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Technical report

Absorption and Emission Spectra of Ni-Doped Glasses and Glass-Ceramics in Connection with Its Co-Ordination Number

Ni 含有ガラスと透明結晶化ガラスの光吸収及び発光スペクトルとその配位数との関係

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The absorption and emission spectra of Ni-doped glasses and transparent glass-ceramics are discussed in relation to its coordination number. The results evidenced that the color changed drastically to deep pink from yellow for the lithium metasilicate crystal based transparent glass-ceramics and to blue from brown for the spinel crystal based transparent glass-ceramics after crystallization, respectively. The absorption spectra of lithium metasilicate and Spinel glasses suggest the existence of a tetrahedral Ni^{2+} ion and a trigonal bipyramid Ni^{2+} ion. On the contrary, tetrahedral Ni^{2+} ions in the lithium metasilicate transparent glass-ceramics and the octahedral Ni^{2+} ion in Spinel transparent glass-ceramics are dominant. The emission at around 580 nm was observed in Spinel transparent glass-ceramics under the excitation of 380 nm, however, a very weak or no emission was observed in the lithium metasilicate glass, lithium metasilicate transparent glass-ceramics and Spinel glass under the excitation of 430 nm. This emission might be due to a $^1T_1(D)\rightarrow{}^3A_2(F)$ transition after the excitation from $^3A_2(F)$ to $^3T_1(P)$ of the octahedral Ni^{2+} ions. In addition, only Spinel transparent glass-ceramics exhibits a broad NIR emission at around 1220 nm under the excitation of a 974 nm laser diode. This emission may be due to $^3T_2(F)\rightarrow{}^3A_2(F)$ transition. It is considered that the tetrahedral Ni^{2+} ion is located between the chains in the lithium metasilicate crystal.

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Key-words : *Ni^{2+} ion, Transparent glass-ceramics, Absorption spectra, VIS–NIR emission spectra, Coordination number*

1. Introduction

Ni-doped glasses tend to absorb over the entire visible spectrum typically producing brown colored glasses, and it was concluded that Ni was present as Ni^{2+} in a wide range of compositions in both four-[Ni(4)] and six-coordination[Ni(6)] with oxygen in the past.1),2) Although the Ni^{2+} ion has a clear preference for octahedral coordination, it was well known that tetrahedral Ni^{2+} ion favorably appeared in high-alkali borate and borosilicate glasses and octahedral Ni^{2+} ion existed in low alkali borate and borosilicate glasses, and their color were pink and green-blue, respectively.3),4) Their optical properties have been recognized using ligand field theory.3) However, recently the modern spectroscopic techniques (EXAFS etc.) have confirmed that a trigonal bipyramid Ni^{2+}[Ni(5)] also presented in many glasses and the brown colored glasses contained both [Ni(4)] ion and Ni[(5)]5)–8) ion, and Ni was found with three coordination numbers (6, 5 and 4) in some glasses.6) The color of glasses changes depending on the fraction of these Ni ions.

The spectroscopy of the Ni^{2+} ion-doped single crystals and glass-ceramics has received much attention in recent years. Much of the present interest focuses on the possibility of Ni^{2+}-doed materials as active media for tunable near infrared lasers.9)–12) In these materials, Ni^{2+} ion occupies octahedral sites and exhibits a broad emission in near infrared region (1100–1600 nm). In contrast, no emission of tetrahedrally coordinated Ni^{2+} ion even at cryogenic temperature has been reported.

In this paper the absorption and emission spectra of Ni-doped glasses and glass-ceramics are discussed in relation to its coordination number.

2. Experimental

2.1 Sample preparation

The compositions of glasses studied are shown in **Table 1**. These glasses are able to convert to transparent glass-ceramics based on $Li_2O\cdot SiO_2$ crystal (LS3) and Spinel crystal [(Mg, Zn) Al_2O_4] (Spinel) by adequate heat treatment.

High purity silica sand, alumina and reagent grade chemicals of Li_2CO_3, K_2CO_3, MgO, ZnO, TiO_2, ZrO_2 and NiO were used as raw materials. Batches corresponding to 50 g of glass were mixed thoroughly and melted in a 50 cc Pt/Rh10 crucible under appropriate condition 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 suitable conditions and cooled slowly in the furnace.

The glasses were heat treated under various conditions 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

Crystalline phases, percent crystallinity and crystalline size were measured by powder X-ray diffraction analysis (XRD, Bruker, AXS Model D5005) under the condition of Cu Kα radiation ($\lambda=0.154$ nm), 40 kV-40 mA, 0.01°/step and 1 s/step. The percent crystallinity was determined using Ohlberg and Strickler's method.13) α-Quartz crystal and parent glasses

Table 1. Glass Compositions (mass%) Studied

Name	SiO_2	Al_2O_3	Li_2O	K_2O	MgO	ZnO	TiO_2	ZrO_2	NiO*
LS3	65	5	26	4	-	-	-	-	0.4
Spinel	46.9	26.54	-	-	5.25	10.59	1.79	8.93	0.4

*: excess wt%.

were used as standard materials. The crystalline size was calculated by Scherrer's equation. True half width was determined by Jones method[14] and α-Quartz was used as a standard.

2.3 Absorption and emission measurements

The absorption spectra were measured with Cary 5E UV–VIS–NIR spectrometer in the range of 300 nm to 2000 nm at room temperature. The emission spectra in UV-VIS region were measured using 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 μm; grating, 600 grooves/mm; resolution, 3 nm) and detected by an InGaAs photodiode.

3. Results and discussion

3.1 Properties of glass and glass-ceramics

Glasses converted to transparent glass-ceramics upon the appropriate heat treatment, and **Fig. 1** shows the XRD patterns of these transparent glass-ceramics. The crystalline phases detected by XRD are $Li_2O \cdot SiO_2$ (JCPDS 00-029-0829) for LS3 and spinel [$(Mg,Zn)Al_2O_4$] (JCPDS 01-070-5187) crystals for Spinel, respectively.

Table 2 summarized the melting conditions, heat treatment conditions, appearances and some properties of glass-ceramics. The percent crystallinity and crystalline size are ranging 45–70% by weight and 15–35 nm, respectively. The glass-ceramics are transparent.

3.2 Absorption spectra

The color changes drastically upon crystallization, brown to deep pink-violet for LS3, and brown to blue for Spinel. The appearance of glasses and glass-ceramics is shown in **Fig. 2**. **Figure 3** shows the absorption spectra of glasses and glass-ceramics. The LS3 and Spinel glasses show the similar spectral pattern and three absorption bands were observed, 430 nm, ≈800 nm and ≈1800 nm, respectively. These spectral patterns are similar to that of $CaMgSi_2O_6$–4% $CaNiSi_2O_6$ glass.[6] In this glass, both [Ni(4)] ion and [Ni(5)] ion coexists. These absorption bands can be assigned to $^3E'(F) \rightarrow {}^3A'(P)$, $^3E'(F) \rightarrow {}^3A''_1$, $^3A''_2(F)$ and $^3E'(F) \rightarrow {}^3E''(F)$ transitions, respectively.[6]

In LS3 transparent glass-ceramics, the spectral pattern is also similar to that of tetrahedral Ni^{2+} ion despite absorption bands shift to longer wavelength, and the absorption intensity increases slightly.[6],[15] This spectral pattern seems to be a typical of tetrahedral Ni^{2+} ion.

On the contrary, new and weak absorption bands appeared, at around 380 nm (shoulder), 580, 620 nm and 1000 nm (shoulder) for Spinel glass-ceramics. This spectral pattern is quite similar to that of Ni^{2+} octahedral in $MgAl_2O_4$ and $MgGa_2O_4$ single crystals,[10],[12] and they can be assigned to $^3A_2 \rightarrow {}^3T_2$, $^3A_2 \rightarrow {}^3T_1$ and $^3A_2 \rightarrow {}^3T_1$ (P) transitions, respectively. The absorption intensity decreases by about 5 times that of glass. Usually the absorption intensity of transition metal ions in tetrahedral symmetry is much greater (over ten times greater) than that of octahedral symmetry due to mixing of the 3d-orbitals with ligand orbitals as well as the 4p orbitals.[3]

The absorption spectra of LS3 glass-ceramics and Spinel glass-ceramics were analyzed by re-convolution method using Voigtian distribution and the ligand field parameters were estimated and are shown in **Table 3**. The parameters for octahedral Ni^{2+} ion (Spinel glass-ceramics) are quite reasonable, and the agreement between observed spectrum and that of predicted is also reasonable.[10],[12]

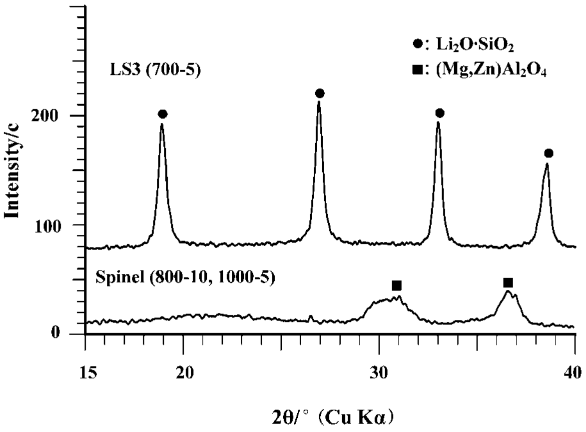

Fig. 1. XRD patterns of transparent glass-ceramics. Heat treatment conditions: LS3; 700°C–5 h, Spinel; 800°C–10 h, 1000°C–5 h.

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

Name	Melting Condition (°C–h)	Heat treatment Condition (°C–h)	Appearance*	Crystalline phases	Percent crystallinity (wt %)	Crystalline Size (nm)
LS3	1300-1	700-5	Yellow Deep pink	$Li_2O \cdot SiO_2$	70±5	35±5
Spinel	1600-2	800-10, 1000-5	Brown Blue	Spinel	45±5	15±5

*: upper: glass, lower: glass-ceramics

Ni^{2+}; LS3 Glass Ni^{2+}; LS3 Glass-ceramics

Ni^{2+}; Spinel Glass Ni^{2+}; Spinel Glass-ceramics

Fig. 2. Appearance of glasses and transparent glass-ceramics.

On the other hand, the parameters for tetrahedral Ni^{2+} ion are not reasonable, especially the 10Dq is extremely large, the calculation of 10Dq[Tetrahedral] = 4/9 × 10Dq[Octahedral] supposes about 4500 cm^{-1} and observed value is about 40% greater than that expected. However, the agreement between observed spectrum and that of predicted is fairly well for tetrahedral symmetry. If the lower frequency band (≈5500 cm^{-1}) would be assigned to $^3T_1(F) \rightarrow {}^3A_{2g}(F)$ transition, the agreement between observed spectrum and that of predicted is not well and B value exceeds that of free ion (>1100 cm^{-1}). Therefore, the assignment shown in Table 3 seems to be

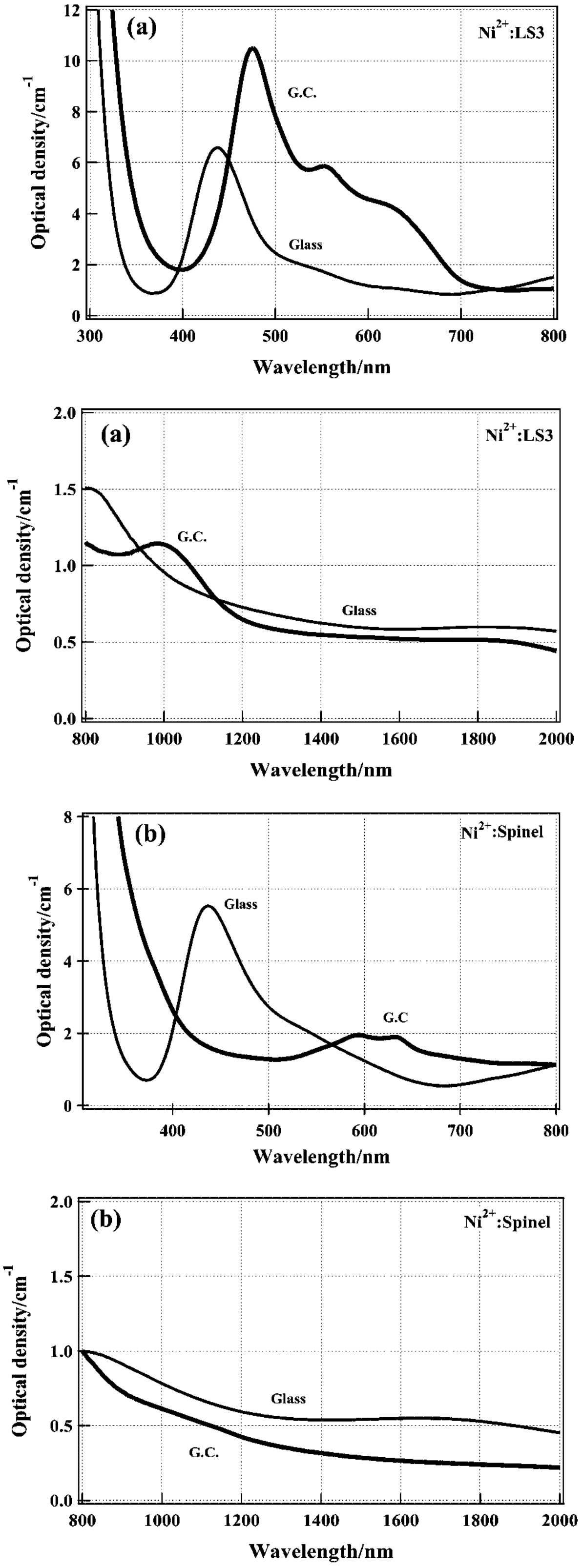

Fig. 3. Absorption spectra of glasses and glass-ceramics at room temperature. (a). LS3 glass and glass-ceramics, (b). Spinel glass and glass-ceramics.

Table 3. Ligand Field Parameters of Ni^{2+} Ion in LS3 and Spinel Glass-Ceramics Calculated by Voigtian Distribution

Sample Name	Observed band ν/cm^{-1}	Gravity center ν/ cm^{-1}	Transition	Predicted ν/ cm^{-1}
LS3 G.C. Tetrahedral	5,450	5,450	$^3T_1(F)\rightarrow{}^3T_{2g}(F)$	5,450
	10,000, 1.3, 1,500 10,600, 0.3, 1,500	10,110	$^3T_1(F)\rightarrow{}^3A_{2g}(F)$	11,676
	17,360, 2.05, 2,000 19,850, 1.52, 2,000 21,250, 2.05, 1,850	19,402	$^3T_1(F)\rightarrow{}^3T_{1g}(P)$	19,460
	10Dq= 6,230 cm^{-1}, B= 973 cm^{-1}, Dq/B= 0.64 (C/B=4.42)			
Spinel G.C. Octahedral	7,100, 0.1, 1,500 9,200, 0.3, 2,200 10,400, 0.52, 2,200	9,760	$^3A_2(F)\rightarrow{}^3T_{2g}(F)$	9,760
	15,800, 0.56, 700 16,850, 0.68, 900	16,440	$^3A_2(F)\rightarrow{}^3T_{1g}(F)$	16,000
	26,315	26,315	$^3A_2(F)\rightarrow{}^3T_{1g}(P)$	26,240
	10Dq =10,000 cm^{-1}, B = 800 cm^{-1}, Dq/B = 1.25 (C/B = 4.71)			
Zn_2SiO_4 Tetrahedral [15]	**10Dq = 4,700 cm^{-1}, B = 781 cm^{-1}, Dq/B = 0.60 (C/B = 4.65)**			
$MgAl_2O_4$ Octahedral [10]	**10Dq = 10,400 cm^{-1} , B = 865 cm^{-1}, Dq/B = 1.2 (C/B = 3.76)**			

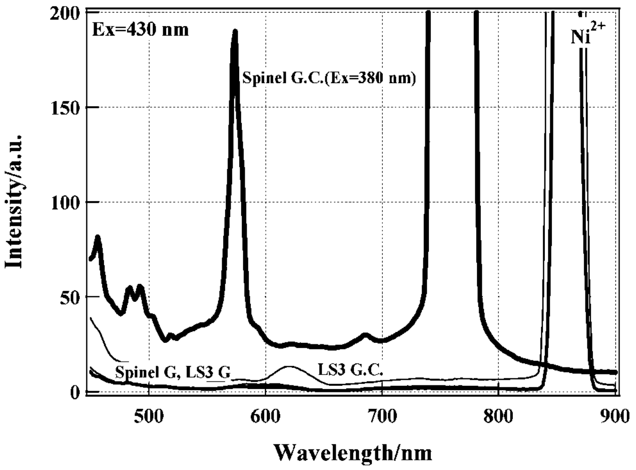

Fig. 4. Emission spectra of glasses and glass-ceramics in VIS region under the excitation of 380 nm (Spinel glass-ceramics) and 430 nm (Spinel glass, LS3 glass and LS3 glass-ceramics) at room temperature.

reasonable.

As mentioned above, the Ni^{2+} ion has a clear preference for octahedral coordination, and spectral data on tetrahedral Ni^{2+} are scarce because it only reluctantly adopts this coordination. There are some spectroscopic studies of tetrahedral Ni^{2+} ion in oxide systems, such as ZnO,$^{16)}$ $Zn_2SiO_4$$^{15)}$ and garnets.$^{17)}$ The lithium metasilicate [$Li_2O\cdot SiO_2$] crystal is also a good host for [Ni(4)] ion. The lithium metasilicate [$Li_2O\cdot SiO_2$] crystal has single chains structure in which each SiO_4 tetrahedra shares two vertices.$^{18)}$ It is considered that Ni^{2+} ion occupies tetrahedral sites between two chains instead of Li$^+$ ions.

3.3 Emission spectra

Figure 4 shows the emission spectra of glasses and glass-ceramics under the excitation of specified wavelength at which the absorption band is observed in near UV region. A strong and sharp emission appears at around 580 nm under the excitation of 380 nm for only Spinel glass-ceramics. However, only a very weak emission is observed at around 600 nm for LS3 glass-ceramics and no emission was observed for Spinel glass and LS3 glass under the excitation of 430 nm. This emission at around 600 nm might be due to the $^1T_1(D)\rightarrow{}^3A_2(F)$ transition after the excitation from $^3A_2(F)$ to $^3T_1$ (P) of octahedral Ni^{2+} ions. This indicates that the emission at around 580–600 nm may be the characteristics of octahedral Ni^{2+}

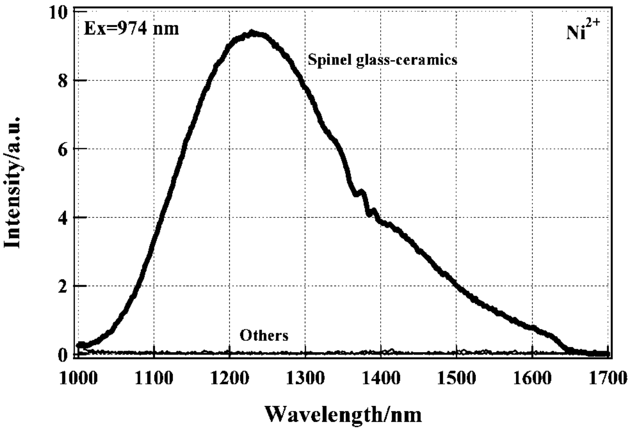

Fig. 5. Emission spectra of glasses and glass-ceramics in NIR region under the excitation of 974 nm laser diode.

ions. It seems that a slight amount of [Ni(6)] might exist in LS3 glass-ceramics. However, the absorption intensity of octahedral Ni^{2+} is much smaller than that of tetrahedral Ni^{2+}, and therefore the absorption bands corresponding to [Ni(6)] can not be detected.

Octahedral Ni^{2+} ion exhibits its characteristic emission in NIR region peaking at around 1300–1400 nm.[9),12)] **Figure 5** shows emission spectra of glasses and glass-ceramics in NIR region under the excitation at 974 nm laser diode at room temperature. Similarly, only Spinel glass-ceramics shows the broad NIR emission peaking at around 1220 nm. On the contrary, no emission can be observed for Spinel glass, LS3 glass and LS3 glass-ceramics.

From above results, it is concluded that [Ni(6)] ion does not exist in LS3 glass and Spinel glass.

4. Conclusion

The absorption and emission spectra of Ni-doped glasses and glass-ceramics are discussed in relation to its coordination number.

The crystalline phases of transparent glass-ceramics are lithium metasilicate crystal ($Li_2O \cdot SiO_2$) for LS3 and spinel crystal $(Mg,Zn)Al_2O_4$ for Spinel, respectively. The percent crystallinity was were 75 ± 5 mass% for LS3 and 40 ± 5 mass% for Spinel, and the crystalline size was 30 ± 5 nm for LS3 and 15 ± 5 nm for Spinel.

The color changed drastically to deep pink from yellow for LS3 and to blue from brown for Spinel after crystallization, respectively. The absorption spectra of LS3 and Spinel glasses suggest the existence of tetrahedral Ni^{2+} ion and trigonal bipyramid Ni^{2+} ion. On the contrary, tetrahedral Ni^{2+} ion for LS3 transparent glass-ceramics and octahedral Ni^{2+} ion Spinel transparent glass-ceramics are dominant.

The emission at around 580 nm was observed in Spinel transparent glass-ceramics under the excitation of 380 nm, however, a very weak or no emission was observed in LS3 glass, LS3 transparent glass-ceramics and Spinel glass under the excitation of 430 nm. This emission might be due to ${}^1T_1(D) \rightarrow {}^3A_2(F)$ transition after the excitation from ${}^3A_2(F)$ to ${}^3T_1(P)$ of octahedral Ni^{2+} ions. In addition, only Spinel transparent glass-ceramics exhibits broad NIR emission at around 1220 nm under the excitation of 974 nm laser diode. This emission may be due to ${}^3T_2(F) \rightarrow {}^3A_2(F)$ transition.

It is considered that tetrahedral Ni^{2+} ion is located between chains in lithium metasilicate crystal.

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