CERAMIC LETTER

Optical Absorption of Cr-Containing Li_2O–SiO_2 System Transparent Glass-Ceramics

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The absorption spectra of Cr-containing Li_2O–SiO_2 transparent glass-ceramics was investigated. The crystalline phases precipitated in glass-ceramics are mainly $Li_2O \cdot 2SiO_2$ with a small amount of α-SiO_2. The percent crystallinity and crystal sizes are 40–77 and 20–42 nm, respectively. A strong absorption band ascribed to the charge transfer of Cr^{6+} ion and a weak *d–d* absorption band ascribed to Cr^{3+} ion were observed in the glass. However, the new absorption bands appeared at around 600–700 nm and the absorption intensity of these bands increased significantly (about 15 times) upon crystallization. It was suggested that the tetrahedrally coordinated Cr^{4+} ion might exist in Li_2O–SiO_2 transparent glass-ceramics.

[Received October 14, 2003; Accepted January 23, 2004]

Key-words: *Li_2O–SiO_2 system, Transparent glass-ceramics, Cr ions, Absorption spectra*

1. Introduction

Many researches on the behavior of Cr ions in glasses, such as valence state and co-ordination number, have been carried out[1)-3)] in association with color generation. The Cr ions existed in glasses were mainly Cr^{3+} and Cr^{6+}, and the redox equilibrium between them was discussed with glass composition and melting atmosphere. However, since Cr^{2+} ion was found[4)] and recent years it was reported the existence of Cr^{4+} in glasses,[5)-7)] the researches on Cr^{2+} and Cr^{4+} ions in glasses and single crystals, especially in laser oscillation materials and opto-electronic devices, is actively taking place. Furthermore, the research on Cr doped transparent glass-ceramics is attempted for the application in various field.[8),9)] In these field, glasses have many advantages comparing with crystalline materials. They are: flexibility and ease of forming to any shape, uniformity and reproducibility and process economy in high-volume manufacturing, etc.

Li_2O–SiO_2 system is well known as a base glass for glass-ceramics, such as chemically machinable glass-ceramics or high strength glass-ceramics. A transparent glass-ceramics can be readily obtained from this system, in which the transparency is substantially comparable to that of glass in NIR region.[10)]

The author investigates various properties of Li_2O–SiO_2 system transparent glass-ceramics. Here the absorption spectra of Cr ion containing Li_2O–SiO_2 system transparent glass-ceramics were investigated, and the possibility of the existence of Cr^{4+} is suggested.

2. Experiment

2.1. Sample preparation

The composition of glass used is $80SiO_2 \cdot 4Al_2O_3 \cdot 13Li_2O \cdot 3P_2O_5 \cdot 0.4Cr_2O_3$(mass%). High purity silica sand, alumina and reagent grade chemicals of Li_2CO_3, $(NH_4)_2HPO_4$ (Carlo Erba) and Cr_2O_3 (Carlo Erba) were used as raw materials. A batch corresponding to 100 g of glass was mixed thoroughly and pre-calcined at 400°C for overnight to remove NH_3. Then it was melted in 100 cc Pt/Rh10 crucible at 1450°C for 3 h in an electric furnace in air, and poured onto iron plate. They were then annealed at 450°C for 30 min and cooled to room temperature in the furnace. The glasses were heat treated for crystallization at various conditions after the first heat treatment at 500°C for 15 h.

The glass and glass-ceramics were cut and polished into the plate of about 0.8 mm in thickness.

2.2. Absorption measurement

Absorption spectra of glass and glass-ceramics were measured at room temperature with Cary 5E UV-VIS-NIR spectrophotometer in the range of 300–1500 nm.

2.3. XRD

Crystalline phases was examined by powder XRD (Bruker, AXS Model D5005). The crystalline size was calculated by Scherrer's equation:

$$d = 0.9\lambda/\beta \cdot \cos\theta. \quad (1)$$

where d is the crystalline size (A), α the wavelength of X-ray (1.54 A), β true half width (radian) and θ diffraction angle (degree). The true half width was determined by Jones method,[11)] and α-quartz was used as a standard.

The percent crystallinity was determined by Ohlberg and Strickler's method[12)] and was calculated by below equation:

$$\text{Percent crystallinity} = 100x(I_g - I_x)/(I_g - I_c) \quad (2)$$

where I_g is the background intensity of glass, I_x the background intensity of specimens and I_c the background intensity of crystal at $2\theta = 23°$. The calibration curve was obtained by mixtures of parent glass and α-quartz with various ratio, and showed a good linearity.

3. Results and discussion

The glass exhibits light green in color. The color of transparent glass-ceramics changes from light green to green-blue, blue, deep blue, and greenish blue depending on heat treatment condition. The crystalline phases precipitated in glass-ceramics are mainly $Li_2O \cdot 2SiO_2$ with a slight amount of Li_2O–SiO_2 crystal at lower temperature. At higher temperature, a small amount of α-quarts crystal also starts to precipitate. **Figure 1** shows XRD patterns of glass-ceramics,