Optical Property of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ Glass-Ceramic Crystallized under High Pressure

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高圧結晶化を行った $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ 系結晶化ガラスの光学特性

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The optical property of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramic, with a near-zero thermal expansion coefficient, crystallized under high pressure has been studied. A hydrostatic pressure of 196 MPa was applied by a hot isostatic pressing (HIP) technique during the nucleation process and the crystal growth process. The temperature coefficient of the optical path length, $1/l \cdot dS/dT$, decreased by $0.6 \times 10^{-6} \text{ K}^{-1}$, because the temperature coefficient of the refractive index, dn/dT , was decreased by the HIP treatment. The decrease in dn/dT was ascribed to the suppression of the temperature coefficient of the molar polarizability, ϕ , of the glass-ceramic crystallized by the HIP treatment. It was concluded that the suppression of ϕ occurs in the crystalline phase during the HIP treatment, based on the fact that the reduced $1/l \cdot dS/dT$ was maintained even after the relaxation of the densified structure in the glass phase upon thermal annealing. The decrease in the number of lattice defects in the crystalline phase was hypothesized to be a cause of the reduced ϕ .

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1. Introduction

$\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS) glass-ceramics with a near-zero thermal expansion coefficient exhibit excellent dimensional stability and thermal shock resistance.^{1,2)} They are widely used in stove cooktops, cookware, woodstove windows, and fire doors. LAS glass-ceramics are produced through the precipitation of nanometer-size crystallites ($< 50 \text{ nm}$) of β -quartz solid solution by appropriate heat treatment to the mother glasses. The near-zero thermal expansion is realized by tailoring the composition and amounts of negative-expansion β -quartz solid solution and positive-expansion residual glass. The crystallinity, chemical composition and the size of the crystallite can be controlled by adjusting the heat-treatment conditions. The thermal expansion coefficient and mechanical properties of the LAS glass-ceramics are mainly controlled by those of the crystalline phase. Since the LAS glass-ceramics possess good transparency and chemical durability as well as dimensional thermal stability, they are also expected to be applied to optical devices.

For the glasses used in optical devices, thermal stability of the optical path length is one of the most important properties. The temperature coefficient of optical path length, $1/l \cdot dS/dT$, is given by

$$\frac{1}{l} \cdot \frac{dS}{dT} = \frac{dn}{dT} + n\alpha, \quad (1)$$

where n is the refractive index, dn/dT the temperature coefficient of the refractive index and α the linear thermal

expansion coefficient. Therefore, in addition to the decrease of α , the reduction of dn/dT is of great importance for realizing good thermal stability of the optical path length. However, in general, it is very difficult to control both α and dn/dT independently by controlling the glass composition and/or heat-treatment conditions. Therefore, in order to control dn/dT independently of α , we investigated the effect of external fields on the optical properties of an LAS glass-ceramic. In this report, we focus on the effect of pressure during the crystallization.

There are many studies about the effect of applied pressure on nucleation or crystal growth, and the corresponding glass-ceramic properties. For example, Eppler et al.³⁾ studied the effect of pressure on the crystallization of an LAS glass, and reported that the crystallinity increased on applying higher pressure. Blinov⁴⁾ reported that high-density crystallites, such as α -eucryptite and α -spodumene, were precipitated during the crystallization of LAS glasses under a pressure of 6 GPa. Fritz et al.⁵⁾ reported that Young's modulus and the bulk modulus of a commercial LAS glass-ceramic decreased with increasing pressure at ambient temperature. Munoz⁶⁾ studied the equilibrium phase relation in the LAS system under high pressure, and reported that the equilibrium phase was changed to a crystalline phase having higher density with increasing pressure and decreasing crystal growth temperature. These results suggest the possibility of controlling the thermal and optical properties of LAS glass-ceramics by applying pressure, although the optical properties were not directly investigated

Table 1. Temperature and Pressure Conditions for Crystallization of Glass-Ceramics

Sample	Nucleation temperature / K	Crystal growth temperature / K	Pressure / MPa
1	1053	1123	0.1
2	1053	1163	0.1
3	1053	1193	0.1
4	1053	1123	196
5	1053	1163	196
6	1053	1193	196

in those studies. In this study, we report on the effect of the pressure applied during crystallization on the optical properties of an LAS glass-ceramic. The change in $1/l \cdot dS/dT$ on applying pressure is discussed from the viewpoint of the molar polarizability.

2. Experimental procedure

The chemical composition of the mother glass of the glass-ceramic used in this study was 66SiO₂, 23Al₂O₃, 4Li₂O, 2TiO₂, 2.5ZrO₂, 1.5P₂O₅, 1Na₂O, and 0.5K₂O mass percent. Small amounts of TiO₂, ZrO₂, and P₂O₅ were added to the glass as nucleating agents. Glasses were formed by melting the appropriate batch materials in a platinum crucible in an electric furnace with air atmosphere. After 16 h at 1853 K, the melts were poured onto a carbon plate and quenched to 973 K, which is below the glass transition temperature (983 K), and held at this temperature for 1 h. Since the minimum nucleation time for this glass is approximately 0.5 h at 1063 K, no nucleation should occur during the quenching. The temperature and pressure conditions for crystallization are given in **Table 1** with their sample numbers. A glass block of 40 mm × 30 mm × 8 mm was heated to 1053 K and maintained at that temperature for 3 h for nucleation. Then the temperature was increased to 1123 K and held there for 1 h for crystal growth. The block was cooled to room temperature after crystal growth. A hot isostatic pressing (HIP) technique was used to apply pressure, because it is the most isotropic pressing method and enables the preparation of larger samples than do other methods such as Bridgman pressing⁵⁾ and girdle pressing.⁷⁾ These heat-treatment processes were performed under atmospheric pressure (0.1 MPa) or 196 MPa. An HIP apparatus (KOBELCO, O₂-Dr.HIP) was used to apply pressurized argon gas.

Powder X-ray diffraction (XRD) patterns were recorded at room temperature in the range of 2θ from 18° to 60° with steps of 0.01° and a scan speed of 1°/min (RIGAKU, RAD-C) using Cu K α radiation. The 2θ angle was calibrated from the Si (111) peak position, within an error of $\pm 0.02^\circ$. The integrated XRD intensity of the (101) peak of β -quartz solid solution, excluding the background, was evaluated in the range of 2θ from 23° to 28° with steps of 0.01° and a scan speed of 0.02°/min. The statistic error of this measurement was within $\pm 1\%$. The lattice constant of the crystal was calculated using the positions of the (100), (101), (112), and (211) peaks of β -quartz solid solution, by the least-squares method within an error of $\pm 4 \times 10^{-4}$ nm.

Density was measured by the Archimedes method with distilled water. The typical error for this measurement was $\pm 3 \times 10^{-4}$ g/cm³. The refractive index was measured at 223, 298, and 353 K by the minimum-deviation method using a spectrometer (Gaertner, L-124) equipped with a mercury lamp as a light source. The details of the measurement are described elsewhere.⁸⁾ The measurement error did not exceed $\pm 4 \times 10^{-5}$. The dn/dT was calculated from the refractive indices at 353 and 223 K. The linear thermal expansion coefficient between 233 K and 373 K was measured with a push-rod dilatometer

Fig. 1. Photograph of LAS glass-ceramic samples. Left is the sample crystallized under atmospheric pressure, and right is the sample crystallized under 196 MPa. Thicknesses of both samples are 1.5 mm. **Fig. 2.** Absorption spectra of glass-ceramic samples 1 and 4.**Table 2.** Physical and Optical Properties of Glass-Ceramics

Sample	Density / g cm ⁻³	α / 10 ⁻⁶ K ⁻¹	dn/dT / 10 ⁻⁶ K ⁻¹	$1/l \cdot dS/dT$ / 10 ⁻⁶ K ⁻¹
1	2.5140	-0.7	13.7	12.6
2	2.5266	-0.7	13.9	12.8
3	2.5365	-0.5	13.5	12.7
4	2.5323	-0.6	13.1	12.2
5	2.5441	-0.5	12.8	12.0
6	2.5520	-0.3	12.6	12.1

(MAC SCIENCE Co., TD5030S) within an error of $\pm 0.05 \times 10^{-6}$ K⁻¹.

3. Results and discussion

3.1 Change of optical properties upon HIP crystallization

The appearance of the samples crystallized under atmospheric pressure and 196 MPa is shown in **Fig. 1**. The optical attenuation spectra of both samples are shown in **Fig. 2**. There was no significant difference in the optical attenuation of the two samples. They showed good transparency in visible and near-infrared regions, which is suitable for application to optical devices.

The refractive indices, dn/dT , and α of the glass-ceramics are listed in **Table 2**. The dn/dT and the product of the refractive index and the thermal expansion coefficient, $n\alpha$, are plotted against the crystal growth temperature in **Fig. 3**. The dn/dT was decreased by applying pressure. However, $n\alpha$ slightly increased upon applying pressure and with increasing crystal growth temperature. **Figure 4** shows $1/l \cdot dS/dT$, which was calculated from dn/dT and $n\alpha$ using Eq. (1). The decrease in dn/dT and the increase in $n\alpha$ against temperature canceled each other out, therefore, $1/l \cdot dS/dT$ was almost constant

Fig. 3. Temperature coefficients of refractive index and products of $n\alpha$ against the crystal growth temperature. Closed and open circles represent the coefficients of the samples prepared under 0.1 and 196 MPa, respectively.

Fig. 4. Temperature coefficients of the optical path length against crystal growth temperature. Closed and open circles represent the coefficients of the samples prepared under 0.1 and 196 MPa, respectively.

against temperature. However, it was found that $1/l \cdot dS/dT$ of the glass-ceramic crystallized under high pressure was smaller than that of the one crystallized at atmospheric pressure. This is due to the fact that the decrease in dn/dT is greater than the increase in $n\alpha$ in HIP crystallization.

Figure 5 shows the XRD patterns of samples 1 and 4. All peaks observed in the XRD patterns were assigned to the peaks of the β -quartz solid solution. Although the integrated intensity from 23° to 28° in 2θ increased by 2% on applying pressure, it is not considered to be a significant change, because the statistic error of this measurement is $\pm 1\%$. Therefore, the crystallinity of the glass-ceramic, which is represented by the integrated intensity, was considered to be constant regardless of the HIP treatment. On the other hand, the lattice constant increased with increasing pressure and crystal growth temperature. However, since this tendency of the lattice constant is different from that of $1/l \cdot dS/dT$, the lattice constant

Fig. 5. XRD patterns of glass-ceramic samples 1 and 4. All peaks are assigned to β -quartz solid solution. Inset shows the (101) peaks in detail.

Fig. 6. Temperature coefficients of molar polarizability against the crystal growth temperature. Closed and open circles represent the coefficients of the samples prepared under 0.1 and 196 MPa, respectively.

is apparently not correlated with $1/l \cdot dS/dT$.

3.2 Effect of molar polarizability on optical properties

The cause of the decrease in $1/l \cdot dS/dT$ upon pressurized crystallization was considered by applying the Lorentz-Lorenz equation (2) and its differential equation (3),⁹⁾

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi P \frac{\rho}{M} \quad (2)$$

$$\frac{dn}{dT} = \frac{(n^2 - 1)(n^2 + 2)}{6n} (\phi - 3\alpha), \quad (3)$$

where ρ , P , M and ϕ are the density (g/cm^3), the molar polarizability (cm^3/mol), the molar weight and the temperature coefficient of the molar polarizability, respectively. The dn/dT depends on both ϕ and α , as shown in Eq. (3), thus, from the relation in Eq. (1), it should be noted that $1/l \cdot dS/dT$ also depends on both ϕ and α . The change of α against the crystal growth temperature and applied pressure was very small, as shown in Table 2. On the other hand, ϕ clearly decreased on applying pressure, although it showed no change against the crystal growth temperature, as shown in Fig. 6. This tendency is the same as that of the change of $1/l \cdot dS/dT$. Therefore, it is strongly suggested that the decrease in $1/l \cdot dS/dT$ is governed

Table 3. Physical and Optical Properties of Glass-Ceramics before and after Annealing

Sample	Density / g/cm ³		1/l·dS/dT / 10 ⁻⁶ K ⁻¹		Lattice constant, a / nm	
	before	after	before	after	before	after
4	2.5323	2.5269	12.2	12.0	0.5164	0.5164
5	2.5441	2.5385	12.0	12.0		
6	2.5520	2.5468	12.1	12.1	0.5151	0.5154

by the value of ϕ .

In order to examine which of the glass and crystalline phases contributes to the change in $1/l \cdot dS/dT$, the density and $1/l \cdot dS/dT$ were measured for the samples annealed at 1053 K for 3 h. The density decreased upon annealing, as shown in **Table 3**, reaching approximately 30% of the total density increase due to the HIP treatment. This density decrease was considered to be due to the structural relaxation of the glass phase, because no change was detected by XRD in the HIP-crystallized specimen after annealing. In spite of a considerable density reduction in the glass phase, however, no change was observed in $1/l \cdot dS/dT$ before and after annealing, as shown in the table. Therefore, it is evident that the cause of the decrease in $1/l \cdot dS/dT$, which was achieved by HIP treatment, is not in the glass phase but in the crystalline phase.

The grain size of the crystals in this glass-ceramic is so small that it is very difficult to investigate the nature of the crystals in the HIP-crystallized specimen in comparison with the specimen crystallized under ambient pressure. In general, the nature of crystals varies with their lattice constants and lattice defects. In this case, however, the lattice constant is not correlated with $1/l \cdot dS/dT$ of the glass-ceramic, as previously mentioned. As for the lattice defects, however, it is reported that the number of lattice defects in a quartz single crystal is decreased by pressurized synthesis.^{10),11)} Therefore, it can be estimated that the number of defects in the crystalline phase of the HIP-treated specimen is less than that in the specimen crystallized under ambient pressure. The defects in the crystals seem to act like nonbridging oxygen ion in glasses. The ϕ factor for the nonbridging oxygen ion is reported to be much larger than that for the bridging oxygen ion.¹²⁾ Therefore, the decrease in the number of lattice defects in the crystalline phase is considered to be a possible explanation for the

reduced $1/l \cdot dS/dT$ in the HIP-crystallized glass-ceramic.

4. Conclusion

The effect of pressure on the optical properties of LAS glass has been studied. It was found that the application of pressure during crystallization led to a decrease in $1/l \cdot dS/dT$ of LAS glass-ceramic. The decrease in $1/l \cdot dS/dT$ was concluded to be due to the decrease in the temperature coefficient of molar polarizability, ϕ , accompanied by the decrease of dn/dT . It was confirmed that the decrease of ϕ occurs in the crystalline phase from the result that the specimen relaxed by annealing maintained the reduced $1/l \cdot dS/dT$. It is suggested that $1/l \cdot dS/dT$ is correlated with the number of lattice defects in the precipitated crystals in the glass-ceramic.

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