

Formation, Absorption and Emission Spectra of Cr⁴⁺ Ions in Li₂O–SiO₂ System Transparent Glass-Ceramics

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Li₂O–SiO₂ 系透明結晶化ガラス中での Cr⁴⁺ イオンの生成と光吸収及び発光スペクトル

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The formation mechanism, optical absorption and emission spectra of Cr⁴⁺ ions-containing Li₂O–SiO₂ system transparent glass-ceramics were investigated. In this material, the main crystalline phase was Li₂O·2SiO₂, and the percent crystallinity and crystal size were 67–72 and 20–33 nm, respectively. The remarkable change in color and absorption spectra was observed upon crystallization. The characteristic emission of tetrahedrally coordinated Cr⁴⁺ ions was identified in the near infrared region, 1000–1600 nm. It was found that tetrahedrally coordinated Cr⁴⁺ ions exist in this transparent glass-ceramics from absorption and emission measurement. The Cr⁴⁺ ions exist in residual high SiO₂ glassy phase, and their ligand field parameters are estimated to be: 10Dq = 10,610 cm⁻¹, B = 690 cm⁻¹ and Dq/B = 1.54. This Dq/B value is just below the crossing point of ³T₂ and ¹E levels (Dq/B = 1.6). The Cr⁴⁺ ions in Li₂O–SiO₂ system transparent glass-ceramics occupy the little stronger ligand field sites than those in aluminate glass reported previously (Dq/B = 1.2). It is considered that the Cr⁴⁺ ions can be formed by the reduction of Cr⁶⁺ ions (chromate ion [CrO₄]²⁻) associated with decreasing the basicity of residual glassy phase during crystallization. In this process the behavior of Li⁺ ions plays a significant role. The [CrO₄] formed is equivalent to [SiO₄] and substitutes [SiO₄] sites in the residual high SiO₂ glassy phase.

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1. Introduction

Nowadays many researches on crystals^{1)–4)} and glasses^{5)–8)} with Cr⁴⁺ ions in tetrahedral coordination are being done because they are able to produce tunable laser emission at longer wavelength. In the area of telecommunications such materials hold the promise of broad-band optical gain at the 1.3 and 1.5 μm optical communication wavelength.

It has been found that the stable Cr⁴⁺ ions can be formed only in aluminate, alumino-silicate and gallate system with higher modifier oxides, and their spectroscopic properties have already been measured.^{5)–7)} According to their results, the formation of tetrahedrally coordinated Cr⁴⁺ ions is related to the interaction between Cr³⁺ ions and oxygen excess defects, such as super oxide ion radicals and peroxy linkage.⁸⁾ Due to the disorder of glass structure the inhomogeneous line-broadening of transition metal ions is caused by site multiplicity. On the other hand, the properties of Cr⁴⁺ doped glass-ceramics have received little attention, despite the possibilities of crystal site control.⁹⁾ The glass-ceramics, as well as glasses, has many advantages comparing with single crystals: flexibility and ease of forming to any shape, uniformity and reproducibility and process economy in high-volume manufacturing, etc.

The author has investigated the behavior of Cr ions in Li₂O–SiO₂ system transparent glass-ceramics,¹⁰⁾ and the possibility of the existence of Cr⁴⁺ ions in this glass-ceramics was suggested. In this paper, the formation mechanism, absorption and emission spectra of Cr⁴⁺ ions in Li₂O–SiO₂ system transparent glass-ceramics were discussed.

2. Experiments

2.1 Sample preparation

The glass composition of 80SiO₂·4Al₂O₃·13Li₂O·3P₂O₅·0.4Cr₂O₃ (mass%) was used. Three glasses were melted under various conditions. (1). A-glass (Oxy): a half of Li₂O was introduced by LiNO₃ and melted in 100 ml Pt/Rh10 crucible in air, (2). B-glass (Air): melted in 100 ml Pt/Rh crucible in air and (3). C-glass: 1.5 mass% carbon was added to batch and melted in covered alumina crucible in air.

High purity silica sand, alumina and reagent grade chemicals of Li₂CO₃, LiNO₃, (NH₃)₂HPO₄ and Cr₂O₃ (Carlo Erba) were used as raw materials. Batches corresponding to 100 g of glass were mixed thoroughly and melted at 1450°C for 2 h under various conditions described above. The molten glasses were poured onto iron plate and pressed by another plate. They were then annealed at 450°C for 30 min. and cooled to room temperature in the furnace.

The glasses were heat treated at 500°C for 15 h for nucleation and subsequently heat treated at various conditions for crystallization. The glasses and glass-ceramics were optically polished into 0.8 mm in thickness.

Crystalline phases, percent crystallinity and crystal size were determined by X-ray diffraction method (XRD). The detail of measurement is given elsewhere.¹¹⁾

2.2 Preparation of polycrystalline Li₂O·2SiO₂: Cr

The polycrystalline Li₂O·2SiO₂: Cr was prepared by a solid state reaction to investigate whether Cr⁴⁺ ions exist in this crystal. A mixture of high purity silica sand, (1/2Li₂CO₃ + 1/2LiNO₃) and Cr₂O₃ (Carlo Erba) corresponding to Li₂O·2SiO₂: Cr₂O₃ (1 mass%) composition was heat treated at 900°C

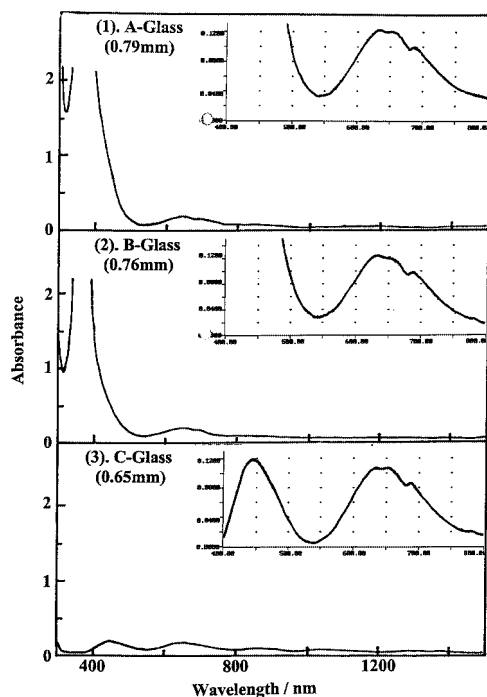


Fig. 1. Absorption spectra of Cr-ions containing glasses at room temperature. A: melted under oxidizing condition, B: melted in air, C: melted under reducing condition.

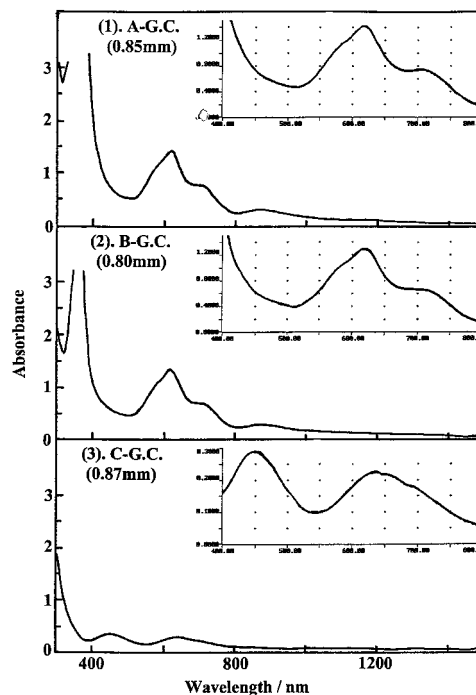


Fig. 2. Absorption spectra of Cr-ions containing transparent glass-ceramics at room temperature. A: melted under oxidizing condition, B: melted in air, C: melted under reducing condition.

for 40 h in air.

2.3 Absorption and emission measurement

The absorption spectra were measured with Cary 5E UV-VIS-NIR spectrophotometer in the range of 300–1500 nm at room temperature. The emission spectra were measured according to Feng and Tanabe⁶⁾ in the range of 800–1670 nm under excitation of 792 nm laser diode at room temperature.

3. Results and discussion

3.1 Absorption and emission spectra of glass and glass-ceramics

The glasses appeared to be yellowish-green (A and B sample) and emerald green (C sample) in color. **Figure 1** shows the absorption spectra of these glasses. The spectral pattern of A and B samples are similar except for UV region. The strong absorption band due to charge transfer of Cr^{6+} ion and a weak absorption band due to d-d transition of Cr^{3+} ion appear at around 370 nm and 650 nm, respectively.¹²⁾ However, the absorption band at around 450 nm due to d-d transition of Cr^{3+} ion is hidden by the strong absorption of Cr^{6+} ion. On the contrary, the absorption band of Cr^{3+} ion in C sample can be observed and that of Cr^{6+} ion disappears. This spectral pattern is very similar to that reported previously.¹²⁾

The transparent glass-ceramics exhibits deep blue (A and B sample) and emerald green (C sample) in color after the heat treatment, 500°C–15 h and 700°C–5 h. The main crystal is $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, and the percent crystallinity and crystal size are about 67–72 and 20–33 nm, respectively. **Figure 2** shows the absorption spectra of these glass-ceramics. The spectral patterns of A and B samples differ from those of glasses. New and strong absorption bands appear in visible (hereafter VIS) and near infrared (NIR) region, the peak position of these bands is about 580, 620, 710, 850 and 1130 nm. The absorption intensity of these band in VIS region increases by about 10 times those of glasses. On the other hand, a remarkable

change in absorption intensity and peak position can not be observed in C sample.

The A and B samples (melted under oxidizing condition) appear to be remarkable change in color and absorption spectra upon crystallization, while not in C sample (melted under reducing condition). According to a ligand field theory,¹³⁾ the absorption intensity of transition metal ions in tetrahedral coordination is much greater than that in octahedral coordination, and it was reported that Cr^{4+} , Cr^{5+} and Cr^{6+} ions occupy the tetrahedral site in crystal and glasses.¹⁴⁾ The electronic configuration of Cr^{6+} ions is d^0 , hence no d-d transition appears. The absorption band of Cr^{5+} ion would appear in NIR region,⁴⁾ and the spectral patterns of A and B samples (**Fig. 2**) are very similar to that of Cr^{4+} ion in single crystals and glasses,^{1)-4),6)} therefore, it is concluded that the most probable cause of this phenomena is due to the Cr^{4+} ions in tetrahedral sites formed in Li_2O - SiO_2 transparent glass-ceramics. The absorption bands in VIS and NIR region can be assigned to ${}^3\text{A}_2 \rightarrow {}^3\text{T}_1$ and ${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$ transition of Cr^{4+} ions in tetrahedral site,⁶⁾ respectively.

Figure 3 shows the emission spectra of glass and glass-ceramics of B sample (melted in air) at room temperature. The emission centered at about 900 nm due to Cr^{3+} ions is observed in glass, whilst in glass-ceramics both the emission of Cr^{3+} ions and the new emission centered at about 1300 nm appear. The latter emission band is ascribed to the ${}^3\text{T}_2({}^3\text{A}_2)$ transition of Cr^{4+} ions in tetrahedral sites.⁶⁾ Consequently, it is confirmed that the Cr^{4+} ions exist in these glass-ceramics from both absorption and emission measurements.

3.2 Cr^{4+} ions site

As mentioned above, it is confirmed that the Cr^{4+} ions exist in these glass-ceramics. However, it is not clear yet whether the Cr^{4+} ions exist in either nano-crystalline $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ phase or residual glassy phase. The polycrystalline $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$: Cr was prepared by solid state reaction in order to investigate

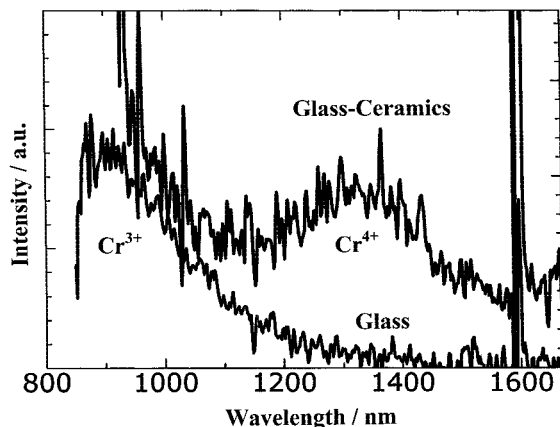


Fig. 3. Emission spectra of Cr-ions containing glass and glass-ceramics at room temperature under excitation at 792 nm laser diode. Glass: Sample B (melted in air), Glass-ceramics: Sample B (melted in air, 500°C-15 h and 700°C-5 h).

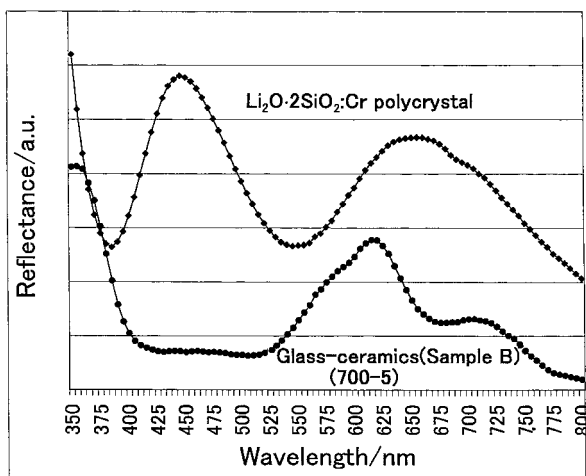


Fig. 4. Diffuse reflectance spectra of synthesized polycrystalline Li₂O·2SiO₂:Cr and glass-ceramics. Glass-ceramics: Sample B (melted in air, 500°C-15 h and 700°C-5 h).

whether the Cr⁴⁺ ions exist in this crystal.

The polycrystalline Li₂O·2SiO₂:Cr appeared to be light-green in color, and XRD showed only Li₂O·2SiO₂ phase. **Figure 4** shows the diffuse reflectance spectra of polycrystalline Li₂O·2SiO₂:Cr and glass-ceramics (B sample, 500°C-15 h and 700°C-5 h). The spectral patterns of polycrystalline and glass-ceramics are different, the former is very similar to the typical spectrum of Cr³⁺ ion (C sample in Fig. 1). This result indicates that the Cr⁴⁺ ions can not be formed in Li₂O·2SiO₂:Cr crystal, accordingly, Cr⁴⁺ ions exist and occupy the tetrahedral site in residual glassy phase. In fact, the existence of Cr⁴⁺ ions in Li₂O·2SiO₂ crystal has not been reported yet.

3.3 Formation of Cr⁴⁺ ions

It is well known that the Cr⁴⁺ ions have been found in aluminate,^{5),7),8)} aluminosilicate⁶⁾ and gallate⁸⁾ glass systems. These glasses contain super oxide ions radicals and peroxy linkage,⁸⁾ which oxidize Cr³⁺ ions to Cr⁴⁺ ions. And the formation of Cr⁴⁺ ions in single crystals has usually been carried out in oxidizing atmosphere.⁴⁾ These results indicate that the formation of Cr⁴⁺ is strongly related to the Cr³⁺ ions, and

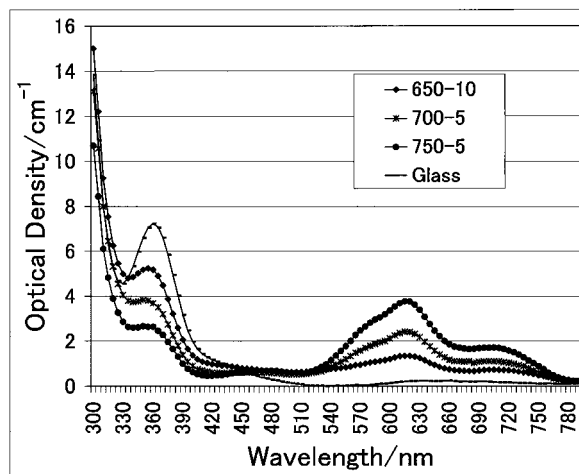


Fig. 5. Absorption spectra of glass and glass-ceramics at room temperature. Glass is melted in air. Cr₂O₃ = 0.1 mass%. Inset denotes 2nd heat treatment condition (°C-h).

consequently the Cr⁴⁺ ions can be formed by the oxidation of Cr³⁺ ions in these materials. The reaction happened in aluminate glasses may be expressed by following equation:⁸⁾



On the contrary, the sample C melted under reducing condition, in which only Cr³⁺ ions was detected by absorption spectrum, did not exhibit a significant change in color and spectral pattern upon crystallization. If the super oxide ions or peroxy linkage would be present in Li₂O-SiO₂ system glass discussed here, the above reaction should take place without heat treatment for crystallization in analogy with aluminate/aluminosilicate glasses, and Cr⁴⁺ ions must be detected in glassy state. However, in Li₂O-SiO₂ system glass, the Cr⁴⁺ ions were formed after the crystallization of glasses melted under oxidizing condition and in air. Therefore, the formation mechanism of Cr⁴⁺ ions in Li₂O-SiO₂ system transparent glass-ceramics seems to differ from those in aluminate/aluminosilicate glasses. It is considered that higher valence state of Cr ions may be responsible for the formation of Cr⁴⁺ ions in this glass system.

In order to clarify the ion species participating in the formation of Cr⁴⁺ ions, the change in absorption spectra of low Cr₂O₃-containing glass (Cr₂O₃ = 0.1 mass%) melted in air was investigated during crystallization. **Figure 5** shows the absorption spectra of glass and glass-ceramics. The absorption bands due to Cr⁶⁺ and Cr⁴⁺ ions are seen at about 370 nm and 500-800 nm, respectively. The peak positions of these bands do not change, while the peak intensity changes depending on the crystallization temperature and time. It should be noted that the peak intensity due to Cr⁶⁺ ion decreases with increasing the peak intensity of Cr⁴⁺ ions. This indicates that there may be a strong correlation between Cr⁶⁺ ions and Cr⁴⁺ ions. The differential spectrum between glass and glass-ceramics is measured, and the relationship between the peak intensity at 370 nm due to Cr⁶⁺ ions and that at 615 nm due to Cr⁴⁺ is shown in **Fig. 6**. The differential spectrum demonstrates the appearance and disappearance of certain ion species, but the increase in scattering by the crystallization is not compensated. Here, the differential spectrum, ([O.D. (cm⁻¹)]), is expressed by:

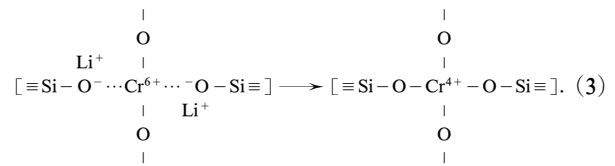
$$([\text{O.D. (cm}^{-1}\text{)}] = [\text{O.D. (cm}^{-1}\text{)}]_{\text{glass-ceramics}} - ([\text{O.D. (cm}^{-1}\text{)}]_{\text{glass}}) \quad (2)$$

A good linearity can be obtained, and it is estimated that the Cr^{6+} ions are strongly related to the formation of Cr^{4+} ions in the crystallization process. If the Cr^{4+} ions would be formed by the thermal reduction of Cr^{6+} simply, the glasses containing Cr^{6+} ions should appear to be the formation of Cr^{4+} ions by the heat treatment. However, this phenomenon has not been reported in any glasses. This result leads to the conclusion that the structural change of glass during crystallization plays an important role for the formation of Cr^{4+} ions.

Nath and Douglas¹⁴⁾ discussed the $\text{Cr}^{6+}/\text{Cr}^{3+}$ equilibrium in $\text{R}_2\text{O}-\text{SiO}_2$ system glasses and concluded that $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio increases with increasing the amount of R_2O . This means that the amount of Cr^{6+} decreases with decreasing R_2O content in glass. In the present case, it was found that the Cr^{4+} ions can be formed during crystallization, but not by the simple thermal reduction. The structural change of glass during crystallization should be considered based on the above results and discussion: (1). Cr^{4+} ions occupy tetrahedral sites, (2). Cr^{4+} ions exist in the residual glassy phase, (3). Cr^{6+} ions

occupy tetrahedral sites.

In the crystallization process, $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ crystal precipitates at first, remaining high SiO_2 containing glassy phase, and then a slight amount of $\text{Li}_2\text{O}\cdot \text{SiO}_2$ and $\alpha\text{-SiO}_2$ crystals begin to precipitate by further heat treatment at higher temperature for longer time. During crystallization, the amount of Li_2O in glassy phase decreases by the formation of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ crystal. According to Nath and Douglas' result, the Cr^{6+} ions should convert to the ions of lower valence state and the amount of Cr^{6+} ions decrease in residual glassy phase, and the Cr^{4+} ions begin to form simultaneously (Fig. 6). Therefore, it is reasonable to consider that Cr^{6+} ions may convert to Cr^{4+} in this process. The next reaction may be suggested:



This equation indicates that the Cr^{6+} ions (chromate ion $[\text{CrO}_4]^{2-}$)¹⁵⁾ exist in glass at first, then Li^+ ions are spent to form $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ crystal, resulted in the decrease in the amount of Li_2O in the residual glassy phase. The decreasing amount of Li_2O corresponds to the decrease in non-bridging oxygen ion and hence the Cr^{6+} ions should be reduced to Cr^{4+} ions. Therefore the significant factor is the behavior of Li^+ ions in this process. Since the tetrahedrally coordinated Cr^{4+} ions $[\text{CrO}_4]$ formed by the above equation are equivalent to $[\text{SiO}_4]$, $[\text{CrO}_4]$ substitutes $[\text{SiO}_4]$ sites in the residual high SiO_2 glassy phase. Consequently, it is considered that the Cr^{4+} ions can be formed by the reduction of tetrahedrally coordinated Cr^{6+} ions (chromate ions $[\text{CrO}_4]^{2-}$) associated with the considerable structural change during crystallization.

3.4 Ligand field analysis of Cr^{4+} ions

The ligand field strength of tetrahedrally coordinated Cr^{4+} ions was analyzed by multi-peak fitting method with a Voigtian distribution.⁶⁾ Figure 7 shows the analytical results in VIS and NIR regions. Assuming that three absorption peaks in VIS and NIR region would be ascribed to ${}^3\text{A}_2 \rightarrow {}^3\text{T}_1$ and ${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$, respectively, the ligand field parameters can be estimated: $10\text{Dq} = 10,610 \text{ cm}^{-1}$, $B = 690 \text{ cm}^{-1}$ and $\text{Dq}/B = 1.54$. This Dq/B is just below the crossing point of ${}^3\text{T}_2$ and ${}^1\text{E}$ levels ($\text{Dq}/B = 1.6$, $\text{Dq}/B > 1.6$, "Strong field" case).¹³⁾ The result is

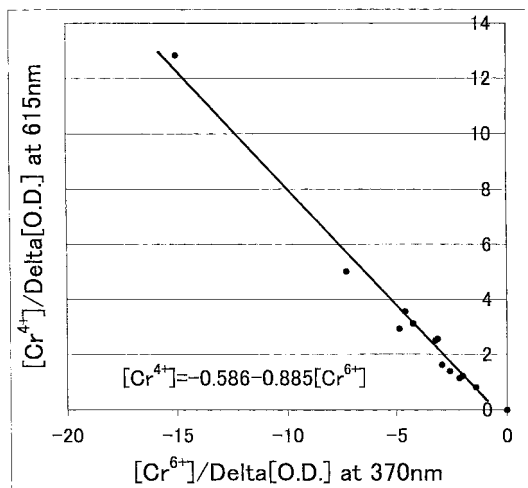


Fig. 6. Relationship between Cr^{6+} absorption (370 nm) and Cr^{4+} absorption (615 nm) in glass-ceramics. $\Delta[\text{O.D. (cm}^{-1}\text{)}] = [\text{O.D. (cm}^{-1}\text{)}]_{\text{glass-ceramics}} - [\text{O.D. (cm}^{-1}\text{)}]_{\text{glass}}$.

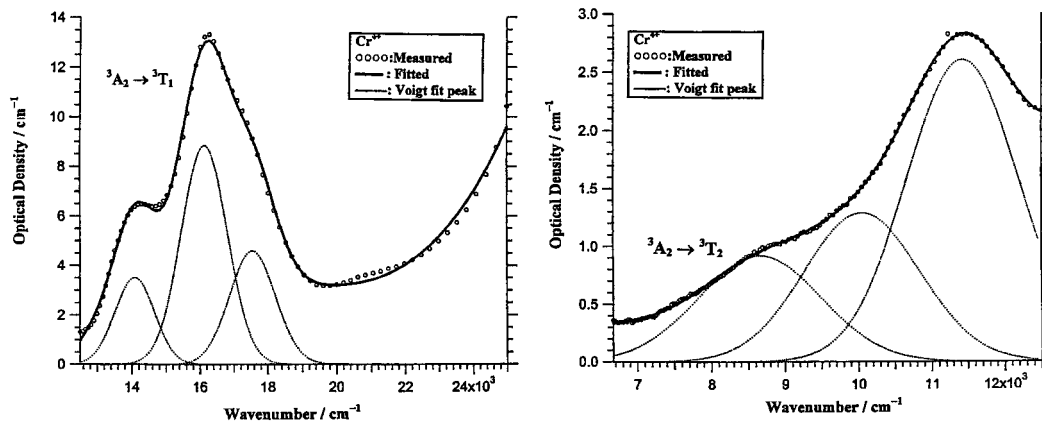


Fig. 7. Multi-peak fitting for absorption spectra of Cr^{4+} ions in glass-ceramics with a Voigtian distribution. Glass-ceramics: Sample B (melted in air, $500^\circ\text{C}-15 \text{ h}$ and $700^\circ\text{C}-5 \text{ h}$).

Table 1. Multi-Peak Fitting for Absorption Spectra of Cr⁴⁺ Ions in Glass-Ceramics with a Voigtian Distribution

Transition	Energy Center (cm ⁻¹)	Band width (cm ⁻¹)	Band Area (cm ⁻¹) ²	Gravity Center (cm ⁻¹)
³ A ₂ → ³ T ₂	8,658	1,175	4,666	10,610 (=10Dq)
	10,050	1,120	7,246	
	11,429	1,082	16,117	
³ A ₂ → ³ T ₁	14,085	810	19,994	16,150
	16,129	958	68,329	
	17,544	952	38,318	

summarized in **Table 1**. The ligand field of Cr⁴⁺ ions in Li₂O–SiO₂ system transparent glass-ceramics is little stronger than that in aluminosilicate glass (10Dq = 10,450 cm⁻¹, B = 870 cm⁻¹ and Dq/B = 1.20).⁶⁾

4. Conclusion

The formation mechanism, absorption and emission spectra of Cr⁴⁺ ions containing Li₂O–SiO₂ system transparent glass-ceramics were investigated. The main crystalline phase was Li₂O·2SiO₂, and their percent crystallinity and crystal size were 67–72 and 20–33 nm, respectively.

The significant change in color and absorption spectra was observed upon crystallization, and the characteristic emission of Cr⁴⁺ ions in tetrahedral sites was identified in the near infrared regions, 1000–1600 nm. It is clarified that the tetrahedrally coordinated Cr⁴⁺ ions were formed and exist in the residual high SiO₂ glassy phase in this transparent glass-ceramics. The ligand field parameters of Cr⁴⁺ were analyzed and they are estimated to be: 10Dq = 10,610 cm⁻¹, B = 690 cm⁻¹ and Dq/B = 1.54. This Dq/B value is just below the crossing point of ³T₂ and ¹E levels (Dq/B = 1.6).

It is considered that the Cr⁴⁺ ions can be formed by the reduction of Cr⁶⁺ ions (chromate ion [CrO₄]²⁻) associated with decreasing the basicity of residual glassy phase during crystallization. In this process the behavior of Li⁺ ions plays a significant role. The [CrO₄] formed is equivalent to [SiO₄] and substitutes [SiO₄] sites in the residual high SiO₂ glassy

phase.

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