Microstructure and Optical Absorption Spectra of Transparent Glass-Ceramics Containing $LiGa_5O_8$:Co^{2+}

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Transparent glass-ceramics containing $LiGa_5O_8$:Co^{2+} have been prepared by heat treatment of glass with a composition of $13Li_2O \cdot 23Ga_2O_3 \cdot 64SiO_2 \cdot xCoO$ (0.1, 0.2, 0.5, 1.0) (mol%). The microstructure and the optical properties have been examined by using X-ray diffraction (XRD), transmission electron microscopy (TEM), and optical absorption measurements. XRD analyses indicated that $LiGa_5O_8$ microcrystals with a crystallite size of 5 to 10 nm precipitated in the specimens heat-treated at temperatures between 750 and 850 °C. Above 850 °C, $LiGaSi_2O_6$ crystals also precipitated. Heat treatment below 850 °C successfully yielded transparent glass-ceramics. The optical absorption spectra at room temperature indicated that the absorption band due to the $^4A_2 \rightarrow {}^4T_1(P)$ transition of Co^{2+} ions in tetrahedral sites showed three peaks (520, 586 and 686 nm) for the glass and three peaks (560, 597, and 646 nm) for the glass-ceramics. This difference in the spectra suggests that some Co^{2+} ions replaced the Ga^{3+} ions in tetrahedral sites of the $LiGa_5O_8$ microcrystals.

Persistent photochemical hole burning (PHB) is a phenomenon in which a site-selective and persistent decrease of absorption or a hole is created in the absorption band of highly dispersed photoreactive guests in host matrices at low temperature. PHB is expected to be a possible means for high-density frequency-domain information storage as well as a tool for high-resolution laser spectroscopy.[1—3] PHB was first observed in $LiGa_5O_8$:Co^{2+} for transition metal-doped systems.[4] The phenomenon was observed in the absorption from the $^4A_2 \rightarrow {}^4T_1(P)$ transition of Co^{2+} substituted in Ga^{3+} tetrahedral sites of $LiGa_5O_8$.

If transparent glass-ceramics containing $LiGa_5O_8$:Co^{2+} can be prepared, it becomes feasible to make the area of a PHB device larger and to prepare a device easily, compared with a single crystal device. The physical properties of lithium gallosilicate glasses, such as the glass transition temperature, viscosity, and thermal expansion, have already been studied.[5] However, crystallization and the crystallized phases of lithium gallosilicate glasses by heat treatment have not been investigated.

In the present study, we have found that $LiGa_5O_8$ spinel crystallite is precipitated from lithium gallosilicate glasses by heat treatment. We prepared transparent glass-ceramics containing $LiGa_5O_8$:Co^{2+} by heat treatment of lithium gallosilicate glasses, and examined the optical absorption spectra of the resultant specimens.

Experimental

Glasses with $13Li_2O \cdot 23Ga_2O_3 \cdot 64SiO_2 \cdot xCoO$ (x=0.1, 0.2, 0.5, and 1.0) molar composition were prepared. The raw materials were mixed thoroughly and melted in a platinum crucible at 1550 °C for 2 h in air. The melt was pressed between iron plates, and annealed at 600 °C. The resultant specimen was a transparent glass of 4 mm thickness. The differential thermal analysis of the glass, which is shown in Fig. 1, revealed that the glass transition temperature was 634 °C and the crystallization temperatures were 730 and 823 °C. Judging from the results of the X-ray diffraction (XRD) analyses, T_{C1} and T_{C2} are the crystallization temperatures of $LiGa_5O_8$ and $LiGaSi_2O_6$, respectively. The specimens were heated at temperatures from 700 to 900 °C for 2 h in air. When the heat treatment was carried out above 750 °C, the color of the specimens changed from deep blue to pale blue.

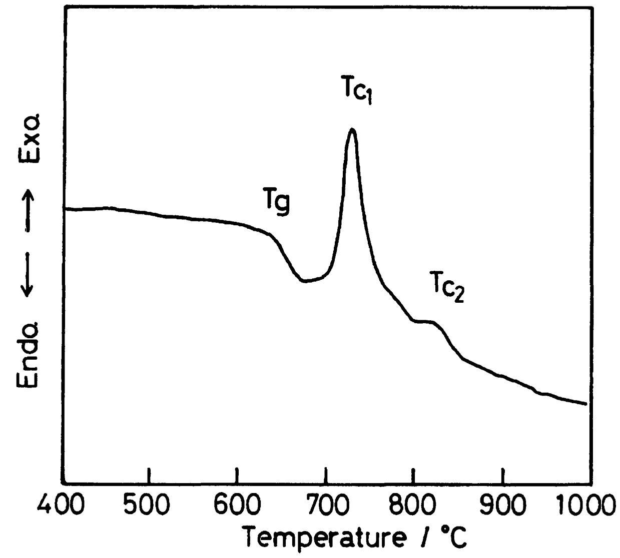

Fig. 1. DTA curve for $13Li_2O \cdot 23Ga_2O_3 \cdot 64SiO_2 \cdot 0.1CoO$ glass. T_g denotes the glass transition temperature. T_{C1} and T_{C2} represent the crystallization temperatures.

The XRD analyses were carried out by using Cu $K\alpha$ radiation to identify the precipitated crystalline phases. The crystallite sizes were evaluated from the full width at half maximum (hereafter referred to as FWHM) of the diffraction peak by using Scherrer's equation.

Transmission electron microscopic (TEM) observation was carried out to investigate the microstructure of the specimens, using a JEOL 2000FX at 200kV.

Optical absorption spectra were measured from 300 to 800 nm at room temperature by using a Shimadzu UV 365 spectrophotometer.

Results and Discussion

The Shape and Size of the Precipitated Crystals. The XRD patterns of the glass and the specimens heat-treated at several temperatures are shown in Fig. 2. The diffraction peaks attributed to $LiGa_5O_8$ were observed for the specimens heat-treated above 750 °C. In the specimens heat-treated above 850 °C, the diffraction peaks due to $LiGaSi_2O_6$ were observed. By using Scherrer's equation with the FWHM values obtained, the crystallite sizes were evaluated. The results are shown in Fig. 3. The crystallite sizes increased with an increase in heat treatment temperature, and varied from 5 to 13 nm as the heat treatment temperature increased from 750 to 900 °C. TEM images of the glass and the specimens heat-treated at several temperatures are shown in Fig. 4. In the specimen heat-treated at 750 °C, spherical $LiGa_5O_8$ nanocrystallites of about 5 nm diameter were precipitated. As the heat treatment temperature increased, the crystallites grew and their size became 15 nm diameter at 900 °C. Also, cubic $LiGaSi_2O_6$ nanocrystallites appeared at 850 °C and their size became 300 nm at 900 °C. The glass-ceramics heat-treated at 850 °C were somewhat translucent. The specimen heat-treated at 900 °C was opaque because of the large crystallite size of the precipitated $LiGaSi_2O_6$ crystals.

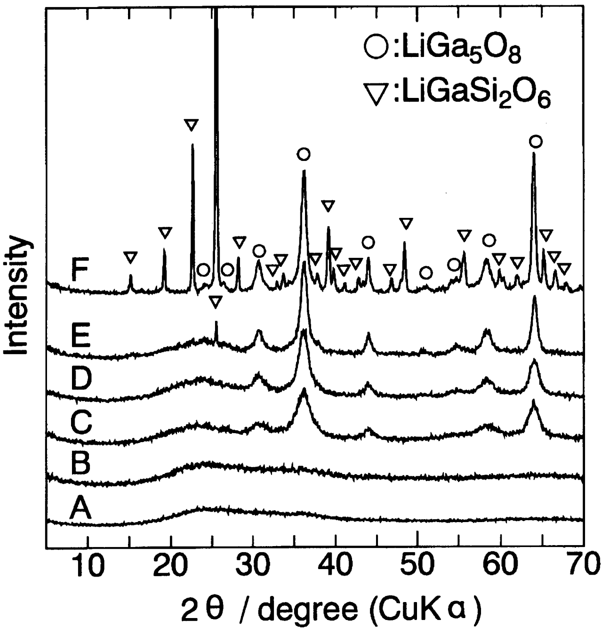

Fig. 2. The variation of the X-ray diffraction patterns with heat treatment temperature for $13Li_2O{\cdot}23Ga_2O_3{\cdot}64SiO_2{\cdot}0.1CoO$ glass. The heat treatment temperatures are: (A) original glass, (B) 700 °C, (C) 750 °C, (D) 800 °C, (E) 850 °C, and (F) 900 °C.

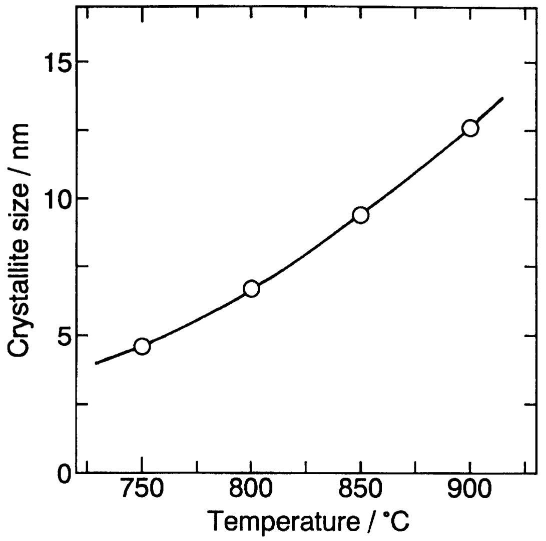

Fig. 3. The relationship between the crystallite size of $LiGa_5O_8$ and the heat treatment temperature.

Optical Absorption Spectra. The absorption spectra of the glass and the heat-treated specimens are shown in Fig. 5. The absorption lines are located in the visible region. As for the glass, the spectrum has three peaks (520, 586, and 636 nm). The absorption spectrum demonstrates that the Co^{2+} ions occupy the tetrahedral sites in the glass.[6,7] When the glass was heated above 750 °C, the absorption spectrum of the heat-treated specimens drastically changed from that of the glass. The spectrum consists of three intense peaks (560, 597, and 646 nm). A weaker absorption band is located at 490 nm. All the specimens heated above 750 °C exhibited similar spectra, although the absorption below 500 nm in their spectra increased with an increase in the heat treatment temperature. This was caused by the scattering of light from the precipitated particles. The appearance of these absorption peaks indicated that the Co^{2+} ions were incorporated into $LiGa_5O_8$, replacing the Ga^{3+} ions in the tetrahedral sites. The unit cell of inverse spinel $LiGa_5O_8$ contains four formula units with twelve octahedral and eight tetrahedral Ga^{3+} sites,[8] which can be substituted by Co^{2+}. When crystallized with small amounts of Co^{2+}, the glass-ceramics become pale blue, which is characteristic of Co^{2+} ions in tetrahedral sites.[4,9,10] The $^4A_2 \rightarrow {}^4T_1(P)$ transition is the only spin-allowed transition for Co^{2+} ions to occur in the visible region and is the origin of the absorption bands seen in Fig. 5. The percentage of Co^{2+} ions occupying octahedral sites is not known, but is presumed to be smaller than that for tetrahedral sites which dominate the optical absorption and are the only ones that concern us here.

Effect of Co^{2+} Ions Concentration. According to crystal field theory, the crystal field strength, D_q, depends on the bonding distance between cations

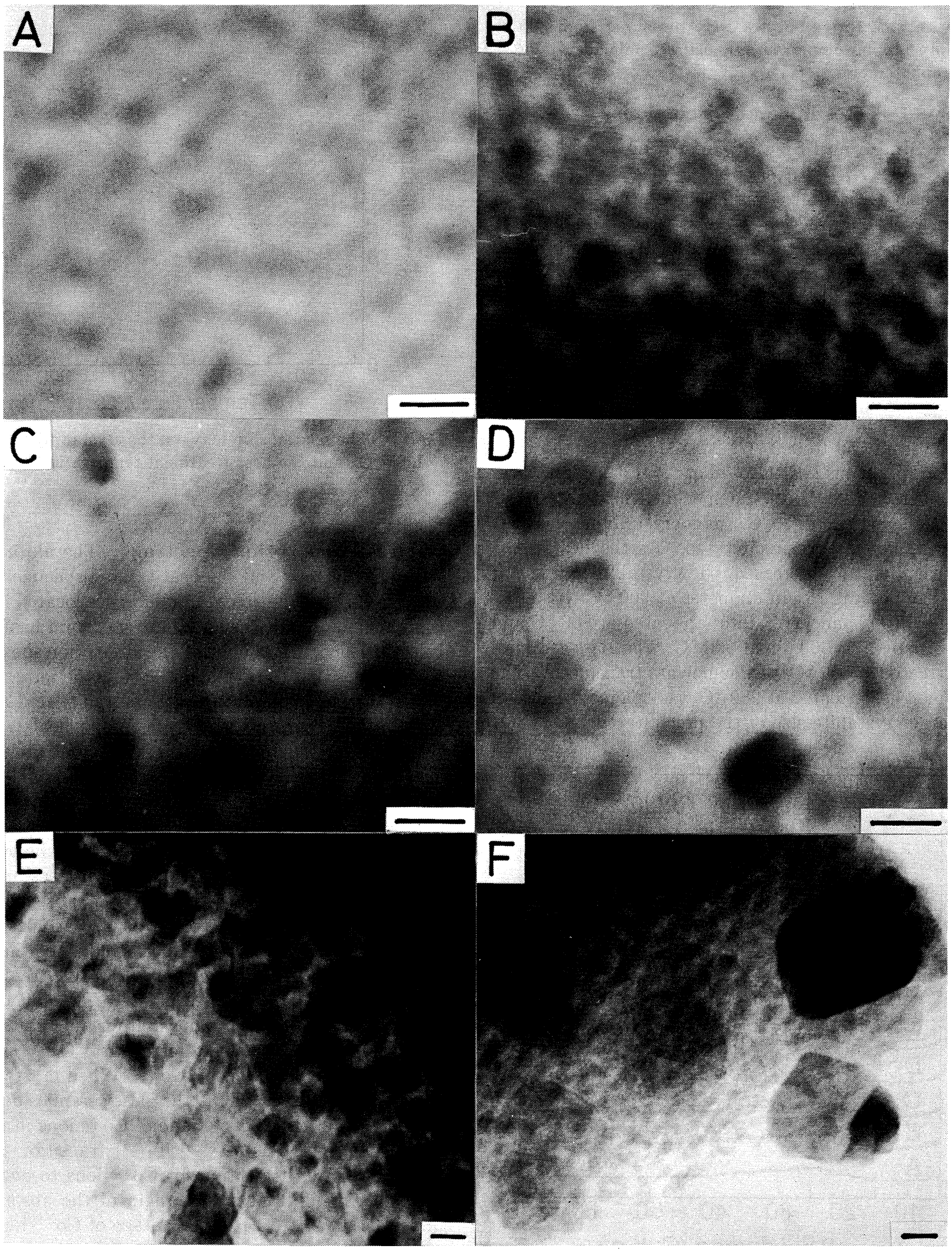

Fig. 4. TEM images of (A) the glass, and the specimens heat-treated at various temperatures: (B) 700 °C, (C) 750 °C, (D) 800 °C, (E) 850 °C, and (F) 900 °C. The bar represents 10 nm.

and anions.[11] For instance, a variation of the average Co^{2+}–O^{2-} distance should cause a shift of the $^4A_2 \rightarrow {}^4T_1(P)$ broad absorption band of Co^{2+}-doped nanocrystallites. Thus, the correlations between the additional Co^{2+} concentration and the lattice constant of precipitated $LiGa_5O_8$ crystals or the absorption spec-

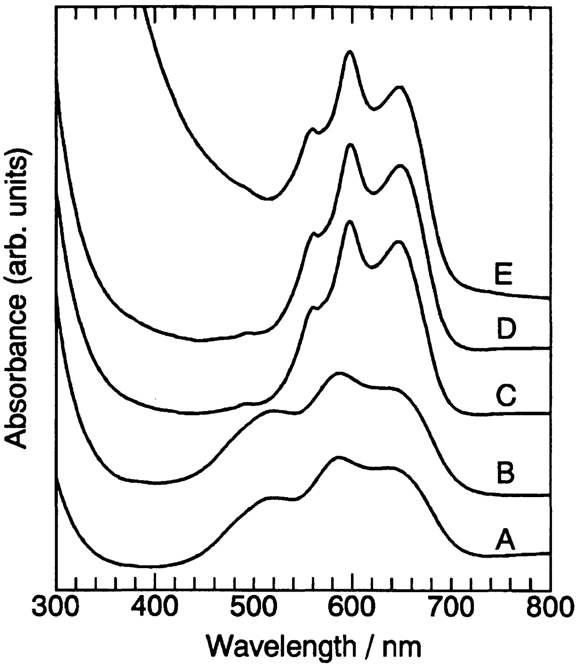

Fig. 5. Absorption spectra in the visible region of (A) the glass, and the specimens heat-treated at various temperatures: (B) 700 °C, (C) 750 °C, (D) 800 °C, and (E) 850 °C.

tra were examined. Figure 6 shows the dependence of the lattice constant on the Co^{2+} concentration. The lattice constant of $LiGa_5O_8$ cited from ASTM cards is also shown. The lattice constants for all the present specimens were larger than that for $LiGa_5O_8$, and the lattice constants increased with an increase in the concentration of Co^{2+} ions. Figure 7 shows the absorption spectra of the specimens with several concentrations of Co^{2+} ions heat-treated at 800 °C. All the specimens manifested similar spectra, although the absorbance of the spectra increased with an increase in the concentration of Co^{2+} ions. The increase in the lattice constant with an increase in Co^{2+} ion concentration indicates that, at least, some Co^{2+} ions replaced the Ga^{3+} ions in the $LiGa_5O_8$ nanocrystallites in the present glass-ceramics. We believe that the discrepancy between the results of the lattice constant and the absorption spectra can be solved in the following way. The crystal field splitting of the energy levels of Co^{2+} ($3d^7$) in a tetrahedral field is the same as the splitting of the energy levels of Cr^{3+} ($3d^3$) in an octahedral field, but the value of the crystal field parameter is significantly smaller in the tetrahedral case.[12] In the present case, the variation of the lattice constant is very small. In other words, the variation of the average Co^{2+}–O^{2-} distance is very small. For these reasons, the crystal field strength, D_q, is only slightly affected by the Co^{2+} ion concentration.

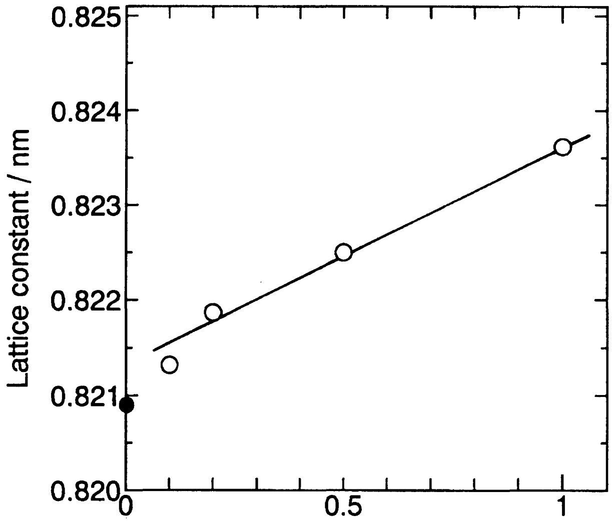

Fig. 6. The relationship between the lattice constant of $LiGa_5O_8$ and the concentration of Co^{2+} ions. The closed circle represents the value from the ASTM cards.

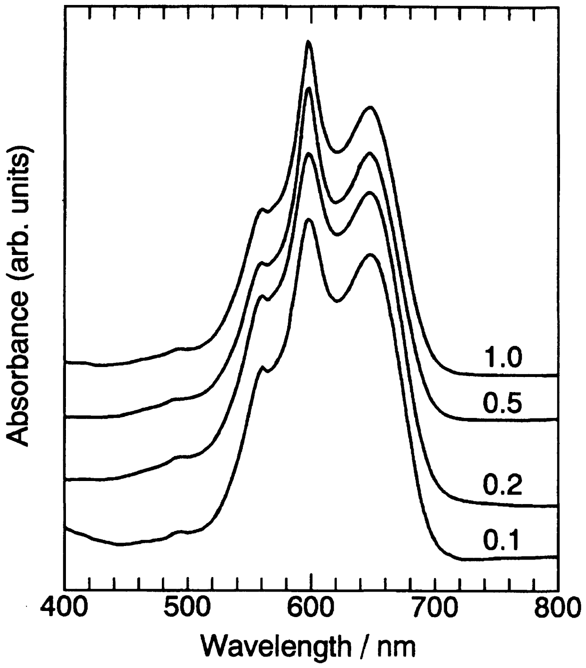

Fig. 7. Absorption spectra of the specimens heat-treated at 800 °C with various concentrations of Co^{2+} ions. The values presented in the figure denote the concentration of Co^{2+} ions.

Conclusions

Transparent glass-ceramics containing $LiGa_5O_8$:Co^{2+} have been prepared by heat treatment of glass with a composition of $13Li_2O \cdot 23Ga_2O_3 \cdot 64SiO_2 \cdot x$CoO ($x$=0.1, 0.2, 0.5, 1.0) (mol%). $LiGa_5O_8$ precipitated from the glass when the heat treatment temperature was above 750 °C. Heat treatment below 850 °C successfully yielded transparent glass-ceramics. The crystallite size of $LiGa_5O_8$ increased from 5 to 10 nm with increasing heat treatment temperature from 750 to 850 °C. The optical absorption spectra at room temperature indicated that the absorption band due to the $^4A_2 \rightarrow ^4T_1(P)$ transition of the Co^{2+} ions in the tetrahedral sites had three peaks (520, 586, and 636 nm) for the glass, and three peaks (560, 597, and 646 nm) for the glass-ceramics. This change of the absorption spectra suggests that Co^{2+} ions were incorporated into the $LiGa_5O_8$ nanocrystallites and replaced the Ga^{3+} ions in the tetrahedral sites.

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