bi, Te_2^- and Bi_2^-.

Consequently it is suggested that the broad NIR luminescence of Te- and Bi-doped glass and glass-ceramics are most likely to be caused by elemental clustering, such as Te_2/Te_2^- and Bi_2/Bi_2^-.

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III. NIR luminescence Characteristics of Bi_2O_3-Containing Glasses

III-1. Effect of Melting Temperature on the Valence State and NIR luminescence Characteristics of Bi_2O_3-Containing Glasses

Abstract

The effect of melting temperature on the redox reaction and NIR luminescent characteristics of $63B_2O_3$-$9Al_2O_3$-$9ZnO$-$9K_2O$-$10Bi_2O_3$ (mol%) glass is investigated and the color center and luminescent center of these glasses are discussed. It was found that the coloration and near-infrared luminescent characteristic of glasses are strongly affected by melting temperature. The color becomes deeper with increasing melting temperature and finally metal colloids precipitate being black color. Near-infrared luminescence starts to appear, reach the maximum luminescent intensity and finally disappears with increasing temperature. The color center and near-infrared luminescent center might be Bi clusters, such as Bi_2, Bi_4, etc.

I. Introduction

Recently Bi-doped glasses which exhibit near infrared (NIR) luminescence, have been received much attention as NIR amplifier and NIR tunable laser materials, and many researches have been done [1-6]. Although many ideas on the luminescent center of these Bi-doped glasses are proposed, such as Bi^{5+} ion [1,2], BiO [3,4] and Bi cluster [5, 6], it is not clear yet. It is known that these glasses often appear to be coloration depending on glass composition and melting conditions, and the metallic particles were sometimes observed in glasses [7-9]. This phenomenon is called as darkening effect or darkening process. This indicates that Bi_2O_3 are readily reduced to metallic colloids. Thus the coloration of Bi-doped glasses can be dealt with redox reaction in glasses. Furthermore, it is quite important to identify what Bi species relate to color center and NIR luminescent center.

The authors are noted the relation between redox reaction and NIR luminescent characteristics in Bi-doped glasses and continue the research on that by controlling melting temperature, glass composition and melting atmosphere. Here, the effect of melting temperature on the redox reaction and NIR luminescent characteristics of Bi-doped glasses is investigated and the color center and luminescent center of these glasses are discussed.

2. Experimental

2. 1. Sample preparation

The glasses of composition $63B_2O_3$·$9Al_2O_3$·$9ZnO$·$9K_2O$·$10Bi_2O_3$ (mol%) were prepared by
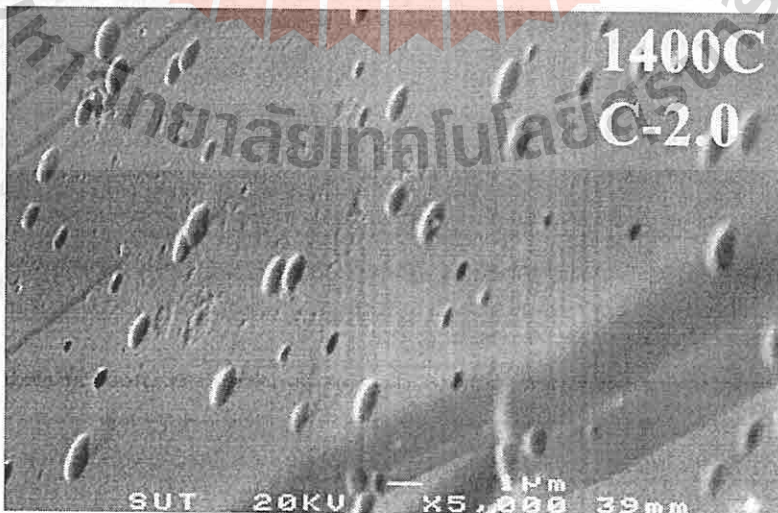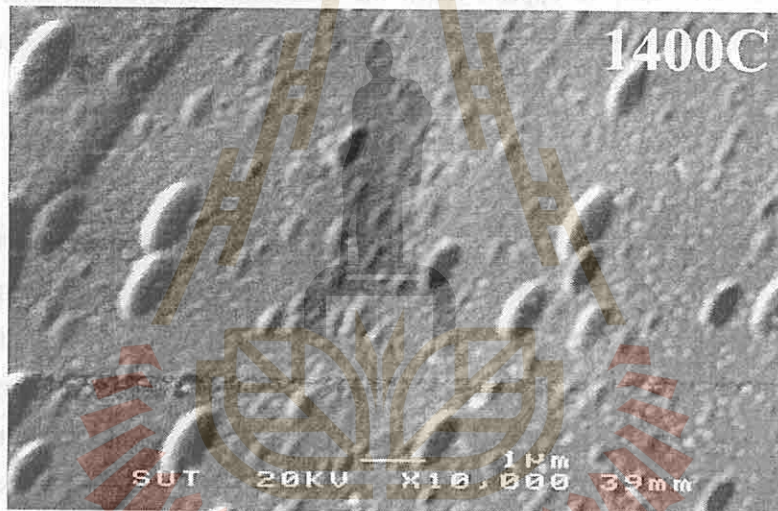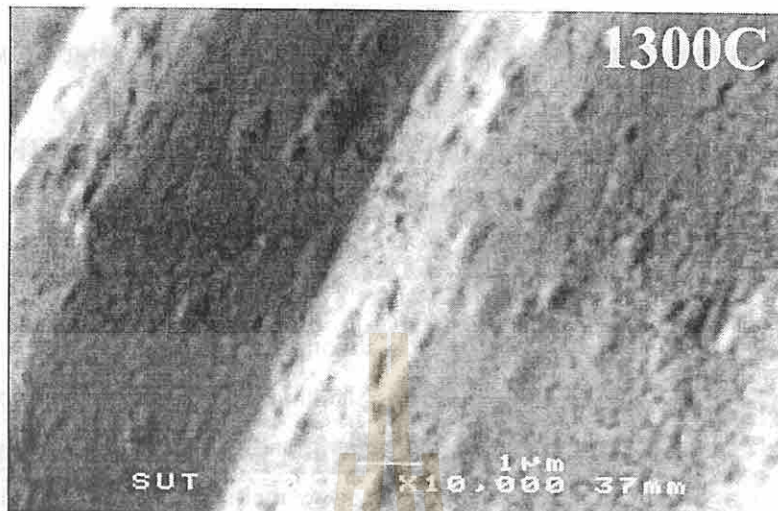
Fig. 1. SEM photos of black-colored Bi-1300, Bi-1400 and Bi-1400C2.0 glasses.

melting at various temperatures. Reagent grade chemicals of H_3BO_3, Al_2O_3, ZnO, K_2CO_3, and Bi_2O_3 were used as raw materials. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucible under various conditions (1000°~1400°C, 15~40 min.) in an electric furnace in air. The Bi-1400 glass was also melted under the strong reducing condition by adding 2.0 % of carbon. After melting they were poured onto iron plate and pressed by another iron plate. Then they were annealed at 450°C for 30 min and cooled slowly to room temperature in the furnace. Glasses were polished optically into about 1.5~2 mm in thickness for optical measurement. Hereafter, these glasses are referred to as Bi-1000, Bi-1100, Bi-1200, Bi-1300, Bi-1400 and Bi-1400-C2.0, respectively.

The fractured surface of glasses was etched by 0.5% HF solution for 1 min at room temperature and observed by scanning electron microscope (SEM, JEOL JSM 6400). X-ray diffraction (XRD) analysis was performed routinely by using Cu-Kα radiation with Bruker AXS Model 5005.

2. 2. Optical measurement

The absorption spectra were measured with Cary 1E ultra-violet-visible (UV-VIS) spectrometer in the range of 300-800 nm at room temperature.

The emission spectra in NIR region (900-1700 nm) were measured under the excitation of 974 nm laser diode at room temperature.

2. 3. XPS

The X-ray photoelectron spectroscopy (XPS) measurement was performed with monohromatized Al-Kα radiation for Bi $4f_{5/2}$ and $4f_{7/2}$ (National Synchrotron Research Center, Thailand). The shift of the energy scale was corrected with a reference of C1s binding energy of residual hydrocarbon at 284.6 eV.

3. Results

3. 1. Appearance and absorption spectra

The colors of glasses change from faint yellow (Bi-1000) to black (Bi-1300, Bi-1400 and Bi-1400C2.0) with increasing temperature as shown in Table 1. In Bi-1400C2.0 glass, silver-white Bi metal (6-8 mm diameter with 5 mm thickness) precipitated at the bottom of crucible. Figure 1 shows scanning electron microscopy (SEM) photos of black-colored glasses (Bi-1300, Bi-1400 and Bi1400-C2.0). Many spherical particles of smaller than 1μm in diameter are observed, and these particles are basically composed of Bi.

Figure 2 shows XRD patterns of Bi-1200, Bi-1300, Bi-1400 and Bi-1400C2.0 glasses. It is clearly seen that two diffraction peaks are detected at 2θ = 27.3° and 2θ = 38.2° in black colored glasses, Bi-1300, Bi-1400 and Bi-1400C2.0. However, no diffraction peaks can be detected in orange-colored Bi-1200 glass. The peak intensity increases with increasing temperature and reducing
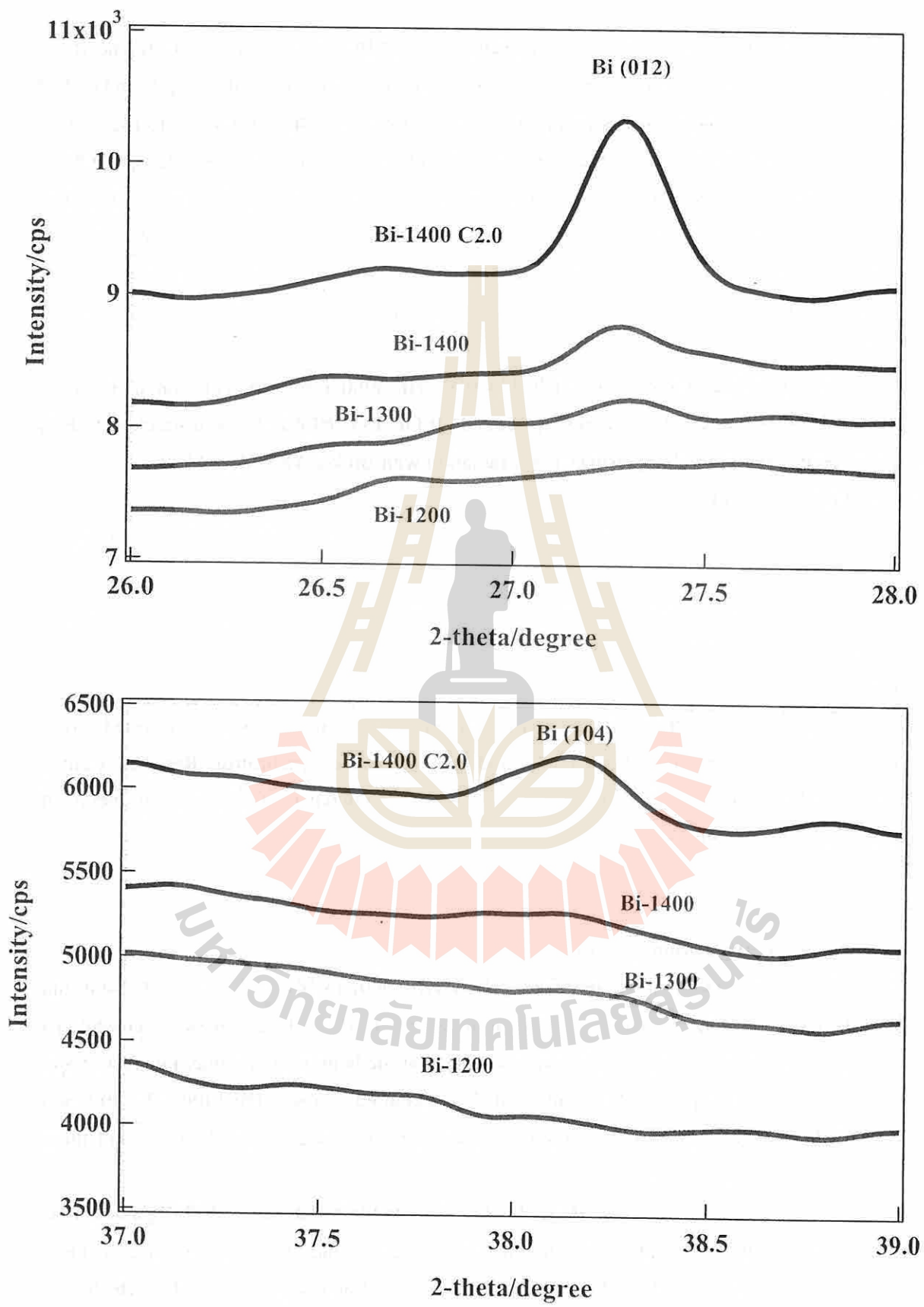
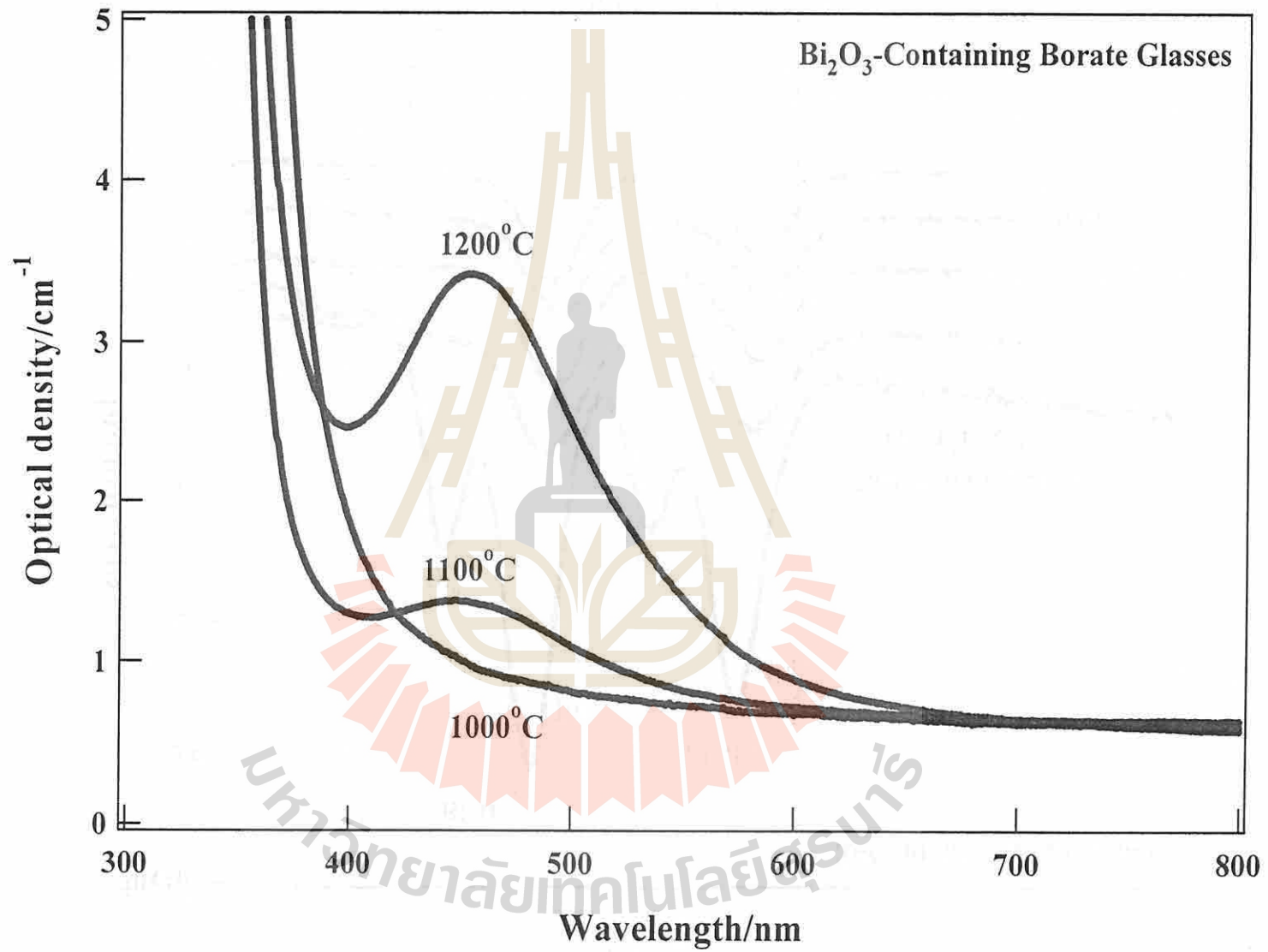Fig. 2. XRD patterns of colored glasses.

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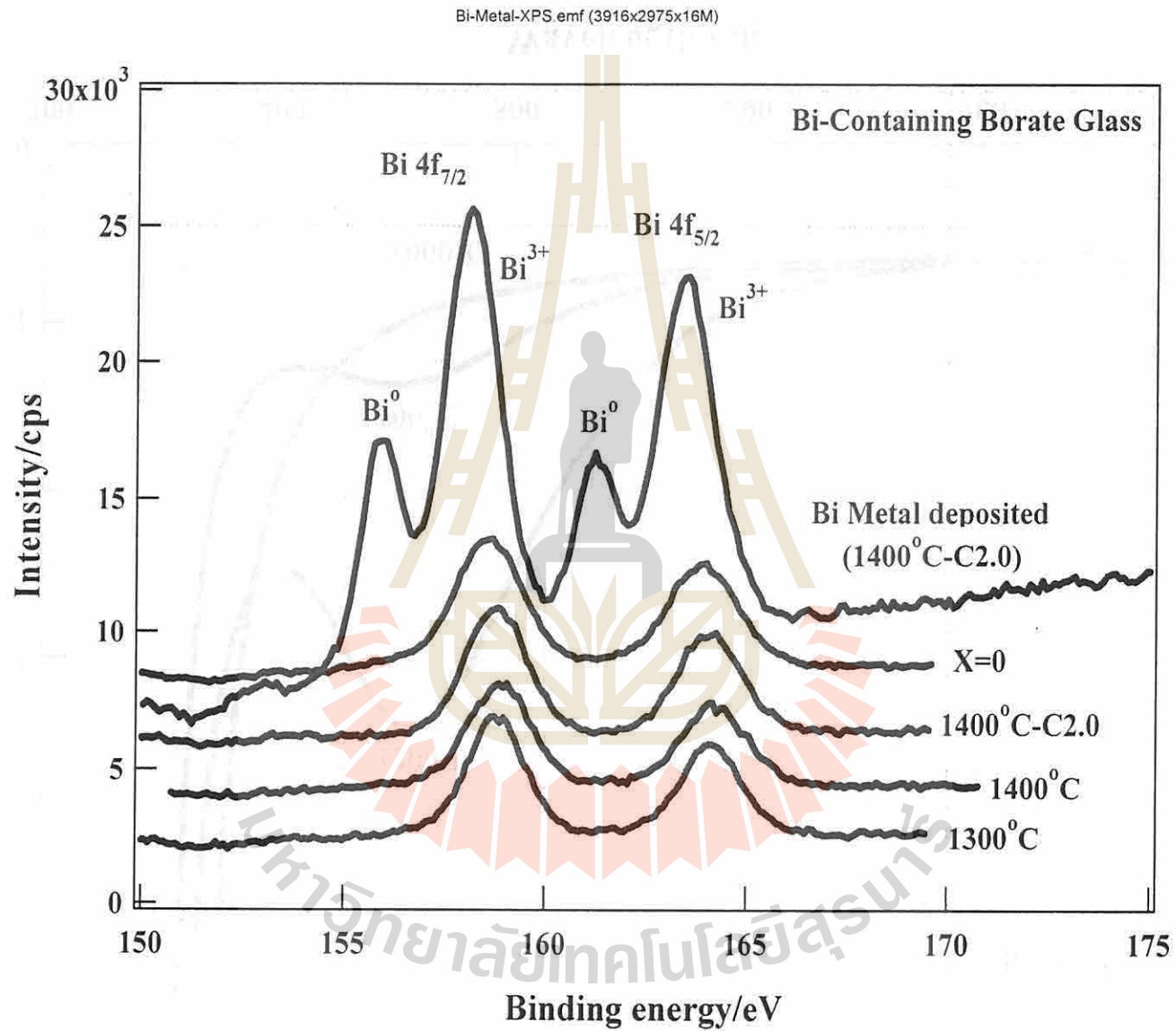Fig. 3. Absorption spectra of Bi-containing glasses melted at various temperatures.

Fig. 4. XPS spectra of Bi-4f for glasses melted at various temperatures.

condition. These peaks can be assigned to (010) and (104) planes of metallic Bi (JCPDS 00-001-0699). Therefore it is concluded that the spherical particles observed in SEM photos could be metallic Bi colloid particles. Thus, Bi_2O_3 is reduced partially to metallic Bi colloids by melting higher temperature and reducing condition [9]. However, it seems that the amount of metallic Bi colloids might be very low, less than 1 wt%. The darkening effect of Bi-containing glasses is confirmed to be the formation process of metallic Bi colloids.

Figure 3 shows the absorption spectra of Bi-containing glasses. The absorption spectra for black glasses could not be measured because of their very deep black coloration. The simple absorption band is observed at around 460 nm in Bi-1100 and Bi-1200 glasses. These spectral patterns are quite similar to those reported previously [3, 4, 10]. On the contrary, however, Peng et al. [11, 12], Suzuki et al. [13] and Khonthon et al. [5] have observed different spectral patterns, in which there were two absorption bands, ~490 nm and ~700 nm in their glasses. This indicates that the different types of color center may present in glasses discussed here.

Table 1. Melting conditions and appearances of glasses.

No.	Melting condition °C–min.	Appearance by naked eye	Absorption bands/nm	
			Band I	Band II
Bi-1000	1000-40	Faint yellow-green	-	-
1100	1100-20	Pale pink-red	460	-
1200	1200-20	Orange-red	460	-
1300	1300-15	Deep brownish-black	-	-
1400	1400-15	Black	-	-
1400-C2.0	1400-15	Black Bi metal deposited	-	-

3. 2. XPS

Figure 4 shows XPS spectra of glasses. Two peaks of Bi $4f_{7/2}$ and Bi $4f_{5/2}$ were detected in all glasses, and these are from Bi^{3+} ions. However, any signal can not be observed in lower energy side, despite the peak position shift slightly to lower energy side and half height width increases slightly with increasing melting temperature. On the contrary, $Bi°$ peaks can also be detected in Bi metal precipitated in Bi-1400C2.0 glass. This result indicates that the detectable amount of lower valence state species of Bi is not present in these glasses.

3. 3. NIR luminescence

Figure 5 shows near infrared (NIR) luminescence of glasses under the excitation of 974 nm laser

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diode. Bi-1000, Bi-1300 and Bi-1400 glasses do not show NIR luminescence. On the contrary, the broad NIR luminescence centered at around 1150 nm can be observed in Bi-1100 and Bi-1200. From the result of XPS measurement, it is clear that Bi^{3+} ion and Bi colloids do not contribute to NIR luminescence.

Table 2. XPS results analyzed by Gaussian distribution.

Glass	Bi $4f_{7/2}$	
	eV	Half width/eV
Bi-1000	158.6	1.038
Bi-1100	158.6	1.09
Bi-1200	158.7	1.12
Bi-1300	158.8	1.163
Bi-1400	158.8	1.18
Bi-1400-C2.0	158.8	1.185
Bi_2O_3*	158.8	1.367

4. Discussion

It was found that the coloration and near-infrared luminescent characteristic of Bi-containing borate glasses are strongly affected by melting temperature. The color became deeper with increasing melting temperature and finally metal colloids precipitated being black color. Near-infrared luminescence started to appear, reached the maximum luminescent intensity and finally disappeared with increasing temperature.

Usually the valence states of metal ions moves to lower side with increasing temperature [14]. Thus the change in valence sate of Bi may be written by:

$$Bi^{3+} \rightarrow [Bi^{2+}, BiO] \rightarrow Bi, Bi_2, Bi_3, Bi_4,--- \rightarrow (Bi)_n \qquad 1)$$

Where Bi_2, Bi_3, Bi_4,--- are Bi clusters and $(Bi)_n$ the Bi metallic colloid. This indicates that the redox equilibrium moves toward reduced side with increasing temperature. As seen clearly in Figure 4 and Table 1, the valence state of Bi moves to lower side with increasing temperature. Bi^{3+} ion and Bi colloids do not contribute to NIR luminescence, and hence, the origin of coloration and NIR luminescence might be intermediate species between Bi^{3+} ion and Bi colloids. A well-defined absorption bands and the strong NIR luminescence were observed in Bi-1200 glass, which is just
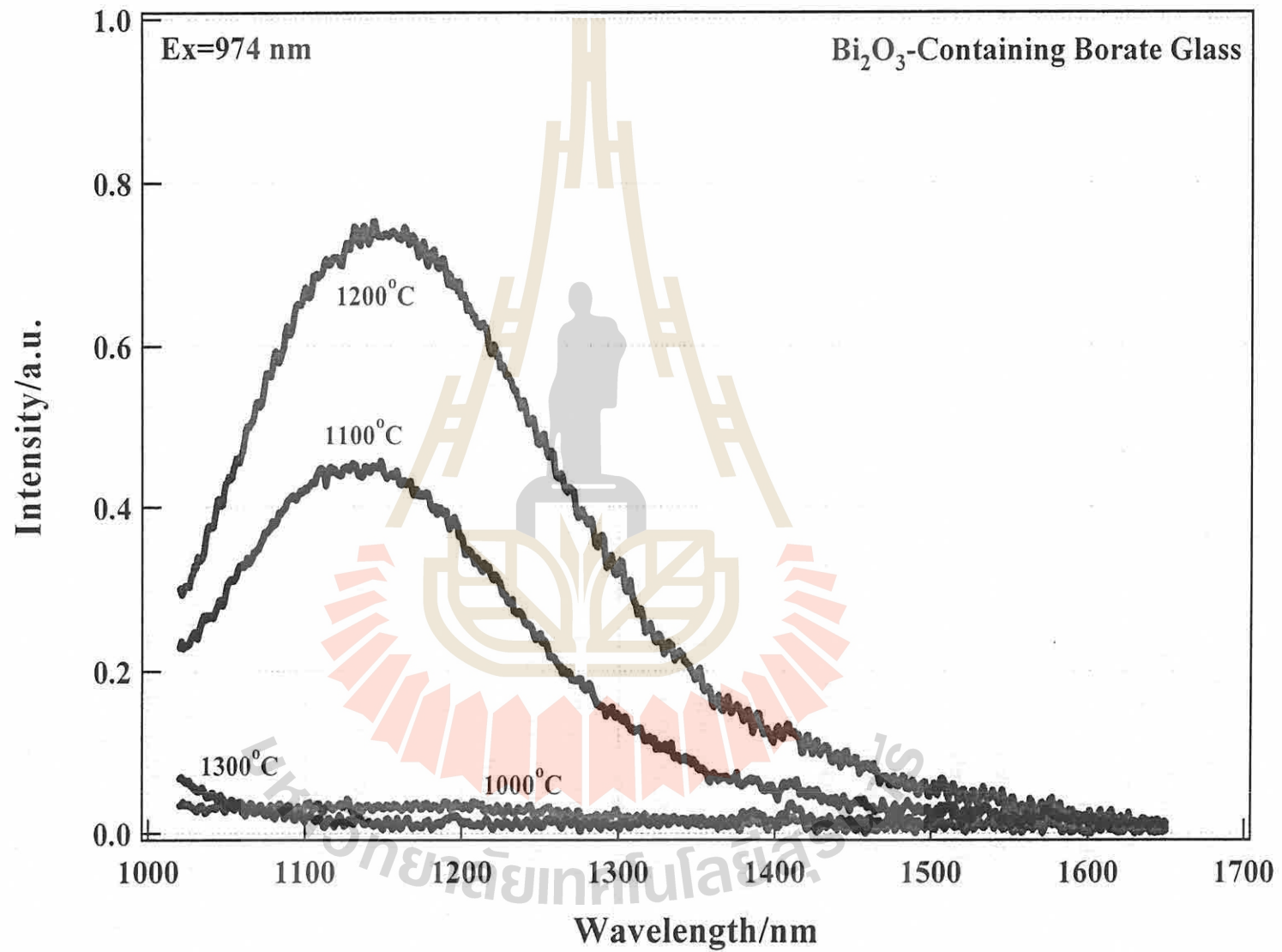
Fig. 5. NIR luminescence of glasses melted under the excitation of 974 nm laser diode at room temperature.

before the beginning of darkening effect Bi-1300). Authors [10] has observed the similar process in Bi-doped soda-lime silicate glass. The annealing at higher temperature induces darkening effect and reduces NIR luminescence for the glass with same composition and same melting condition. However, the glass annealed at lower temperature was colorless and transparent and exhibits higher intensity of NIR luminescence [10]. It seems that this process corresponds to Bi, Bi_2, Bi_3, Bi_4,--- $\rightarrow$ $(Bi)_n$ in Eq. 1). This kind of process has often been observed in the formation of noble-metal colloids [15]. In this process, reduced noble-metal atoms gather together, grows and finally form metal colloids by further heating.

Thus the darkening effect can be interpreted as the process of colloid formation from atomic or molecular Bi. Therefore, it was concluded that the color center and luminescent center is likely to be caused by Bi clusters, Bi_2, Bi_3, Bi_4,---. Reng et al [3, 4] measured VIS luminescence and found luminescence at around 640 nm, and they concluded that this luminescence might come from BiO. However, the authors could not detect this luminescence.

5. Conclusion

The effects of melting temperature on the redox reaction and NIR luminescent characteristics of $63B_2O_3$-$9Al_2O_3$-$9ZnO$-$9K_2O$-$10Bi_2O_3$ (mol%) glass were investigated and the color center and luminescent center of these glasses are discussed.

It was found that the coloration and near-infrared luminescent characteristic of glasses are strongly affected by melting temperature. The color becomes deeper with increasing melting temperature and finally metal colloids precipitate being black color. Near-infrared luminescence starts to appear, reach the maximum luminescent intensity and finally disappears with increasing temperature.

The color center and near-infrared luminescent center is likely to be caused by Bi clusters, such as Bi_2, Bi_3, Bi_4, etc.

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III-2. Effect of Glass Composition on the NIR luminescence Characteristics of Bi_2O_3-Containing Borate Glasses

Abstract

The effect of glass composition on the redox equilibrium and NIR luminescent characteristics of $90[(80-X)B_2O_3 \cdot 10Al_2O_3 \cdot 10ZnO \cdot XK_2O] \cdot 10Bi_2O_3$ (mol%, X=0, 10, 20, 30)) glasses is investigated and the color center and luminescent center of these glasses are discussed. It was found that the coloration and near-infrared luminescent characteristic of glasses are strongly affected by glass composition. The color becomes deeper with decreasing K_2O content. Near-infrared luminescence appears in low K_2O-containing glasses (X=0 and 10). The compositional effect on NIR luminescence is discussed based on optical basicity of glass. The color center and near-infrared luminescent center is likely to be caused by Bi clusters, such as Bi_2, Bi_3, Bi_4, etc.

I. Introduction

Recently Bi-doped glasses which exhibit near infrared (NIR) luminescence, have been received much attention as NIR amplifier and NIR tunable laser materials, and many researches have been done [1-6]. Although many ideas on the luminescent center of these Bi-doped glasses are proposed, such as Bi^{5+} ion [1,2], BiO [3,4] and Bi cluster [5, 6], it is not clear yet. It is known that these glasses often appear to be coloration depending on glass composition and melting conditions, and the metallic particles were sometimes observed in glasses [7-9]. This phenomenon is called as darkening effect or darkening process. This indicates that Bi_2O_3 are readily reduced to metallic colloids. Thus the coloration of Bi-doped glasses can be dealt with redox equilibrium in glasses. Furthermore, it is quite important to identify what Bi species relate to color center and NIR luminescent center.

The authors are noted the relation between redox equilibrium and NIR luminescent characteristics in Bi-doped glasses and continue the research on that by controlling melting temperature, glass composition and melting atmosphere. Here, the effect of glass composition on the redox equilibrium and NIR luminescent characteristics of Bi-doped borate glasses is investigated and the color center and luminescent center of these glasses are discussed.

2. Experimental

2. 1. Sample preparation

Four glasses were prepared, and their compositions were expressed by $90[10Al_2O_3 \cdot (80-X)B_2O_3 \cdot 10ZnO \cdot XK_2O] \cdot 10Bi_2O_3$ (mol%, X=0, 10, 20, 30). Reagent grade chemicals of H_3BO_3, Al_2O_3, ZnO, K_2CO_3, and Bi_2O_3 were used as raw materials. Batches corresponding to 25 g of

glass were mixed thoroughly and melted in 50 cc alumina crucible under various conditions (1200°C, 15~20 min.) in an electric furnace in air. After melting they were poured onto iron plate and pressed quickly by another iron plate. Then they were annealed at 450°C for 30 min and cooled slowly to room temperature in the furnace. Glasses were ground and polished optically into about 1.5~2 mm in thickness for optical measurement. Hereafter, glasses are referred to as Bi-0, Bi-10, Bi-20 and Bi-30, respectively.

2. 2. Optical measurement

The absorption spectra were measured with Cary 1E ultra-violet-visible (UV-VIS) spectrometer in the range of 300-800 nm at room temperature.

The emission spectra in NIR region (900-1700 nm) were measured under the excitation of 974 nm laser diode at room temperature.

2. 3. XPS

The X-ray photoelectron spectroscopy (XPS) measurement was performed with monohromatized Al-Kα radiation for Bi $4f_{5/2}$ and $4f_{7/2}$ (NSRC, National Synchrotron Research Center, Thailand). The shift of the energy scale was corrected with a reference of C1s binding energy of residual hydrocarbon at 284.6 eV.

3. Results

3. 1. Absorption spectra

The colors of glasses change from reddish-orange (Bi-0) to yellow (Bi-30) with increasing amount of K_2O as shown in Table 1. Bi-20 and Bi-30 glasses are readily to phase-separate during casting.

Figure 1 shows absorption spectra of Bi-containing glasses. The strong absorption is observed in near ultra-violet (UV) to blue region in visible range for Bi-20 and Bi-30 glasses. Two absorption bands are observed at around 470 and 710 nm in Bi-0 glass. The absorption band at around 460 nm is observed in Bi-10 glass. The absorption bands at around 460~470 nm of Bi-0 and Bi-10 glasses are analyzed with Gaussian distribution, and the result is shown in Table 1. Thus the band at around 460-470 nm can be separated into two bands, ~455 nm (Band I) and ~490 nm (Band II). Band II is dominant in Bi-0 glass, but Band I is dominant in Bi-10 glass.

It is well known that Bi^{3+} ion has strong absorption in UV region and Bi^{5+} has a strong absorption band in shorter wavelength in VIS region. Therefore, the absorption edge shift to longer wavelength with increasing K_2O contents. and the absorption edge reaches at around 400 nm for Bi-30 glass. In the case of Bi-20 glass, the scattering also overlaps on the spectrum because of phase separation. It should be noted that the drastic change in absorption spectra was observed between Bi-10 and Bi-20.
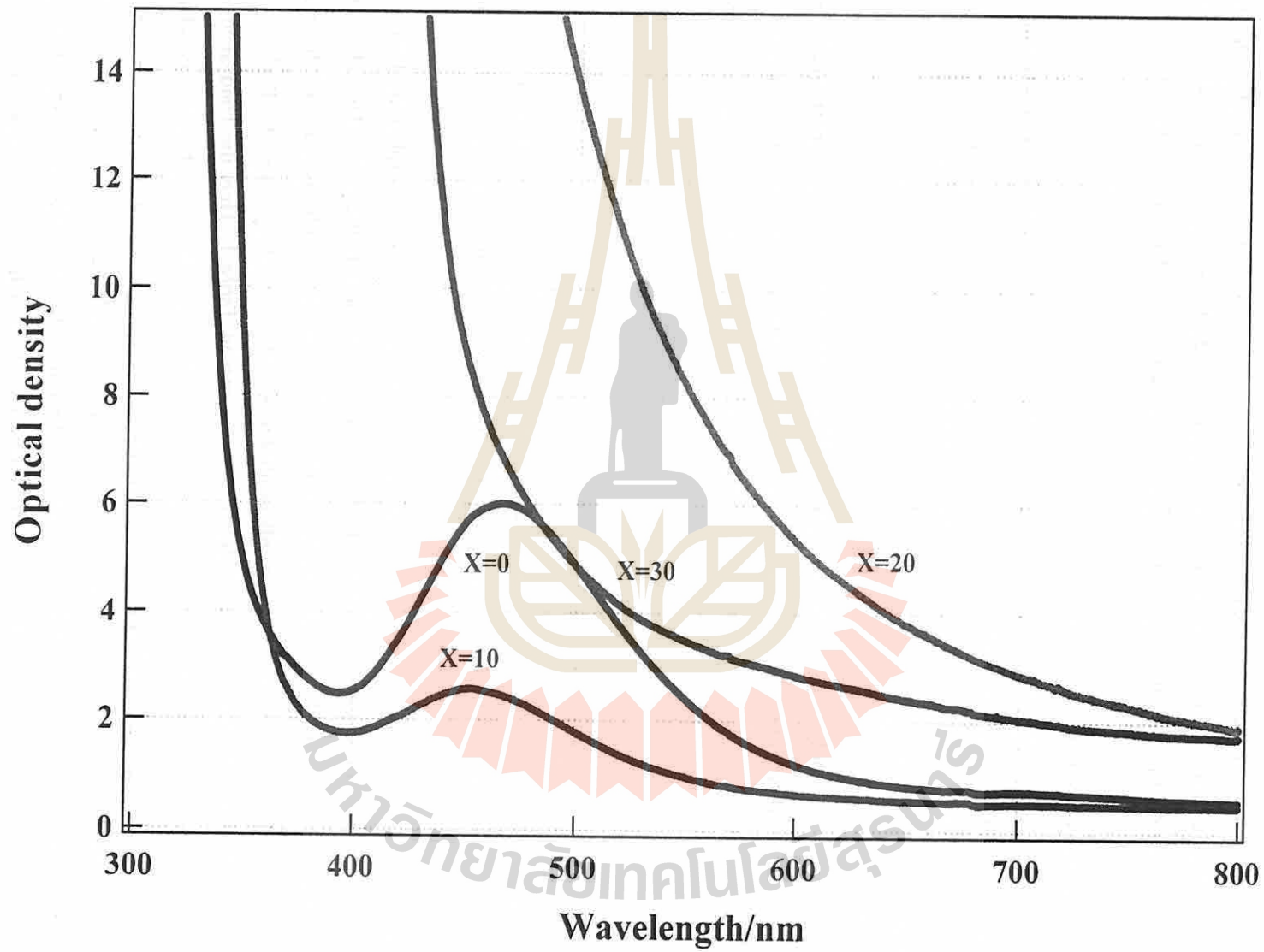
Fig. 1. Absorption spectra of glasses at room temperature.

Table 1. Appearances and absorption bands analyzed by Gaussian distribution.

Name	Appearance/by naked eye	Absorption bands		
		Band I	Band II	Band III
Bi-0	Reddish-orange	455 nm	**488 nm***	717 nm
Bi-10	Orange	**452 nm***	490 nm	–
Bi-20	Yellow-brown, partly phase separated	-	-	-
Bi-30	Brown, partly phase separated	-	-	-
[3, 4, 10]		~460 nm	–	–
[5, 11, 12, 13]		–	~490 nm	~710 nm

*: dominant

As shown above, it was found that three absorption bands were observed in Bi-0 glass. Two different spectral patterns have been reported in Bi- doped glasses. One is only one absorption band at around 460 nm reported by Reng et al. [3, 4] and Khonthon et al. [10] Another is two absorption bands at ~490 nm and ~700 nm reported by many researchers [5, 11, 12, 13]. The color of glasses is also different, the former one is orange and the latter one is reddish-brown to pink. This suggests that two color centers are present in Bi-doped glasses, for example C1 center (~460 nm) and C2 center (~490 nm and ~710 nm). These color centers changes depending on glass composition, melting temperature and melting atmosphere. Bi-0 glass may have two color centers, C1 and C2.

Authors reported that the former color center (C1 center) is likely to be caused by Bi clusters, such as Bi_2, Bi_3, ---. On the contrary, the latter color center (C2 center) may be due to cluster radicals, such as Bi_2^-, Bi_3^-, --- by ESR measurement.

3. 2. XPS

Figure 2 shows XPS spectra of glasses. Two peaks of Bi $4f_{7/2}$ and Bi $4f_{5/2}$ were detected in all glasses, and these are from Bi^{3+} ions. However, any signal can not be observed in lower energy side, despite the peak position shift slightly to lower energy side and half height width increases slightly with increasing melting temperature. This result indicates that the detectable amount of lower valence state species of Bi is not present in these glasses.

3. 3. NIR luminescence

Figure 3 shows near infrared (NIR) luminescence of glasses under the excitation of 974 nm laser diode. Bi-0 and Bi-10 glasses exhibit NIR luminescence peaking at around 1100 nm, but Bi-20 and Bi-30 glasses do not show NIR luminescence. The intensity of NIR luminescence of Bi-0 glass is higher that that of Bi-10 glass.

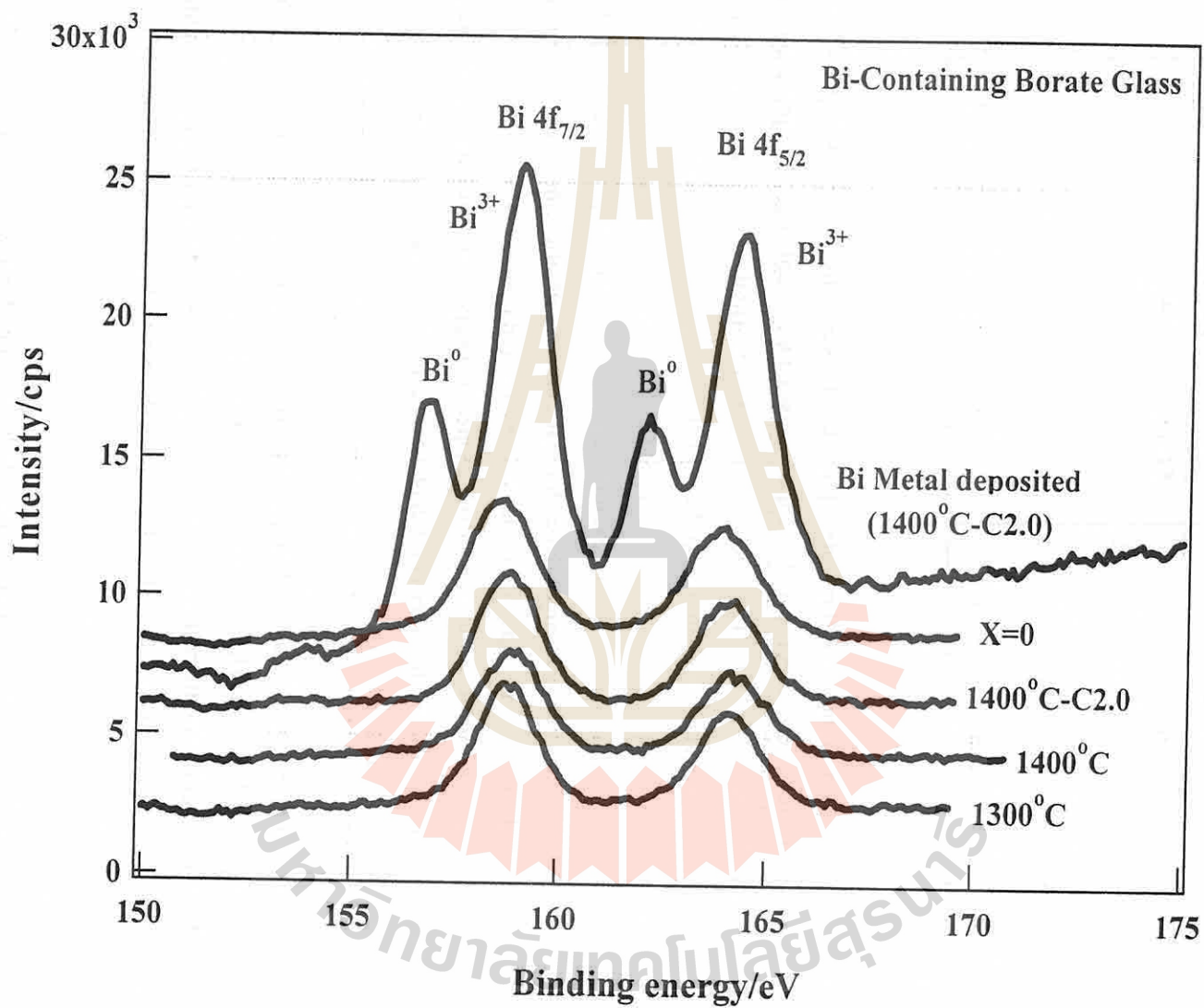As shown before, Bi-20 and Bi-30 glasses contain Bi^{3+} ions and do not exhibit any NIR

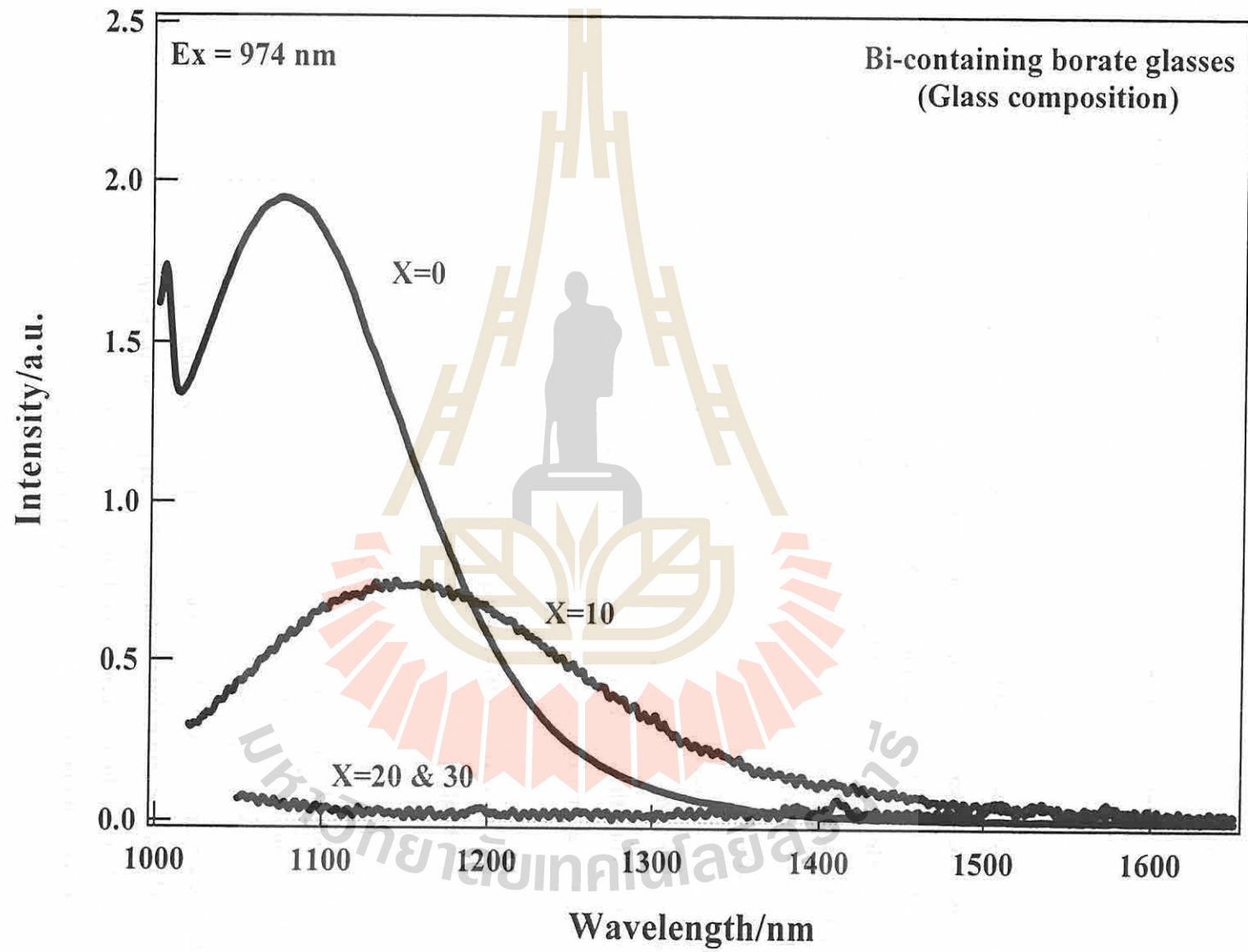Fig. 2. XPS spectra of Bi4f for various glasses.

Fig. 3. NIR luminescence spectra of glasses under the excitation of 974 nm laser diode.
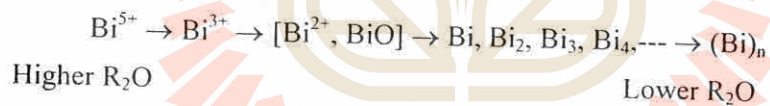
luminescence, and hence these ions do not contribute to NIR luminescent.

4. Discussion

It was found that the coloration and near-infrared luminescent characteristic of Bi-containing borate glasses are strongly affected by glass composition. The color becomes deeper with decreasing K_2O content. The intensity of NIR luminescence decreases gradually and finally disappears with increasing amount of K_2O.

The glass composition also affects to redox equilibrium of metal ions in glasses. Generally higher oxidation state was induced by an increase in the basicity of glass (increasing alkali content) [14]. On these glasses discussed here, the coloration decreases with increase in K_2O content. This shows that the Bi3+ ions is dominant in X=20and 30 glasses comparing with X=0 and X=10 glasses. Murata and Mouri [15] discussed NIR luminescence characteristics of various Bi-doped glasses based on optical basicity. They concluded that the optical basicity of $\Lambda = 0.4$ is critical, and no NIR luminescence was observed above this value. According to Duffy's optical basicity concept [16], the optical basicity, Λ, of all glasses were calculated. Λ is 0.45 for X=0, 0.50 for X=10, 0.55 for X=20 and 0.59 for X=30 glasses, respectively. However, weak luminescence was detected in X=10 ($\Lambda = 0.50$) glass melted at 1000°C (see previous chapter III-1) compared with the results of Murata and Mouri. This indicates that the formation of of color center and luminescent center of Bi-containing glasses is 2

The change in valence sate of Bi may be written by:

$$Bi^{5+} \rightarrow Bi^{3+} \rightarrow [Bi^{2+}, BiO] \rightarrow Bi, Bi_2, Bi_3, Bi_4, \text{---} \rightarrow (Bi)_n$$

Higher R_2O \qquad\qquad\qquad\qquad\qquad Lower R_2O

where Bi_2, Bi_3, Bi_4,--- are Bi clusters and $(Bi)_n$ is Bi metallic colloid. However, metal colloids were not formed in the glass discussed here.

Bi^{3+} ion has a strong absorption in UV region but no characteristic absorption appears in VIS region. On the contrary Bi colloids show very deep black color. These two species don't contribute to NIR luminescence. Reng et al [3, 4] measured VIS luminescence and found luminescence at around 640 nm, and they concluded that this luminescence might come from BiO or Bi^+. However, the authors could not detect this luminescence, and hence it is considered that the color center and luminescent center of Bi-containing borate glasses is Bi molecule/electron trapped Bi molecule, such as Bi_2, Bi_2^-,etc.

The absorption spectrum of Bi-0 glass is different from that of Bi-10 glass. The peak position shifts to longer wavelength slightly and a new absorption band appears at around 700 nm. This spectral pattern is quite similar to those op pink colored Bi-doped glasses [5, 11-13]. And the NIR

luminescence is also different slightly. Khonthon et al. [5] observed that pink colored spinel transparent glass-ceramics shows similar absorption and NIR luminescence spectra to Bi-0 glass, and hence it seems that the color center and luminescent center of both glasses are the same.

5. Conclusion

The effect of glass composition on the redox equilibrium and NIR luminescent characteristics of $90[(80–X)B_2O_3 \cdot 10Al_2O_3 \cdot 10ZnO \cdot XK_2O] \cdot 10Bi_2O_3$ (mol%, X=0, 10, 20, 30)) glasses is investigated and the color center and luminescent center of these glasses are discussed based on optical basicity.

It was found that the coloration and near-infrared (NIR) luminescent characteristic of glasses are strongly affected by glass composition. The color becomes deeper with decreasing K_2O content. Near-infrared luminescence appears in low K_2O-containing glasses (X=0 and 10). The compositional effect on NIR luminescence is discussed based on optical basicity of glass.

The color center and nNIR luminescent center is likely to be caused by Bi clusters, such as Bi_2, Bi_3, Bi_4, etc.

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III-3. Effect of Carbon Addition on the NIR luminescence Characteristics of Bi_2O_3-Doped Soda-Lime-Silicate Glass

Abstract

The effect of melting atmosphere on coloration and near-infrared luminescent characteristics of Bi-doped soda-lime-silicate glass was investigated by adding various amount of carbon to the batch. The colorless and transparent Bi-doped soda-lime-silicate glass was prepared, and the broad near-infrared luminescence peaking at around 1200 nm was observed. It is suggested that the color center and luminescent center is likely to be caused by reduced Bi species such as Bi_2, Bi_3, Bi_4 by considering the change in valence state of Bi based on redox equilibrium.

I. Introduction

Recently Bi-doped glasses which exhibit near infrared (NIR) luminescence, have been received much attention as NIR amplifier and NIR tunable laser materials, and many researches have been done [1-6]. Although a few ideas on the luminescent center of these Bi-doped glasses are proposed, such as Bi^{5+} ion [1,2], BiO [3,4] and Bi cluster [5, 6], it is not clear yet. It is known that these glasses often appear to be coloration depending on melting conditions, kinds of crucibles and additives, and the metallic particles were sometimes observed in glasses [7-9]. This indicates that Bi_2O_3 are readily reduced to metallic colloids, and this behavior can be dealt with redox reaction in glasses similar to transition metal ions. Furthermore, it seems to be quite important to know what species of Te and Bi formed by redox reaction relating to color center and luminescent center.

The authors are noted the relation between redox reaction and NIR luminescent characteristics in Bi-doped glasses and continue the research on that by controlling melting temperature, glass composition and melting atmosphere, and discovered colorless and transparent Bi-doped soda-lime silicate glass which exhibits broad near-infrared luminescence [6]. Here, the effect of melting atmosphere on the redox reaction of Bi-doped glasses is investigated and the color center and luminescent center of these glasses are discussed.

2. Experimental

2. 1. Sample Preparation

The compositions of glasses studied are $72SiO_2 \cdot 2Al_2O_3 \cdot 4MgO \cdot 8CaO \cdot 13Na_2O \cdot 1K_2O \cdot 0.5 Bi_2O_3 \cdot XCarbon$ (wt %, X=0, 0.5, 1.0, 1.5), and the base glass composition is the typical window glass. Hereafter, these glasses are referred to as C-X.

High purity silica sand, alumina and reagent grade chemicals of Na_2CO_3, K_2CO_3, MgO, $CaCO_3$, Bi_2O_3 and carbon were used as raw materials. In order to control the melting atmosphere, carbon was
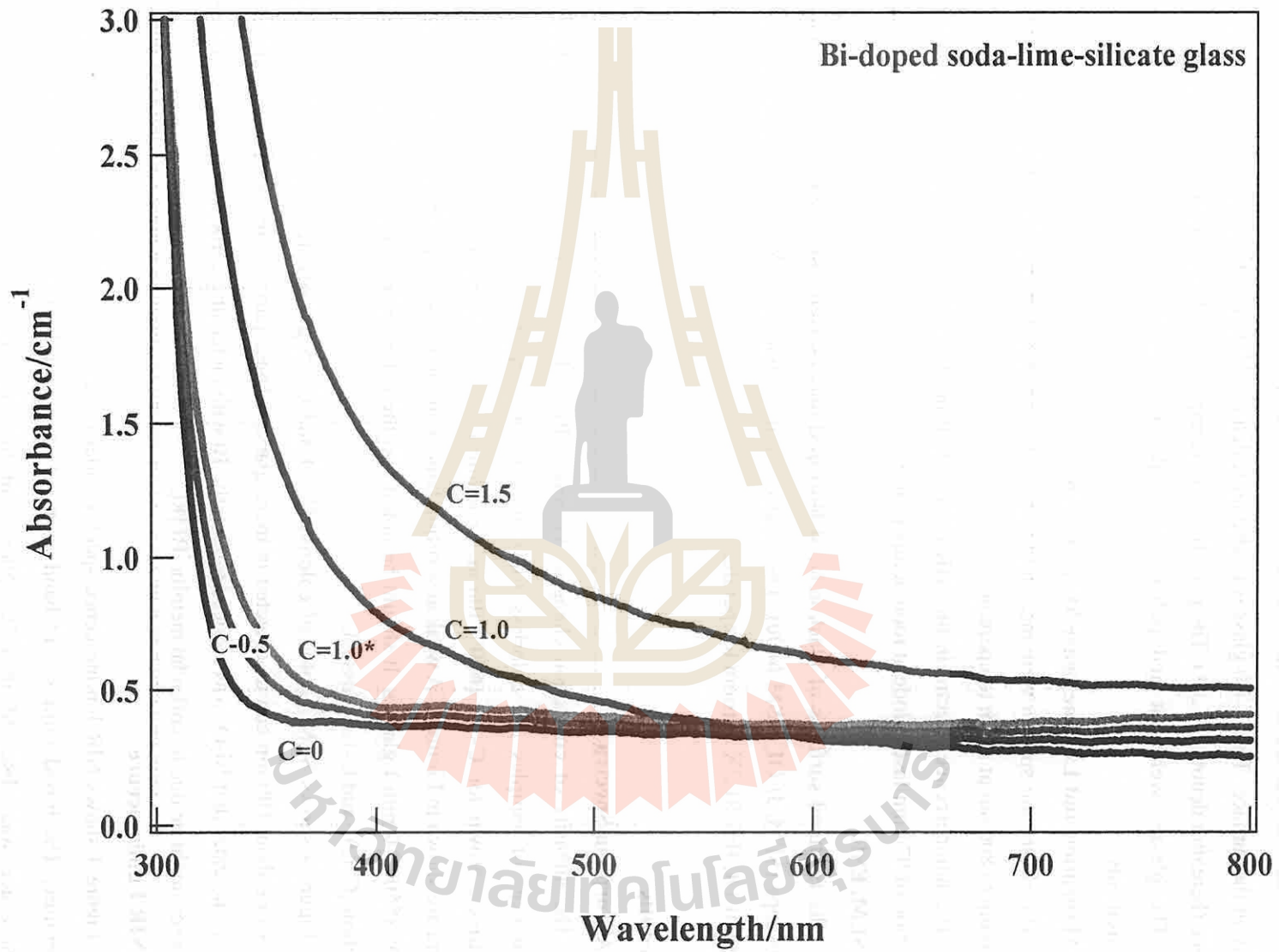
Fig. 1. UV-VIS absorption spectra of soda-lime-silicate glasses melted under various conditions.

added to batches. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucibles at 1450°C for 1 h in an electric furnace in air. After melting they were poured onto an iron plate and pressed by other one. Then they were annealed at 650°C for 30 min and cooled slowly in the furnace. The C-1.0 glass was also annealed at 550°C for 0 min and cooled slowly in the furnace (hereafter denote C-1.0*). The glass transition temperature (Tg) of these glasses is 550°C.

The glasses were cut and polished optically into about 2 mm in thickness for optical measurements.

2. 2. Absorption and Luminescence Measurements

The absorption spectra were measured with a Cary 5E UV-VIS-NIR Spectrometer in the range of 300 nm to 800 nm at room temperature.

The luminescence spectra in the NIR region (950 nm to 1,650 nm) were measured under the excitation of 974 nm laser diode at room temperature.

2. 3. SEM, ESR

The fractured surfaces of black colored Bi-doped glasses were observed by scanning electron microscope (SEM, JEOL, JSM 6400). The electron spin resonance (ESR) spectra were measured by using a JEOL JES-RE2X at room temperature.

3. Results

3. 1. Absorption Spectra

The intensity of coloration changes systematically with the amount of carbon addition. The appearances of samples are colorless for C-0 and C-0.5, faint yellow for C-1.0* (550°C-0min. annealing), brown for C-1.0 (650°–30min. annealing) and black-brown for C-1.5. The absorption spectra are shown in Figure 1. A weak absorption band at around 450 nm can be observed in C-0.5 and C-1.0* (550°C-0 min.) glasses. It should be noted that the color changes by the change of annealing condition (C-1.0* and C-1.0 glasses).

Figure 2 shows SEM photos of colored C-1.0 and C-1.5 glasses. It is clearly seen that small particles of about 100 nm can be detected in these glasses. These particles might be colloidal metallic Bi. This indicates that Bi_2O_3 was reduced to metallic Bi with increasing carbon content. The coloration of glasses might be due to colloidal metallic Bi [8].

3. 2. NIR Luminescence

Figure 4 shows NIR luminescence spectra under the excitation of 974 nm laser diode at room temperature. The broad luminescent band centered at around 1200 nm is detected. The strongest luminescence was observed in C-0.5 glass, and the intensity of luminescence decreases with increasing amount of carbon. No NIR luminescence can be observed in C-0 glass. It should be noted that the differenct luminescent characteristics was observed in C-1.0* and C-1.0 glasses. These glasses
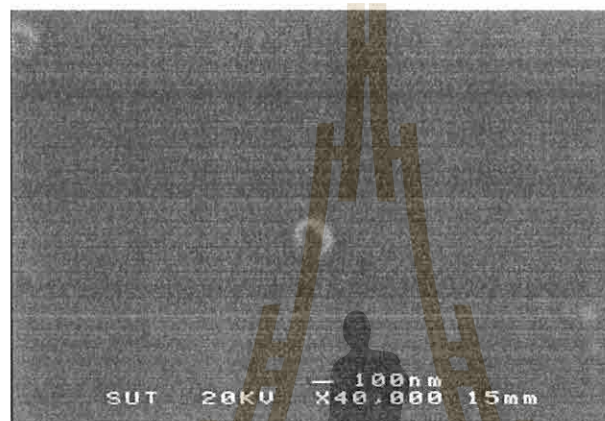
Bi-Soda-lime-silicate glass C:1.0

Bi-Soda-lime-silicate glass C:1.5

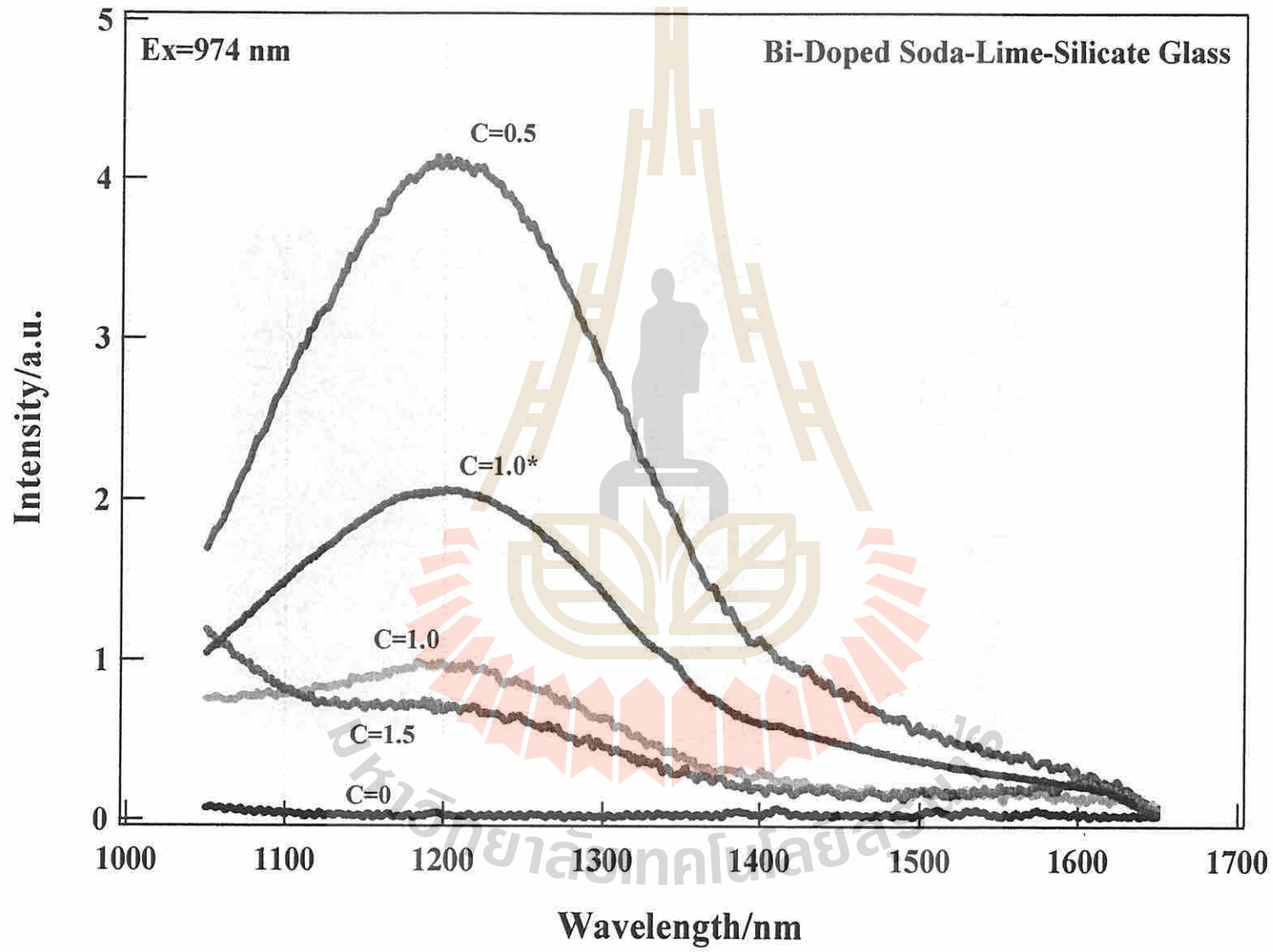Fig. 2. SEM photos of C=1.0 and C=1.5 glasses.

Fig. 3. NIR luminescence spectra of soda-lime-silicate glasses under the excitation of 974 nm laser diode.
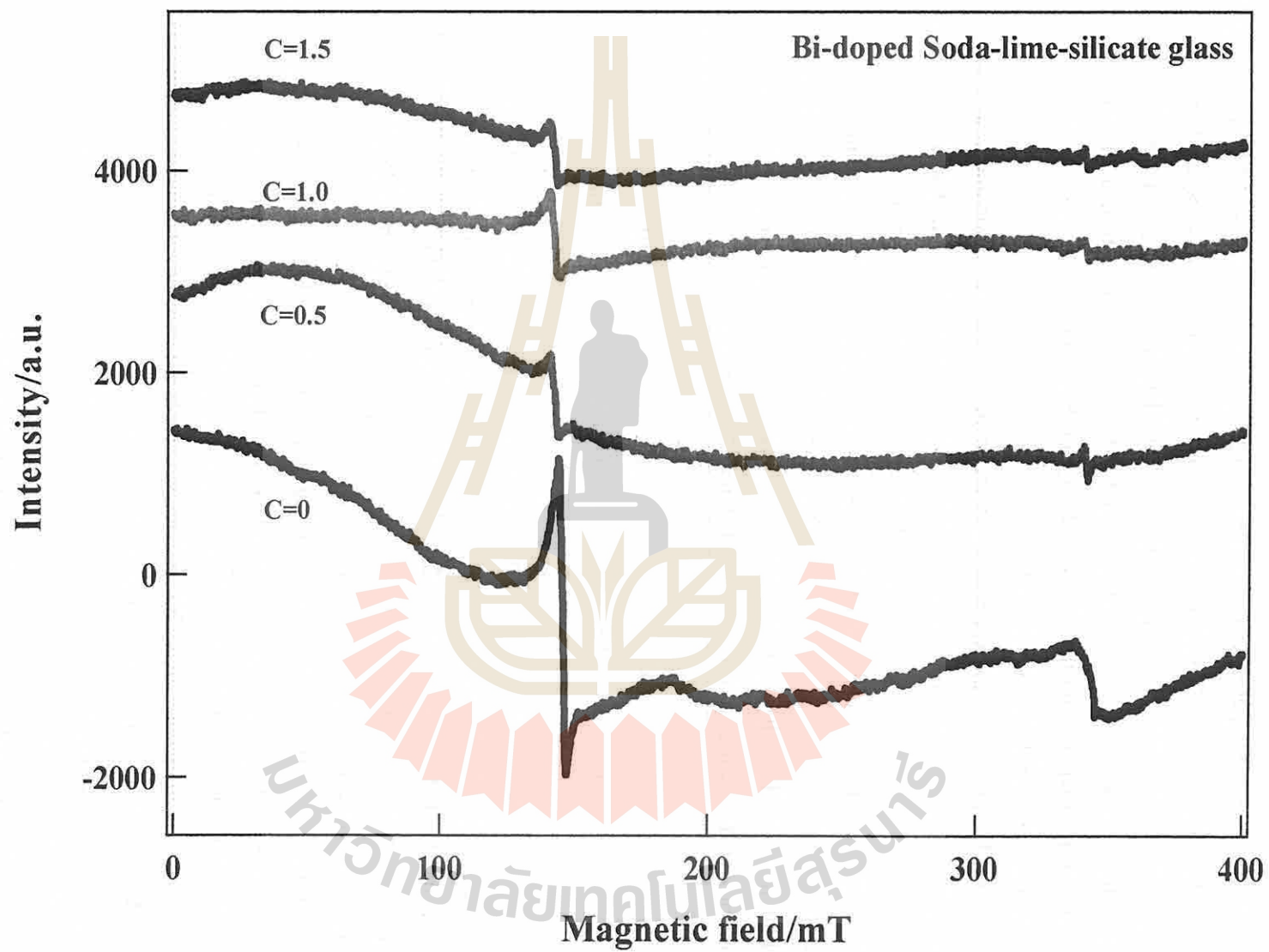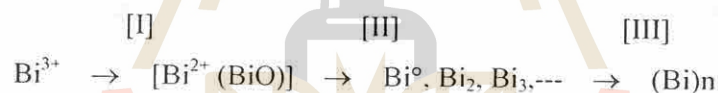
Fig. 4. ESR spectra of glasses.

have a same batch composition but different annealing condition.

4. Discussion

A weak absorption band was observed at around 450 nm in C-0.5 and C-1.0* glasses. J. Reng et al. [4] and Sumimiya et al. [12] have also observed the absorption band at same position. On the other hand, however, Fujimoto et al. [1,2], Peng et al. [3] and Khonthon et al. [5] observed the absorption bands at different positions, around 500 nm and 700 nm. This suggests that the absorption band observed here is different from the observed absorption bands previously, 500 nm and 700 nm. This means the presence of different color centers.

It was observed the glass annealed at lower temperature is less color and exhibits an intense luminescence than that annealed at higher temperature despite the same batch composition and melting condition (C-1.0* and C1.0 glasses). This result suggests the formation process of color center and luminescent center. As mentioned previously, Bi^{3+} ion and Bi colloids are dominant in C-0 glass (without carbon) and C-1.5 glass (highest carbon), respectively, and these species do not contribute NIR luminescence. This change in valence state can exactly be considered as a redox reaction with carbon amount. The change in valence state of Bi may be written by:

$$
\begin{array}{ccccc}
 & [\text{I}] & & [\text{II}] & & [\text{III}] \\
Bi^{3+} & \rightarrow & [Bi^{2+}(BiO)] & \rightarrow & Bi^{\circ}, Bi_2, Bi_3, \text{---} & \rightarrow & (Bi)n
\end{array}
$$

It seems that the phenomenon observed here may be the process [IV]. Atomic or molecular Bi gathers together, grows and forms the colloid. This process is often observed in the formation process of noble-metal colloid [13]. Therefore, the glass becomes to be black in color and the NIR luminescence decreases with the formation of Bi colloid. Thus, the origin of color center and NIR luminescent center is likely to be caused by Bi cluster, such Bi, Bi_2, Bi_3, Bi_4 etc.

In order to confirm the color center and luminescent center, the ESR spectra were measured. Figure 4 shows ESR spectra of glasses. Two ESR signals were observed at g~4.24 and g~2.0 in all glasses. The intensity of the ESR signal at g~4.24 decreased markedly with increasing amount of carbon. This signal is believed to be due to impurities, such as Fe^{3+} ion [14]. Thus the concentration of Fe^{3+} ion decreases with increasing amount of carbon addition.

The authors [5] detected the ESR signal at g~2.0 in Bi-doped spinel glass and glass-ceramics which exhibited NIR luminescence.

On the contrary, ESR signal at g~2.0 was not detected in C-0 glass, the intensity of this signal reached the maximum at C-0.5 and decreased gradually with increasing amount of carbon addition. The authors [5] detected the ESR signal at g~2.0 in Bi-doped alkaline-earth alumino-silixcate glass

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and glass-ceramics which exhibited NIR luminescence, and hence, this signal may relate to color center or luminescent center of Bi-doped glasses. However, the origin of this signal is still unknown.

4. Conclusion

The effect of melting atmosphere on coloration and near-infrared luminescent characteristics of Bi-doped soda-lime-silicate glass was investigated by adding various amount of carbon to the batch, and the origin of NIR luminescence was also discussed.

The appearance of these glasses changed systematically from colorless/transparent to deep brown by the amount of carbon addition. A very weak absorption band can be observed at around 450 nm in glass melted in mild reducing condition. A broad near-infrared luminescence peaking at about 1200 nm was observed in the glass melted under mild reducing condition. This glass was colorless and transparent.

It is suggested that the color center and luminescent center is likely to be caused by reduced Bi species such as Bi_2, Bi_3, Bi_4 by considering the change in valence state of Bi based on redox equilibrium.

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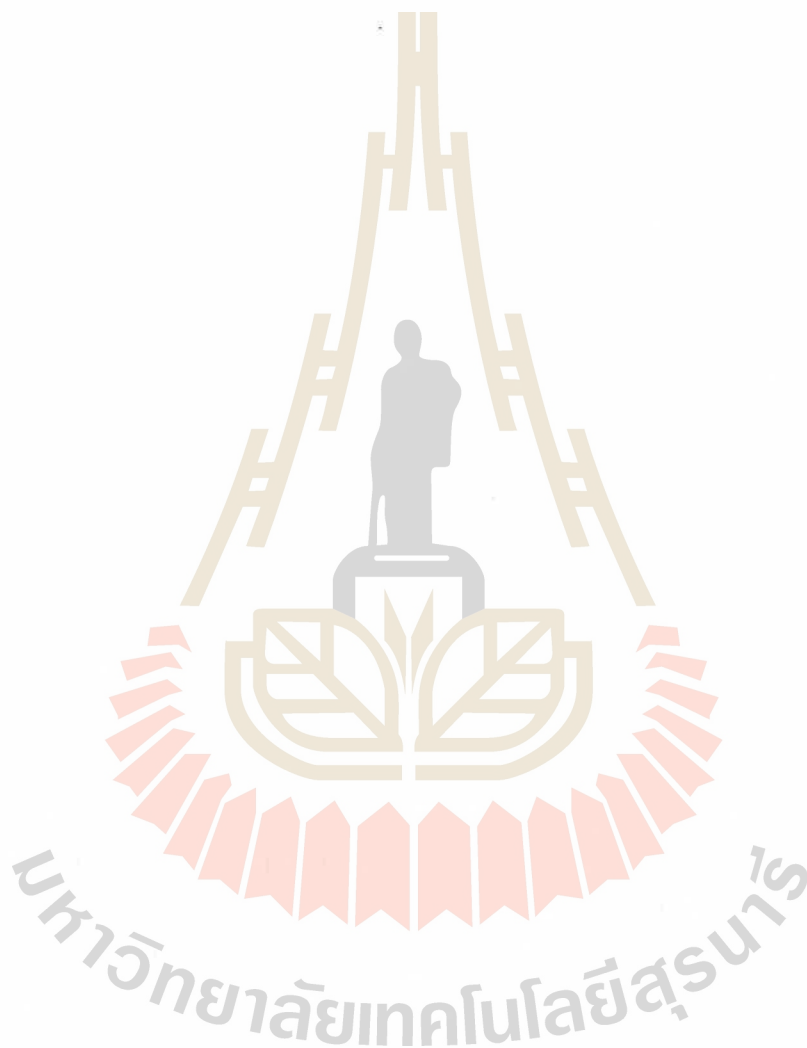
IV. NIR Luminescence Characteristics of TeO$_2$-Containing Glasses

IV-1. Melting temperature and glass composition dependence on the NIR luminescence characteristics of Te-containing borate glasses

Abstract

The effects of melting temperature and glass composition on the Near-infrared (NIR) luminescent characteristics of Te-containing borate glasses are investigated and compared with previous works. Three absorption bands are detected at around ~370 nm, ~430 nm and ~530 nm, however, the absorption band at around ~600 nm could not be detected in all borate glasses. And no NIR luminescence was observed under the excitation of a 974 nm laser diode. The NIR luminescence was observed in Te-green and Te-purple glasses, which showed the absorption band at around ~600 nm. This absorption band was ascribed to $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te$_2^-$. Consequently, it is suggested that the NIR luminescence of Te-containing green and purple glass seems to be due to Te$_2^-$ center.

1. Introduction

Among non-silicate glasses, such as heavy metal oxide and non-oxide glasses, high TeO$_2$ containing glasses are promising candidate materials for photonics applications, unifying the following features (1) wide transmission window, (2) good glass stability and durability and (3) high refractive index, better non-linear optical properties and relatively low phonon energy. Broad band erbium doped fiber amplifiers (EDFAs) have been demonstrated using TeO$_2$-based fibers as erbium hosts [1, 2].

However, high TeO$_2$ containing glasses often show coloration, pale green, brilliant purple to dark red, depending on glass composition and melting conditions [3, 4]. The color centers of these glasses have already been reported [4, 5]. According to their reports, the color centers of pale green glasses are clusters of Te$_2$ and Te$_2^-$ species [5] and those of brilliant purple glasses are Te metallic colloids [4].

Recently, the authors have found near-infrared (NIR) luminescence centered at 1250 nm with 250 nm of half width from pale green and purple TeO$_2$-containing glasses for the first time to our knowledge [6, 7]. We concluded that NIR luminescent centers might be Te$_2$ or Te$_2^-$ species. Thus, the valence state of Te may change depending on glass composition and melting conditions, which produce color center and luminescent center in the glasses. In this study, the effects of melting temperature and glass compositions on the NIR luminescent characteristics of Te-containing borate glasses are investigated and compared with previous works [6, 7].

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2. Experimental

2.1. Sample preparation

Two series of glasses were prepared. Glasses of Series I are the composition of $62B_2O_3 \cdot 9Al_2O_3 \cdot 9ZnO \cdot 9K_2O \cdot 10TeO_2$ (mol%), those of Series II are $90[(80-X)B_2O_3 \cdot 10Al_2O_3 \cdot 10ZnO \cdot XK_2O] \cdot 10TeO_2$ (mol%, X=0, 10, 20 and 30). Reagent grade chemicals of H_3BO_3, Al_2O_3, ZnO, K_2CO_3 and TeO2 were used as raw materials. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucibles under various conditions (850°~1300°C for 15~60 min) in an electric furnace in air for Series I glasses. Glasses of Series II were melted in 50 cc alumina crucibles at 1200°C for 20 min in an electric furnace in air. After melting they were poured onto iron plate and pressed by another iron plate. Then they were annealed at 450°C for 30 min and cooled slowly to room temperature in the furnace. All glasses were polished optically into about 1.5~2.0 mm in thickness for optical measurement. Hereafter, these glasses are referred to as Te-850, Te-1000, Te-1100, Te-1200, Te-1300, X=0, X=10, X=20 and X=30, respectively.

2.2. Optical measurement

The absorption spectra (300~800 nm) were measured using a Cary 1E ultraviolet-visible (UV-VIS) spectrometer at room temperature.

The NIR luminescence spectra (1000~1700 nm) were measured under the excitation of a 974 nm laser diode at room temperature. The optical setup for NIR luminescence measurement is shown in Fig. 1. Emission from the samples was dispersed by a single monochromator (blaze, 1.0 mm; grating, 600 grooves/mm; resolution 3 nm) and detected by InGaAs photodiode.

3. Results and discussion

3.1. Appearance and absorption spectra

The colors of Series I glasses change from colorless (Te-850) to brown (Te-1300) with increase in melting temperature. In glasses of Series II, color changes from reddish orange (X=10) to colorless (X=30) with increase in X (increasing amount of K_2O). However, X=0 glass revealed phase separation during casting. The melting conditions and appearance of these glasses are summarized in Table 1.

Figure 2 shows the absorption spectra of Te-containing borate glasses. The absorption spectra were analyzed and separated into three bands using peak fitting with Gaussian distribution. The results are shown in Table 1. Basically, three absorption bands can be observed, ~370 nm (Band I), ~430 nm (Band II) and ~530 nm (Band III), respectively. The assignment of these absorption bands are already known that Band I is the exciton transition, Band II $^3\Sigma g^- \rightarrow ^3\Sigma u^-$ transition of Te_2 and Band III Te metallic colloids[4), 5)]. In Series I glasses, the UV absorption increases with an increase in melting temperature. It seems that the melting temperature affects the change in valence of Te. According to
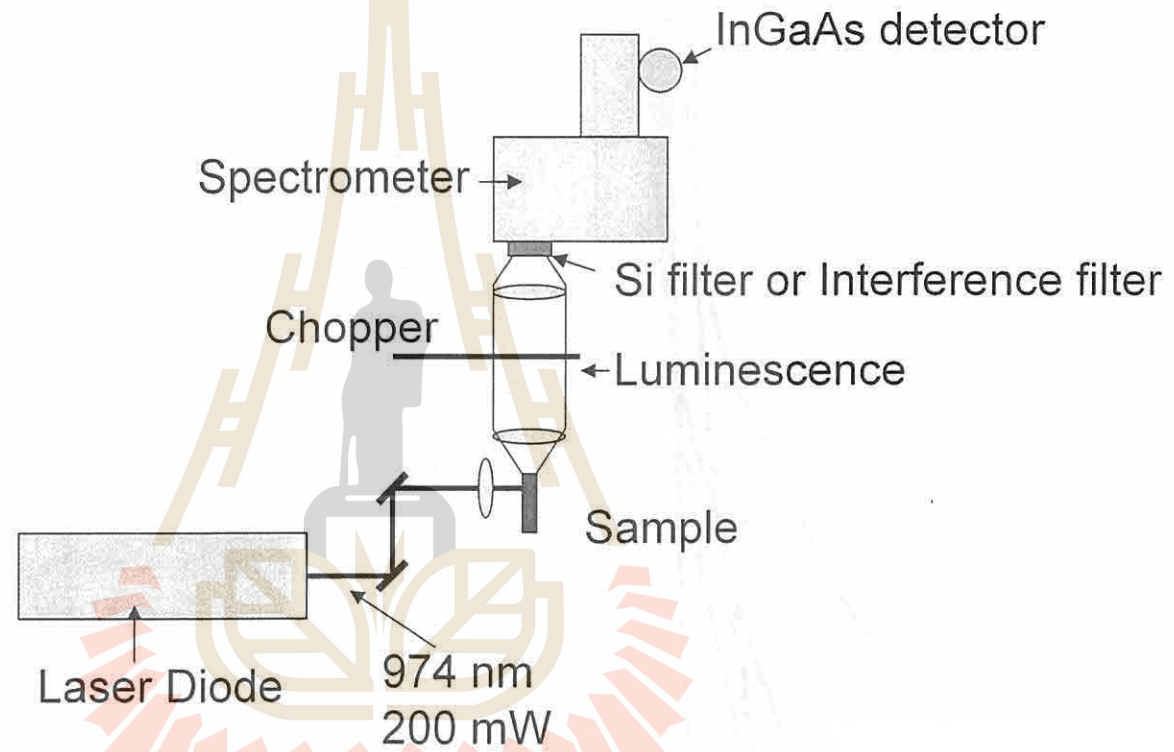
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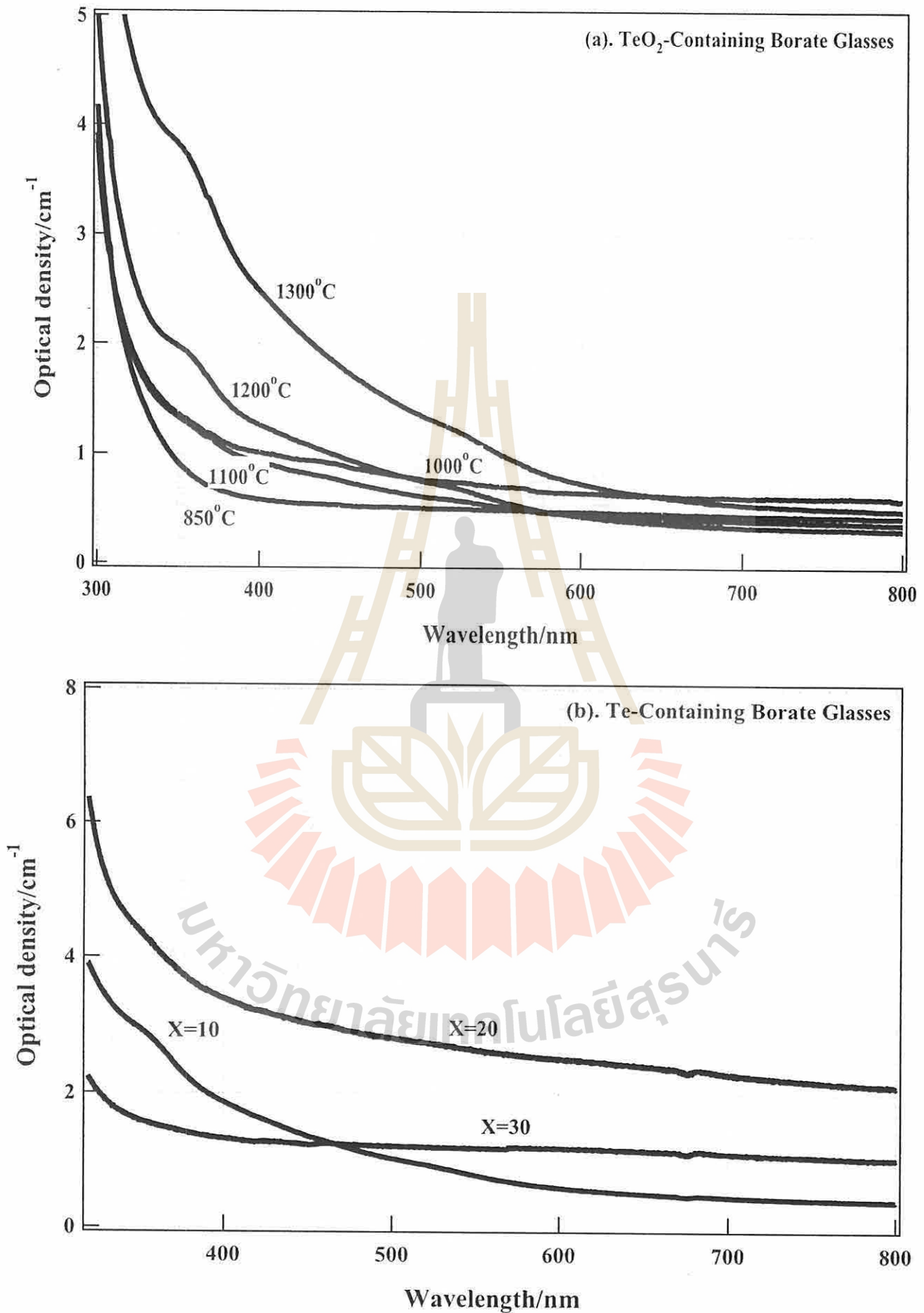Fig. 1. Optical setup for NIR luminescence measurement.

Fig. 2. Absorption spectra of Te-containing borate glasses.
(a) Effect of melting temperature, (b) Effect of glass composition.

Table 1. Melting conditions, appearances and absorption bands.

Glass No.	Melting condition °C–min.	Appearance	Absorption bands/nm			
			I	II	III	IV
Te-850	850-60	Colorless	-	-	-	-
Te-1000	1000-20	Pale orange	370	430*	530*	-
Te-1100	1100-20	Orange brown	370	430*	530*	-
Te-1200	1200-20	Reddish orange	370	430*	530	-
Te-1300	1300-15	Reddish brown	370	430*	530	-
X=0	1200-20	Phase separation	-	-	-	-
X=10	1200-20	Reddish orange	370	430*	530*	-
X=20	1200-20	Pale orange	370	430*	530*	-
X=30	1200-20	Colorless	-	-	-	-
ZTP[6]	1200-60	Brilliant purple	375	417	537	600
Te-SL[6]	1450-60	Pale green	374	444	526*	625
Te-Spinel [6]	1600-60	Brownish pink	-	420 488*	556	599

*: very weak

redox equilibrium, the higher melting temperature provides a lower valence state of metal ions, and hence the increase in UV absorption might be due to the Te species of a lower valence state.

However, these spectral patterns are different from those reported previously (ZTP, Te-SL and Te-Spinel in Table 1) [6]. The former three absorption bands are the same, but Band IV can not be detected in all borate glasses discussed in this study. The assignment of Band IV has already been done and is ascribed to $^2\Pi g \rightarrow ^2\Pi u$ transition of Te_2^- [5]. It is considered that the color center of Te_2^- is lacking in all borate glasses from these results. Lindner et al. [5] reported that the absorption band due to Te_2^- appeared at 606 nm in Te-doped blue and green sodalite crystal. This position is nearly the same as those in ZTP, Te-SL and Te-Spinel glasses. Thus, the absorption band due to Te_2^- center appeared at around 600 nm in many host materials. If Te_2^- centers are present in borate glasses, the absorption band should appear at around 600 nm. However, this band could not be detected in all borate glasses, and therefore, it is concluded that Te_2^- center is lacking or of a very low concentration in borate glasses.

Te_2 or Te_2^- species may be formed during reduction process of TeO_2 to metallic colloids $(Te)n$ in glasses and they gather together and precipitate Te metallic colloids[4]. Zinc tellurium phosphate glass

(ZTP) appeared to be brilliant purple and many small particles were observed by scanning electron microscope (SEM) observation in this glass [6]. These particles were confirmed to be Te-metallic colloids and the strong absorption at around 537 nm was derived from the surface plasmon resonance absorption of Te-metallic colloids [4]. This glass contained the same amount of TeO_2 (10 mol%) as that in borate glasses and was melted at nearly the same temperature (1200°C-2h). This indicates that ZTP glass was prepared under higher reducing condition than borate glasses. According to Duffy's optical basicity concept [8], Λ values for both glasses were calculated without TeO_2: ZTP: 0.42 and X=0: 0.46, X=10: 0.50, X=20: 0.55 and X=30: 0.59, respectively. The Λ value of ZTP is smaller than those of borate glasses. The smaller Λ value provides higher reducing condition, and therefore, a large amount of Te metallic colloids (Te)n was formed in ZTP glass compared with borate glasses. This tendency can be clearly seen in Series II glasses. Thus, the reduction process did not proceed enough in borate glasses and the amount of Te_2 or Te_2^- species seems to be very low. This implies the lacking or very weak absorption of Band IV in borate glasses.

3.2. NIR luminescence

No NIR luminescence can be detected in all borate glasses under the excitation of 974 nm laser diode at room temperature. However, as reported previously[6),7)], ZTP, Te-SL and Te-Spinel glasses and glass-ceramics exhibited NIR luminescence centered at around 1200~1250 nm (Fig.3).

In Table 1, the color center of borate glasses is different from those of ZTP, Te-SL and Te-Spinel glass and glass-ceramics. Especially, the band IV (~600 nm) is lacking in all borate glasses. This color center has been ascribed to Te_2^-. Murata et al. [9] discussed the NIR luminescence characteristics of various Bi-doped glasses based on optical basicity concept without any reducing agents, and they reported that the generation of NIR luminescence was affected strongly by optical basicity of base glass. They concluded that Λ of 0.4 was the critical point (above 0.4 no NIR luminescence was observed). As discussed in the previous section, the concentration of the color center due to Te_2 or Te_2^- species might be very low resulting in the lacking of absorption bands and NIR luminescence in all borate glasses. On the contrary, the Λ values for Te-SL and Te-Spinel are 0.58 and 0.47. These values are much larger than that of ZTP glass. However, a small amount of carbon was added into Te-SL glass, which was melted at the higher temperature (1450°C), and Te-Spinel glass was melted at much higher temperature (1600°C). The reducing agent and higher melting temperature enhance the reducing condition, and hence it seems that Te-SL and Te-Spinel glass and glass-ceramics exhibited NIR luminescence.

Consequently, it is suggested that the NIR luminescence of green and purple Te-containing glass seems to be due to by Te_2^-.

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4. Conclusion

The effects of the melting temperature and glass compositions on the Near-infrared (NIR) luminescent characteristics of Te-containing borate glasses are investigated and compared with previous works.

Three absorption bands are detected at around ~370 nm, ~430 nm and ~530 nm, however, the absorption band at around ~600 nm can not be detected in all borate glasses. Also no NIR luminescence was observed under the excitation of a 974 nm laser diode. The NIR luminescence was observed in Te-green and Te-purple glasses, which showed the absorption band at around ~600 nm. This absorption band was derived from $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te_2^-.

Consequently, it is suggested that the NIR luminescence of green and purple Te-containing glass seems to be due to by Te_2^-.

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IV- 2. Effect of Carbon Addition and TeO$_2$ Concentration on the Near-Infrared Luminescent Characteristics of Te-Doped Soda-lime-silicate Glasses

Abstract

The effects of carbon addition and TeO$_2$ concentration on the near-infrared (NIR) luminescent characteristics of Te-doped soda-lime silicate glasses are investigated. Three absorption bands were detected in all glasses at around 330~380 nm, ~430 nm and ~630 nm, respectively. The last absorption band (~630 nm) has been ascribed to $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te$_2^-$. The broad NIR luminescence centered at 1200 nm was detected under the excitation of 974 nm laser diode except for glasses of lower carbon addition. The NIR luminescence was found to be strongly affected by melting atmosphere and TeO$_2$ concentration. It is considered that the absorption band, ~630 nm, is related strongly to the NIR luminescence of Te-doped soda-lime-silicate glasses. Consequently, it is suggested that the origin of NIR luminescence detected in Te-doped soda-lime-silicate glasses is likely to be caused by Te$_2^-$ center.

1. Introduction

Tellurite glasses (high TeO$_2$-containing glasses) have received much attention as promising candidates for new glass because of their special properties [1-5], high nonlinear refractive indices [6], large nonlinear optical sensitivity [6-9], relatively low phonon energy in blue [10] and green band emission [11], wide transmission window and good stability [3, 4, 12, 13]. In addition these glasses are well known to be good hosts for some rare earth and heavy metal ions with small multi-phonon decay rate [6, 14, 15], and they are potential materials for up-conversion lasers [16, 17], optial fiber amplifiers [18], such as tellurite-base Er-doped fiber amplifier [19], non-linear optical devices, such as optical switching [6], optical memory, etc. [6].

However, high TeO$_2$ containing glasses often show the coloration, pale green to brilliant purple, depending on glass compositions and melting conditions [20, 21]. Few researchs [20, 22] has been reported on the coloration and color centers of TeO$_2$-containing glasses, their coloration change from pale green to brilliant purple depending on melting conditions and glass compositions. The color center of pale-green TeO$_2$-containing glasses is clusters of Te: Te$_2$ and Te$_2^-$ [22], and that of brilliant purple TeO$_2$ glasses is Te metallic colloids [20].

Recently, the authors have found near-infrared (NIR) luminescence centered at 1250 nm with 250 nm of half width from pale-green and purple TeO$_2$-containing glasses for the first time to our knowledge [23-25], and we concluded that NIR luminescent center might be Te$_2$ and Te$_2^-$. In this paper, the effects of carbon addition and TeO$_2$ concentration on the NIR luminescent characteristics of

Te-doped soda-lime-silicate glasses are investigated and compared with previous work [23].

2. Experimental

2. 1. Sample preparation

Two series of glasses were prepared. Glasses of series I were the composition of $72SiO_2 \cdot 2Al_2O_3 \cdot 4MgO \cdot 8CaO \cdot 13Na_2O \cdot 1K_2O \cdot 1TeO_2 \cdot XCarbon$ (X=0~1.0, wt%), and those of series II were $72SiO_2 \cdot 2Al_2O_3 \cdot 4MgO \cdot 8CaO \cdot 13Na_2O \cdot 1K_2O \cdot XTeO_2 \cdot 0.3Carbon$ (X=0.2~2.0, wt%).

High purity silica sand, alumina, reagent grade chemicals of MgO, $CaCO_3$, Na_2CO_3, K_2CO_3, carbon and TeO_2 were used as raw materials. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucible at 1450°C for 1h in an electric furnace in air. After melting they were poured onto iron plate and pressed by another iron plate. Then they were annealed at 600°C for 30 min and cooled slowly to room temperature in the furnace.

The glasses were cut and polished optically into about 2.0 mm in thickness for optical measurement. Hereafter, these glasses are referred to as C-0, C-0.1, C-0.2, etc. for series I glasses and Te-0.2, Te-0.5, Te-0.7, etc. for series II glasses, respectively.

2.2. Optical measurement

The absorption spectra (300 ~ 800 nm) were measured using Cary 1E ultraviolet-visible (UV-VIS) spectrometer at room temperature.

The NIR luminescence spectra (1000 ~ 1700 nm) were measured under the excitation of 974 nm laser diode at room temperature. Emission from the sample was dispersed by a single monochromator (blaze< 1.0 mm; grating, 600 grooves/mm; resolution, 3 nm) and detected by an InGaAs photodiode.

3. Results and discussion

3. 1. Appearance and absorption spectra

The appearances of Series I change from colorless (C-0) to dark green (C-1.0) with increase in the amount of carbon. In glasses of Series II, colors change from green (Te-0.2) to pale green (Te-2.0) with increasing amount of TeO_2. Figure 1 shows absorption spectra of Te-doped soda-lime-silicate glasses. Appearances and absorption bands of these glasses are summarized in Table 1.

Basically, three absorption bands can be observed in all glasses, 330~380 nm, ~430 nm and ~630 nm, respectively. In series I glasses, weak absorption bands can be detected even in C-0 glass. The absorbance increases with increase in the amount of carbon, and the absorbance is very high in whole wavelength region in C-0.5 and C-1.0 glasses.

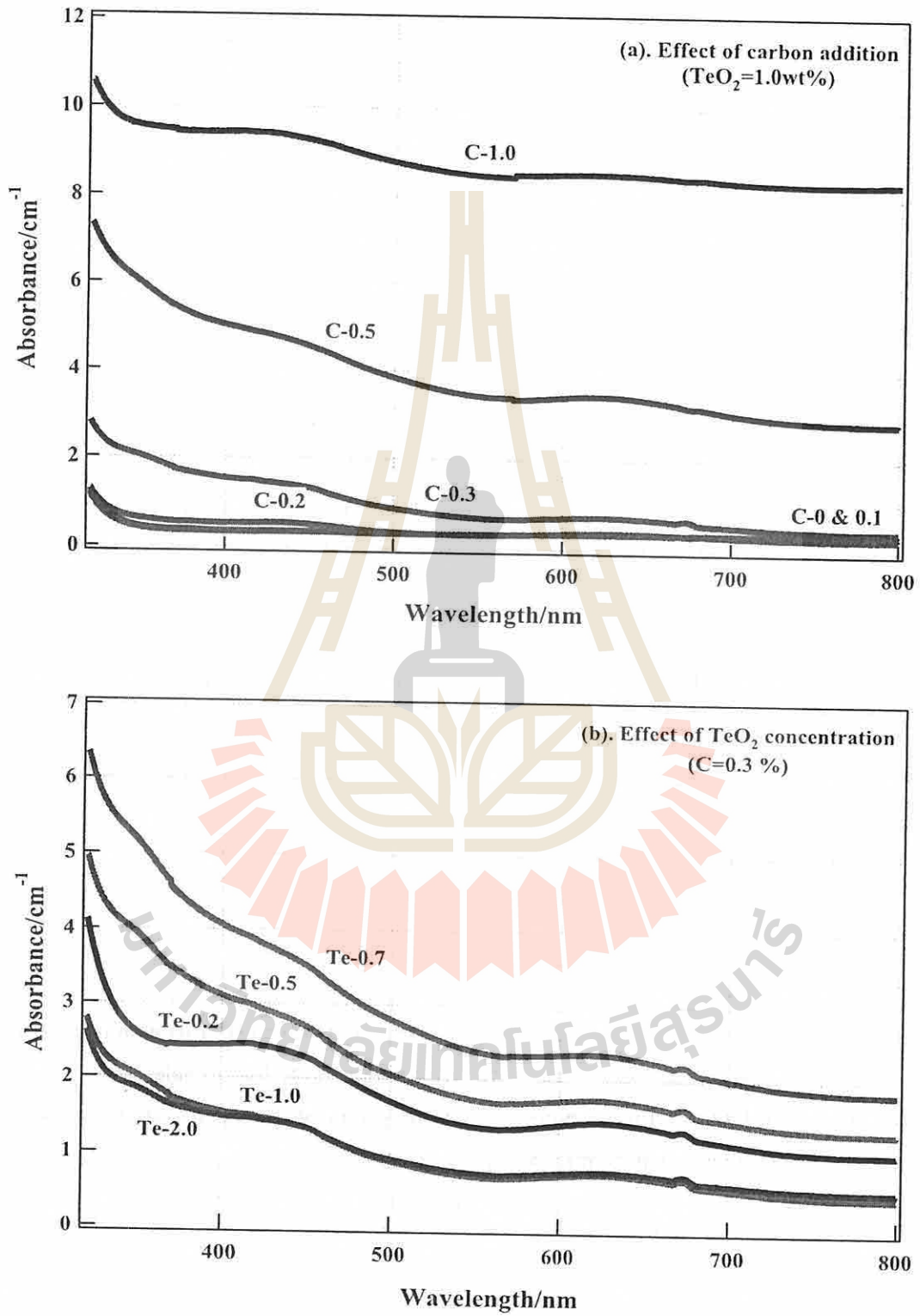On the contrary, the absorbance increases with increase in the amount of TeO_2 and decreases

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Fig. 1. Absorption spectra of Te-doped glasses. (a) Effect of carbon addition (TeO_2=1.0 wt%), (b) Effect of TeO_2 concentration (Carbon=0.3 wt%).

again in series II glasses. However, the absorption band owing to Te-metallic colloids (~530 nm) can

Table 1. Melting conditions, appearances and observed absorption bands.

No.	Melting condition	Appearance	Absorption bands/nm			
	°C–min		I	II	III	IV
C-0	1450-60	Colorless	~380	432*	–	638*
C-0.1	1450-60	Pale green	~380	432*	–	638*
C-0.2	1450-60	Green	377	432	–	638*
C-0.5	1450-60	Dark green	355	436	–	638
C-1.0	1450-60	Dark-green	375	438	–	634
Te-0.2	1450-60	Green	367	437	–	635
Te-0.5	1450-60	Green, partly brownish green	344	432	–	634
Te-0.7	1450-60	Green, partly brownish green	349	435	–	634
Te-1.0	1450-60	Green	327	435	–	633
Te-2.0	1450-60	Pale green	331	436	–	633
Te-1200**	1200-20	Reddish orange	356	431*	523	–

*: very weak,

**: $63B_2O_3 \cdot 9Al_2O_3 \cdot 9ZnO \cdot 9K_2O \cdot 10TeO_2$ (mol%), they were melted in alumina crucible in air [25].

not be observed in all glasses discussed here.

The assignment of these absorption bands has been already known that the band I is due to exciton transition, band II $^3\Sigma g^- \rightarrow {}^3\Sigma u^-$ transition of Te_2 and band IV $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te_2^- [20, 21], respectively.

For comparison with Te-doped soda-lime-silicate glasses, the absorption bands of Te-containing borate glass are also shown in Table 1. The band III was observed but band IV could not be detected in borate glasses.

3.2. NIR luminescence

Figure 2 shows the NIR luminescence spectra of glasses under the excitation of 974 nm laser diode at room temperature. In these glasses, the strong and broad emission can be observed at around 1200 nm except for glasses of lower carbon addition (C-0, C-0.1 and C-0.2 glasses). In series I glasses, the luminescence untensity increases with increase in the amount of carbon (Fig. 3(a)). On the contrary,
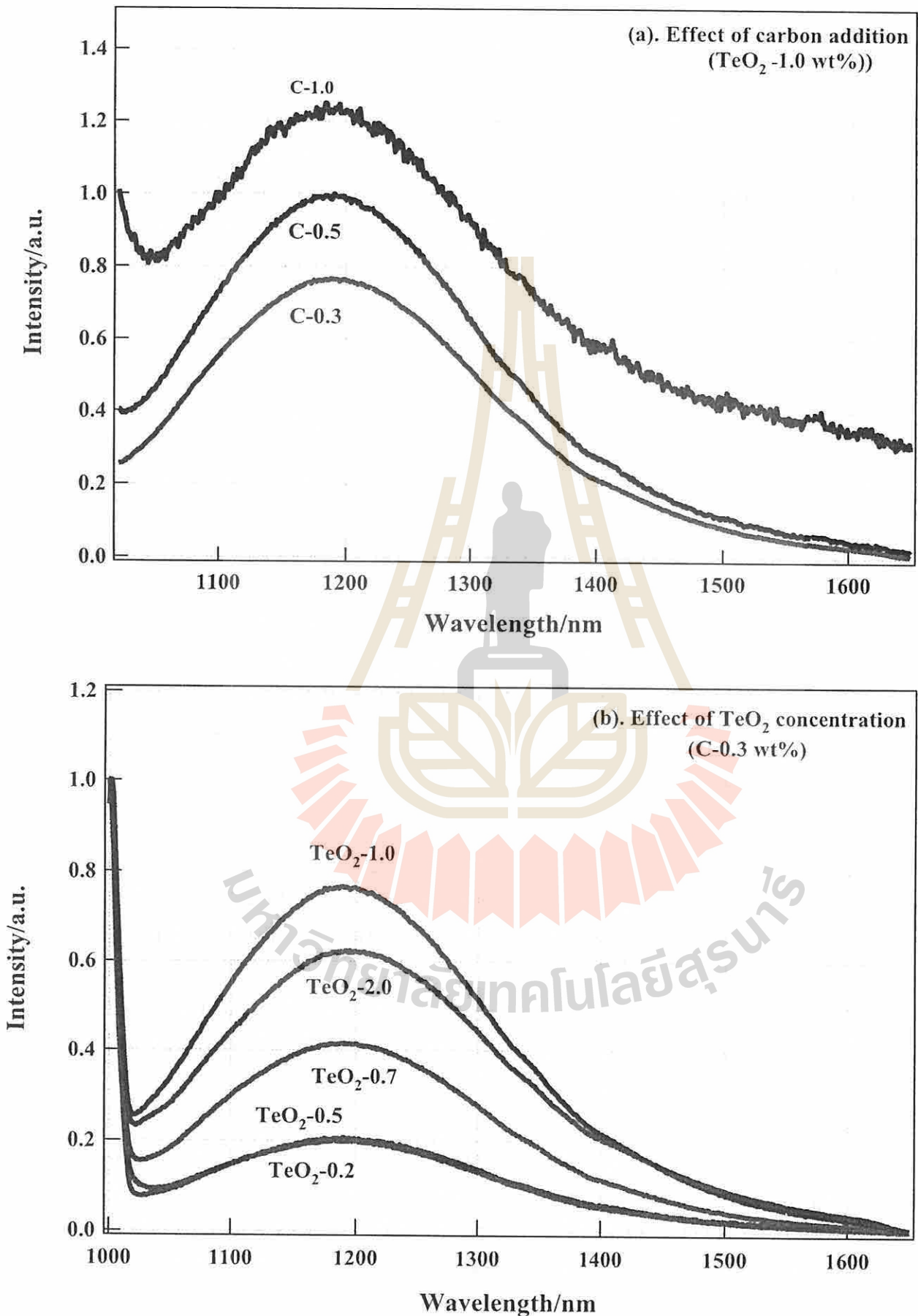
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Fig. 2. NIR luminescence spectra of Te-doped glasses. (a) Effect of carbon addition (TeO$_2$=1.0 wt%), (b) Effect of TeO$_2$ concentration (Carbon=0.3 wt%).
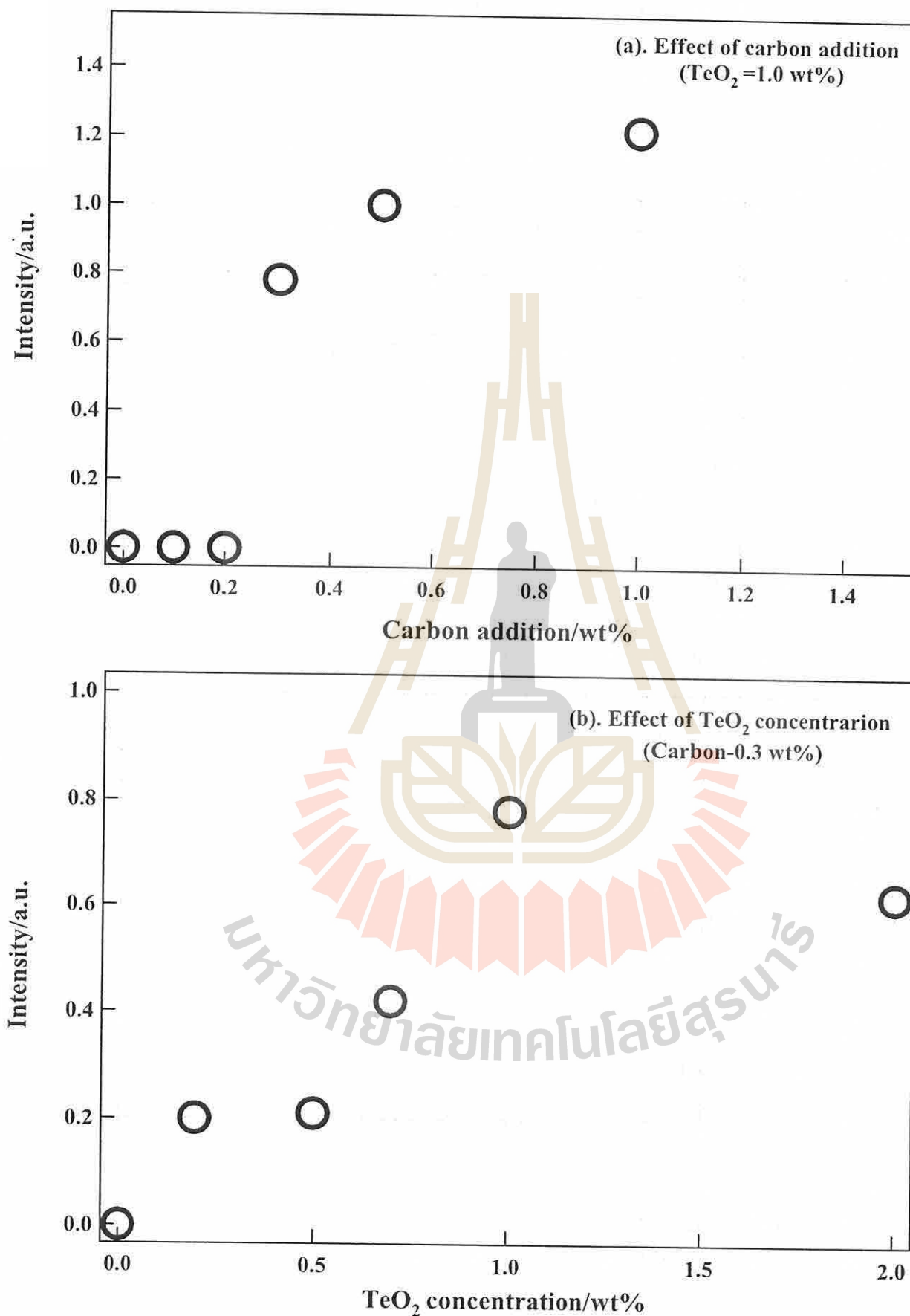
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Fig. 3. NIR luminescence intensity of Te-doped glasses. (a) Effect of carbon addition (TeO$_2$=1.0 wt%), (b) Effect of TeO$_2$ concentration (Carbon=0.3 wt%).

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the luminescent intensity of series II glasses increases with increase in TeO_2 concentration and reaches the maximum at TeO2 = 1.0 wt% and decreases slightly again at TeO_2 = 2.0 wt% (Gig. 3(b)). Thus the intensity of NIR luminescence was strongly affected by melting atmosphere and TeO_2 concentration.

The authors have investigated color generation and NIR luminescence characteristics of Te-containing borate glasses melted under various conditions [25]. Although the coloration of glasses changed depending on melting temperature and glass composition, the green-colored glass could not be obtained. In these glasses, three absorption bands were observed, ~350 nm, ~430 nm and ~520 nm, however, the band at around ~630 nm could not be detected. One example of borate glasses is shown in Table 1. As mentioned previously, the band at around ~530 nm is due to Te metallic colloids [20]. These borate glasses did not exhibit any NIR luminescence under the excitation of 974 nm laser diode.

Lindner et al. [22] have reported that two luminescence bands could be observed at 562 nm and 862 nm under the excitation of 457 nm, and they concluded that the former luminescence band was ascribed to $^3\Sigma u^- \rightarrow {}^3\Sigma g^-$ transition of Te_2 and the latter was due to $^2\Pi u \rightarrow {}^2\Pi g$ transition of Te_2^-. However, they did not observe the NIR luminescence (>1000 nm). On the contrary, band IV (~630 nm) was observed in all Te-doped soda-lime-silicate glasses discussed here, and the NIR luminescence was detected under the excitation of 974 nm except for glasses low carbon addition (C=0, C=0.1 and C=0.2). All borate glasses without absorption band IV did not show any NIR luminescence. Therefore, it is considered that the color center of band IV (~630 nm) is strongly related to NIR luminescence.

Consequently, it is suggested that the NIR luminescence detected from Te-doped soda-lime-silicate glasses is likely to be caused by Te_2^-.

4. Conclusion

The effects of carbon addition and TeO_2 concentration on the near-infrared (NIR) luminescent characteristics of Te-doped soda-lime-silicate glasses were investigated and compared with previous works. All glasses appear to be green in color. The color becomes to be deeper with increase in the amount of carbon addition at constant TeO_2 concentration. And also the color changes from green to brownish green and again pale green with increases in TeO_2 concentration at constant carbon amount. Three absorption bands were detected in all glasses at around 330~380 nm, ~430 nm and ~630 nm, respectively. The last absorption band (~630 nm) has been ascribed to $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te_2^-.

The broad NIR luminescence centered at 1200 nm was detected under the excitation of 974 nm laser diode except for glasses of lower carbon addition. The NIR luminescence was found to be strongly affected by melting atmosphere and TeO_2 concentration. It is considered that the absorption band, ~630 nm, is related strongly to the NIR luminescence of Te-doped glasses.

Consequently, it is suggested that the origin of NIR luminescence detected in Te-doped

soda-lime-silicate glasses is likely to be caused by Te_2^-.

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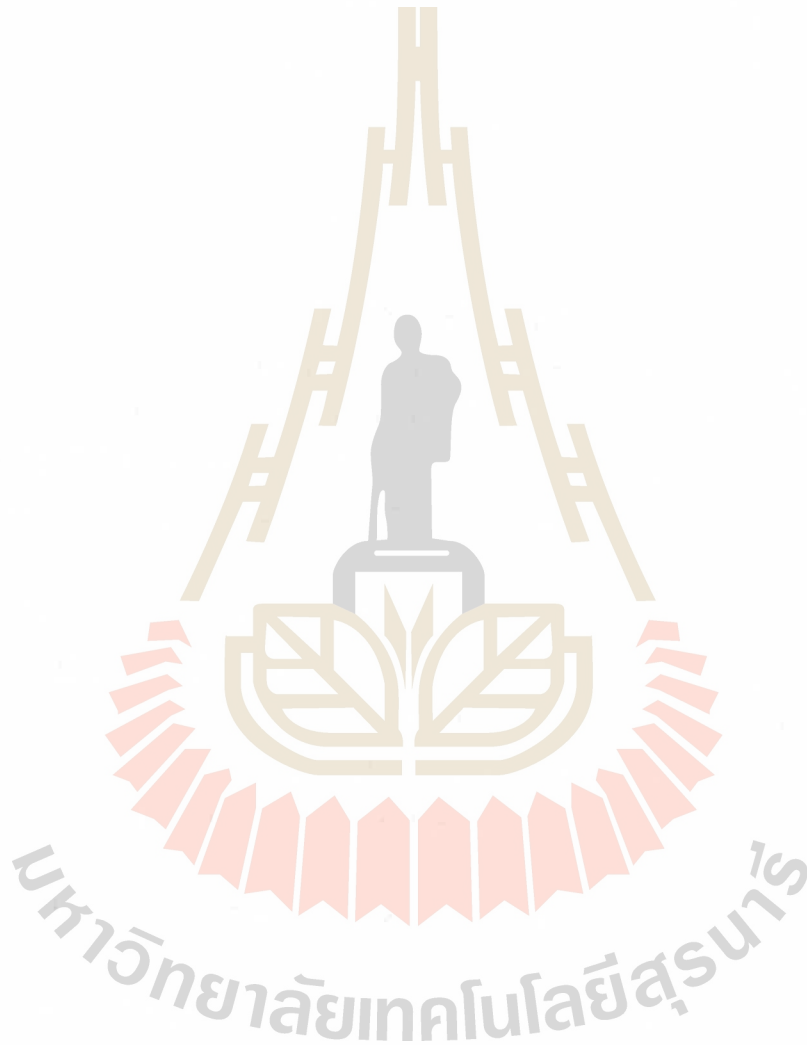
V. STRUCTURE AND PROPERTIES OF TeO$_2$- CONTAINING BORATE GLASSES

Abstract

The structure and properties of TeO$_2$–containing B$_2$O$_3$-Al$_2$O$_3$-ZnO glasses were investigated. The glass transition temperature (Tg) decreases monotonically with increase in the amount of TeO$_2$. The density and molar volume also increases and decreases gradually with increasing amount of TeO$_2$. This reveals that TeO$_2$ is incorporated into borate structure as a glass former. XANES spectra indicates that TeO$_4$ trigonal bipyramids structural units present uniformly in these glasses and this structural unit shares corners with BO$_3$ and BO$_4$ structural units.

1. Introduction

Tellurite glasses (high TeO$_2$–containing glasses) have received much attention as promising candidates for new glass because of their special properties [1,-4], high nonlinear refractive indices [5], large nonlinear optical sensitivity [5-8], relatively low phonon energy in the blue [9] and green band emission [10], wide transmission window and good stability and durability [3, 4, 11, 12]. In addition these glasses are well known to be good hosts for some rare earth and heavy metal ions with small multi-phonon decay rate [5, 13, 14] and they are potential materials for up-conversion lasers [15, 16], optical filter amplifiers [17], such as tellurite-base Er-doped fiber amplifier [11], non-linear optical devices, such as optical switching, optical memories, etc. [5].

However, high TeO$_2$-containing glasses often show the coloration, pale green to brilliant purple, depending on glass compositions and melting conditions [18, 19, 20]. This indicates that TeO$_2$ is readily reduced to low valence state species, such as Te$_2$, Te$_2^-$, (Te)$_n$, etc. according to redox equilibrium. On the contrary, glasses exhibit colorless to pale yellow melted at low temperature and higher alkali concentration [19].

In this study, properties and structure of TeO$_2$–containing borate glasses were investigated.

2. Experiment

2. 1. Sample preparation

TeO$_2$–containing borate glasses of (100-X)[80B$_2$O$_3$·10Al$_2$O$_3$·10ZnO]·XTeO$_2$ (X = 0–30) were prepared by conventional melt-quench method. High purity alumina and reagent grade chemicals of H$_3$BO$_3$, ZnO, TeO$_2$ were used as raw materials. Batches corresponding to 30 g of glass were mixed

thoroughly and melted in 50 cc alumina crucible at 1000–1200°C for 30 min depending on the glass composition in an electric furnace in air. After melting they were poured on to iron plate and pressed by another one. Then they were annealed at 400°–500°C for 30 min depending on the glass composition in the furnace, and cooled to room temperature in the furnace.

All glasses were polished optically into about 1.5–2.0 mm and also pulverized into #200 pass for DTA and X-ray absorption measurement. Hereafter, these glasses are referred to as Te-0, Te-10, Te-20, Te-30, respectively.

2. 2. Density measurement

The density of glasses was measured by Archimedes method using H_2O as a liquid at room temperature (30°C).

2. 3. DTA and TDA

The differential thermal analysis (DTA) was carried out routinely using Perkin Elmer DTA-7 at the heating rate of 10°C/min. Glass transition temperature (Tg), dilatometric softening point (Td) and thermal expansion coefficient were measured for some glasses using fused silica single push rod type dilatometer (Netsch 402E) at the heating rate of 5°C/min.

2. 4. X-ray absorption spectra

Te L_{III} (4341 eV) edge X-ray absorption near edge structure (XANES) spectra were obtained on BL-8 beam line at Siam Photon Laboratory (NSRC, Thailand). The primary beam was obtained by a double crystal Si(111) monochromator. The energy steps and scan time were 0.2 eV/step and 5 times, respectively. The FL mode was applied. The reagent grade chemical of α–TeO_2 (para-tellurite) was used as a standard.

3. Results and discussion

3. 1. Properties of glasses

The properties of glasses are summarized in Table 1. Though Te-0 glass exhibits slight opaque because of phase separation, other glasses show pale yellow to pale brown.

Figure 1 shows the composition dependence of glass transition temperature. The glass transition temperature decreases linearly with increase in X. Figure 2 shows the density and molar volume of glasses
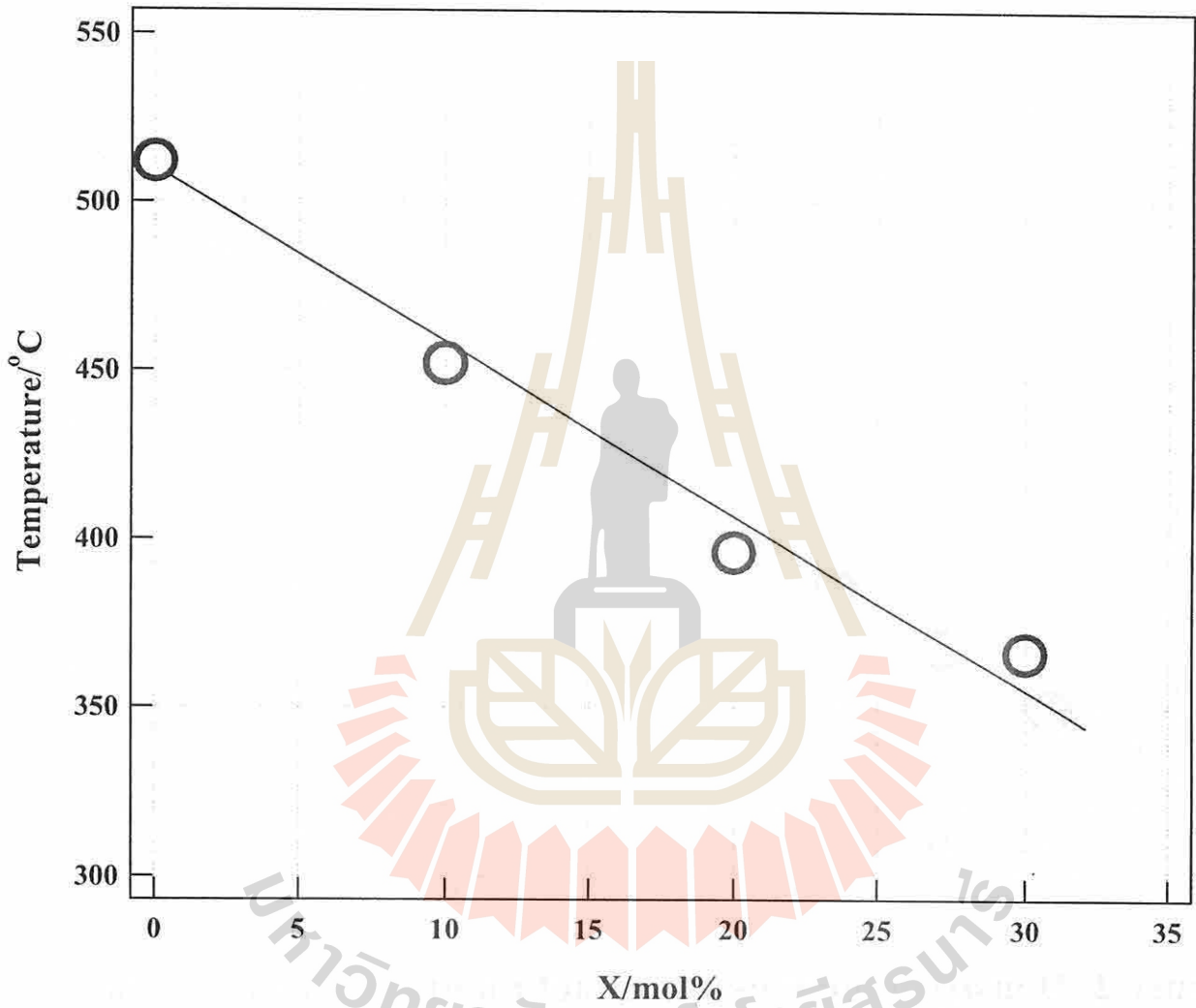
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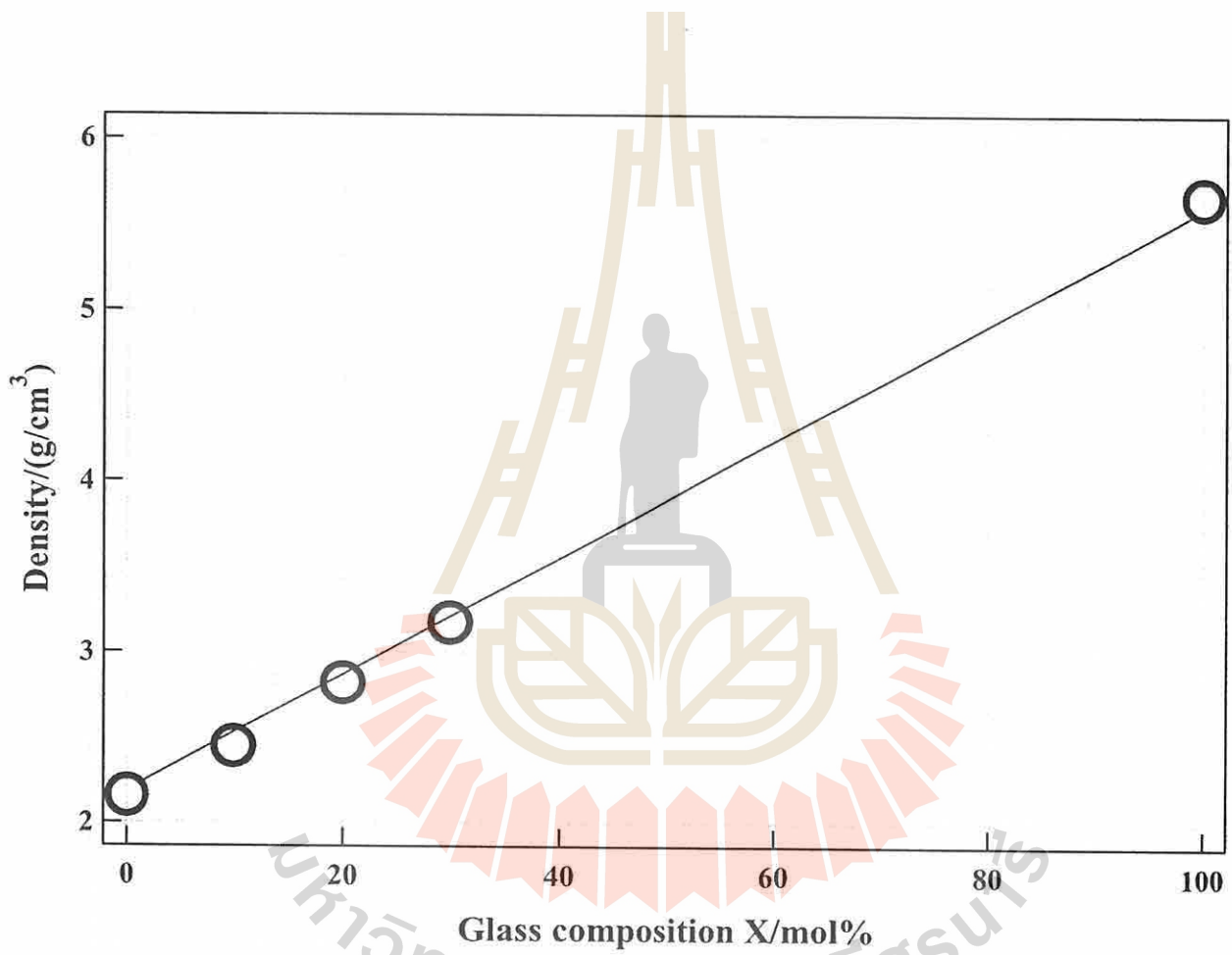**igure1. Glass transition temperature as a function of glass composition**

Figure 2. Density of glasses as a function of glass composition

Table 1. Properties of TeO_2-containing borate glasses.

Glass	Appearance	Glass transition temperature Tg/°C	Density g/cm³	Molar volume cm³/mol
Te-0	Slightly opaque*	512	2.154	34.44
Te-10	Pale yellow	452	2.445	33.78
Te-20	Pale yellow	396	2.817	32.37
Te-30	Pale brown	366	3.172	31.44
α–TeO_2 (standard)	Pale yellow (Para-tellurite)	≈ 300**	5.66	28.20

*: phase separation, **: $98TeO_2 \cdot 2Ga_2O_3$ (mol%) glass [24]

as a function of glass composition. Molar volume may be calculated as follows:

$$M.V. = Molar\ weight\ /\ density\ (cm^3/Mol) \qquad 1)$$

The density increases linearly with increase in X, on the contrary, molar volume shows different manner of change. The molar volume of TeO_2-containing borate glasses decreases almost linearly with increase in X. The density and molar volume of crystalline α–TeO_2 (para-tellurite) are also shown in these figures. By extrapolation of density and molar volume to 100% of TeO_2 (para-tellurite crystal), a good linearity can be obtained.

TeO_2 can not be formed as a glass by itself and is not pure glass forming oxides unlike SiO_2, B_2O_3, etc. However, the addition of slight amount of second oxides leads to be formed as a glass. Thus, TeO_2 can be regarded as pseudo glass forming oxide. On the contrary, borate glasses often show boric oxide anomaly, which shows the minimum or maximum in relation between properties and composition by adding modifier oxides. In these glasses, no abnormal change in properties was observed, and hence TeO_2 are incorporated into B_2O_3 network structure gradually.

3. 2. X-ray absorption spectra

Figure 3 shows the XANES spectra of Te-containing glasses. The pre peak was observed at around 4345.5 eV for all glasses and TeO_2 standard (para-tellurite). The peak position does not change, but the peak intensity changes. The XANES spectra show that the valence state of Te ions was basically 4 in all glasses. For crystalline para-tellurite, this pre-peak looks like shoulder, however, this pre-peak becomes to
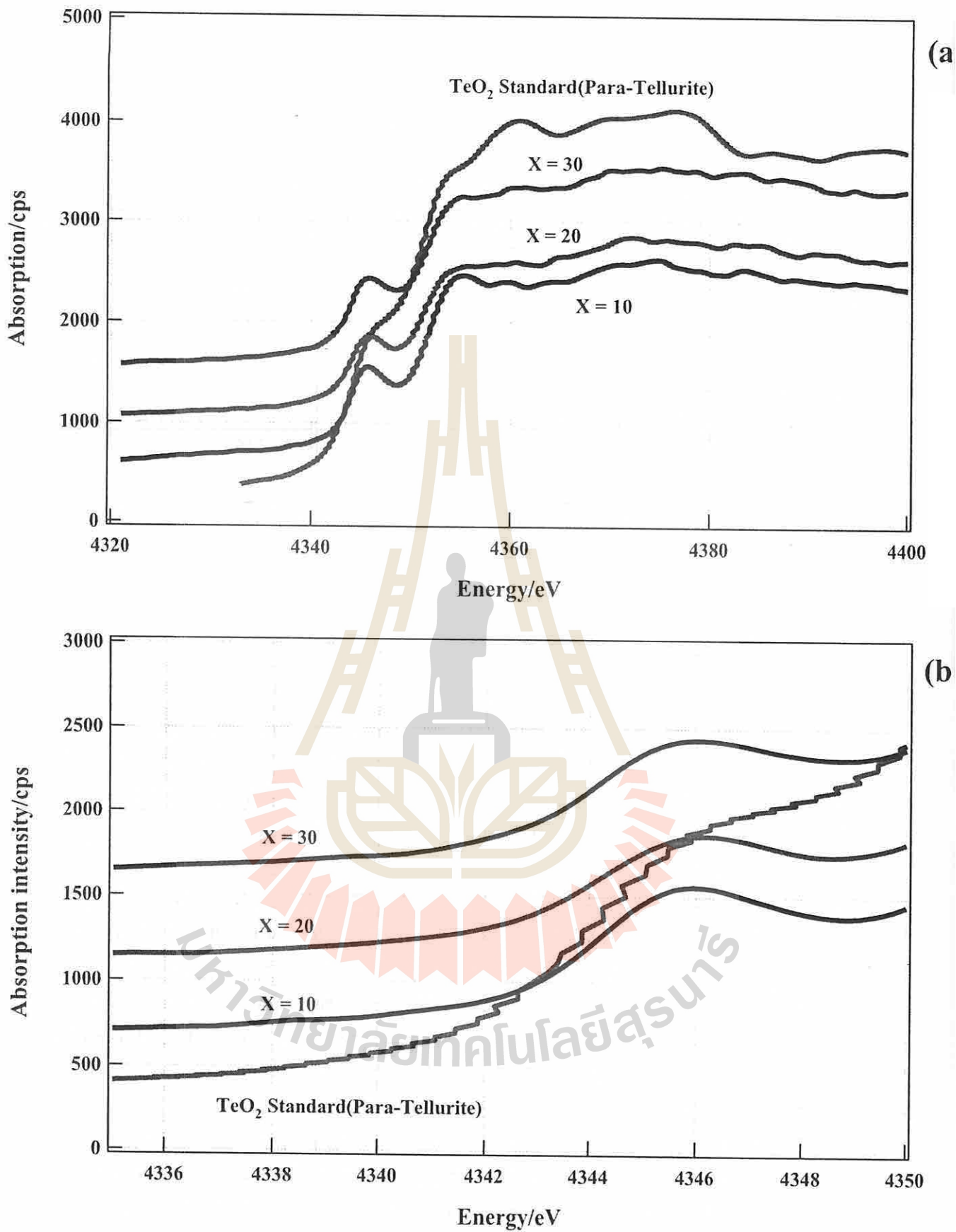
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Figure 3. Te L_III edge XANES spectra of TeO₂-containing glasses
(a) Glasses with the reference TeO₂(para-tellurite)
(b) Zoom of the pre-edge

be more clear and distinct in glasses.

In crystalline $\alpha-$ TeO$_2$ (para-tellurite), TeO$_4$ trigonal bipyramidal structural unit shares their corners and forms three dimensional structure [21]. This trigonal bipyramids structural unit is converted to trigonal pyramids by the addition of modifier oxides [22-24]. Thus, the pre-peak in XANES spectra becomes to be more clear and distinct.

However, in B$_2$O$_3$-Al$_2$O$_3$-ZnO-TeO$_2$ glasses, the amount of modifier oxide is only 10 mol% and Al$_2$O$_3$ are present. Therefore, the amount of non-bridging oxygen ions must be the minimum, and TeO$_2$ incorporated might not form trigonal pyramid. TeO$_4$ trigonal bipyramids structural unit disperses uniformly in B$_2$O$_3$ structural network and forms isolated TeO$_4$ and they share corners with BO$_3$ or BO$_4$ structural units. It seems that the intensity of pre-peak might increase.

Conclusion

The structure and properties of TeO$_2$–containing B$_2$O$_3$-Al$_2$O$_3$-ZnO glasses were investigated. The glass transition temperature (Tg) decreases monotonically with increase in the amount of TeO$_2$. The density and molar volume also increases and decreases gradually with increasing amount of TeO$_2$. This reveals that TeO$_2$ is incorporated into borate structure as a glass former.

XANES spectra indicates that TeO$_4$ trigonal bipyramids structural units present uniformly in these glasses and this structural unit shares corners with BO$_3$ and BO$_4$ structural units.

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VI. Summary and Conclusions

The color center, near-infrared (NIR) luminescent characteristics of Te- and Bi-containing glasses were investigated based on redox equilibrium. Particularly, the factors affecting the redox equilibrium, melting temperature, glass compositions and addition of reducing agent (carbon), were investigated in detail in Te- and Bi-containing borate and borosilicate glasses. And the structure and properties of Te and Bi-containing glasses were also investigated.

It was found that the formation of color center and NIR luminescence characteristics of Te- and Bi-containing glasses and glass-ceramics were strongly affected by redox equilibrium. In oxidized side, color center and NIR luminescent center were not formed, and hence the NIR luminescence could not be detected. On the contrary, the darkening effect due to the formation process of Te and Bi metallic colloids, took place in strong reduced side, and also no NIR luminescence was observed. Therefore, the color center and NIR luminescent center can be formed mild to medium reducing condition and the NIR luminescence centered at 1100 ~ 1300 nm can be detected. It is suggested that the color center and NIR luminescent center in Te- and Bi-containing glasses is likely to be caused by Te-and Bi-clusters, electron trapped Te- and Bi-clusters and Bi^+, such as, Te_2, Te_2^-, Bi_2, Bi_3, Bi_2^-,etc.

New type NIR luminescent materials of Te-doped glasses and glass-ceramics which exhibit broad NIR luminescence were discovered for the first time to our knowledge.

The glass transition temperature (Tg) decreased monotonically with an increase in TeO_2 and Bi_2O_3 contents. The density also increases linearly with increasing amount of TeO_2 in TeO_2 containing glasss. On the contrary, the molar volume of Bi-containing glasses showed the minimum at about Bi_2O_3=10 mol%, indicating boron anomaly. XANES spectra indicate that TeO_4 trigonal bipyramids structural units are present uniformly in these glasses and this structural unit shares edges with BO_3 and BO_4 structural units. And BiO_6 octahedral structural units are present in Bi-containing glasses and this structural unit shares corners with BO_3 and BO_4 structural units. Thus, it is confirmed that TeO_2 acts as glass former, but Bi_2O_3 acts as modifier.

List of Publications and Presentations

I. Publications

(1). Sasithorn Khonthon, Shigeki Morimoto, Yusuke Arai and Yasutake Ohishi, "**Luminescence characteristics of Te- and Bi-doped glasses and glass-ceramics**", *Journal of the Japan Ceramic Society*, 115 (2007) 259-263.

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Luminescence Characteristics of Te- and Bi-Doped Glasses and Glass-Ceramics

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The luminescence characteristics of Te- and Bi-doped glasses and glass-ceramics were investigated and the origin of coloration and near infrared luminescence was discussed. The colorations of these glasses and glass-ceramics might be due to the elemental clustering, such as Te_2/Te_2^- and Bi_2/Bi_2^-. The broad near infrared (NIR) luminescence can be detected in Te- and Bi-doped glasses and glass-ceramics. The electron spin resonance (ESR) signal at $g \approx 2.0$ was observed in Te- and Bi-doped glasses and glass-ceramics, which exhibit NIR luminescence, and therefore this ESR signal is strongly related to the NIR luminescence. The ESR signal at $g \approx 2.0$ might be derived from molecular ions of Te and Bi, Te_2^- and Bi_2^-. Consequently, it is suggested that the broad NIR luminescence of Te- and Bi-doped glass and glass-ceramics are most likely to be caused by elemental clustering, such as Te_2/Te_2^- and Bi_2/Bi_2^-.   [Received December 6, 2007; Accepted February 15, 2007]

1.   Introduction

The demand to increase the transmission capacity of wavelength division multiplexing (WDM) system is indispensable due to rapid development of the telecommunication. Many attempts have been made on broadening and flattening of gain spectra of optical fiber amplifiers such as Er-doped fiber amplifiers (EDFAs),[1] tellurite-base Er-doped fiber amplifier (EDFA),[2] Tm-doped fiber amplifiers [TDFAs],[3] fiber Raman amplifiers (FRAs).[4] Broadband tunable lasers such as Ti^{3+}: Al_2O_3 (Sapphire),[5] Cr^{4+}: $Y_3Al_5O_{12}$ (YAG),[6] Cr^{3+}: $LiCaAlF_6$ (LiCAF)[7] were realized by using transition metals as active ions.

Recently Fujimoto et al.[8] discovered a new infrared luminescence from a Bi-doped silica glass with long life time. The glass has three excitation/absorption bands at 500 nm, 700 nm and 800 nm. These excitation bands are intrinsic for luminescent bands at 750, 1120 and 1250 nm, respectively.[8] These spectroscopic properties are different from previous Bi-luminescent materials, and 1250 nm wide band luminescence is useful for optical amplifier of telecommunication with optical fiber. Fujimoto et al.[8],[9] proposed that this near infrared (NIR) luminescence comes from Bi^{5+} ion. On the other hand, Peng et al.[10],[11] estimated to be due to BiO or Bi metal.

The color generation of glasses in visible region is basically caused by impurities, such as transition metal ions, rare earth ions, metallic and semiconductor particles, etc. There are numerous other sources of visible coloration in glasses which are of interest. Included in this group are blue-sulfur, pink-selenium, and purple-tellurium glasses whose colors are

associated with elemental clustering.[12] Many researches on the luminescence properties of Te-doped crystals have been done.[13]-[16] The research on the luminescence properties of elemental clustering must be of interest.

The luminescent properties of Te- and Bi-doped glasses and transparent glass-ceramics were investigated and the origin of coloration and NIR luminescence was discussed in this paper.

2.   Experimental

2.1   Sample preparation

The compositions (mass%) of glasses studied are shown in **Table 1**. High purity silica sand, alumina and reagent grade chemicals of Li_2CO_3, Na_2CO_3, K_2CO_3, $CaCO_3$, H_3PO_4, H_3BO_3, MgO, ZnO, TiO_2, ZrO_2, TeO_2, Bi_2O_3 and carbon were used as raw materials. The addition of a slight amount of carbon produces a mild reducing condition. Batches corresponding to 25 g of glass were mixed thoroughly and melted in a 50 cc Pt/Rh10 or alumina crucibles under appropriate condition in an electric furnace in air. The melting conditions of glasses are shown in **Table 2**. After melting they were poured onto iron plate and pressed by another iron plate. Glasses were heat treated for nucleation and crystallization.

The glasses and glass-ceramics were cut and polished optically into about 1 mm in thickness for optical measurement.

2.2   XRD, SEM and ESR

X-ray diffraction (XRD) analysis was performed routinely to determine crystalline phases, percent crystallinity and crystal size[17],[18] using Bruker AXS Model D5005. The fractured surface of glasses and glass-ceramics was observed by scanning electron microscope (SEM) (JEOL, JSM 6400).

Table 1.   Glass Compositions (mass%) Studied

Name	SiO_2	Al_2O_3	ZnO	MgO	CaO	Na_2O	K_2O	TeO_2	Bi_2O_3	carbon
Te-Sp.	46.9	26.54	10.59	5.25	TiO_2:1.75, ZrO_2:8.93			0.2	–	–
Te-SL.	72	2	–	4	8	13	1	1.6	–	0.08
Te-ZTP	P_2O_5: 33.17, ZnO: 35.87							14.07	–	–
Bi-L-2S	80	4	–	P_2O_5: 3, Li_2O: 13.0				–	6.0	–
Bi-AlPO₄	28.07	23.82	P_2O_5: 33.17, B_2O_3: 4.07, Na_2O: 10.86					–	6.0	–
Bi-Sp.	46.9	26.54	10.59	5.25	TiO_2:1.75, ZrO_2:8.93			–	6.0	–

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Table 2. Melting Conditions, Heat Treatment Conditions for Crystallization, Appearance and Some Properties of Glass-Ceramics

Name	Melting condition °C-h,	Heat treatment °C-h	Appearance*	Crystals		
				Phases	Percent mass%	Size nm
Te-Sp.	1600-1, Pt/Rh10	800-10, 1000-5	Pale brown Brown-pink	Spinel	45±5	15±5
Te-SL.	1450-1, Pt/Rh10	–	Pale green	–	–	–
Te-ZTP	1200-1, Alumina	–	Brilliant pink	–	–	–
Bi-L·2S	1450-1, Pt/Rh10	500-10, 650-5	Pale yellow Brown	Lithium disilicate	70±5	25±5
Bi-AlPO₄	1600-1, Pt/Rh10	500-10, 600-5	Brown Deep brown	AlPO₄	50±5	20±5
Bi-Sp.	1600-1, Pt/Rh10	800-10, 1000-5	Pale pink Pink	Spinel	45±5	15±5

*: upper=glass, lower=glass-ceramics

The electron spin resonance (ESR) spectra were measured using JEOL JES RE-2X at room temperature.

2.3 Absorption and emission measurements

The absorption spectra were measured with Cary 1E ultraviolet-visible (UV–VIS) spectrometer in the range of 300 nm to 800 nm at room temperature. The emission spectra in UV–VIS region were measured with Perkin–Elmer Luminescence Spectrometer LS50B at room temperature. The emission spectra in NIR region (1000 nm to 1700 nm) were measured under the excitation of 974 nm laser diode at room temperature. Emission from the sample was dispersed by a single monochromator (blaze, 1.0 mm; grating, 600 grooves/mm; resolution, 3 nm) and detected by an InGaAs photodiode.

3. Results

Some glasses are able to convert to transparent glass-ceramics based on lithium disilicate $(Li_2O \cdot 2SiO_2)$ for L·2S, AlPO₄ (tridymite type) for AlPO₄ and spinel $[(Mg, Zn) Al_2O_4]$ crystals for Sp. The crystalline phases, crystal size and percent crystallinity are summarized in Table 2. The percent crystallinity and crystal size are ranging 45–70±5% and 15–25 ±5 nm, respectively. All glass-ceramics are highly transparent.

3.1 Absorption spectra

(a) Te-doped glasses and glass-ceramics

Appearance of samples are pale green for Te-SL, brilliant purple for Te-ZTP and brown-pink for Te-Sp. glass-ceramics, and absorption spectra are shown in Fig. 1(a). Three absorption bands are observed at around 377, 444 and 625 nm for green Te-SL glass. For Te-ZTP glass, the strong absorption band at 537 nm with a shoulder at around 420 nm appears. On the contrary, the shoulder at around 420 nm is observed in Sp. glass-ceramics.

The absorption bands may be classified into four bands, and they are summarized in Table 3. The absorption spectra were analyzed with Gaussian distribution.

For green Te-SL glass, the absorption band at 440 nm is ascribed to $^3\Sigma_g \rightarrow {}^3\Sigma_u$ transition of Te_2 color center and the absorption band at 625 nm can be assigned to $^2\pi_g \rightarrow {}^2\pi_u$ transition of Te_2^- color center.[14] The 377 nm band may relate to exciton transition.[14] The strong absorption band at 537 nm of Te-ZTP glass seems to be due to colloidal metallic Te.[19] Actually, many particle of about 200 nm in diameter are actually observed in Te-ZTP glass, and a small particle was
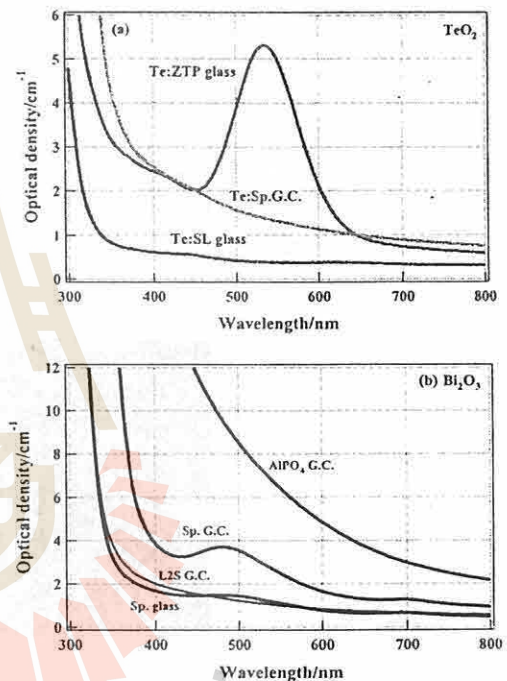

Fig. 1. Absorption spectra of Te- and Bi-doped glass and glass-ceramics. (a) Te-doped glasses and glass-ceramics, (b) Bi-doped glass and glass-ceramics. G.C.: glass-ceramics.

also detected in Te-Sp. glass-ceramics as shown in Fig. 2(a). This indicates that TeO_2 was reduced to metallic Te. This pink coloration might be due to the surface plasmon resonance absorption of Te colloids.

(b) Bi-doped Sp. glasses and glass-ceramics

Appearances of samples are yellow-brown for Bi-L·2S glass-ceramics, deep brown for Bi-AlPO₄ glass-ceramics and pale pink to pink for Bi-Sp. glass and glass-ceramics, and their absorption spectra are shown in Fig. 1(b). Two absorption bands at around 480 nm and 700 nm appear in pink Sp. glass and glass-ceramics. This spectral pattern is the same as those

reported previously.[8]-[11] On the contrary, no specific absorption band can be detected in Bi-L·2S and Bi-AlPO₄ glass-ceramics. Figure 2(b) shows that particles of 100–200 nm in diameter precipitated in Bi-AlPO₄ glass-ceramics, while no particles can be detected in Bi-Sp. glass-ceramics. These particles may be colloidal metallic Bi.[20] This indicates that Bi_2O_3 was reduced to metallic Bi in Bi-AlPO₄ glass-ceramics.

3.2 Luminescence in UV–VIS and NIR region

Figure 3 shows UV–VIS luminescence of Te- and Bi-doped glasses and glass-ceramics at room temperature. The strong and structured blue luminescence was observed in Te-doped glasses and glass-ceramics. The weak sub luminescence band is detected in red region. The intensity of these luminescence bands is proportional to TeO_2 content in samples.

In Bi-doped L·2S glass-ceramics and Sp. glass, strong blue luminescence is detected with weak luminescence band at

Table 3. Appearance and Absorption Bands Analyzed by Gaussian Distribution

Name	Appearance	Band I nm	Band II nm	Band III nm	Band IV nm
Te-SL	Pale green	377	444	(526)*	625
Te-ZTP	Brilliant pink	375	417	537	(600)*
Te-Sp. G.C.	Brown-pink	–	420 (448)*	(556)*	(599)*
Bi-L·2S G.C.	Brown	–	–	–	–
Bi-AlPO₄ G.C.	Deep brown	–	–	–	–
Bi-Sp. G	Pale Pink	(370)*	480	–	700
Bi-Sp. G.C.	Pink	(370)*	480	–	700

*: very weak

around 800 nm. On the contrary, a very weak and structured blue luminescence is observed in AlPO₄ and Sp. glass-ceramics, and red luminescence disappears. The luminescence intensity decreases markedly by the heat treatment for crystallization in Sp. glass. It is well known that the blue luminescence of Bi-containing glass is derived from Bi^{3+} ions in materials,

Figure 4 shows the NIR luminescence spectra of Te- and Bi-doped glasses and glass-ceramics under the excitation of 974 nm laser diode at room temperature. A broad NIR luminescence at around 1200 nm can be observed in all Te-doped glasses and glass-ceramics. It should be noted that a weak and rather sharp luminescence can also be detected at around 1020 nm in Te-Sp. glass-ceramics.

On the other hand, pink colored Bi-Sp. glass and glass-ceramics exhibit NIR luminescence at around 1100 nm with a shoulder at around 1450 nm. However, no NIR luminescence can be observed in other two Bi-doped glass-ceramics (L·2S and AlPO₄ glass-ceramics).

3.3 ESR spectra

In order to determine the luminescent center of Te- and Bi-doped glasses and glass-ceramics, the ESR spectra were measured. The ESR spectra are shown in **Fig. 5**. Two ESR signals were detected, $g \approx 4.7$ and $g \approx 2.0$ for both Te- and Bi-doped glasses and glass-ceramics. The ESR signals at $g \approx 4.7$ may be derived from impurities, such as Fe^{3+} ion in the sample.

It is noteworthy that ESR spectrum of Bi-doped Sp. glass and glass-ceramics is identical with that of Te-doped Sp. glass-ceramics. The ESR signal at $g \approx 2.0$ can also be observed in Bi-Sp. glass and Sp. glass-ceramics which exhibit NIR

(a)Te: ZTP Glass

(a)Te: Spinel Glass-ceramics

(b) Bi: AlPO₄ Glass-ceramics

(b) Bi: Spinel Glass-ceramics

Fig. 2. SEM photos of Te- and Bi-doped glasses and glass-ceramics. (a) Te-doped glass and glass-ceramics, (b) Bi-doped glass and glass-ceramics.
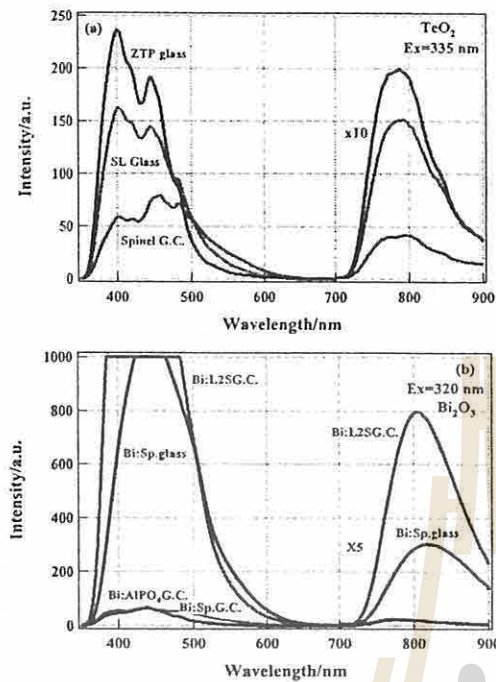
Fig. 3. UV–VIS emission spectra of Te- and Bi-doped glass and glass-ceramics at room temperature. (a) Te-doped glass and glass-ceramics. The intensity has been multiplied by 10 times in the range of 700–900 nm, (b) Bi-doped glass and glass-ceramics. The intensity has been multiplied by 5 times in the range of 700–900 nm.
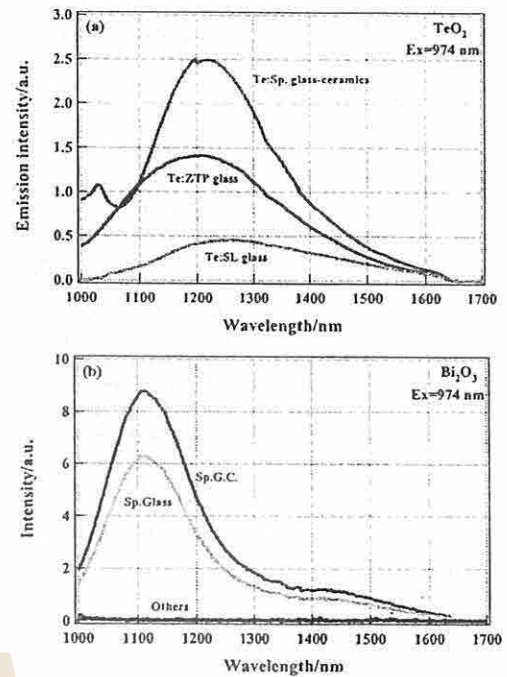
Fig. 4. NIR emission spectra of Te- and Bi-doped glass and glass-ceramics under the excitation of 974 nm laser diode at room temperature. (a) Te-doped glass and glass-ceramics, (b) Bi-doped glass and glass-ceramics.

luminescence. However, the ESR signals at $g \approx 2.0$ can not be detected in Bi–AlPO$_4$ G.C. and Bi–L·2S G.C. which do not exhibit NIR luminescence, and hence this ESR signal is strongly related to NIR luminescence.

4. Discussion

4.1 Te-doped glasses and glass-ceramics

It was found that colorations of Te-doped glasses and glass-ceramics might be due to elemental clustering of Te, such as Te$_2$ and Te$_2^-$. The dimer of Te cluster is believed to be stable species.[21],[22] In glasses and glass-ceramics, it is clear that TeO$_2$ was reduced to elemental Te during melting, and they aggregated to colloidal size. This colloidal metallic Te results in the pink coloration of ZTP glass. However, the NIR luminescence does not seem to be due to colloidal Te because the NIR luminescence is not proportional to the amount of colloidal Te.

In ESR spectra shown in Fig. 5(a), two ESR signals were detected, $g \approx 4.7$ and $g \approx 2.0$. The ESR signals at $g \approx 4.7$ may be derived from impurities, such as Fe^{3+} ion in the sample. The ESR signals at $g \approx 2.0$ of SL and Sp. glass-ceramics have fine structure. This signal often appears in halide crystals and it is assigned to self-trapped hole or V_k center.[23],[24] This means that ESR signal at $g \approx 2.0$ is derived from halogen molecular ion, X$_2^-$. The similar ESR spectrum was obtained in Se-doped borosilicate glass and it is believed to be due to Se$_2^-$ ions.[25] Since Te clustering such as Te$_2^-$/Te$_2$ exists in Te-doped glasses as mentioned previously, ESR signals at $g \approx 2.0$ can be assigned to Te$_2^-$ ions. The NIR luminescent intensity seems to be proportional to the intensity of $g \approx 2.0$ signals of
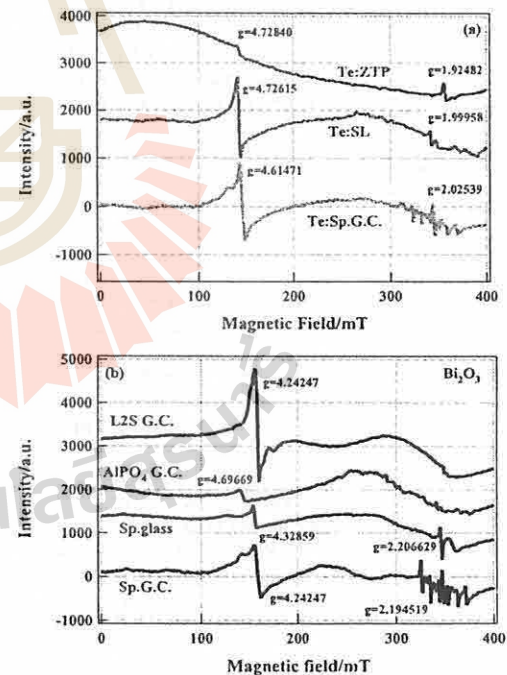

Fig. 5. ESR spectra of Bi-doped glass and glass-ceramics at room temperature. (a) Te-doped glass and glass-ceramics, (b). Bi-doped glass and glass-ceramics.
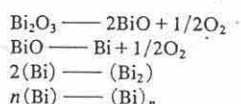
ESR spectra.

4.2 Bi-doped glasses and glass-ceramics

The origin of the pink coloration and NIR luminescence of Bi-doped glasses and glass-ceramics are not clear yet. Here, the origin of the coloration and NIR luminescence of Bi-doped glasses and glass-ceramics will be discussed.

It is well known that the blue luminescence of Bi-containing glass is derived from Bi^{3+} ions in materials,[26] therefore a large amount of Bi^{3+} ions present in Bi-L·2S glass-ceramics and Bi-Sp. glass. On the contrary, Bi^{3+} ion scarcely exists in Bi-AlPO$_4$ glass-ceramics and Bi-Sp. glass-ceramics. This indicates that Bi^{3+} ion was reduced to lower valence state by further heat treatment for crystallization in Bi-AlPO$_4$ glass-ceramics and Bi-Sp. glass-ceramics.

The darkening effect of high Bi_2O_3-containing glasses was reported,[20] When glasses containing a large amount of Bi_2O_3 were melted at higher temperature, brown-black glasses could be obtained, and nano-scale Bi particles were detected by transmission electron microscope (TEM) observation.[20] The nano-scale Bi particles can also be detected in this study (Fig. 2(b)). This darkening effect was related to a redox process partially reducing Bi^{3+} ions to a lower valence state, and hence the next process may be given:

$$Bi_2O_3 \longrightarrow 2BiO + 1/2O_2$$
$$BiO \longrightarrow Bi + 1/2O_2$$
$$2(Bi) \longrightarrow (Bi_2)$$
$$n(Bi) \longrightarrow (Bi)_n$$

Here, (Bi) indicates elemental Bi, (Bi$_2$) the molecular Bi and (Bi)n the metallic colloidal Bi. Above reactions go to right side at higher temperature and reducing condition.

From the result mentioned previously, it is clear that Bi^{3+} ions (L·2S glass-ceramics) and colloidal metallic Bi (AlPO$_4$ glass-ceramics) are not responsible for pink coloration and NIR luminescence. The NIR luminescence can be observed only for pink Sp. glass and glass-ceramics.

It should be noted that ESR spectrum of Bi-doped Sp. glass-ceramics is identical with that of Te-doped Sp. glass-ceramics. The ESR signal at $g \approx 2.0$ can also be observed in Bi-Sp. glass and Bi-Sp. glass-ceramics which exhibit NIR luminescence. This ESR signal can not be detected in AlPO$_4$ and L·2S glass-ceramics which did not exhibit NIR luminescence. Therefore, it seems that the ESR signal at $g \approx 2.0$ is strongly related to NIR luminescence and pink coloration. In analogy with Te-doped Sp. glass and Sp. glass-ceramics, this ESR signal may come from Bi molecular ions, Bi_2^-.

In Se-pink glasses, the analytical concentration of Se is usually few hundreds ppm, and the Se molecule or molecular ions contributing the color generation is believed to be few% of total Se presented in glasses.[27] Therefore, the concentration of Te and Bi molecular ions in glasses and glass-ceramics may be very low, $\approx 10-30$ ppm.

5. Conclusion

The luminescence characteristics of Te- and Bi-doped glasses and glass-ceramics were investigated and the origin of coloration and near infrared luminescence was discussed. The colorations of these glasses and glass-ceramics might be due to the elemental clustering such as Te_2/Te_2^- and Bi_2/Bi_2^-. The broad NIR luminescence can be detected in Te- and Bi-doped glasses and glass-ceramics. The ESR signal at $g \approx 2.0$ can be observed in Te- and Bi-doped glasses and glass-ceramics which exhibit NIR luminescence, and therefore this ESR signal is strongly related to the NIR luminescence. The ESR signal at $g \approx 2.0$ might be derived from molecular ions of Te and Bi,

Te_2^- and Bi_2^-.

Consequently it is suggested that the broad NIR luminescence of Te- and Bi-doped glass and glass-ceramics are most likely to be caused by elemental clustering, such as Te_2/Te_2^- and Bi_2/Bi_2^-.

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Ultrabroadband near-infrared emission from a colorless bismuth-doped glass

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The characteristics of bismuth-doped glasses were investigated as colorless ultrabroadband near-infrared gain media. The colorless Bi-doped soda-lime-silicate glass was prepared under controlled redox conditions, and it realized the broadest near-infrared emission of about 600 nm in full width at half maximum, centered at 1000 nm, under 720 nm excitation. The emission band extended toward shorter wavelengths compared with the shortest wavelength for the Bi-doped glass ever reported. The colorless Bi-doped glass developed in this work has a good potential for the broadband gain media for amplifiers and tunable lasers. © 2007 American Institute of Physics.
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Broadband amplifiers and tunable lasers in the near-infrared region are indispensable in developing dense wavelength-division-multiplexing network systems. Much work has been reported on broadening and flattening of gain spectra of rare-earth-doped fiber amplifiers (RDFAs) and fiber Raman amplifiers (FRAs). However, these amplifiers have some disadvantages. The gain bandwidths of RDFAs are limited at most to 100 nm due to narrow f-f transitions in nature. Multiwavelength pumping FRAs have complicated system structures and require high power excitation sources. We have investigated transition metal ion-doped glass ceramics as ultrabroadband optical amplification media by single wavelength pumping.[1,2] Recently, bismuth-doped glasses have been attracted much attention because of their near-infrared emission.[3–8] Optical amplification at 1.3 μm was realized using Bi:Al codoped SiO_2 glass by pumping at 800 nm.[4] In addition, Dianov *et al.* reported laser oscillations in the spectral region between 1150 and 1300 nm using Bi-doped alumino silicate fiber.[9]

We have studied Bi-doped glasses as broadband gain media focusing on the control of their emission bands. The broad emission of more than 500 nm in full width at half maximum (FWHM) under 900 nm laser excitation was achieved in Bi-doped lithium-alumino-silicate (Bi-LAS) glasses.[10,11] However, optical characteristics and mechanisms of the Bi-doped glasses are not understood at present. Furthermore, the Bi-doped glasses already reported had deep coloration. Deeply colored optical gain materials are not always desirable as the coloration deteriorates laser or amplification performance. We have investigated the effect of host glass composition to an emission bandwidth and coloration of Bi-doped glasses. We chose a soda-lime-silicate glass as a host glass. We have fabricated the colorless Bi-doped soda-lime-silicate glass with high transparency and found that it realized the broadest emission of about 600 nm FWHM that is the broadest bandwidth ever reported. In this letter, we will present the characteristics of the Bi-doped soda-lime-silicate glass as colorless ultrabroad near-infrared gain media.

The Bi-doped soda-lime-silicate glasses were prepared by an ordinary melt-quenching method. Batch compositions of the glasses were $13Na_2O-8CaO-4MgO-2Al_2O_3-K_2O-72SiO_2-0.5Bi_2O_3-xC$ ($x=0$, 1.5, 2.5, 3.0, and 4.0 wt %). From now on, these glasses are referred to as xC–BiSL. Bi_2O_3 was used as a dopant, and carbon powder, that evolved out of the glass during melting, was used to control the redox condition of the melts. The raw materials were mixed thoroughly and melted in an alumina crucible for 1 h at 1450 °C under nitrogen atmosphere. Bubble-free glasses were obtained by quenching the resultant melts on a steel plate preheated to the glass transition temperature of 650 °C and cooled slowly to room temperature in an electric furnace so as to release stress induced during the quenching process.

The bulk glass samples were cut to a thickness of 1–2 mm and polished to optical quality before subjecting them to the following measurements. Absorption spectra were measured by using a double-beam spectrophotometer (Perkin-Elmer, Lambda 900). A prism coupler (Metricon, 2010) was used to measure the refractive indices of the glasses. The bulk glass samples were excited with a Ti^{3+}:sapphire laser (Coherent 890) in the 700–920 nm wavelength range. The excitation light was mechanically chopped at 47 Hz in the emission measurements. Emission from the samples was dispersed by a single monochromator (blaze wavelength of 1.0 μm, groove number of 600 grooves/mm) and detected by a photomultiplier (Hamamatsu Photonics, H9170-75) or indium-gallium-arsenic *PIN* photodiode (Hamamatsu Photonics, G5852-11). Emission decay curves were measured by the photomultiplier and accumulated using a digital oscilloscope (Yokogawa, DL-1640). Lifetimes $\tau_{1/e}$ of each emission were obtained as the first e-folding time of the decay curves.

1.5, 2.5, and 3.0C–BiSL glasses were prepared and they were transparent. The color of the glass was changed by addition of the carbon. The 1.5C–BiSL glass was colorless,
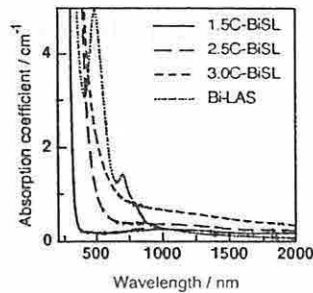
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FIG. 1. Optical absorption spectra of 1.5, 2.5, and 3.0–C-BiSL glasses. The absorption spectrum of a Bi-LAS glass is also shown for comparison by the dotted line.
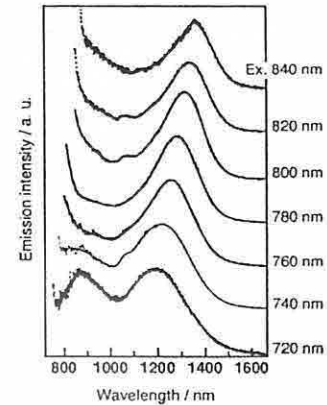

FIG. 2. Normalized near-infrared emission spectra of a 1.5C–BiSL glass. The excitation wavelengths are indicated by each spectrum. The substantial increases at the shorter wavelength region in each spectrum were due to the excitation laser.

and the 2.5 and 3.0C–BiSL glasses were yellow and brown, respectively. For a 4.0C–BiSL glass, the metal bismuths were slightly precipitated in the crucible when the glass melt was cast. Figure 1 shows the optical absorption spectra of the resultant glass samples. The absorption spectrum of a Bi-LAS glass is also shown for comparison by the dotted line in the figure. The absorption edge of the 1.5C–BiSL glass was about 300 nm. There were no distinct peaks at 500, 750, and 800 nm that were observed in the Bi:Al codoped SiO_2 glass and Bi-LAS glasses.[3,10] Increasing the carbon concentration caused redshift of the absorption edge.

Near-infrared emissions were confirmed from all xC–BiSL glasses under 800 nm excitation, although the emission from a 0C–BiSL glass was very weak. The largest and broadest emission was confirmed from the 1.5C–BiSL glass, and the intensity substantially decreased with increasing the carbon concentration. The amount of the carbon in the glass batch affected the redox condition of the glass melts, thus the moderately reduced condition was inevitable in realizing the near-infrared emission from xC–BiSL glasses. The emission is most likely caused by electric transition of Bi^{5+},[12] Bi^+,[8] complex of Bi^+ and $AlO^{4/2-}$,[9] or Bi clusters,[13] but the origin is still controversial. Taking the experimental results mentioned above into account, we would like to point out that some reduced species such as Bi clusters (dimer, trimer, or tetramer, for instance) and Bi^+ should be considered as origins for the emission center.

Figure 2 shows the normalized emission spectra of the 1.5C–BiSL glass excited from 720 to 840 nm. The excitation wavelengths are indicated by each spectrum. Substantial emission increases at shorter wavelengths in each spectrum were due to the excitation laser. Emission peaks were observed at 900 and 1400 nm when excited at 840 nm. Varying the excitation wavelength from 840 to 720 nm, blueshift of the peak at 1400 nm, which was observed for 840 nm excitation, occurred and peak intensities increased. The emission band with FWHM as wide as 600 nm was obtained under the 720 nm laser excitation. This is the widest emission bandwidth from Bi-doped glasses ever reported. Though a similar emission band at 1200 nm was observed from the Bi-LAS glasses, the 900 nm emission band was not observed from the Bi-LAS glasses.[10]

Figure 3 shows the decay curves of near-infrared emissions from the 1.5C–BiSL glass measured at 950 and 1300 nm. Those emission wavelengths are included in the emission bands at 900 and 1200 nm, respectively. The lifetimes $\tau_{1/e}$ at 950 and 1300 nm were 40 and 337 μs, respec-

tively. The $\tau_{1/e}$ at 950 nm was different from that of Bi-LAS glass, while the $\tau_{1/e}$ at 1350 nm was similar to that of Bi-LAS glass. This clear difference in lifetimes suggests that the emission centers of the 900 and 1200 nm emissions were completely different. Another unknown emission center that did not exist in the Bi-LAS glass extended the total emission band toward short wavelengths in the case of the 1.5C–BiSL glass. The emission can cover the visible to near-infrared region (at least 750–1600 nm), while that of the Bi-LAS glass covers from 920 to 2000 nm.[11] It is suggested that choosing an appropriate host matrix is very effective in controlling the emission band of the Bi-doped glass.

Figure 4(a) shows the curve fitting of the emission spectrum of the 1.5C–BiSL glass excited at 720 nm. The band was well fitted to two Gaussian peaks denoted as A and B. Wavelength dependence of the lifetime $\tau_{1/e}$ is shown in Fig. 4(b) with the emission spectrum in Fig. 4(a). We can see the distinct change in $\tau_{1/e}$ with the emission wavelength. This is because the total emission spectrum consists of the two emission bands with different emission lifetimes as mentioned above.

The stimulated emission cross sections σ_{em} can be estimated from the Füchtbauer-Ladenburg equation by assuming a Gaussian-shaped emission band.[7]
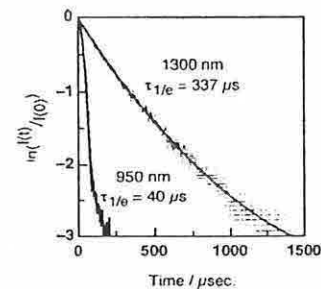

FIG. 3. Decay curves of near-infrared emission at 950 and 1300 nm from a 1.5C–BiSL glass under 720 nm laser excitation.
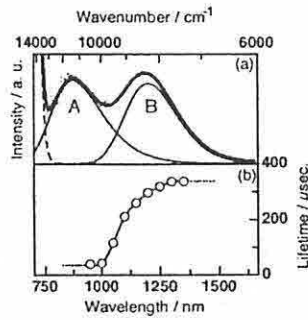
FIG. 4. (a) Curve fitting of the emission spectrum of a 1.5C–BiSL glass excited at 720 nm to two Gaussian peaks denoted as A and B. The strongest peak indicated by the dashed line is due to the excitation laser. (b) Lifetime $\tau_{1/e}$ of a 1.5C-BiSL glass under 720 nm laser excitation as a function of wavelength. The line in the figure is a guide to the eyes.

$$\sigma_{em} = \frac{\lambda_0^2}{4\pi n^2 \tau}\left(\frac{\ln 2}{\pi}\right)^{1/2}\frac{1}{\Delta\nu}, \qquad (1)$$

where λ_0 is the peak wavelength, n is the refractive index of the host material, τ is the emission lifetime, and $\Delta\nu$ is the FWHM of the emission. The properties of peaks A and B of Fig. 4(a) are given in Table I. σ_{em} for peaks A and B were 3.8×10^{-20} and 1.5×10^{-20} cm^2, respectively. The products of the stimulated emission cross section and the lifetime, $\sigma_{em}\tau$, that is proportional to the amplification gain and inversed laser oscillation threshold, were 1.5×10^{-24} and 5.1×10^{-24} cm^2 s for peaks A and B, respectively. The values were higher than that of Ti^{3+}:sapphire [$\sigma_{em}\tau = 1.4 \times 10^{-24}$ cm^2 s (Ref. 14)]. The high $\sigma_{em}\tau$ indicate that the Bi-doped soda-lime-silicate glass developed in this work has a good potential for the broadband gain media for amplifiers and tunable lasers.

TABLE I. Properties of Gaussian peaks A and B in the emission spectrum shown in Fig. 4(a).

	A	B
λ_0 (nm)	874	1199
$\Delta\nu$ (cm^{-1})	2724	1568
τ (μs)	40	337
n	1.512	1.508
σ_{em} (cm^2)	3.8×10^{-20}	1.5×10^{-20}
$\sigma_{em}\tau$ (cm^2 s)	1.5×10^{-24}	5.1×10^{-24}

In summary, the characteristics of Bi-doped soda-limesilicate glasses were investigated as ultrabroadband near-infrared gain media. The colorless transparent Bi-doped soda-lime-silicate glass was prepared under controlled redox conditions, and it realized the broadest emission band of about 600 nm in FWHM, centered at 1000 nm, under 720 nm excitation. This is the widest emission bandwidth from Bi-doped glasses ever reported. Extending the emission band toward shorter wavelengths compared with the shortest wavelength for the Bi-doped glass ever reported suggests that we can control the emission band of the Bi-doped glass by choosing the appropriate host matrix. In addition, covering the visible to near-infrared region (at least 750–1600 nm) will open wide applications including medical uses and optical measurements. The emission band consisted of at least two emission centers, and the $\sigma_{em}\tau$, representing its efficiency as optical gain media, at the peaks were obtained as 1.5×10^{-24} and 5.1×10^{-24} cm^2 s. These high $\sigma_{em}\tau$, higher than that of Ti^{3+}:sapphire, indicate that the Bi-doped soda-lime-silicate glass developed in this work has a good potential for the broadband gain media for amplifiers and tunable lasers.

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NEAR INFRARED LUMINESCENCE FROM BI-DOPED SODA-LIME-SILICATE GLASSES

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Abstract

The effect of melting atmosphere on the luminescent characteristics of Bi-doped soda-lime-silicate glasses was investigated, and the origin of NIR luminescence was also discussed. The appearance of these glasses changed from colorless and transparent to deep brown depending on the melting atmosphere (amount of carbon addition). The characteristic absorption bands can not be observed in all glasses. The colorless and transparent glass (C1.50) exhibit both UV-VIS and NIR luminescence. The UV-VIS luminescence comes from Bi^{3+} ion, which remains in glasses. On the contrary, the NIR luminescence is derived from Bi clustering, such as Bi_2 or Bi_2^-, and therefore transparent colorless C1.5 glass contains both Bi^{3+} ion and Bi_2 or Bi_2^-. The ESR measurements confirmed that the ESR signals derived from molecular clustering of Bi, Bi_2^- can be detected at g~2.0. Consequently, it is found that the molecular clustering of Bi, Bi_2 or Bi_2^-, might be produced under the mild reducing condition.

Keywords: Bismuth cluster, soda-lime-silicate glass, absorption spectra, near infrared luminescence (NIR), electron spin resonance (ESR)

Introduction

There are several reports on visible luminescence from Bi-doped glasses and crystals. Srivastava (1998, 2002) reported luminescence from Bi^{2+}:$CaBPO_4$ at 15 K and luminescence from Bi^{3+}:$Y_2Sn_2O_7$. These spectra are both very wide, and the excitation and luminescence peaks exist at around 240 nm and 380 nm, respectively. Although the excitation and luminescence peaks change with the host crystals, the excitation peaks are located between the violet and ultraviolet regions and luminescence peaks between the blue and green regions. This visible luminescence is believed to be derived from Bi^{3+} ions (Blasse, 1997; Srivastava, 2002).

Recently Fujimoto and Nakatsuka (2004) discovered a new infrared luminescence from a Bi-doped silica glass with a long life-time. The glass has three excitation/absorption bands at 500, 700, and 800 nm. These excitation bands

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are intrinsic for luminescent bands at 750, 1,120, and 1,250 nm, respectively. These spectroscopic properties are quite different from previous Bi-luminescent materials, and the 1,250 nm wide band luminescence is useful for an optical amplifier of telecommunications with an optical fiber. Fujimoto and Nakatsuka (2004) proposed that this near infrared (NIR luminescence) comes from Bi^{5+} ion. On the other hand, Peng *et al.* (2004, 2006) estimated to be due to BiO or Bi metal.

The authors have found new NIR luminescent Bi-doped glasses. In this paper, the effect of melting atmosphere on the luminescent characteristics of Bi-doped soda-lime-silicate glasses was investigated, and the origin of NIR luminescence was also discussed and proposed that the color generation and NIR luminescence of Bi-doped glasses is likely to be caused by molecular clustering of Bi, Bi_2, or Bi_2^-.

Experiment

Sample Preparation

The compositions of glasses studied are shown in Table 1, and the base glass composition is the typical window glass.

High purity silica sand, alumina and reagent grade chemicals of Na_2CO_3, K_2CO_3, MgO, $CaCO_3$, Bi_2O_3 and carbon were used as raw materials. In order to control the melting atmosphere, carbon was added to batches. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucibles at 1,450°C for 1 h in an electric

furnace in air. After melting they were poured onto an iron plate and pressed by other one. Then they were annealed at 650°C for 30 min and cooled slowly in the furnace.

The glasses were cut and polished optically into about 2 mm thick for optical measurements.

Absorption and Luminescence Measurements

The absorption spectra were measured with a Cary 5E UV-VIS-NIR Spectrometer in the range of 300 nm to 800 nm at room temperature. The luminescence spectra in the UV-VIS (300 nm to 900 nm) region were measured using a Perkin-Elmer Luminescence Spectrometer LS50B at room temperature.

The luminescence spectra in the NIR region (950 nm to 1,650 nm) were measured under the excitation of 800 nm of a Ti: Sapphire tunable laser operated by an Ar laser.

SEM, ESR

The fractured surfaces of colored Bi-doped glasses were observed by scanning electron microscope (SEM, JEOL, JSM 6400). The electron spin resonance (ESR) spectra were measured by using a JEOL JES-RE2X.

Results and Discussion

Absorption Spectra

The appearances of samples are colorless for C0 and C1.5, yellow-orange for C2.5, and deep brown for C3 and C4. The absorption

Table 1. Glass compositions (wt %) studied

Glass	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	Bi_2O_3*	Carbon*
C0	72	2	4	8	13	1	0.5	-
C1.5	72	2	4	8	13	1	0.5	1.5
C2.5	72	2	4	8	13	1	0.5	2.5
C3	72	2	4	8	13	1	0.5	3.0
C4	72	2	4	8	13	1	0.5	4.0

* *excess wt%*

spectra are shown in Figure 1. The characteristic absorption band can not be observed in all glasses. The absorption intensity of C4 is lower than that of C3 because of the precipitation of Bi metal at the bottom of crucible due to the strong reducing condition during melting for C4. This phenomenon will be discussed later.

Figure 2 shows SEM photos of colored C2.5~4.0 glasses. It is clearly seen that small particles can be detected in these glasses. These particles might be colloidal metallic Bi. This indicates that Bi_2O_3 was reduced to metallic Bi with increasing carbon content. The coloration of glasses might be due to colloidal metallic Bi (Sanz et al., 2006).

Luminescence in VIS Region

The UV-VIS luminescence spectra of glasses are shown in Figure 3 under the excitation of 300 nm at room temperature. Strong and broad luminescence bands were observed centered at 400 nm and 800 nm for C0, C1.5, and C4 glasses. The emission intensity of 400 nm and 800 nm band decreases markedly with increasing of the amount of carbon for C2.5 and C3.0, however, the intensity of those luminescence increases again for C4.

It is well known that UV-VIS luminescence at $\approx$ 400 nm comes from Bi^{3+}, and it was assigned to $^3P_1 \rightarrow {}^1S_0$ transition (Blasse, 1997; Kishimoto, Tsuda and Sakaguchi, 2004). The strong 400 and 800 nm bands observed in C0, C-1.5, and C-4 glasses are derived from

Bi^{3+} ions. However, the structured 400 nm band in C2.5 and C3 glasses may not be from Bi^{3+} ions but from another Bi-related center. It should be noted that a considerable amount of Bi^{3+} ion is still remained in C-4 glass despite the strong reducing condition. As mentioned
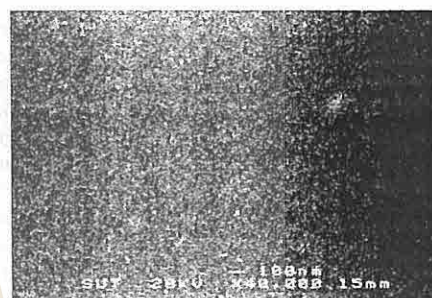

Bi-Soda lime silicate glass C:2.5

Bi-Soda lime silicate glass C:3.0

Bi-Soda lime silicate glass C:4.0

Figure 1. Absorption spectra of Bi-doped soda-lime-silicate glasses

Figure 2. SEM photos of Bi-doped soda-lime-silicate glasses

previously, the metallic Bi colloids deposited on the bottom of the crucible during melting for C4. It seems that the Bi_2O_3 was reduced to metallic colloids in the early stage of melting and deposited as colloids on the bottom of the crucible. Thus the concentration of Bi in glass decreased and the valence state of Bi may revert again to higher state, such as Bi^{3+}, during further melting.

NIR Luminescence

Figure 4 shows NIR luminescence spectra under the excitation of 800 nm at room temperature. Three emission bands, ≈950 nm, 1,070 nm, and 1,300 nm, can be observed in glasses with carbon. However, no NIR luminescence can be observed in C0 glass without carbon. The broad and strong emission at around 1,300 nm appears only in C1.5 glass, and this emission for another glasses is much weaker (≈1/10) than that of C1.5 glass. On the contrary, there is no remarkable difference in the intensity of the 1,070 nm emission band.

C0 glass does not exhibit NIR luminescence. As shown before, C0 glass contains a large amount of Bi^{3+} ion but not metallic colloid. Consequently it is found that Bi^{3+} ion is not the origin of NIR luminescence. On the other hand, C2.5 and C3 glasses which contains a large number of metallic Bi colloids and exhibit very weak NIR luminescence. This indicates that the NIR luminescence is not from metallic Bi colloids. Only colorless and transparent C1.5 glass shows strong NIR luminescence.

There are numerous sources of visible coloration in glasses which are of special interest. Included in this group are blue-sulfur, pink-selenium and purple tellurium glasses whose colors are associated with elemental clustering (Sigel, 1977). The selenium pink glass is the most famous among them and has been already commercialized.

Previous research (Peng *et al.*, 2004, 2005; Morimoto *et al.*, 2006) reported that Bi-doped glasses and glass-ceramics, which exhibit NIR luminescence, appeared to be pink to reddish brown in color. It has proposed that the pink coloration and NIR luminescence is likely to be caused by molecular clustering of Bi, such as Bi_2 and Bi_2^- (Morimoto *et al.*, 2006). Therefore, this result implies that such molecular clustering, Bi_2 and Bi_2^-, are present in these glasses. It is very interesting to note that the transparent and colorless Bi-doped glass discussed here (C1.5) also exhibits NIR luminescence. This indicates that C1.5 glass contains molecular clustering of Bi, such as Bi_2 and Bi_2^- and their concentration might be quite low.

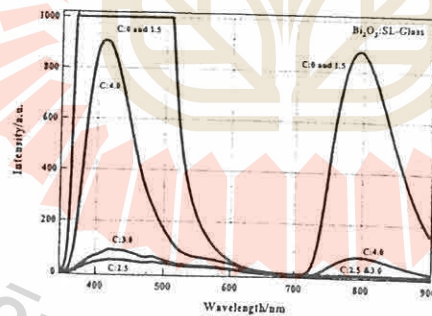In order to confirm the luminescent center, the ESR spectra were measured and

Figure 3. UV-VIS luminescence of Bi-doped soda-lime-silicate glasses under the excitation of 300 nm at room temperature
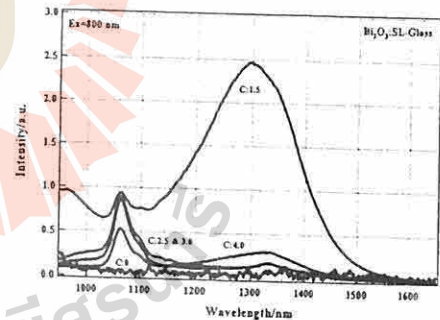

Figure 4. NIR luminescence of Bi-doped soda-lime-silicate glasses under the excitation of 800 nm at room temperature

ESR wide scan spectra are shown in Figure 5. Three ESR signals were observed at g~4.24, g~2.5, and g~2.0 in C1.5 glass, while two ESR signals were observed at g~4.24 and g~2.0 for C2.5, C3, and C4 glasses. C0 glass shows only one ESR signals at g~4.24. The ESR signal at g~4.24 may be due to impurities such as Fe^{3+} ion, but the signal at g~2.5 is not clear. C0 glass does not show NIR luminescence and the ESR signal at g~2.0, and hence it is considered that the ESR signal at g~2.0 is strongly related to NIR luminescence. The intensity of ESR signal at g~2.0 does not change by samples as shown in Figure 5, however the intensity of NIR luminescence is different. This may be due to concentration quenching. ESR signal at g~2.0 might be due to molecular clustering of Bi, such as Bi_2 or Bi_2^-.

The ESR signal at g~2.0 has often been observed in UV-irradiated alkali halide crystals (Nistor et al., 2000), Se-containing glasses (Guha et al., 1998) and Te-containing glasses (Lindner et al., 1996). This signal is due to the Vk center or self-trapped center (X_2^-) in alkali halide crystals. Likewise in Se-containing glasses and Te-containing glasses, the ESR signal at g~2.0 is believed to be due to Se_2^- and Te_2^- centers. In analogy with above examples, the ESR signal at g~2.0 observed here is likely to caused by the molecular clustering of Bi, Bi_2^-.
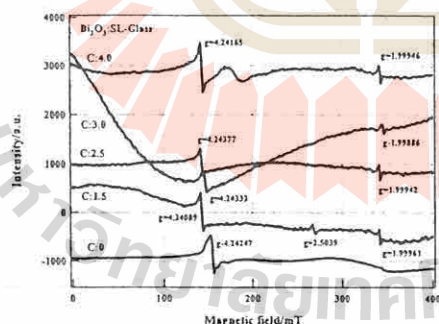

Figure 5. ESR spectra of Bi-doped soda-lime-silicate glasses at room temperature

Thus the strong NIR luminescence can be obtained from C1.5 glass, and this glass may contain a relatively large amount of molecular clustering of Bi, Bi_2^-. However, the glasses C2.5, C3, and C4, which were melted under strong reducing condition, do not exhibit the strong NIR luminescence. These glasses contain a large amount of metallic Bi colloids. This effect is related to a redox process partially reducing Bi^{3+} ions to a lower valence state, and hence the next process may be given:

$$Bi_2O_3 \rightarrow 2BiO + 1/2O_2, \; BiO \rightarrow Bi + 1/2O_2, \; 2(Bi) \rightarrow (Bi_2), \; n(Bi) \rightarrow (Bi)_n \quad (1)$$
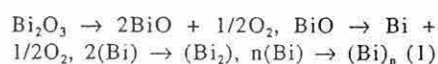
Here, (Bi) indicates elemental Bi, (Bi_2) the molecular Bi and $(Bi)_n$ the metallic Bi colloid. Above reactions go to right side with increasing amount of carbon (strong reducing condition). C1.5 glass exhibits the strong NIR luminescence, and hence a relatively large amount of molecular clustering of Bi, Bi_2^-, may be produced comparing with C2.5, C3, and C4 glasses. Consequently, it is found that the molecular clustering of Bi, Bi_2, or Bi_2^-, might be produced under the mild reducing condition.

Conclusion

The effect of melting atmosphere on the luminescent characteristics of Bi-doped soda-lime-silicate glasses was investigated, and the origin of NIR luminescence was also discussed.

The appearance of these glasses changed from colorless and transparent to deep brown depending on the melting atmosphere (amount of carbon addition). The characteristic absorption bands can not be observed in all glasses. The colorless and transparent glass (C1.50) exhibit both UV-VIS and NIR luminescence. The UV-VIS luminescence comes from Bi^{3+} ion, which remains in glasses. On the contrary, the NIR luminescence is derived from Bi clustering, such as Bi_2 or Bi_2^-, and therefore transparent colorless C1.5 glass contains both Bi^{3+} ion and Bi_2 or Bi_2^-. The ESR measurements confirmed that the ESR signals derived from molecular clustering of Bi, Bi_2^- can be detected at g~2.0.

Consequently, it is found that the molecular clustering of Bi, Bi_2, or Bi_2^-, might be produced under the mild reducing condition.

Acknowledgement

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On the near-infrared luminescence from TeO₂ containing borate glasses

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The effects of melting temperature and glass composition on the Near-infrared (NIR) luminescent characteristics of Te-containing borate glasses are investigated and compared with previous works. Three absorption bands are detected at around ~370 nm, ~430 nm and ~530 nm, however, the absorption band at around ~600 nm could not be detected in all borate glasses. And no NIR luminescence was observed under the excitation of a 974 nm laser diode. The NIR luminescence was observed in Te-green and Te-purple glasses, which showed the absorption band at around ~600 nm. This absorption band was ascribed to $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te_2^-. Consequently, it is suggested that the origin of NIR luminescence of Te-containing green and purple glass is likely to be caused by Te_2^- center.

1. Introduction

Among non-silicate glasses, such as heavy metal oxide and non-oxide glasses, high TeO₂ containing glasses are promising candidate materials for photonics applications, unifying the following features (1) wide transmission window, (2) good glass stability and durability and (3) high refractive index, better nonlinear optical properties and relatively low phonon energy. Broad band erbium doped fiber amplifiers (EDFAs) have been demonstrated using TeO₂-based fibers as erbium hosts.[1),2)]

However, high TeO₂ containing glasses often show coloration, pale green, brilliant purple to dark red, depending on glass composition and melting conditions.[3),4)] The color centers of these glasses have already been reported.[4),5)] According to their reports, the color centers of pale green glasses are clusters of Te_2 and Te_2^- species[5)] and those of brilliant purple glasses are Te metallic colloids.[4)]

Recently, the authors have found near-infrared (NIR) luminescence centered at 1250 nm with 250 nm of half width from pale green and purple TeO₂-containing glasses for the first time to our knowledge.[6),7)] We concluded that NIR luminescent centers might be Te_2 or Te_2^- species. Thus, the valence state of Te may change depending on glass composition and melting conditions, which produce color center and luminescent center in the glasses. In this study, the effects of melting temperature and glass compositions on the NIR luminescent characteristics of Te-containing borate glasses are investigated and compared with previous works.[6),7)]

2. Experimental

2.1 Sample preparation

Two series of glasses were prepared. Glasses of Series I are the composition of $62B_2O_3 \cdot 9Al_2O_3 \cdot 9ZnO \cdot 9K_2O \cdot 10TeO_2$ (mol%),

those of Series II are $90[(80-X)B_2O_3 \cdot 10Al_2O_3 \cdot 10ZnO \cdot XK_2O] \cdot 10TeO_2$ (mol%, $X = 0, 10, 20$ and 30). Reagent grade chemicals of H_3BO_3, Al_2O_3, ZnO, K_2CO_3 and TeO2 were used as raw materials. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucibles under various conditions (850°–1300°C for 15–60 min) in an electric furnace in air for Series I glasses. Glasses of Series II were melted in 50 cc alumina crucibles at 1200°C for 20 min in an electric furnace in air. After melting they were poured onto iron plate and pressed by another iron plate. Then, they were annealed at 450°C for 30 min and cooled slowly to room temperature in the furnace. All glasses were polished optically into about 1.5–2.0 mm in thickness for optical measurement. Hereafter, these glasses are referred to as Te-850, Te-1000, Te-1100, Te-1200, Te-1300, $X = 0$, $X = 10$, $X = 20$ and $X = 30$, respectively.

2.2 Optical measurement

The absorption spectra (300–800 nm) were measured using a Cary 1E ultraviolet-visible (UV-VIS) spectrometer at room temperature.

The NIR luminescence spectra (1000–1700 nm) were measured under the excitation of a 974 nm laser diode at room temperature. The optical setup for NIR luminescence measurement is shown in **Fig. 1**. Emission from the samples was dispersed by a single monochromator (blaze, 1.0 mm; grating, 600 grooves/mm; resolution 3 nm) and detected by InGaAs photodiode.

3. Results and discussion

3.1 Appearance and absorption spectra

The colors of Series I glasses change from colorless (Te-850) to brown (Te-1300) with increase in melting temperature. In glasses of Series II, color changes from reddish orange ($X = 10$) to colorless ($X = 30$) with increase in X (increasing amount of
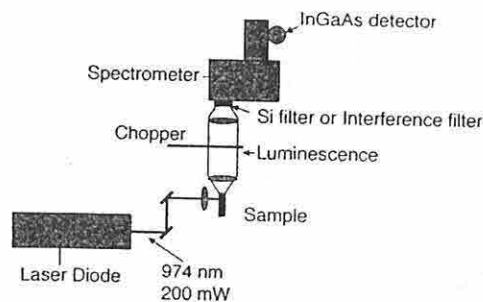
Fig. 1. Optical setup for NIR luminescence measurement.

K_2O). However, $X = 0$ glass revealed phase separation during casting. The melting conditions and appearance of these glasses are summarized in **Table 1**.

Figure 2 shows the absorption spectra of Te-containing borate glasses. The absorption spectra were analyzed and separated into three bands using peak fitting with Gaussian distribution. The results are shown in Table 1. Basically, three absorption bands can be observed, ~370 nm (Band I), ~430 nm (Band II) and ~530 nm (Band III), respectively. The assignment of these absorption bands are already known that Band I is the exciton transition, Band II $^3\Sigma g^- \rightarrow ^3\Sigma u^-$ transition of Te_2 and Band III Te metallic colloids.[4),5)] In Series I glasses, the UV absorption increases with an increase in melting temperature. It seems that the melting temperature affects the change in valence of Te. According to redox equilibrium, the higher melting temperature provides a lower valence state of metal ions, and hence the increase in UV absorption might be due to the Te species of a lower valence state.

However, these spectral patterns are different from those reported previously (ZTP, Te-SL and Te-Spinel in Table 1).[6)] The former three absorption bands are the same, but Band IV cannot be detected in all borate glasses discussed in this study. The assignment of Band IV has already been done and is ascribed to $^2\Pi g \rightarrow ^2\Pi u$ transition of Te_2^-.[5)] It is considered that the color cen-

ter of Te_2^- is lacking in all borate glasses from these results. Lindner et al.[5)] reported that the absorption band due to Te_2^- appeared at 606 nm in Te-doped blue and green sodalite crystal. This position is nearly the same as those in ZTP, Te-SL and Te-Spinel glasses. Thus, the absorption band due to Te_2^- center appeared at around 600 nm in many host materials. If Te_2^- centers are present in borate glasses, the absorption band should appear at around 600 nm. However, this band could not be detected in all borate glasses, and therefore, it is concluded that Te_2^- center is lacking or of a very low concentration in borate glasses.

Te_2 or Te_2^- species may be formed during reduction process of TeO_2 to metallic colloids $(Te)n$ in glasses and they gather together and precipitate Te metallic colloids.[4)] Zinc tellurium phosphate glass (ZTP) appeared to be brilliant purple and many small particles were observed by scanning electron microscope (SEM) observation in this glass.[6)] These particles were confirmed to be Te-metallic colloids and the strong absorption at around 537 nm was derived from the surface plasmon resonance absorption of Te-metallic colloids.[4)] This glass contained the same amount of TeO_2 (10 mol%) as that in borate glasses and was melted at nearly the same temperature (1200°C-2 h). This indicates that ZTP glass was prepared under higher reducing condition than borate glasses. According to Duffy's optical basicity concept,[8)] Λ values for both glasses were calculated without TeO_2: ZTP: 0.43 and $X = 0$: 0.46, $X = 10$: 0.50, $X = 20$: 0.55 and $X = 30$, respectively. The Λ value of ZTP is smaller than those f borate glasses. The smaller Λ value provides higher reducing condition, and therefore, a large amount of Te metallic colloids $(Te)n$ was formed in ZTP glass compared with borate glasses. This tendency can be clearly seen in Series II glasses. Thus, the reduction process did not proceed enough in borate glasses and the amount of Te_2 or Te_2^- species seems to be very low. This implies the lacking or very weak absorption of Band IV in borate glasses.

3.2 NIR luminescence
No NIR luminescence can be detected in all borate glasses under the excitation of 974 nm laser diode at room temperature.

Table 1. Melting Conditions, Appearances and Absorption Bands of Te-containing Glasses

| Glass No.	Melting conditions °C-min	Appearance	Absorption bands/nm			
			I	II	III	IV
Te-850	850-60	Colorless	–	–	–	
Te-1000	1000-20	Pale orange	370	430**	530**	
Te-1100	1100-20	Orange brown	370	430**	530**	
Te-1200	1200-20	Reddish orange	370	430**	530	
Te-1300	1300-15	Reddish brown	370	430**	530	
X = 0	1200-20	Phase separation	–	–	–	
X = 10	1200-20	Reddish orange	370	430**	530**	
X = 20	1200-20	Pale orange	370	430**	530**	
X = 30	1200-20	Colorless	–	–	–	
ZTP*	1200-60	Brilliant purple	375	417	537	600
Te-SL*	1450-60	Pale green	374	444	526**	625
Te-Spinel*	1600-60	Brownish pink	–	420 488**	556	599

*: Reference 6), **: very weak.
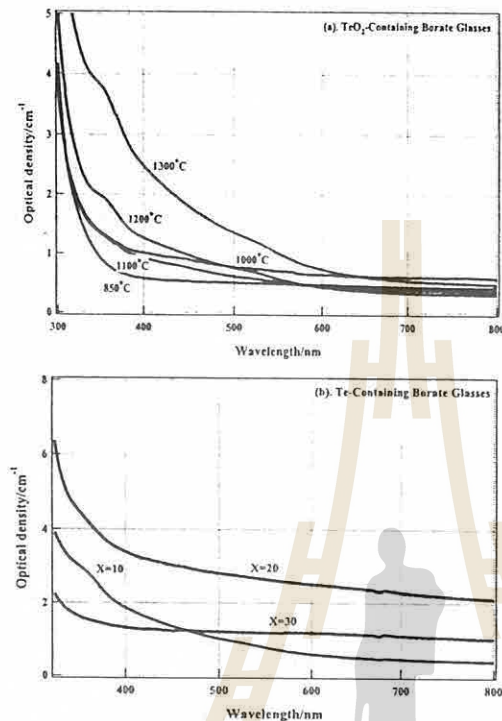
Fig. 2. Absorption spectra of Te-containing borate glasses. (a) Effect of melting temperature, (b) Effect of glass composition.
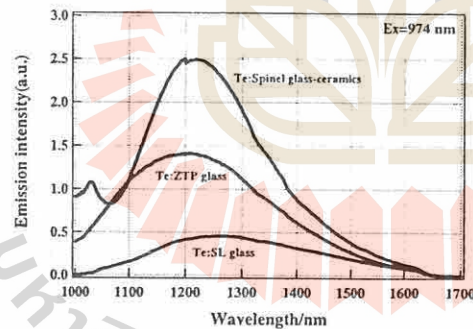

Fig. 3. NIR luminescence spectra of Te-containing glasses and glass-ceramics.[6]

However, as reported previously,[6),7)] ZTP, Te-SL and Te-Spinel glasses and glass-ceramics exhibited NIR luminescence centered at around 1200–1250 nm (**Fig. 3**).

In Table 1, the color center of borate glasses is different from those of ZTP, Te-SL and Te-Spinel glass and glass-ceramics. Especially, the band IV (~600 nm) is lacking in all borate glasses. This color center has been ascribed to Te_2^-. Murata et al.[9)] discussed the NIR luminescence characteristics of various

Bi-doped glasses based on optical basicity concept without any reducing agents, and they reported that the generation of NIR luminescence was affected strongly by optical basicity of base glass. They concluded that Λ of 0.4 was the critical point (above 0.4 no NIR luminescence was observed). As discussed in the previous section, the concentration of the color center due to Te_2 or Te_2^- species might be very low, resulting in the lacking of absorption bands and NIR luminescence in all borate glasses. On the contrary, the Λ values for Te-SL and Te-Spinel are 0.58 and 0.47. These values are much larger than that of ZTP glass. However, a small amount of carbon was added into Te-SL glass, which was melted at a higher temperature (1450°C), and Te-Spinel glass was melted at a much higher temperature (1600°C). The reducing agent and higher melting temperature enhance the reducing condition, and hence it seems that Te-SL and Te-Spinel glass and glass-ceramics exhibited NIR luminescence.

Consequently, it is suggested that the origin of NIR luminescence of Te-containing glasses is likely to be caused by Te_2^-.

4. Conclusion

The effects of the melting temperature and glass composition on the Near-infrared (NIR) luminescent characteristics of Te-containing borate glasses are investigated and compared with previous works.

Three absorption bands are detected at around ~370 nm, ~430 nm and ~530 nm, however, the absorption band at around ~600 nm cannot be detected in all borate glasses. Also, no NIR luminescence was observed under the excitation of a 974 nm laser diode. The NIR luminescence was observed in Te-green and Te-purple glasses, which showed the absorption band at around ~600 nm. This absorption band was derived from $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te_2^-.

Consequently, it is suggested that the origin of NIR luminescence of Te-containing green and purple glass is likely to be caused by Te_2^- center. (As with abstract, not sure of the real meaning of the sentence...)

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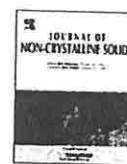
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Effect of carbon addition and TeO$_2$ concentration on NIR luminescent characteristics of TeO$_2$-doped soda-lime–silicate glasses

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ABSTRACT

The effects of carbon addition and TeO$_2$ concentration on the near-infrared (NIR) luminescent characteristics of Te-doped soda-lime–silicate glasses are investigated. Three absorption bands were detected in all glasses at around 330–380 nm, ~430 nm and ~630 nm, respectively. The last absorption band (~630 nm) has been ascribed to $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te$_2^-$. The broad NIR luminescence centered at 1200 nm was detected under the excitation of 974 nm laser diode except for glasses of lower carbon addition. The NIR luminescence was found to be strongly affected by melting atmosphere and TeO$_2$ concentration. It is considered that the absorption band, ~630 nm, is related strongly to the NIR luminescence of Te-doped soda-lime–silicate glasses. Consequently, it is suggested that the origin of NIR luminescence detected in Te-doped soda-lime–silicate glasses is likely to be caused by Te$_2^-$.

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1. Introduction

Tellurite glasses (high TeO$_2$-containing glasses) have received much attention as promising candidates for new glass because of their special properties [1–5], high nonlinear refractive indices [6], large nonlinear optical sensibility [6–9], relatively low phonon energy in the blue [10] and green band emission [11], wide transmission window and good stability and durability [3,4,12,13]. In addition these glasses are well known to be good hosts for some rare earth and heavy metal ions with small multi-phonon decay rate [6,14,15], and they are potential materials for up-conversion lasers [16,17], optical fiber amplifiers [18], such as tellurite-base Er-doped fiber amplifier [19], nonlinear optical devices, such as optical switching [6], optical memory, etc. [6].

However, high TeO$_2$-containing glasses often show the coloration, pale green to brilliant purple, depending on glass compositions and melting conditions [20,21]. Few research [20,22] has been reported on the coloration and color centers of TeO$_2$-containing glasses, their coloration change from pale green to brilliant purple depending on melting conditions and glass compositions. The color center of pale green TeO$_2$-containing glasses is clusters of Te:Te$_2$ and Te$_2^-$ [22], that of brilliant purple TeO$_2$ glasses is Te-metallic colloids [20].

Recently, the authors have found near-infrared (NIR) luminescence centered at 1250 nm with 250 nm of half width from pale green and purple TeO$_2$-containing glasses for the first time to our knowledge [23–25], and we concluded that the NIR luminescent center might be Te$_2$ and Te$_2^-$. In this paper, the effects of carbon addition and TeO$_2$ concentration on NIR luminescent characteristics of TeO$_2$-doped soda-lime–silicate glasses are investigated and compared with previous work [23].

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2. Experimental

2.1. Sample preparation

Two series of glasses were prepared. In series (I) glasses, compositions was $72SiO_2 \cdot 2Al_2O_3 \cdot 4MgO \cdot 8CaO \cdot 13Na_2O \cdot 1K_2O \cdot 1TeO_2 \cdot X$carbon (X = 0–1, wt%). Series (II) glasses, compositions was $72SiO_2 \cdot 2Al_2O_3 \cdot 4MgO \cdot 8CaO \cdot 13Na_2O \cdot 1K_2O \cdot XTeO_2 \cdot 0.3$carbon (X = 0.2–2, wt%).

High purity silica sand, alumina and reagent grade chemicals of MgO, $CaCO_3$, Na_2CO_3, K_2CO_3, TeO_2 and carbon were used as raw materials. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucible at 1450 °C for 1 h in an electric furnace in air. After melting they were poured onto iron plate and pressed by another iron plate. Then they were annealed at 600 °C for 30 min and cooled slowly in the furnace.

The glasses were cut and polished optically into about 2 mm in thickness for optical measurements. Hereafter, these glasses are referred to as C-0, C-0.1, C-0.2, C-0.3, C-0.5, C-1.0 and Te-0.2, Te-0.5, Te-0.7, Te-1.0, Te-2.0, respectively.

2.2. Absorption and luminescence measurement

The absorption spectra were measured with Cary 1E ultraviolet-visible (UV–Vis) spectrometer in the range of 300 nm to 800 nm at room temperature.

The luminescence spectra in the NIR region (1000–1700 nm) were measured under the excitation of 974 nm laser diode at room temperature. Emission from the sample were dispersed by a single monochromator (blaze, 1.0 nm; grating, 600 grooves/mm; resolution, 3 nm) and detected by an InGaAs photodiode.

3. Result and discussion

3.1. Absorption spectra

The appearances of glasses in series I change from colorless (C-0) to dark green–black (C-1.0) with increase in the amount of carbon addition. In series II, color of glasses change from green (Te-0.2) to pale green (Te-2.0) with increase in TeO_2 concentration. Fig. 1 shows absorption spectra of TeO_2-doped soda-lime–silicate glasses of series I and II glasses. Appearances and absorption bands of glasses are summarized in Table 1.

Three absorption bands can be observed in all glasses, 330–380 nm, ~430 nm, ~630 nm, respectively. In series I glasses, weak absorption bands can be detected even in C-0 glass, the absorbance increases with increase in the amount of carbon, and the absor-
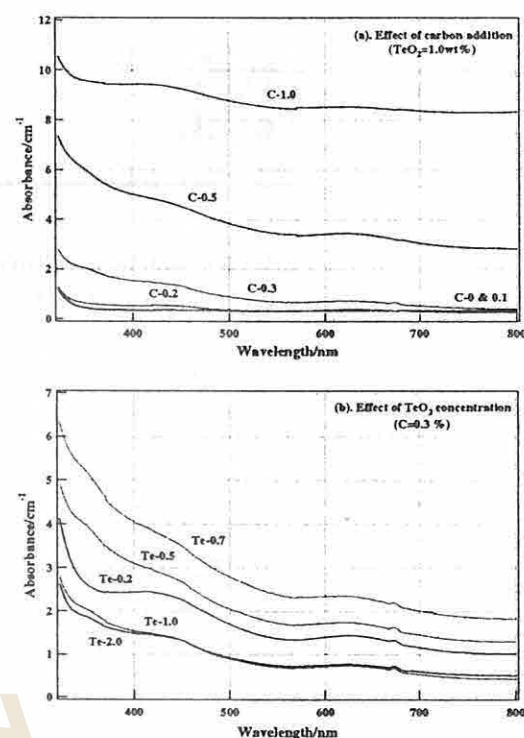

Fig. 1. Absorption spectra of TeO_2-doped glasses. (a) Effect of carbon addition (TeO_2 = 1.0 wt%).(b)Effect of TeO_2 concentration (Carbon = 0.3 wt%).

bance is very high in whole wavelength region in C-0.5 and C-1.0 glasses.

On the other hand, the absorbance of series II glasses increases with increase in the amount of TeO_2 (0.2–1.0 wt%) and decreases again. However, the absorption band owing to Te-metallic colloids (~530 nm) cannot be observed in all glasses discussed here.

The assignment of these absorption bands has been already known that absorption band (I) is due to exciton transition, band (II) $^3\Sigma g^- \to {}^3\Sigma u^-$ transition of Te_2, band (III) Te metallic colloids and band (IV) $^2\Pi g \to {}^2\Pi u$ transition of Te_2^- [20,21], respectively.

Table 1
Melting conditions, appearance and absorption bands of glasses studied

No.	Melting condition (°C min)	Appearance	Absorption bands/nm			
			I	II	III	IV
C-0	1450–60	Colorless	~380[a]	432	–	638[a]
C-0.1	1450–60	Pale green	~380[a]	432	–	638[a]
C-0.2	1450–60	Green	377[a]	432	–	638[a]
C-0.3	1450–60	Green	327	435	–	633
C-0.5	1450–60	Dark green	355	436	–	638
C-1.0	1450–60	Dark green-black	375	438	–	634
Te-0.2	1450–60	Green	367	437	–	635
Te-0.5	1450–60	Green, partly brownish green	344	432	–	633
Te-0.7	1450–60	Green, partly brownish green	349	435	–	634
Te-1.0	1450–60	Green	327	435	–	633
Te-2.0	1450–60	Green	331	436	–	633
Te-1200[b]	1200–20	Reddish orange	370	430	530	–

[a] Very weak.
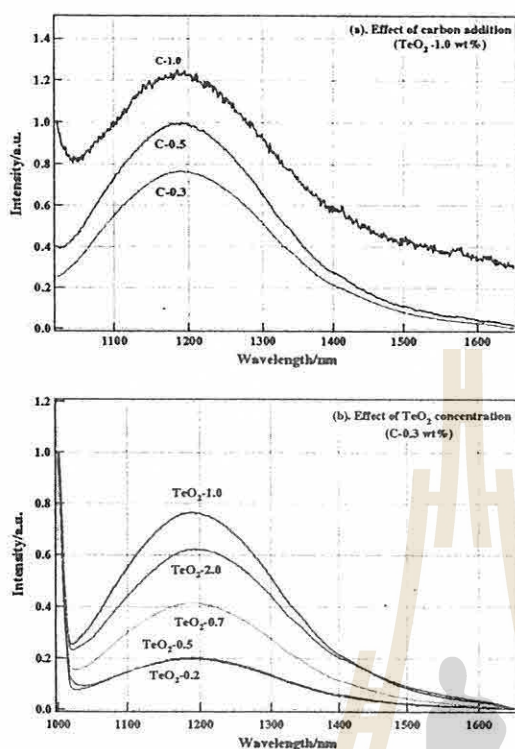[b] $63B_2O_3 \cdot 9Al_2O_3 \cdot 9ZnO \cdot 9K_2O \cdot 10TeO_2$ (mol%) melted in alumina crucible [25].

Fig. 2. NIR luminescence spectra of TeO$_2$-doped soda-lime–silicate glasses. (a) Effect of carbon addition (TeO$_2$ = 1.0 wt%). (b) Effect of TeO$_2$ concentration (Carbon = 0.3 wt%).
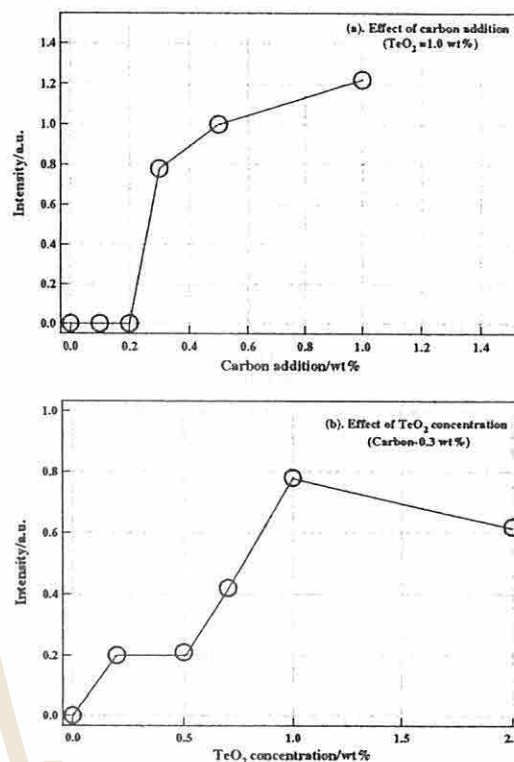

Fig. 3. NIR luminescence intensity of TeO$_2$-doped soda-lime-silicate glasses. (a) Effect of carbon addition (TeO$_2$ = 1.0 wt%). (b) Effect of TeO$_2$ concentration (Carbon = 0.3 wt%).

For comparison with Te-doped soda-lime–silicate glasses, the absorption bands of Te-containing borate glasses are also shown in Table 1. The band III was observed but the band IV could not be detected in borate glasses.

3.2. NIR luminescence

Fig. 2 shows the NIR luminescence spectra of glasses under the excitation of 974 nm laser diode at room temperature. In these glasses, the strong and broad emission band can be observed at around 1200 nm except for glasses of lower carbon addition (C-0, C-0.1 and C-0.2 glasses). In series I glasses, the luminescent intensity increases with increase in the amount of carbon (Fig. 3(a)). On the contrary, the luminescent intensity of series II glasses increases with increase in TeO$_2$ concentration and reaches to the maximum at TeO$_2$ = 1.0 wt% and decrease slightly again at TeO$_2$ = 2.0 wt% (Fig. 3(b)). Thus the intensity of NIR luminescence was strongly affected by melting atmosphere and TeO$_2$ concentration.

The authors have investigated color generation and NIR luminescence characteristics of Te-containing borate glasses melted under various conditions [25]. Though the coloration of glasses changed depending on melting conditions and glass compositions, the green-colored glass could not be obtained. In these glasses, three absorption bands were observed, ~370 nm, ~430 nm and ~530 nm, however, the band at around ~630 nm could not be detected. One example of borate glasses is shown in Table 1. As mentioned previously, the band at ~530 nm is due to Te–metallic

colloids [20]. These borate glasses did not exhibit any NIR luminescence under the excitation of 974 nm laser diode.

Lindner et al. [22] have reported that two luminescence bands could be observed at 562 nm and 862 nm under the excitation of 457 nm, and they concluded that the former band was ascribed to $^3\Sigma u^- \rightarrow {}^3\Sigma g^-$ transition of Te$_2$ and the latter was due to $^2\Pi u \rightarrow {}^2\Pi g$ of Te$_2^-$. However, they did not observe the NIR luminescence (>1000 nm). On the contrary, band IV (~630 nm) was observed in all Te-doped soda-lime–silicate glasses discussed here, and the NIR luminescence was detected under the excitation of 974 nm except for glasses of low carbon addition (C-0, C-0.1 and C-0.2). All borate glasses without absorption band IV did not show any NIR luminescence. Therefore, it is considered that the color center of band IV (~630 nm) is strongly related to NIR luminescence.

Consequently, it is suggested that the NIR luminescent center of Te-doped soda-lime–silicate glasses is likely to be caused by Te$_2^-$.

4. Conclusion

The effects of carbon addition and TeO$_2$ concentration on the NIR luminescent characteristics of Te-doped soda-lime–silicate glasses are investigated. All glasses appear to be green in color. The color becomes to be deeper with increase in the amount of carbon addition at constant TeO$_2$ concentration. And also the color changes from green to brownish green and again pale green with increase in TeO$_2$ concentration at constant carbon amount. Three absorption bands were detected in all glasses, 330–380 nm,

$\sim$430 nm and $\sim$630 nm, respectively. The last absorption band ($\sim$630 nm) has been ascribed to $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te_2^-.

The broad NIR luminescence centered at around 1200 nm was detected under the excitation of 974 nm laser diode except for glasses of lower carbon addition. The NIR luminescence was found to be strongly affected by melting atmosphere and TeO_2 concentration. It is considered that the absorption band ($\sim$630 nm), is related strongly to NIR luminescence of Te-doped soda-lime–silicate glasses.

Consequently, it is suggested that the origin of NIR luminescence detected in Te-doped soda-lime–silicate glasses is likely to be caused by Te_2^- center.

Acknowledgement

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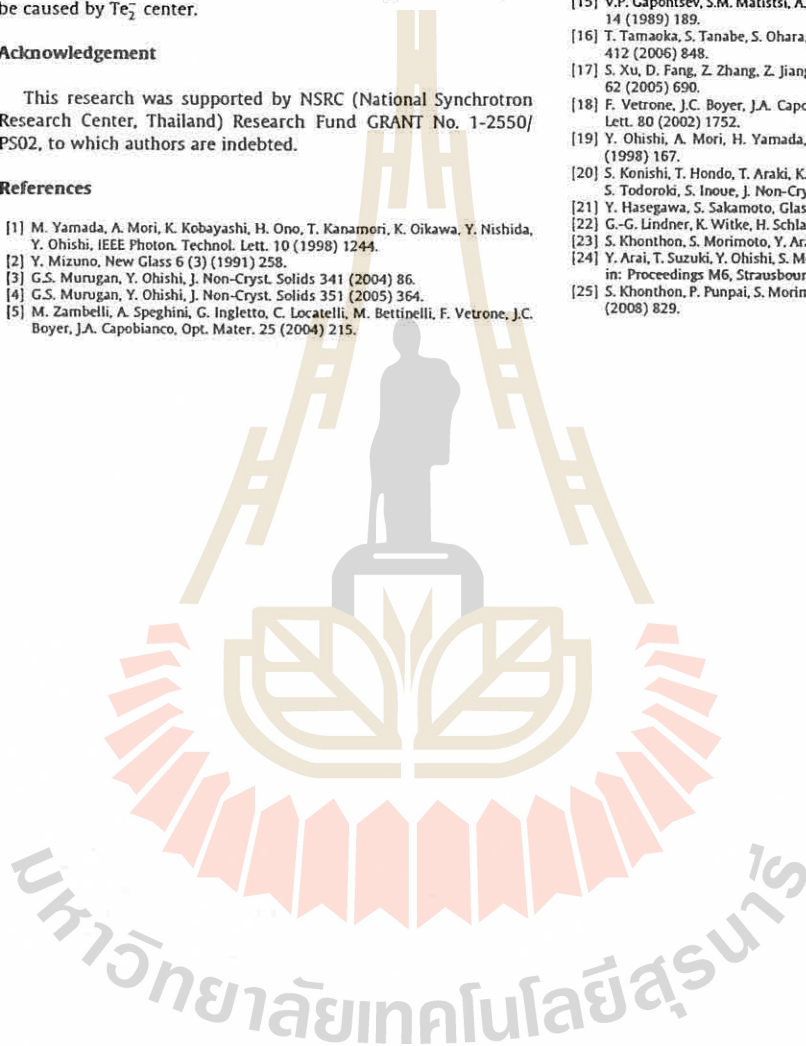
Redox equilibrium and NIR luminescence of Bi_2O_3-containing glasses

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ABSTRACT

The relationship between factors affecting redox equilibrium, melting temperature, glass composition and carbon addition, and near infrared luminescence (NIR) characteristics of Bi-containing glasses was investigated, and the color center and luminescent center of these glasses were discussed based on redox equilibrium. It was found that the coloration and NIR luminescent characteristics of Bi-containing glasses are strongly affected by redox equilibrium. It was confirmed that the darkening effect (black coloration) of Bi-containing glasses is the formation process of metallic Bi colloids. The highest NIR luminescent intensity was obtained in glasses just before the beginning of darkening effect. Absorption and luminescence measurements suggest that there are few color centers and luminescent centers in these glasses. It is suggested that the color center and NIR luminescent center is likely to be caused by lower valence state species of Bi, such as Bi clusters (e.g. dimmer, tirmer, etc.) and Bi^+.

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1. Introduction

Since Fujimoto and Nakatsuka [1] discovered the NIR luminescence from Bi-doped silica glass in 2001, Bi-doped glasses have received much attention as a candidate of NIR amplifier and NIR tunable laser materials, and many researches have been done (e.g. [2–5]). In 2005, Dianov et al. [6] reported the laser oscillation in the spectral region between 1150 and 1300 nm using Bi-doped alumino-silicate glass fiber. Although, many ideas on the color center and the luminescent center of these Bi-containing glasses are proposed, such as Bi^{5+} ion [1], Bi^+ ion [2,3] and Bi cluster [4,5], the origin of NIR luminescence is still unknown.

It is well known that these glasses often appear to be coloration depending on glass composition and melting conditions, and small particles were sometimes observed in glasses [7–9]. These small particles are believed to be metallic Bi colloids [9] and this phenomenon is called as darkening effect or darkening process (black coloration). This indicates that Bi_2O_3 are very sensitive to preparation conditions and readily reduced to metallic Bi. Thus the coloration of Bi-doped glasses can be considered based on the redox equilibrium in glasses. Furthermore, it is quite important to identify what kinds of Bi species respond to color center and NIR luminescent center.

In this paper, the relationship between factors affecting redox equilibrium, melting temperature, glass composition and carbon addition, and NIR luminescent characteristics of Bi-containing glasses are investigated, and the color center and luminescent center of these glasses are discussed based on redox equilibrium.

2. Experimental

2.1. Sample preparation

Three series of glasses were prepared. The compositions of glasses are as follows.

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Series I: $63B_2O_3 \cdot 9Al_2O_3 \cdot 9ZnO \cdot 9K_2O \cdot 10Bi_2O_3$ (mol%).
Series II: $90[(80 - X)B_2O_3 \cdot 10Al_2O_3 \cdot 10ZnO \cdot XK_2O] \cdot 10Bi_2O_3$
($X = 0$, 10, 20 and 30 mol%).
Series III: $72SiO_2 \cdot 2Al_2O_3 \cdot 4MgO \cdot 8CaO \cdot 13Na_2O \cdot 1K_2O \cdot 0.5Bi_2O_3 \cdot X$ Carbon (wt%, $X = 0-1.5$).

High purity silica sand, alumina and reagent grade chemicals of H_3BO_3, MgO, $CaCO_3$, ZnO, Na_2CO_3, K_2CO_3, Bi_2O_3 and carbon were used as raw materials. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucible under various conditions in an electric furnace in air. Glasses of Series I were melted at 1000–1400 °C for 15–40 min. Then they were annealed at 450 °C for 30 min and cooled slowly to room temperature in the furnace. These glasses are referred to as Bi-1000, Bi-1100, Bi-1200, Bi-1300 and Bi-1400, respectively. The Bi-1400 glass was also melted under strong reducing condition by adding 2.0% of carbon (Bi-1400-C2.0).

Glasses of Series II are melted in 50 cc alumina crucible at 1200 °C for 20 min, after melting they were poured onto iron plate and pressed by another iron plate. Then they were annealed at 450 °C for 30 min and cooled slowly to room temperature in the furnace. These glasses are referred to as $X = 0$, 10, 20 and 30, respectively.

Glasses of Series III are melted in 50 cc alumina crucible at 1450 °C for 1 h, after melting they were poured onto iron plate and pressed by another iron plate. Then they were annealed at 650 °C for 30 min and cooled slowly to room temperature in the furnace. These glasses are referred to as C-X. The C-1.0 glass was also annealed at 550 °C for 5 min and cooled slowly to room temperature in the furnace (hereafter denotes C-1.0*).

All glasses were ground and polished optically into about $20 \times 30 \times 2$ mm for optical measurement.

The fractured surface of glasses was etched by 0.5% HF solution for 1 min at room temperature and observed by scanning electron microscope (SEM, JEOL JSM 6400).

2.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were performed using a spectrometer with monochromatized Mg Kα radiation at acceleration voltage of 15 kV with electron shower.

The shift of the energy scale was corrected with a reference of C 1 s binding energy of residual hydrocarbon at 284.6 eV.

2.3. X-ray diffraction (XRD)

The crystalline phases of colored glasses were examined by powder X-ray diffraction analysis (XRD) (Bruker, AXS Model D5005). The condition of measurement is: Cu Kα radiation, slit system: 1°–1°, 0.02°/step, 100 s/step, $2\theta = 26-28°$ and $2\theta = 37-39°$. These regions of 2θ correspond to metallic Bi (0 1 2) and Bi (1 0 4) planes.

2.4. Optical measurement

The absorption spectra were measured with Cary 5E ultra-violet-visible (UV–VIS–NIR) spectrometer in the range of 300–800 nm at room temperature.

The luminescence spectra in NIR region (900–1700 nm) were measured under the excitation of 974 nm laser diode at room temperature. Luminescence from the samples was dispersed by a single monochromator (blaze, 1.0 mm; grating, 600 grooves/mm; resolution, 3 nm) and detected by an InGaAs photodiode.

3. Results

3.1. Appearance and absorption spectra

The melting condition and appearance of glasses are summarized in Table 1. The colors of glasses of Series I change from faint yellow (Bi-1000) to black (Bi-1300, Bi-1400, Bi-1400 C-2.0) with increase in temperature. In Bi-1400 C-2.0 glass, silver-white colored Bi metal (6~8 mm in diameter with 5 mm thickness) precipitated at the bottom of crucible. The color changes from reddish brown to yellow with increase in X (amount of K_2O) in Series II glasses. $X = 20$ and 30 glasses showed phase separation, especially $X = 20$ glass. In Series III glasses, the color changes systematically from colorless to brown–black with increase in the amount of carbon addition. It should be noted that the color changes by the change of annealing condition (C-1.0* and C-1.0 glasses). C-1.0* glass annealed at lower temperature is colorless, but C-1.0 glass annealed at higher temperature exhibits brown.

Table 1
Melting conditions, appearances and absorption bands of glasses studied.

No.	Melting condition (°C – min)	Appearance	Absorption bands/nm		
			I	II	III
Series-I Bi-1000	1000 – 40	Faint yellow–green	–	–	–
1100	1100 – 20	Pale orange	460	–	–
1200	1200 – 20	Orange–red	460	–	–
1300	1300 – 15	Black	–	–	–
1400	1400 – 15	Black	–	–	–
1400-C2.0	1400 – 15	Black, Bi Metal	–	–	–
Series-II $X = 0$	1200 – 20	Reddish-orange	455	497	717**
10	1200 – 20	Orange–red	460	–	–
20	1200 – 20	Yellow–brown phase separated	–	–	–
30	1200 – 20	Yellow phase separated	–	–	–
Series-III C-0	1450 – 60	Colorless	–	–	–
C-0.5	1450 – 60	Colorless	460**	–	–
C-1.0*	1450 – 60	Colorless	460**	–	–
C-1.0	1450 – 60	Brown	–	–	–
C-1.5	1450 – 60	Brown–black	–	–	–
Fujimoto et al. [1,2], Khonthon et al. [5], Peng et al. [10,11];			–	490	710
Ren et al. [3,4]			~460	–	–

* Annealed at 550 °C for 5 min.
** Very weak.

Figs. 1 and 2 show SEM photos of brown to black colored glasses. Many spherical particles of smaller than 1 μm are observed and their shape becomes to be more clear and distinct with increasing melting temperature and reducing condition for Bi-1300, Bi-1400 and Bi-1400 C2.0 glasses. Furthermore, it is clearly seen that small particles of about 100 nm can be detected in C-1.0 and C-1.5 glasses. These particles might be metallic Bi colloids [9].

Fig. 3 shows the XPS spectra of glasses of Series I and II. The XPS spectrum of Bi metal precipitated at the bottom of crucible is also shown in Fig. 3. Two peaks of Bi $4f_{7/2}$ and Bi $4f_{5/2}$ were detected in all glasses, and these are from Bi^{3+} ions. However, any signal can not be observed in lower energy side, despite the peak position shifts slightly to lower energy side and half height width increases slightly with increasing melting temperature. On the contrary, $Bi°$

peaks can also be detected in Bi metal precipitated in Bi-1400 C2.0 glass. This result indicates that the detectable amount of lower valence state species of Bi is not present in these glasses.

Fig. 4 shows XRD patterns of Bi-1200, Bi-1300, Bi-1400 and Bi-1400 C2.0 glass. It is clearly seen that two diffraction peaks are detected at $2\theta = 27.3°$ and $2\theta = 38.2°$ in black colored glasses, Bi-1300, Bi-1400 and Bi-1400 C2.0. However, no diffraction peaks can be
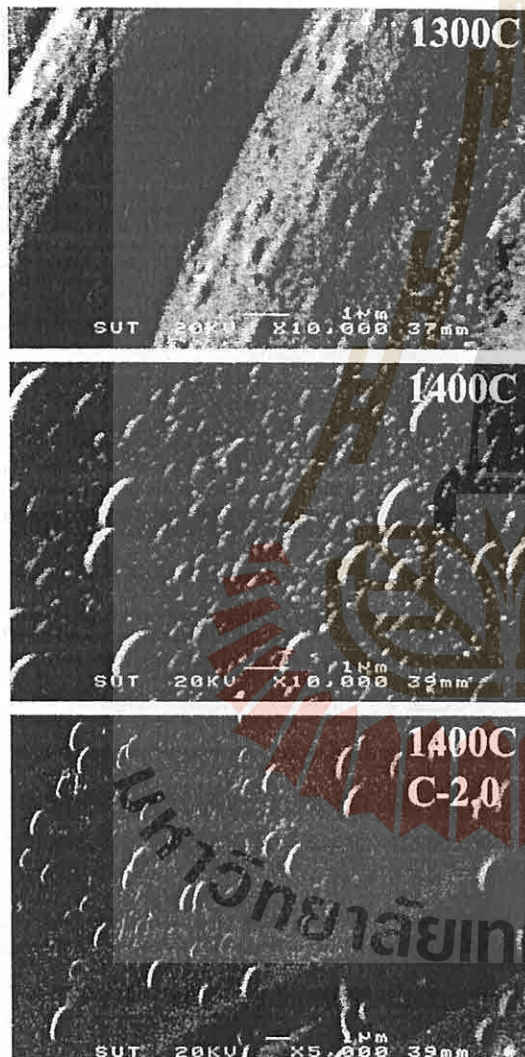
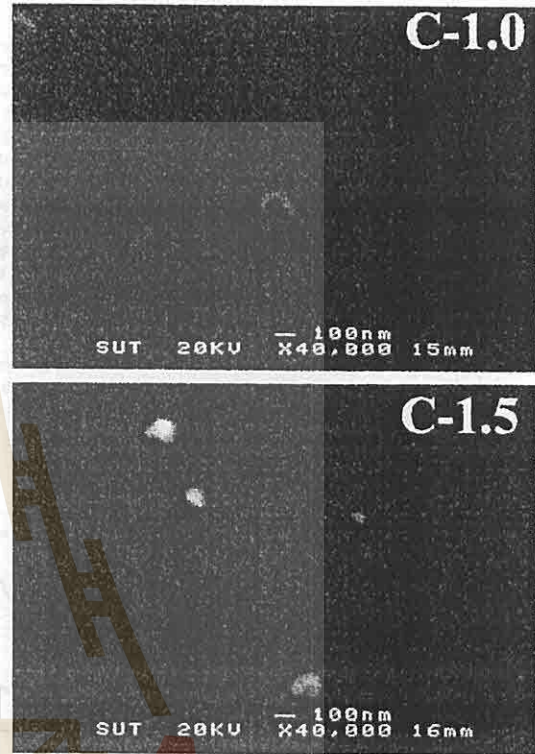Fig. 1. SEM photos of Bi-1300, Bi1400 and Bi-1400-C2.0 glasses.

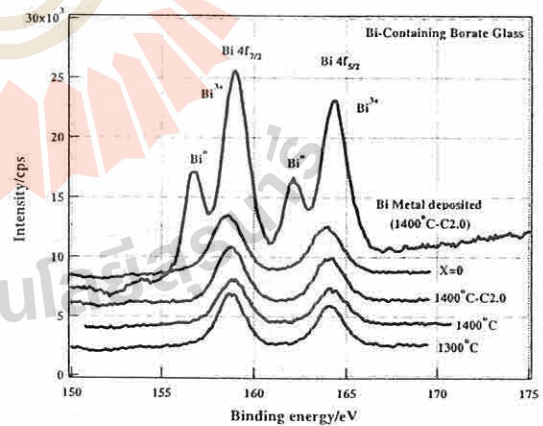Fig. 2. SEM photos of C-1.0 and C-1.5 glasses.

Fig. 3. XPS spectra of Bi-4f for various glasses.

detected in orange–red colored Bi-1200 glass. The peak intensity increases with increasing melting temperature and reducing condition. These peaks can be assigned to (012) and (104) planes of metallic Bi (JCPDS 00-001-0699). Therefore, it is concluded that the spherical particle observed in SEM photos could be metallic Bi colloid particles. Thus, Bi_2O_3 is reduced partially to metallic Bi colloids by melting higher temperature and reducing condition. However, it seems that the amount of metallic Bi colloids might be very low, less than 1 wt%. The darkening effect of Bi-containing glasses is confirmed to be the formation process of metallic Bi colloids.

The absorption spectra of glasses are shown in Figs. 5 and 6. The absorption spectra for black colored glasses (Bi-1300, Bi-1400 and Bi-1400 C2.0) could not be measured because of their very deep coloration. The simple absorption band is observed at around 460 nm in Bi-1100 and Bi-1200 glasses, and the absorption intensity of Bi-1200 glass is higher than that of Bi-1100 glass (Fig. 5a). The observed spectra were analyzed and separated into few absorption bands using curve fitting method with Gaussian distribution and the result is also shown in Table 1. The spectral patterns of these glasses are very similar to that reported previously [2,3]. However, Fujimoto and Nakatsuka [1], Peng et al. [10,11] and Khonthon et al. [4] reported another spectral patterns (Table 1). They have basically two absorption bands, ~490 and ~700 nm in VIS region.

The absorption spectra of Series II glasses are shown in Fig. 5b. It seems that the absorption band of $X = 0$ glass shifts slightly to longer wave length compared with $X = 10$, Bi-1100 and Bi-1200 glasses.
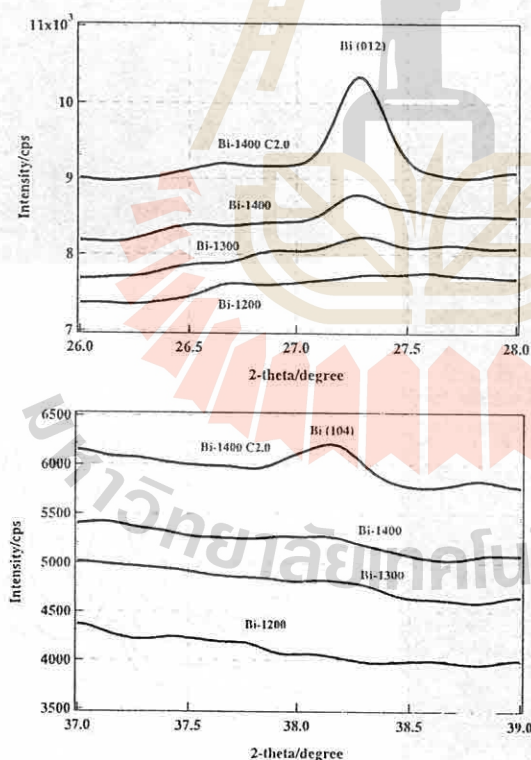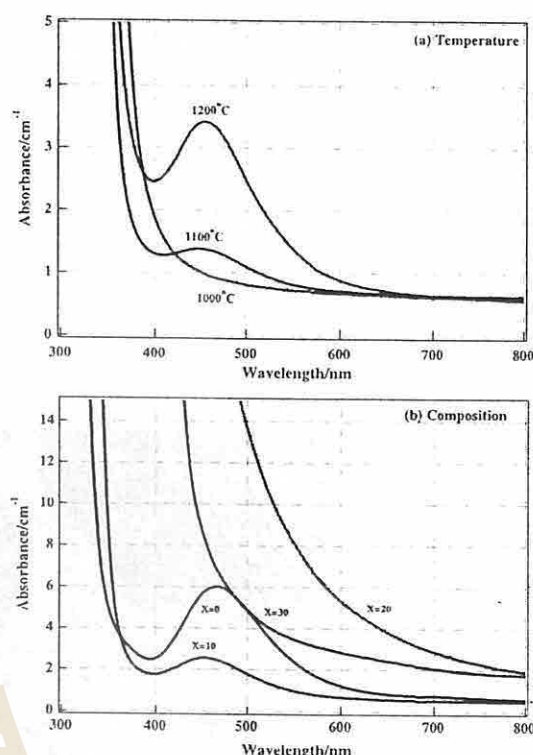

Fig. 5. UV–VIS absorption spectra of Series I and II borate glasses at room temperature. (a) Temperature dependence, (b) composition dependence.

It should be noted that a new and weak absorption band appears at around 700 nm in $X = 0$ glass. The spectral pattern of $X = 0$ glass is similar to those reported by Fujimoto and Nakatsuka [1], Peng et al. [10,11] and Khonthon et al. [4]. And the spectral pattern of $X = 10$ glass is also similar to those of Bi-1100, Bi-1200 glasses and that reported by Ren et al. [2,3]. There is no characteristic absorption band in $X = 20$ and 30 glasses.

In Series III glasses, a weak absorption band at around 460 nm can be observed in C-0.5 and C-1.0* (550 °C – 0 min.) glasses (Fig. 6). These spectral patterns are also similar to those of Bi-1200, Bi-1300 and $X = 10$ glasses. This suggests that few kinds of color centers might be present in these glasses.

3.2. NIR luminescence

Figs. 7 and 8 show NIR luminescence of glasses under the excitation of 974 nm laser diode. In Series I glasses, Bi-1300 and Bi-1400 and Bi-1400 C-2.0 glasses do not show NIR luminescence. On the contrary, the broad NIR luminescence centered at around 1150 nm can be observed in Bi-1100 and Bi-1200 glasses. The NIR luminescence intensity of Bi-1000 glass is very weak. From the result of XPS and XRD measurement, it is clear that Bi^{3+} ion and Bi colloids do not respond to the generation of NIR luminescence.

In Series II glasses, a relatively strong NIR luminescence was observed centered at around 1080 nm for $X = 0$ glass, and this spectral pattern is different from those of Bi-1100 and Bi-1200 glasses. On the other hand, the luminescence centered at around 1150 nm was
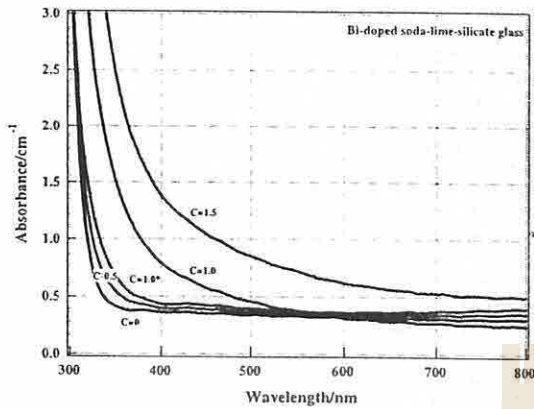

Fig. 4. XRD patterns of Series I glasses.

Fig. 6. UV–VIS absorption spectra of Series III soda-lime-silicate glasses at room temperature.
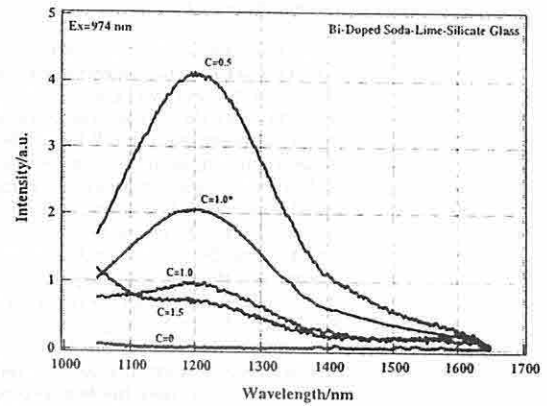

Fig. 8. NIR luminescence spectra of Series III soda-lime-silicate glasses under the excitation of 974 nm laser diode at room temperature.

detected in X = 10 glass, and this spectral pattern is quite similar to those of Bi-1100 and Bi-1200 glasses. It is considered that the change in NIR luminescence spectrum of X = 0 glass is due to the new absorption bands, 497 and 717 nm. This revealed that different luminescent center is present in these glasses.
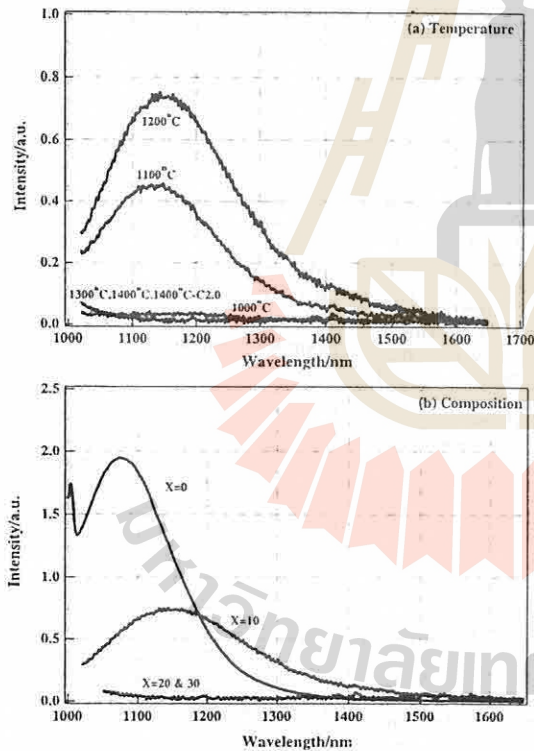

Fig. 7. NIR luminescence spectra of Series I and II borate glasses under the excitation of 974 nm laser diode at room temperature. (a) Temperature dependence, (b) composition dependence.

In Series III glasses, the broad NIR luminescent bands centered at around 1200 nm were detected except for C-0 glass. The strongest luminescence was observed in C-0.5 glass, and the luminescent intensity decreases with increasing amount of carbon. The luminescent intensity of C-0.5 glass is higher than those of glasses in Series I and II. No NIR luminescence can be observed in C-0 glass. It should be noted that the different luminescent characteristics was observed in C-1.0* and C-1.0 glasses. The glass annealed at lower temperature (C-1.0*) exhibits stronger NIR luminescence than that of glass annealed higher temperature (C-1.0).

4. Discussion

4.1. Melting temperature

It was found that the coloration and near-infrared luminescent characteristic of Bi-containing borate glasses were strongly affected by melting temperature. The color became deeper and deeper with increasing melting temperature and finally Bi metallic colloids precipitated being black color. Near-infrared luminescence started to appear, reached the maximum and finally disappeared with increasing melting temperature.

Generally the redox equilibrium of metal ions moves toward reduced side (lower valence state) with increasing melting temperature [12]. Thus the change in valence sate of Bi may be written by:

$$Bi^{3+} \overset{[I]}{\to} Bi^{2+} \overset{[II]}{\to} Bi^{+} \overset{[III]}{\to} Bi/Bi_2, \ Bi_2^{-}, \ Bi_3, \ etc. \overset{[IV]}{\to} (Bi)_n \qquad (1)$$

where Bi_2, Bi_2^{-}, Bi_3, etc., are Bi clusters and $(Bi)_n$ the Bi metallic colloid. The metallic Bi colloids were confirmed to be present in black colored glasses melted at higher temperature by XRD (Fig. 4). It is concluded that the darkening effect (black coloration) of Bi-containing glasses is the formation process of metallic Bi colloids (process IV in Eq. (1)). This process has often been observed in the formation of noble-metal colloids [13]. Bi^{3+} ion and metallic Bi colloids do not respond to NIR luminescence, and hence, the origin of coloration and NIR luminescence might be intermediate species between Bi^{3+} ion and Bi colloids. The NIR luminescent intensity becomes to be higher just before the beginning of darkening effect, therefore the color center and luminescent center might be low valence state species of Bi species, such as Bi clusters (e.g. dimmer, trimer, etc.) and Bi^{+}.

4.2. Glass composition

The glass composition also affects to redox equilibrium of metal ions in glasses. Generally, higher oxidation state was induced by an increase in the basicity of glass (increasing alkali content) [12]. In Series II glasses, the coloration decreases with increase in K_2O content. This shows that the Bi^{3+} ions is dominant in $X = 20$ and 30 glasses comparing with $X = 0$ and $X = 10$ glasses. Murata and Mouri [14] discussed NIR luminescence characteristics of various Bi-doped glasses based on optical basicity. They concluded that the optical basicity of $\Lambda = 0.4$ is critical, and no NIR luminescence was observed above this value. According to Duffy's optical basicity concept [15], the optical basicity, Λ, of all glasses were calculated. Λ is 0.45 for $X = 0$, 0.50 for $X = 10$ (Bi-1000–Bi-1400 C2.0), 0.55 for $X = 20$ and 0.59 for $X = 30$ glasses, respectively. However, a very weak NIR luminescence was detected in $X = 10$ ($\Lambda = 0.50$) glass melted at 1000 °C compared with the result of Murata and Mouri [14]. On the other hand, NIR luminescence could not be detected in $X = 20$ and 30 glasses. This indicates that the formation of color center and luminescent center of Bi-containing glasses is apparently influenced by optical basicity of glasses regardless of the critical point, 0.4.

The absorption spectrum of $X = 0$ glass is different from those of $X = 10$, Bi-1100 and Bi-1200 glasses. The peak position shifts to longer wavelength slightly and a new and weak absorption band appears at around 700 nm. This spectral pattern is quite similar to those of pink colored Bi-doped glasses [4,10,11]. And the NIR luminescence is also different slightly. Khonthon et al. [4] observed that pink colored spinel transparent glass ceramics shows similar absorption and NIR luminescence spectra to $X = 0$ glass, and hence it seems that the color center and NIR luminescent center of both glasses are the same. On the contrary, Bi-1100, Bi-1200, $X = 10$ glasses exhibit different absorption spectra and luminescence spectra. Therefore, these glasses might have a different color center and luminescent center from those of $X = 0$ glass (Table 1).

4.3. Effect of carbon addition

The reducing agent such as carbon affects directly to the redox equilibrium of opponent oxides [12], the concentration of lower valence state of Bi species increases with increase in the amount of reducing agent (carbon).

As mentioned previously, the basicity of glasses strongly affected to the NIR luminescence characteristics of glasses. The optical basicity of soda-lime-silicate glass discussed here (without carbon) is calculated to be $\Lambda = 0.58$, which is much greater than critical value of 0.4 [14], and hence the NIR luminescence could not be detected in C-0 glass even melted at 1450 °C. However, the NIR luminescence started to appear and reach the maximum at C-0.5 and decreased again with an increase in the amount of carbon. Furthermore, the darkening effect also appears in the glass added large amount of carbon, C-1.0 and C-1.5 glasses. Thus, the effect of reducing agent is very large, and suitable amount of reducing agents enhances the NIR luminescence. This indicates that the higher concentration of color center and luminescent center may be formed at that condition. And the colorless and transparent materials could also be obtained with lower amount of Bi_2O_3 concentration (in this glass only 0.5 wt% Bi_2O_3 compared with Series I and II glasses).

It was observed that the annealing condition also influences NIR luminescent characteristics. Higher annealing temperature induces darkening effect despite the same batch composition and melting condition (C-1.0* and C1.0 glasses). The glass annealed at lower temperature (C-1.0*) exhibits colorless and stronger NIR luminescence than that of brown glass annealed at higher temperature (C-1.0). It seems that this phenomenon observed here may be the

process [IV] in Eq. (1). Atomic or molecular Bi gathers together grows and forms the colloid. This process is often observed in the formation process of noble-metal colloids [13]. Therefore, the glass becomes to be black in color and the NIR luminescence decreases with the formation of Bi colloid.

Finally, it is considered that the color center and luminescence center of Bi-doped glasses may be the Bi species just before the formation of Bi metallic colloids, lower valence state species of Bi such as Bi clusters (e.g. dimmer, trimer, etc.) and Bi*, and the concentration of color center and luminescent center seems to be very low few tenth of ppm [16].

5. Conclusion

The relationship between factors affecting redox equilibrium melting temperature, glass composition and carbon addition, and NIR luminescence of Bi-containing glasses are investigated, and the color center and luminescent center of these glasses are discussed based on redox equilibrium.

It was found that the coloration and NIR luminescent characteristics of Bi-doped glasses are strongly affected by melting temperature, glass composition, carbon addition and annealing condition. The color becomes deeper with increasing melting temperature and finally metal colloids precipitate being black color. And also the color changes from reddish orange to pale yellow with increasing alkali content. The color changes from colorless to brown–black color with increasing amount of carbon addition. Higher annealing temperature induces darkening effect. It was confirmed that the darkening effect (black coloration) of Bi-containing glasses is the formation process of metallic Bi colloids.

NIR luminescence starts to appear, reach the maximum and finally disappears with increasing temperature, decreasing alkali content and increase in the amount of carbon addition. Higher annealing temperature reduces NIR luminescent intensity. Thus the luminescent characteristics of Bi-containing glasses are found to be affected strongly by redox equilibrium of Bi and the highest intensity might be obtained in the glass just before the beginning of darkening effect (formation process of Bi metallic colloid).

Optical absorption and NIR luminescence measurement suggest that there are few color centers and luminescent centers in the glasses. It is suggested that the color center and NIR luminescence center is likely to be caused by lower valence state species of Bi such as Bi clusters (e.g. dimmer, trimer, etc.) and Bi*.

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LUMINESCENCE CHARACTERISTICS OF Se-, Te- AND Bi-DOPED GALSSES AND TRANSPARENT GLASS-CERAMICS

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KEY WORDS: UV-VIS and NIR luminescence, glass, transparent glass-ceramics, Se-, Te- and Bi molecule

ABSTRACT

The origin of coloration and luminescence of Se-, Te- and Bi-doped glasses and glass-ceramics were investigated. NIR luminescence was observed at around 1100 nm and 1200 nm in Bi-doped and Te-doped glasses and glass-ceramics, respectively. On the contrary, no NIR luminescence could be observed in Se-doped glass. It is suggested that the origin of coloration and NIR luminescence in these hosts is most likely to be caused by molecular Se_2 (Se_2^-), Te_2 (Te_2^-) and Bi_2 (Bi_2^-).

INTRODUCTION

Broad band tunable lasers such as Ti^{3+}:Al_2O_3[1], Cr^{4+}:YAG[2], Cr^{3+}:LiCAF[3] were realized by using transition metals as active ions. If other active ions were active in glasses or transparent glass-ceramics, ultra-broadband optical amplifiers could be realized. The characteristics of broad band NIR emission from Se-, Te- and Bi- doped glasses and transparent glass-ceramics were investigated and the origin of color generation and NIR emission were also discussed.

EXPERIMENTAL

Four kinds of glasses were prepared by conventional melt-quench method. Spinel glasses were heat treated subsequently for crystallization. Glasses and glass-ceramics were cut and polished optically into about 1mm in thickness for optical measurement. NIR luminescence was measured under the excitation of 974 nm laser diode.

RESULTS & DISCUSSION

The glasses appeared to be pink, green and purple, and pink in color for Se-, Te- and Bi doped glasses and glass-ceramics, respectively. Absorption spectra suggested that the color generation of these glasses and glass-ceramics might be due to molecular Se_2/Se_2^- for Se-pink, molecular Te_2/Te_2^- for Te-green, nano-size metallic particles of Te for Te-purple and molecular Bi_2/Bi_2^- for Bi-pink, respectively.

Figure 1 shows the NIR luminescence spectra of glasses and glass-ceramics. The broad NIR luminescence was clearly observed in Bi- and Te-doped glass and glass-ceramics.
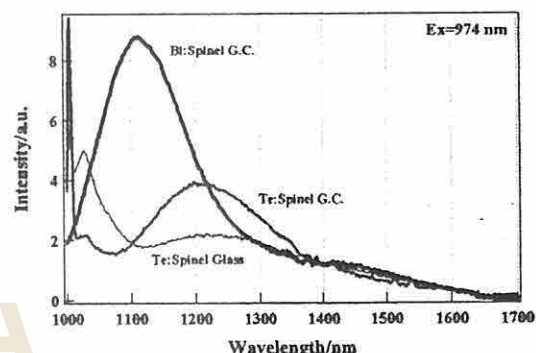

Fig. 1. NIR luminescence spectra of Te- and Bi-doped glasses and glass-ceramics under the excitation of 974 nm laser diode at room temperature.

In Bi-doped glass-ceramics, emission peaking at around 1100 nm is observed. On the contrary, two emission bands appear at around 1030 nm and 1200 nm in Te-doped glass-ceramics. The origin of these two emission bands might be different [4].

CONCLUSION

Broad NIR emission could be observed in Te- and Bi-doped glasses and transparent glass-ceramics. However, no NIR emission was observed in Se-doped glasses. It is suggested that the origin of coloration and NIR luminescence in these hosts is most likely to be caused by molecular Se_2 (Se_2^-), Te_2 (Te_2^-) and Bi_2 (Bi_2^-).

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Luminescence characteristics of Te- and Bi-doped glasses and glass-ceramics

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The origin of coloration and luminescence of Te- and Bi-doped glasses and glass-ceramics were investigated. The broad NIR luminescence was observed in both glasses and glass-ceramics ranging 1000-1600 nm. It is suggested the origin of coloration and NIR luminescence is most likely to be caused by elemental clustering of Te and Bi, Te_2 (Te_2^-) and Bi_2 (Bi_2^-).

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1. Introduction

The color generation of glasses in visible region is basically caused by impurities, such as transition metal ions, rare earth ions, metallic and semiconductor particles, etc. There are numerous other sources of visible coloration in glasses which are of interest. Included in this group are blue-sulfur, pink-selenium and green to purple tellurium whose colors are associated with elemental clustering. The investigation of the luminescence properties derived from elemental clustering must be of interest. The luminescence properties of elemental clustering, Te- and Bi-doped glasses and glass-ceramics were investigated.

2. Experimental

The glass compositions (wt%) used and melting conditions are shown in Table 1. Glasses were prepared by conventional melt-quench method. Te-Sp., Bi-Sp., Bi-AlPO₄ and Bi-L2S glasses converted to transparent glass-ceramics by subsequent heat treatment, 800°C–10 and 1000°C–5 h for Te-Sp. and Bi-Sp., 500°C–10 h and 600°C–5 h for Bi-AlPO₄ and 500°C–10 h and 650°C–5 h for Bi-L2S, respectively. The glasses and glass-ceramics were cut and polished optically into 1 mm in thickness for optical measurement.

Table 1. Compositions (wt%) and melting conditions of glasses studied.

Name	Melting condition*	SiO_2	Al_2O_3	ZnO	MgO	CaO	Na_2O	K_2O	TeO_2	Bi_2O_3	C
Te-Sp.	1600-1, Pt/Rh10	46.9	26.54	10.59	5.25	TiO_2:1.79, ZrO_2: 8.93			0.2	–	–
Te-SL	1450-1, Pt/Rh10	72	2		4	8	13	1	1.6	–	0.08
Te-ZTP	1200-1, Alumina	P_2O_5: 50.06, ZnO: 35.87							14.07		–
Bi-Sp.	1600-1, Pt/Rh10	46.9	26.54	10.59	5.25	TiO_2:1.79, ZrO_2: 8.93			–	5.0	–
Bi-AlPO₄	1600-1, Pt/Rh10	28.07	23.82	P_2O_5: 33.17, B_2O_3: 4.07, Na_2O: 10.86					–	5.0	–
Bi-L2S	1450-1, Pt/Rh10	80	4	P_2O_5: 3.0, Li_2O: 13.0					–	5.0	–

*: °C – h, kinds of crucible

Optical absorption and luminescence measurement were carried out using Cary 5E UV-VIS-NIR spectrometer and Perkin-Elmer LS50B Luminescence spectrometer. The luminescence spectra of NIR region was measured under the excitation of 974 nm laser diode. The luminescence from sample was dispersed by a single monochromator and detected by an InGaAs photodiode. ESR spectra were measured with JEOL JES RE-2X.

3. Results and discussion

The colors of samples are brown-pink for Te-Sp. glass-ceramics, pale green for Te-SL glass, brilliant purple for Te-ZTP glass and pink for Bi-Sp. glass-ceramics, respectively. And those of Bi-doped samples are pink for Sp. glass and glass-ceramics, dark brown for AlPO₄ G.C. and yellow-brown for L2S G.C. Figure 1and 2 show absorption spectra of glasses and glass-ceramics. The absorption spectra of Te-doped glasses and glass-ceramics are similar to those of Te-doped ultramarine [1] and ZnO-TeO₂-P₂O₅ glasses [2]. It is believed that the coloration of Te-doped glasses and glass-ceramics are due to the elemental clustering of Te, Te_2/Te_2^- (Te-SL, Te-Sp.) [1] and

colloidal metallic Te (Te-ZTP) [2].

The absorption spectra of Bi-doped Sp. glass and glass-ceramics are identical with that reported previously [3] and also similar to that of Te-doped glasses and Se-doped glasses [4].

Figure 3 and 4 show the NIR luminescence of Te-doped and Bi-doped glasses and glass-ceramics under the excitation of 974 nm laser diode. It is clearly seen that broad NIR luminescence can be observed in Te-doped glasses, Te-doped Sp. G.C., Bi-doped Sp. glass and Bi-doped Sp.G.C. The peak positions of Te-doped glasses are located at around 1200 nm and differ slightly from each other. A weak and rather sharp luminescence also appears at around 1020 nm in Sp. G.C. On the other hand, the luminescence centered at around 1100 nm with a shoulder at 1400 nm is observed in Bi-doped Sp. glass and glass-ceramics. Only pink colored Bi-doped Sp. glass and glass-ceramics exhibit NIR luminescence.
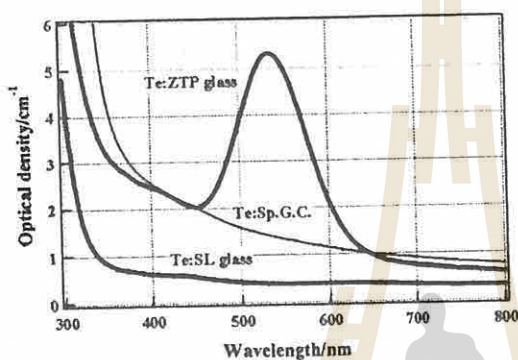
Fig. 1. Absorption spectra of Te-doped glasses and glass-ceramics.
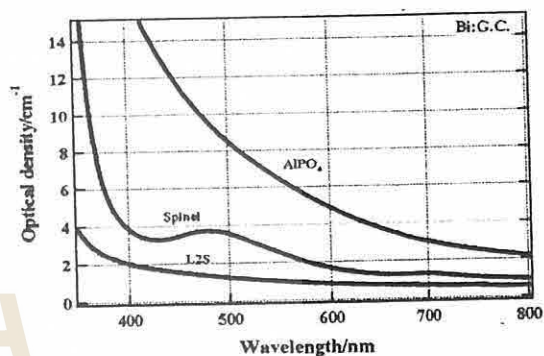
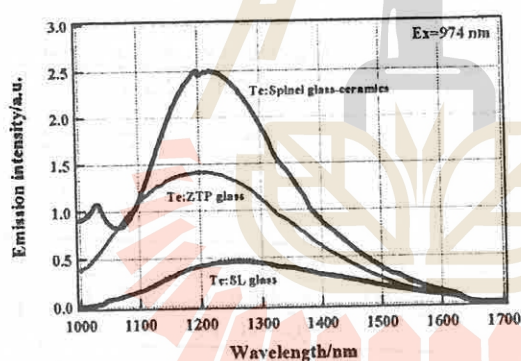Fig. 2. Absorption spectra of Bi-doped glass-ceramics.

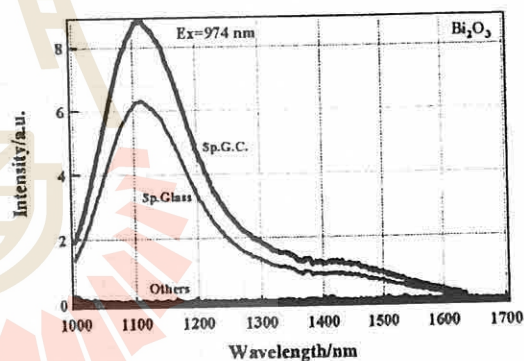Fig. 3. NIR luminescence of Te-doped glasses and glass-ceramics at room temperature.

Fig. 4. NIR luminescence of Bi-doped glass-ceramics.

It is found that the elemental clustering of Te exists in glasses and glass-ceramics, and hence the broad NIR luminescence may be due to these species. However, the origin of pink coloration and luminescence of Bi-doped samples are not clear yet. These will be discussed in detail at the conference.

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Opto-electronics-Oral

Tellurium Ion-Doped Transparent Glass-Ceramics As A Novel Active Medium For Broadband Near-Infrared Amplifiers And Tunable Lasers

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Broadband amplifiers in near-infrared region are key devices for the wavelength-division-multiplexing (WDM) network systems. Much work has been done to realize broadband optical amplifications for WDM use using rare-earth-doped fibers and fiber Raman amplifiers, and to develop new broadband gain media is still desired. We report it for the first time to our knowledge that we have observed broad near-infrared emission from tellurium ion-doped transparent spinel glass-ceramics (Te-spinel glass). The Te-spinel glasses were prepared by a conventional melt-quenching method, and subsequently heating at 800°C -10hrs and 1000°C -5hrs for nucleation and crystallization. Both of the as-prepared glasses and post-annealed glass-ceramics had good transparency in the visible to near-infrared region. Broad fluorescence, with a full width half maximum of about 250nm and centered at 1250nm, was confirmed under 974nm laser excitation. The fluorescence lifetime τ at 300K was about 600μsec. It lengthened by decreasing the temperature, and $\tau = 1.0 - 1.2$msec. was observed in 5 - 200K. We shows that the Te-spinel glasses have a potential for the novel broadband gain media for amplifiers and tunable lasers.
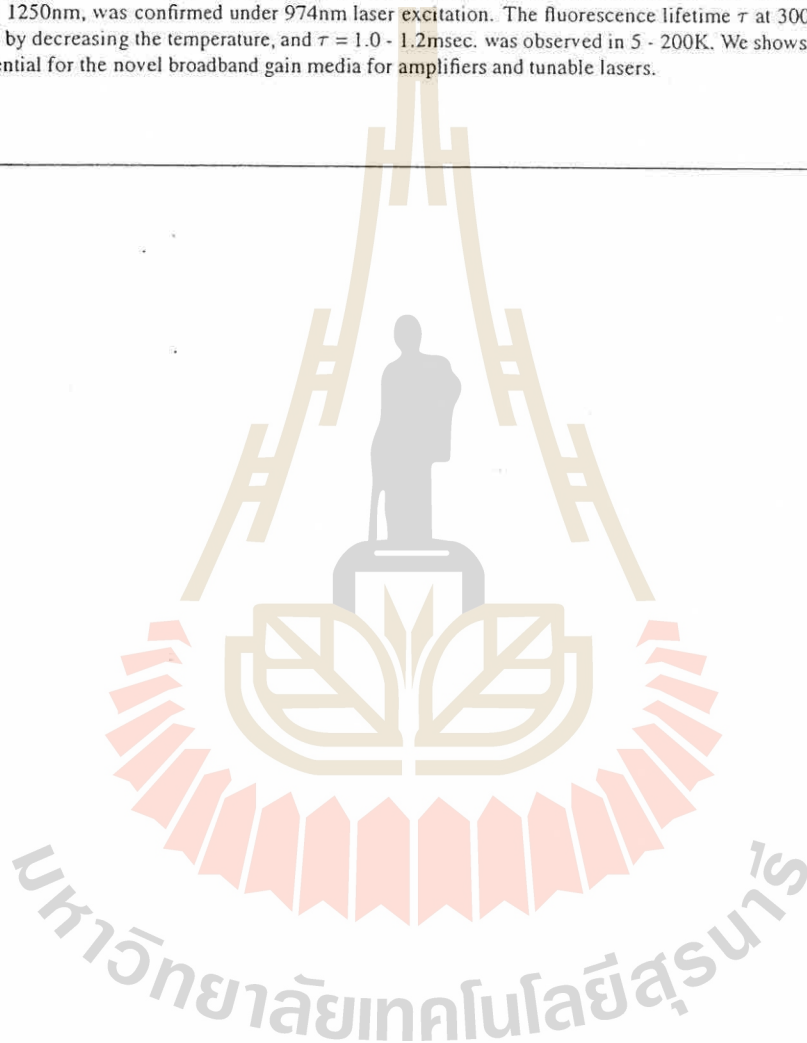
1A02   Melting Temperature and glass composition dependence on the NIR luminescence characteristics of Bi-containing borate glasses

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Melting temperature and glass composition dependence on the NIR luminescence characteristics of Bi-containin borate glasses were investigated based on redox reaction. It was suggested that the color center and luminescen center seems to be Bi clusters, such as Bi, Bi_2, Bi_2^-, etc.

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1. Introduction

Although many ideas on the near-infrared luminescence center of Bi-doped glasses have been proposed such as Bi^{5+} ion, BiO and Bi clusters, it is not clear yet. It is known that these glasses often appear to be blac coloration depending on glass composition and melting conditions, and particles were sometimes observed i glasses. Here, the melting temperature and glass composition dependence on the NIR luminescence characteristic of Bi-containing borate glasses were investigated based on redox reaction.

2. Experimental

Two series of glasses were prepared. Series I was $63B_2O_3 \cdot 9Al_2O_3 \cdot 9ZnO \cdot 9K_2O \cdot 10Bi_2O_3$ (mol%) and we melted in alumina crucible under various conditions(1000°~1400°C for 15~40 min.). Series II wa $90[(80-X)B_2O_3 \cdot 10Al_2O_3 \cdot 10ZnO \cdot XK_2O] \cdot 10Bi_2O_3$ (X=0, 10, 20, 30, mol%) and were melted in alumina crucible 1200°C for 20 min. Glasses were polished optically into 1.5~2.0mm in thickness for optical measurement.

Optical absorption and NIR luminescence were measured. SEM observation and XPS measurement we also carried out.

3. Results and discussion

The color changes from pale yellow to black with increase in melting temperature. SEM photos are shov in Fig. 1. Many spherical particles of about 1μm diameter can be observed. The silver-white colored metallic also deposited at the bottom of crucible in the glass melted under strong reducing condition. Therefore, the particles seem to be Bi metallic colloids. XPS measurement confirmed these particles were Bi metallic colloid peak fitting of XPS spectra (Fig.2). The colors of glasses become deeper with decreasing X in Series II glasses.

NIR luminescence can be detected in Bi-1200 and Bi-1300 glasses in Series I and in X=0, 10 glasses Series II (Fig. 3). From Fig. 2, it is considered that there might be two color centers and luminescent centers. Th it is found that the NIR luminescence characteristics were strongly affected by redox reaction.

The NIR luminescent center was formed just before the beginning of darkening effect (Bi metallic collo formation), and hence it is suggested that the color center and luminescent center might be Bi clusters, such as Bi_2, Bi_2^-, etc.

4. Conclusion

Melting temperature and glass composition dependence on the NIR luminescence characteristics Bi-containing borate glasses were investigated based on redox reaction. It was suggested that the color center a luminescent center seems to be Bi clusters, such as Bi, Bi_2, Bi_2^-, etc.

Acknowledgement

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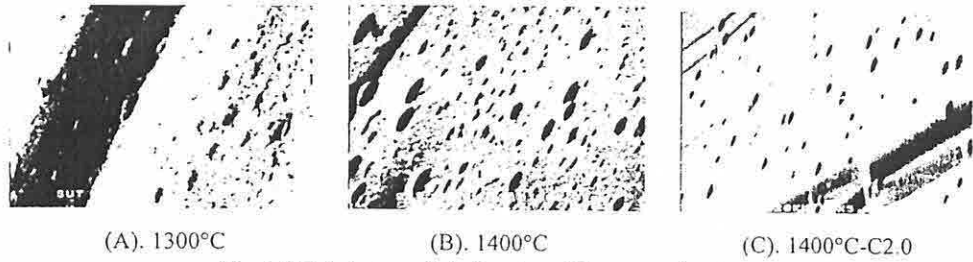

(A). 1300°C   (B). 1400°C   (C). 1400°C-C2.0

Fig. 1. SEM photos of black-colored Bi- containing borate glasses.
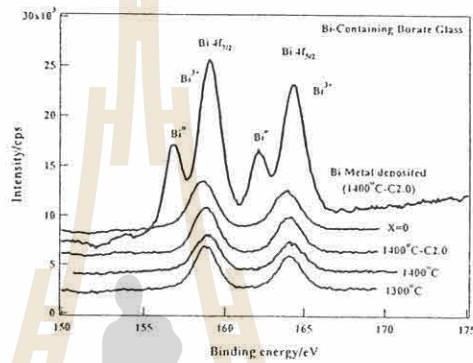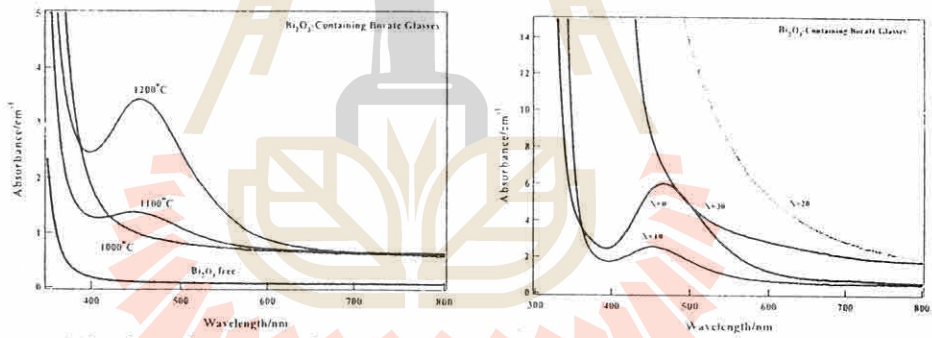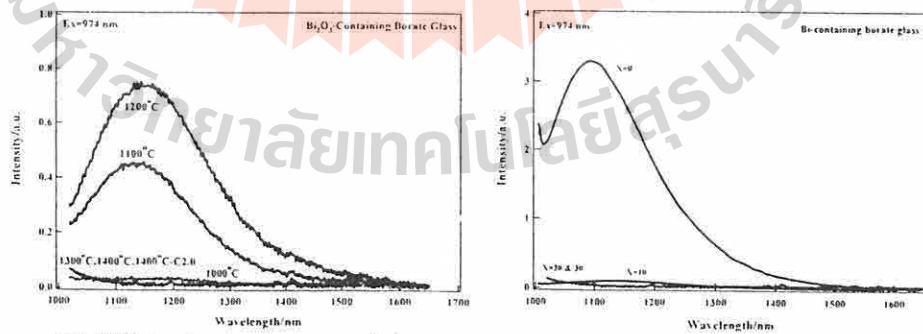

Fig. 2. XPS spectra various glasses and Bi metal deposited.

(A). Absorption spectra of glasses.
Temperature dependence.

(B). Absorption spectra of glasses.
Composition dependence.

(C). NIR luminescence spectra of glasses.
Temperature dependence.

(D). NIR luminescence spectra of glasses.
Composition dependence.

Fig. 3. Absorption and NIR luminescence spectra of glasses.

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78th Glasses & Photonics Materials conference, Toyohashi, Japan 29-30/Nov/2007

P06   Near-infrared Luminescent Center of Te-Containing Glasses

Khonthon, S. (SUT), ○Punpai, P. (SUT),
Morimoto, S. (SUT), Arai, Y. (TTI) and Ohishi, Y. (TTI)

The near-infrared luminescent center of Te-containing glasses was investigated by optical absorption and NIR luminescence measurement. The NIR luminescence can be detected in some limited gasses. It was suggested the NIR luminescent center might be Te_2^-.
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1. Introduction

The color generations of glasses in visible region are well known, they are caused by many kind of impurities such as transition metal ions, rare earth ions, metallic and semiconductor particles, etc. Many researches were interested in the influence of elemental clustering to the color center and luminescence center of glasses, but the near-infrared luminescent center of Te-containing glasses is not clear yet. Many ideas propose that the color center and luminescence center might be due to Te clusters. The near-infrared luminescent center of Te-containing glasses was investigated in this research.

2. Experimental

Two series of glasses were prepared. Series I was $63B_2O_3 \cdot 9Al_2O_3 \cdot 9ZnO \cdot 9K_2O \cdot 10TeO_2$ (mol%) and melted in alumina crucible under different melting condition (different melting temperature). Series II was $90[(80-X)B_2O_3 \cdot 10Al_2O_3 \cdot 10ZnO \cdot XK_2O] \cdot 10TeO_2$ (X=0-30 mol%) were melted in alumina crucible at 1200°C for 20 min. After melting they were poured onto iron plate and pressed by another iron plate, and then they were annealed at 450°C for 30 min and cooled slowly in the furnace. Glasses were polished optically into 1.5-2.0 mm in thickness for the optical measurement. Optical absorption and NIR luminescence were measured.

Table 1. Melting conditions, appearance and absorption bands of glasses studied.

No.	Melting condition °C–min	Appearance	Absorption bands/nm			
			I	II	III	IV
Te-850	850-60	Colorless	–	–	–	–
1000	1000-20	Pale orange	370	430	530	–
1100	1100-20	Pale reddish brown	370	430	530	–
1200	1200-20	Reddish orange	370	430	530	–
1300	1300-15	Reddish brown	370	(430 ?)	530	–
X=0	1200-20	Phase separation	–	–	–	–
10	1200-20	Reddish orange	370	430	530	–
20	1200-20	Pale orange	370	–	–	–
30	1200-20	Colorless	–	–	–	–
ZTP*	1200-60	Brilliant purple	375	417	537	600
Te-SL*	1450-60	Pale green	374	444		625
Te-Sp.*	1600-60	Brownish pink	–	420 (448 ?)	(556 ?)	600

*: S. Khonthon et al., J. Ceram. Soc. Japan, 115 (2007) 259.

3. Result and discussion

The melting conditions, appearance and absorption bands were summarized in Table 1. In Series I, the color of glasses changes from colorless to reddish brown with increase in melting temperature. In series II, color of glasses changes from reddish orange to colorless with increase in X, X=0 was phase separated during casting. Absorption bands of ZTP*, Te-SL* and Te-Sp.* were also shown in Table 1 for comparison.

Fig.1, 2 and 3 show absorption spectra of Te-containing borate glasses (series I), Te-containing borate glasses (series II) and Te-doped glasses and glass-ceramics, respectively.

The NIR luminescence can not be detected in all borate glasses. On the contrary, ZTP*, Te-SL* and Te-Sp.* exhibit NIR luminescence centered at around 1200 nm (Fig.4) and a weak and rather sharp luminescence also appears at around 1020 nm in Sp GC.

Three absorption bands are observed in all borate glasses, ~370 nm, ~430 nm and ~530 nm. However, absorption band at around ~600 nm can not be detected in all borate glasses. These absorption bands can be assigned already, exciton transition (≈ 370 nm), $^3\Sigma_g^- \rightarrow {}^3\Sigma_u^-$ transition of Te_2 (≈ 430), Te metallic colloid (≈ 530) and $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te_2^- (≈ 600). Therefore, it was found that the center is not present in borate

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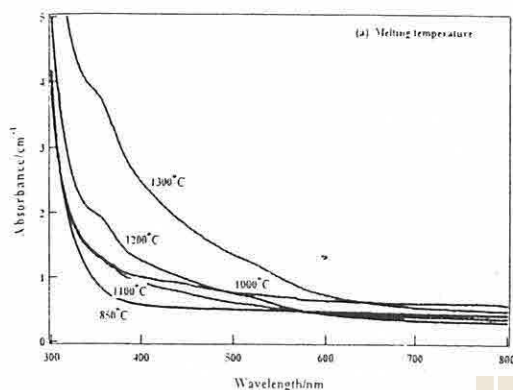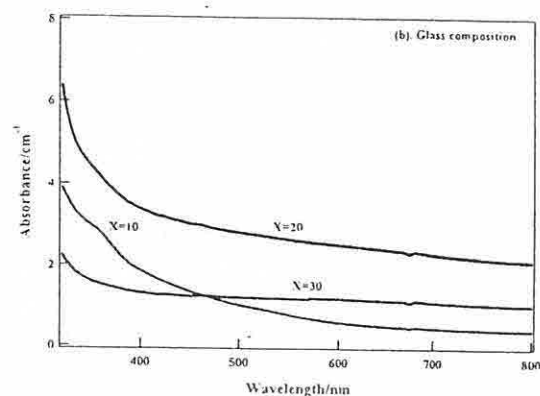Fig.1. Absorption spectra of Te-containing borate glasses. Series I.

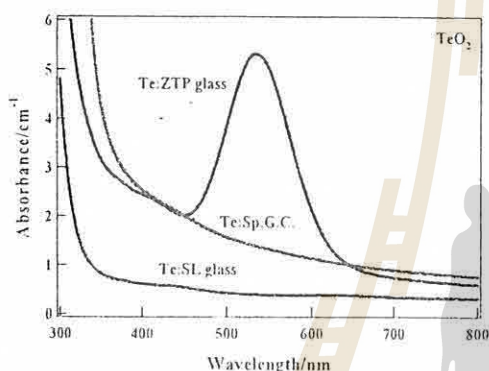Fig.2. Absorption spectra of Te-containing borate glasses. Series II.

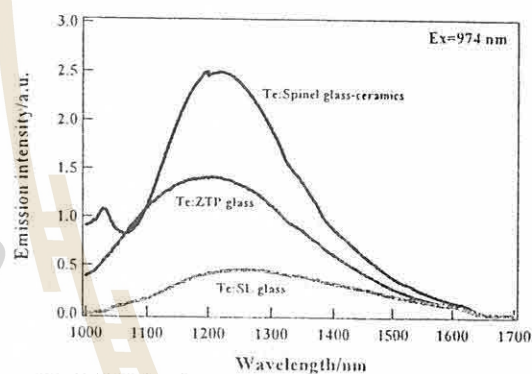Fig.3. Absorption spectra of Te-doped glasses and glass ceramics.

Fig 4. NIR luminescence spectra of Te-doped glasses and glass ceramics.

glasses, which do not exhibit NIR luminescence. Consequently, it was suggested that the NIR luminescent center of Te-doped glasses might be Te_2^-.

4. Conclusion

The near-infrared luminescent center of Te-containing glasses was investigated by optical absorption and NIR luminescence measurement. The NIR luminescence can be detected in some limited gasses. It was suggested that NIR luminescent center might be Te_2^-.

Acknowledgement

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On the NIR Luminescence Characteristics of Bi$_2$O$_3$-Containing Borate Glasses

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Abstract

The effects of melting temperature and glass composition on the NIR luminescent characteristics of $90[(80-X)B_2O_3 \cdot 10Al_2O_3 \cdot 10ZnO \cdot XK_2O] \cdot 10\ Bi_2O_3$ (X=0–30 mol%) glasses are investigated and the color center and luminescent center of these glasses are discussed based on redox reaction. It was found that the coloration and near–infrared luminescent characteristic of glasses are strongly affected by melting temperature and glass composition. The color becomes deeper with increasing melting temperature and finally metal colloids precipitate being black color. The same tendency can be observed in composition series, higher NIR luminescent intensity with lower K_2O content. Near-infrared luminescence starts to appear, reach the maximum intensity and finally disappears with increasing temperature and decreasing alkali content. Thus the luminescent characteristics of Bi-containing glasses are found to be influenced strongly by redox reaction of Bi and the highest luminescent intensity might be obtained in the glass just before the beginning of darkening effect (formation process of Bi metallic colloid). It was suggested that the color center and near-infrared luminescent center is likely to be caused by Bi clusters, such as Bi, Bi_2, Bi_2^-, Bi_3, Bi_4, etc.

Keywords: Bismuth, Borate glass, melting temperature, darkening effect, Bi clusters

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Near-Infrared Luminescent Center of
Te-Doped Soda-lime-silicate Glasses

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Abstract

The effects of carbon addition and TeO_2 concentration on the near-infrared (NIR) luminescent characteristics of Te-doped soda-lime silicate glasses are investigated. Three absorption bands were detected at around 330~380 nm, ~430 nm and ~630 nm, respectively. The last absorption band (~630 nm) has been ascribed to $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te_2^-. The NIR luminescence centered at 1200 nm was detected under the excitation of 974 nm laser diode except for glasses of lower carbon addition. The NIR luminescence was found to be strongly affected by melting atmosphere and TeO_2 concentration. It is considered that the absorption band, ~630 nm, is related strongly to the NIR luminescence of Te-doped soda-lime-silicate glasses. Consequently, it is suggested that the origin of NIR luminescence detected in Te-doped soda-lime-silicate glasses is likely to be caused by Te_2^- center.

Keywords: Tellurium, soda-lime-silicate glass, color center, NIR luminescent center, clusters

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