Optical Properties of Transparent Glass-Ceramics
Containing ZnGa$_2$O$_4$: Cr$^{3+}$ Microcrystals

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Transparent glass-ceramics containing ZnGa$_2$O$_4$: Cr$^{3+}$ have been prepared by the heat treatment of glass in sodium zinc gallate silicate system for the purpose of evaluating optical properties of the ZnGa$_2$O$_4$: Cr$^{3+}$ microcrystal precipitated in the glass matrix. Average crystallite size of the ZnGa$_2$O$_4$: Cr$^{3+}$ microcrystal estimated from the full width at half maximum of X-ray diffraction peak is about 100 Å. The optical absorption spectra indicate that the ligand field strength around the Cr$^{3+}$ ion is higher in the ZnGa$_2$O$_4$: Cr$^{3+}$ microcrystal than in the glass, which is coincident with the fact that the R-line is observed in the emission spectrum of the transparent glass-ceramics while the emission spectrum of glass manifests a broad Stokes' shifted band. We have analyzed temperature dependence of peak position of R$_1$- and R$_2$-lines for the ZnGa$_2$O$_4$: Cr$^{3+}$ microcrystal and polycrystal by assuming the Raman process for the electronic transition and the Debye model for the vibrational density of state. The Debye temperatures of ZnGa$_2$O$_4$: Cr$^{3+}$ microcrystal estimated from the R$_1$- and R$_2$-lines are 640 and 530 K, respectively. On the other hand, the Debye temperatures of ZnGa$_2$O$_4$: Cr$^{3+}$ polycrystal estimated from the R$_1$- and R$_2$-lines are 690 and 600 K, respectively. The difference in the Debye temperature between microcrystal and polycrystal is mainly attributed to the softening of phonons in the ZnGa$_2$O$_4$: Cr$^{3+}$ microcrystal.

KEY WORDS: Transparent glass-ceramics/ Microcrystal/ ZnGa$_2$O$_4$: Cr$^{3+}$/ Optical properties/ Raman process/ Debye model/

1. INTRODUCTION

The optical properties of Cr$^{3+}$ ion in oxide glasses have been studied extensively in the past. The ligand field strength for Cr$^{3+}$ ion in oxide glasses is generally low, and consequently, the emission from the $^4T_2$ to $^4A_2$ is dominant even at low temperatures in most of the oxide glasses.$^{1-4}$ The transition from the $^4T_2$ to $^4A_2$ gives rise to a Stokes' shifted broad band in the red to infrared region. The emission due to the transition from the $^2E$ to $^4A_2$, what is called R-line, is barely observed at room temperature in the oxide glasses. In contrast, the R-line is evidently observed in Cr$^{3+}$-doped aluminate crystals such as spinel and ruby since high ligand field is attained in these materials.$^5$ Also, the emission intensity of the Stokes' shifted band as well as the R-line is lower in oxide glasses than in aluminate and gallate crystals.$^6$ Thus, from a point of view of practical application as a fluorescence material utilizing Cr$^{3+}$ ion, oxide glasses are inferior. Nonetheless, glass is an attractive substance as an optical material because of high transparency and easiness to form any shapes. One way to obtain high emission intensity from Cr$^{3+}$ ion in oxide glass is to introduce microcrystalline phases doped with Cr$^{3+}$ ion into the glass.

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Recently, transparent glass-ceramics containing Cr$^{3+}$-doped microcrystals have been prepared mainly with the aim of application to a solid-state laser and a luminescence solar concentrator. The crystallization process, microstructure and optical properties of transparent glass-ceramics containing Cr$^{3+}$-doped aluminate and other crystals have been investigated. The Cr$^{3+}$ ion is effective as a photo-active center in these transparent glass-ceramics because of its high emission intensity. Besides, the Cr$^{3+}$ ion plays a role of a nucleating agent in the precipitation process of microcrystal from the glass, as revealed from the crystallization processes of MgAl$_2$O$_4$:Cr$^{3+}$ and ZnAl$_2$O$_4$:Cr$^{3+}$. The latter property is advantageous for the formation of Cr$^{3+}$-doped microcrystals. Furthermore, the transparent glass-ceramics allow us to deduce optical properties of microcrystals, which are different than those of bulk crystals. It is known that the size of microcrystal has influence on the vibrational properties. Since many optical processes in a solid are intimately related to the vibrational properties, we can obtain information about the lattice vibration of microcrystals from optical measurements. In the present investigation, an attempt was made to prepare transparent glass-ceramics containing ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystals. We report optical absorption and emission properties of transparent glass-ceramics and vibrational properties of ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystals deduced from the optical measurements of the transparent glass-ceramics.

2. EXPERIMENTAL

2.1 Preparation of specimens

Glass with the composition of 6Na$_2$O·18ZnO·18Ga$_2$O$_3$·51SiO$_2$·3TiO$_2$·4ZrO$_2$·0.05Cr$_2$O$_3$ (molar ratio) was prepared from reagent-grade Na$_2$CO$_3$, ZnO, Ga$_2$O$_3$, SiO$_2$, TiO$_2$, ZrO$_2$ and Cr$_2$O$_3$. TiO$_2$ and ZrO$_2$ were added because they were effective for lowering the temperature for melting as well as efficient as a nucleating agent. The raw materials were mixed thoroughly and melted in a platinum crucible at 1,600°C for 2 h in air. The melt was poured onto a stainless steel plate and quenched by being pressed with an iron plate. The resultant specimen was transparent and exhibited green color due to the Cr$^{3+}$ ion. The amorphous state was ascertained by using X-ray diffraction analysis with CuKα radiation. The glass was heat-treated for 12 h at 680°C, which was higher by about 50°C than the glass transition temperature determined by means of the differential thermal analysis. Subsequently, the specimen was reheated at 800°C for 12 h in air. The resultant specimen was subjected to the X-ray diffraction to identify precipitated crystalline phases and to evaluate the average crystallite size. The crystallite size was estimated from the full width at half maximum (FWHM) of the X-ray diffraction peak by using the Scherrer's equation.

ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal was prepared by using the conventional solid state reaction. Reagent-grade ZnO, Ga$_2$O$_3$ and Cr$_2$O$_3$ powders were mixed thoroughly so that the composition was ZnO·Ga$_2$O$_3$·0.005Cr$_2$O$_3$ (molar ratio). The mixed powders were calcined at 1,300°C for 1 h in air. After cooled to room temperature, the specimen was pulverized. The procedure of the calcination and pulverization was repeated three times. Then, the resultant powders were cast into a pellet under a hydrostatic pressure, and sintered at 1,400°C for 3 h in air. The X-ray diffraction analysis was carried out on the sintered material in order to ascertain that the specimen was a ZnGa$_2$O$_4$ single phase.
2.2 Measurements of optical properties

Optical absorption spectra were measured at room temperature by using a spectrophotometer (Hitachi-330) with a Xe lamp as the light source. Emission spectra were measured at 8 to 600 K by using an Ar ion laser (Coherent Innova 70) as the excitation source. The emission was detected by using a fluorescence spectrophotometer (Hitachi-850). For the measurements below room temperature, the specimen was cooled by using a cryogenic refrigerator (Iwatani Plantech, Model CRT-006-1000) equipped with a compressor (Iwatani Plantech, Model CA101). With this apparatus, one can obtain low temperatures down to 8 K utilizing the adiabatic expansion of helium gas supplied from the compressor. For the measurements at 600 K from room temperature, the specimen was heated by using Nichrome wires; the specimen was contacted with two alumina rods around which Nichrome wires were coiled, and a current was supplied to the wires.

3. RESULTS

Figure 1 shows the X-ray diffraction patterns of the glass, transparent glass-ceramic and polycrystal specimens. All the diffraction lines in the X-ray diffraction patterns of the transparent glass-ceramics and the polycrystal are attributable to ZnGa$_2$O$_4$. The average crystallite size of ZnGa$_2$O$_4$ precipitated in the transparent glass-ceramics was estimated to be about 100 Å from the FWHM of the diffraction peak corresponding to the reflection from the (440) plane. The lattice constant of the ZnGa$_2$O$_4$ microcrystal and polycrystal was also evaluated from the position of diffraction peaks. The results are shown in Table 1. The lattice constant of the ZnGa$_2$O$_4$ microcrystal is almost identical with that of the ZnGa$_2$O$_4$ polycrystal.

Optical absorption spectra of the glass and transparent glass-ceramics are shown in Fig. 2. According to the Tanabe-Sugano diagram, the absorption bands at around 15,900 cm$^{-1}$ and...
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Table 1. Average crystallite size and lattice constant of ZnGa₂O₄:Cr³⁺ microcrystal precipitated in the transparent glass-ceramics and ZnGa₂O₄:Cr³⁺ polycrystal.

<table>
<thead>
<tr>
<th>Crystallite size</th>
<th>Lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Å)</td>
<td>(Å)</td>
</tr>
<tr>
<td>ZnGa₂O₄:Cr³⁺</td>
<td></td>
</tr>
<tr>
<td>Microcrystal</td>
<td>100</td>
</tr>
<tr>
<td>Polycrystal</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 2. Ligand field strength, Dq, and Racah parameter, B, for the Cr³⁺ ion in the 6Na₂O-18ZnO-18Ga₂O₃-51SiO₂-3TiO₂-4ZrO₂-0.05Cr₂O₃ glass and ZnGa₂O₄:Cr³⁺ microcrystal precipitated from the glass.

<table>
<thead>
<tr>
<th></th>
<th>Dq (cm⁻¹)</th>
<th>B (cm⁻¹)</th>
<th>Dq/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>1,590</td>
<td>827</td>
<td>1.9</td>
</tr>
<tr>
<td>ZnGa₂O₄:Cr³⁺ microcrystal</td>
<td>1,630</td>
<td>610</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Fig. 2. Optical absorption spectra of glass and transparent glass-ceramics measured at room temperature. The assignments of the absorption peaks are presented in the text.

23,500 cm⁻¹ observed for the glass correspond to the ⁴A₂→⁴T₂ and ⁴A₂→⁴T₁ transitions, respectively. Similarly, the absorption bands at around 16,300 cm⁻¹ and 22,500 cm⁻¹ in the spectrum of the transparent glass-ceramics are assigned to the ⁴A₂→⁴T₂ and ⁴A₂→⁴T₁ transitions, respectively. When the absorption peak positions are represented by ν₁ and ν₂ where ν₁ and ν₂ respectively correspond to the ⁴A₂→⁴T₂ and ⁴A₂→⁴T₁ transitions, following equations hold:¹⁸

\[
\nu_1 = 10Dq,
\]

\[
\nu_2 = 7.5B + 15Dq - \frac{1}{2} (225B^2 + 100Dq^2 - 180BDq)^{1/2},
\]

(1a)

(1b)
where $Dq$ is the ligand field strength and $B$ is the Racah parameter. By using Eqs. (1a) and (1b), we evaluated the values of $Dq$ and $B$ for the glass and transparent glass-ceramics. The results are shown in Table 2.

![Emission spectra of glass, transparent glass-ceramics, and ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal measured at room temperature. The excitation was carried out by using an Ar ion laser (all lines).](image1)

**Fig. 3.** Emission spectra of glass, transparent glass-ceramics, and ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal measured at room temperature. The excitation was carried out by using an Ar ion laser (all lines).

![Temperature variation of emission spectrum of ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal precipitated in the transparent glass-ceramics. It should be noted that the scale of the abscissa for the top two spectra is different than that for the bottom three spectra.](image2)

**Fig. 4.** Temperature variation of emission spectrum of ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal precipitated in the transparent glass-ceramics. It should be noted that the scale of the abscissa for the top two spectra is different than that for the bottom three spectra.
In Fig. 3 are shown the emission spectra of glass, transparent glass-ceramics, and ZnGa₂O₄:Cr³⁺ polycrystal measured at room temperature. The glass manifests a broad and weak Stokes' shifted band at around 13,000 cm⁻¹. In contrast, intense peaks with narrow linewidth are observed at around 14,500 and 14,550 cm⁻¹ in the spectrum of the ZnGa₂O₄:Cr³⁺ polycrystal. These peaks are R₁- and R₂-lines, respectively. These lines also appear in the spectrum of the transparent glass-ceramics, although the intensity is lower compared with the spectrum of the polycrystal. The emission bands at around 13,900, 14,000, 14,100 and 14,400 cm⁻¹, which are observed for both transparent glass-ceramics and polycrystal, are assigned to the vibronic sidebands of the transition from the ⁴E to ⁴A₂ levels. The emission bands observed in the region higher than 14,600 cm⁻¹ are ascribed to the hot bands. Figure 4 shows the temperature variation of emission spectrum for ZnGa₂O₄:Cr³⁺ microcrystal precipitated in the transparent glass-ceramics. In this figure, the scales of the abscissa for the top two spectra are different than those for the bottom three spectra. The R₁- and R₂-lines manifest broad linewidth and low intensity in the spectra above room temperature. In particular, the R-lines are barely observed in the spectra above 450 K. Figure 5 shows the temperature dependence of emission spectrum of ZnGa₂O₄:Cr³⁺ polycrystal. The temperature variations of R-lines are similar to those for the ZnGa₂O₄:Cr³⁺ microcrystal; the linewidth of the R-lines increases and the intensity of those lines decreases with an increase in temperature.

![Emission Spectrum Diagram](image)

**Fig. 5.** Temperature variation of emission spectrum of ZnGa₂O₄:Cr³⁺ polycrystal. The scale of the abscissa for the top two spectra is different than that for the bottom four spectra.

4. DISCUSSION

As shown in Table 2, the ligand field strength Dq is larger for the transparent glass-ceramics than for the glass. This fact indicates that Cr³⁺ ions are incorporated in the ZnGa₂O₄.
microcrystalline phases in the transparent glass-ceramics and the ZnGa₂O₄ microcrystal offers higher ligand field to the Cr³⁺ ion than the glass. The B value is smaller for the transparent glass-ceramics than for the glass, indicating that the interaction between the 3d orbitals of Cr³⁺ ion and the 2p orbitals of oxide ions is larger in the ZnGa₂O₄ : Cr³⁺ microcrystal than in the glass. Presumably, the interionic separation between Cr³⁺ and O²⁻ is shorter in the ZnGa₂O₄ : Cr³⁺ microcrystal than in the glass, leading to the higher ligand field strength and smaller B value for the ZnGa₂O₄ : Cr³⁺ microcrystal. The high ligand field strength in ZnGa₂O₄ is also reflected in the emission spectra. As shown in Fig. 3, the emission bands which correspond to the transition from the ⁴E to ⁴A₂ are clearly observed for the ZnGa₂O₄ : Cr³⁺ microcrystal while the emission spectrum of the glass consists of only broad Stokes' shifted band due to the ⁴T₂⁻⁴A₂ transition.

It is known that the peak position of zero-phonon line changes with temperature. In Raman process, the temperature dependence of peak position of zero-phonon line is expressed by the following equation when the Debye model is assumed for the vibrational density of state:¹⁹

\[ \varepsilon(T) = \varepsilon(0) + a \left( \frac{T}{3kT} \right)^{1/2} - \frac{kT}{\hbar} \int_0^{\infty} \frac{\epsilon^3}{\epsilon^3 - 1} d\epsilon. \tag{2a} \]

Here \( a \) is given by

\[ a = \frac{3k\omega_p^4}{4\pi^3 \rho v^3} \left( \left| \langle i | \mathcal{V}^{(0)} | i \rangle \right|^2 + \sum_{\sigma_i} \left| \langle i | \mathcal{V}^{(1)} | m \rangle \right|^2 W_{\sigma_i m} \right), \tag{2b} \]

where \( \hbar \) is the Planck constant, \( \omega_p \) is the cut-off frequency in the Debye model, \( \rho \) is the density, \( v \)

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**Fig. 6.** Temperature dependence of peak position of \( R_1 \) and \( R_2 \)-lines for ZnGa₂O₄ : Cr³⁺ microcrystal precipitated in the transparent glass-ceramics and for the ZnGa₂O₄ : Cr³⁺ polycrystal. The open and closed symbols correspond to the ZnGa₂O₄ : Cr³⁺ microcrystal and polycrystal, respectively. \( R_1 \) and \( R_2 \) denote the \( R_1 \)- and \( R_2 \)-lines, respectively. The solid curves are drawn by assuming the Raman process for the electronic transition and the Debye model for the vibrational density of state (Eqs. (2a) and (2b)).
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is the sound velocity, $V^{(i)}$ and $V^{(m)}$ are relevant to the local strain field, and $W_i$ and $W_m$ are the energy levels of $i$-th and $m$-th states, respectively. In Fig. 6 are shown the temperature variations of peak positions of $R_1$- and $R_2$-lines for the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal precipitated in the transparent glass-ceramics and for the ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal. The open and closed symbols represent the experimental data for the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal and ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal, respectively. The solid curves are calculated ones, which were fitted to the experimental data by using Eqs. (2a) and (2b) with parameters $\varepsilon(0)$, $\alpha$ and $\theta_D$ given in Table 3.

Only the experimental data obtained below room temperature were adopted in the calculation, because it was difficult to determine the accurate peak positions of linewidth of $R_1$- and $R_2$-lines in the emission spectra above room temperature owing to the broadness and weakness of intensity. Table 3 indicates that the Debye temperature obtained from the temperature dependence of the $R_1$-line is not identical with the Debye temperature derived from the $R_2$-line. The reason for this incompatibility is unclear, but the properties of phonons relevant to the electronic transitions corresponding to $R_1$- and $R_2$-lines may be different from each other. In this sense, the Debye temperatures obtained from the present optical measurements are inevitably different than those derived from the other properties such as specific heat, Debye-Waller factor, and recoil-free fraction.

Table 3 also shows that the Debye temperature for the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal is lower than that for the ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal. As well known, there is a general tendency that the Debye temperature decreases with a decrease in the size of crystal because of the softening of phonons on the surface of the microcrystal. For instance, it was reported that the Debye temperature of microcrystalline Au of 60 A is 134 K while that of bulk Au is 168 K. In the present case, we speculate that the lower Debye temperature of the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal compared with the polycrystal is mainly attributed to the softening of lattice vibration at the interface between microcrystal and glass matrix.

As for the Au microcrystal, in contrast with the dependence of the Debye temperature on the size of crystal, the lattice constant is independent of the size of the crystal. A similar result was obtained for the present ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal, as indicated in Table 1; the lattice constant of the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal is almost identical to that of polycrystal.

It is found from Figs. 3 to 5 that the intensity of the $R_1$- and $R_2$-lines is lower and the linewidth of these lines is broader for the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal than for the polycrystal. The broad linewidth for the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal implies the site-to-site distribution of Cr$^{3+}$ ions in this material. The wide distribution of Cr$^{3+}$ ion sites arises from possible

Table 3. Peak position of $R_1$- and $R_2$-lines at 0 K, $\varepsilon(0)$, the parameter $\alpha$ in Eqs. 2a and 2b, and Debye temperature, $\theta_D$, for ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal precipitated in the transparent glass-ceramics and ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal.

<table>
<thead>
<tr>
<th>Line</th>
<th>$\varepsilon(0)$ (cm$^{-1}$)</th>
<th>$\alpha$ (cm$^{-1}$)</th>
<th>$\theta_D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$-line</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal</td>
<td>14,544</td>
<td>-410</td>
<td>640</td>
</tr>
<tr>
<td>ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal</td>
<td>14,547</td>
<td>-450</td>
<td>690</td>
</tr>
<tr>
<td>$R_2$-line</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal</td>
<td>14,586</td>
<td>-340</td>
<td>530</td>
</tr>
<tr>
<td>ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal</td>
<td>14,587</td>
<td>-350</td>
<td>600</td>
</tr>
</tbody>
</table>

(131)
incorporation of Ti and Zr into the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystalline phase as well as the existence of Cr$^{3+}$ ions on the surface region of the microcrystal. The lower intensity for the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal may reflect lower ligand field strength compared with the ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal.

5. CONCLUSION

Transparent glass-ceramics containing ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystals were successfully prepared by the heat treatment of 6Na$_2$O:18ZnO:18Ga$_2$O$_3$:51SiO$_2$:3TiO$_2$:4ZrO$_2$:0.05Cr$_2$O$_3$ (molar ratio) glass. Incorporation of Cr$^{3+}$ ions into the ZnGa$_2$O$_4$ microcrystalline phase was demonstrated from the optical absorption and emission spectra. As revealed from the full width at half maximum of X-ray diffraction peak, the average crystallite size of ZnGa$_2$O$_4$:Cr$^{3+}$ is about 100 Å. The ligand field strength around the Cr$^{3+}$ ion is higher in the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal than in the glass, resulting in the appearance of R-lines in the emission spectrum of the transparent glass-ceramics. The temperature dependence of peak position of the R$_1$- and R$_2$-lines for the transparent glass-ceramics and ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal is describable in terms of the Raman process assuming the Debye model for the vibrational density of state. The Debye temperature of the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal is lower than that of the ZnGa$_2$O$_4$:Cr$^{3+}$ polycrystal, indicating that the softening of phonons takes place in the ZnGa$_2$O$_4$:Cr$^{3+}$ microcrystal.

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