High performance transparent glass-ceramics for optical components

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Glass-ceramics based on nepheline crystal (Na₃[Na,K][Al₃SiO₁₀]) system was modified to satisfy the thermal and optical properties required for a band-pass filter (BPF) in telecommunication systems using optical fibers. The suitable coefficient of thermal expansion was achieved in a glass-ceramic containing more potassium oxide than the conventional nepheline glass-ceramics, in nepheline–kalsilite (K[AlSiO₄]) binary system. An addition of the moderate amount of nucleating agents is a key parameter to obtain high transparency of the glass-ceramics. The optimized nepheline–kalsilite glass-ceramic showed higher mechanical strength as compared with the monolithic glassy material used in the same application.

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Table 1. Glass composition and properties of the substrate for BPF described in the Japanese patent 3399883

|                  | Example 1 | Example 2 |
|------------------|-----------|-----------|
| SiO₂             | 41.39     | 39.39     |
| B₂O₃             |           | 2.00      |
| TiO₂             | 30.00     | 30.00     |
| BaO              | 3.50      | 3.50      |
| Li₂O             | 2.00      | 2.00      |
| Na₂O             | 14.10     | 14.10     |
| K₂O              | 9.00      | 9.00      |
| Sb₂O₃            | 0.01      | 0.01      |
| CTE (×10⁻²/°C)(−20–70°C) | 110  | 100       |
| Young’s modulus (GPa) | 85    | 87        |

*Glass composition is in wt %.

1. Introduction

In telecommunication systems using optical fibers, wavelength division multiple (WDM) technology is widely used, where a band-pass filter (BPF) comprising many dielectric layers is an essential component. The BPF is designed to transmit a sharp signal of certain wavelength so that many signals can be transmitted in the glass fiber simultaneously. The center wavelength of the signal is defined by the thickness and refractive index of the dielectric layers. Changes in environmental conditions, particularly temperature, can shift this wavelength and cause errors in the operation of the telecommunication device.

To ensure reliable behavior, the coefficient of thermal expansion (CTE) of the glass substrate for the BPF is very important. A substrate with a high CTE applies stress to the dielectric layers of the BPF proportional to the temperature changes, which can compensate the wavelength shift due to the change in the refractive index of the dielectric layers with temperatures.1,2) Preferred range of CTE at room temperature is identified to be 100–120 × 10⁻⁷/°C.2) From our knowledge, the most popular glass substrate in this application is WMS-02 provided by OHARA. Although the detail chemical composition of WMS-02 is not disclosed, this glass comprises SiO₂, TiO₂, R₂O₅ (R₂O₅: Alkali oxides) as main components from the patent.1) Some of the data described in the patent is listed in Table 1.

Although these kinds of glasses are widely used in the industry, glasses are generally brittle, and hence they tend to break during fabrication of the BPF due to high stresses occurring in thick layers. Also, a higher Young’s modulus is preferable to avoid warpage of the substrate. These issues are more problematic when the bandwidth for filter transmission becomes narrower, because more dielectric layers are needed on the substrate.

Glass-ceramics are generally advantageous for better mechanical properties as compared with monolithic glassy materials.3,5) Since some of the glass-ceramics have high transparency,6,7) it seems to be reasonable to apply glass-ceramics into BPF applications. The glass-ceramic precipitating nepheline (Na₃-[Na,K][Al₃SiO₁₀]) known as transparent materials with high CTE,3–10) Nepheline group minerals include two major minerals, nepheline and kalsilite (K[AlSiO₄]), and these form solid-solutions.11)

Some of the chemical composition and the CTE data of nepheline glass-ceramics in the early works by Duke3–5) are listed in Table 2. Titanium oxide is used as a nucleating agent. The CTE increases after crystallization, meaning that the CTE of nepheline crystal is higher than that of the parent glass. However, it is not clear whether this CTE value is suitable for the BPF application because the temperature range of the measurement is 0–300°C in their study. Also, the transparency data is not available in these literatures. Besides, the chemical compositions of their study focused on the Na-rich region in the NaAlSiO₄–KAlSiO₄ binary system, so that the properties of the K-rich glass-ceramics are not known. It is also unclear whether the mechanical strength of these glass-ceramics has an advantage against monolithic glassy material in the BPF application.

Therefore, it is necessary to investigate the relation between the chemical compositions and the properties of the glass-ceramics to satisfy the joint requirements of appropriate CTE, high trans-
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cate glass-ceramics,\(^{21}\) the glass added with a small amount of ZrO\(_2\) to this composition was also evaluated to see the effect of ZrO\(_2\). The contents of Na\(_2\)O and K\(_2\)O in parent glasses were varied to see the change of the crystalline phases and the CTEs of the glass-ceramics. Concentrations of nucleating agents (TiO\(_2\) and ZrO\(_2\)) were also varied to see their effect on the transparencies of the glass-ceramics. MgO was added to some glasses because this oxide is known to increase Young’s modulus of glass.\(^{13}\) During the investigation, the microstructures in the glass-ceramics were observed and related to the transparencies of the glass-ceramics.

### 2.2 Preparation of glass-ceramic samples

Parent glasses were prepared by lab-scale melting by a conventional method. Reagent grade SiO\(_2\), Al\(_2\)O\(_3\), Na\(_2\)CO\(_3\), Na\(_2\)SO\(_4\), K\(_2\)CO\(_3\), BaCO\(_3\), MgO, TiO\(_2\), and ZrO\(_2\) were used as starting materials to obtain 600 g of glass melt. Approximately 0.4–0.5 wt% of SO\(_3\) was added to the glass batch as a refining agent. Using a platinum crucible, the glass batches were melted at 1650°C for 5–6 h in air. The glass melt was homogenized using a platinum stirrer and poured onto a carbon plate to form slab samples. These were cut into pieces and heat-treated for crystallization according to the heat schedule shown in Fig. 1. The obtained glass-ceramics were cut and polished into suitable samples for characterization.

### 2.3 Evaluation of optical properties

The optical transmission of the glass-ceramics was measured for wavelengths between 300 nm and 1600 nm using a U-3500 (HITACHI) spectrometer. The internal transmittance was calculated by subtracting the absorption spectra for two samples of different thicknesses. The transmission loss of glass-ceramics is generally caused by light scattering. Since the transmittance of samples in the near-IR region is relatively high, it is sometimes difficult to compare the transmittance between samples. Therefore, an index to evaluate light scattering is introduced in this study.

Light scattering of glass-ceramics is described by Rayleigh scattering theory if the crystal size is much smaller than the wavelength.\(^{6}\)

The scattering factor \(F\) is described by the following equations:

\[
I/I_0 = \exp(-Ft)
\]

\[
F = \left(\frac{24\pi^2n_i^4}{\lambda^4}V\cdot NV\cdot \left[(n_2^2 - n_1^2)/(n_2^2 + 2n_i^2)\right]^2\right)
\]

where, \(t\) is the sample thickness, \(n_i\) is the refractive index of the glass phase, \(n_2\) is the refractive index of the crystal phase, \(V\) is the particle volume, \(N\) is the numerical density of particles, and \(\lambda\) is the wavelength.

### 2.4 Design of glass compositions

For easy understanding of chemical compositions of glass-ceramics, we classified the oxides components used in our study into two categories. One is “crystal components”, which create nepheline-kalsilite crystals. This includes SiO\(_2\), Al\(_2\)O\(_3\), Na\(_2\)O, and K\(_2\)O. The other is “other components”, which include nucleating agents. In Tables 3 and 4, the glass compositions investigated in this study are described in this manner, with the sum total of “crystal components” equal to 100%. Actual glass samples were prepared by converting all compositions into concentrations in wt% with sum total of 100%.

As mentioned in section 1, since it is not clear yet if the disclosed compositions of nepheline glass-ceramics are applicable to the BPF, we started our study to know the properties of the typical glass composition in the literature. The glass composition D, without As\(_2\)O\(_3\) in the reference 8 (see Table 2), was selected because detail data for a crystallization process is available. Since ZrO\(_2\) is another well known nucleating agent in sili

| Table 3. Chemical compositions and properties of glass-ceramics containing different amount of K\(_2\)O and Na\(_2\)O |
|---------------------------------------------------------------|
| **Composition of crystal components (mol%)**                  |
| SiO\(_2\) | 55    | 55    | 55    |
| Al\(_2\)O\(_3\) | 24    | 24    | 24    |
| Na\(_2\)O | 15.8  | 15.8  | 15.8  |
| K\(_2\)O | 5.2   | 5.2   | 10.5  |
| total       | 100   | 100   | 100   |
| **Composition of other components (mol%)**                    |
| MgO         | 0     | 0     | 0     |
| TiO\(_2\)   | 7.3   | 7.3   | 7.3   |
| ZrO\(_2\)   | 0     | 1     | 1     |
| **Properties of glass-ceramics**                              |
| Density (g/cm\(^3\)) | 2.64  | 2.69  | 2.66  | 2.64 |
| CTE (×10\(^{-6}\)/°C) | 105   | 105   | 108   | 112  |
| Young’s Modulus (GPa) | 85    | 88    | 89    | 88   |


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the wavelength of the light. Combining these two equations, we obtain the following equation:

\[ -\ln\left(\frac{I}{I_0}\right) = C \cdot t \cdot \lambda^{-4} \]  

(3)

where, \( C \) represents the scattering constant. Therefore, if the light loss is due to scattering, a straight line should be obtained by plotting the logarithm of the internal transmittance against \( \lambda^{-4} \) according to Eq. (3). We use the constant \( C \) as the index of transmission capability of glass-ceramics in this study.

2.4 Physical characterization

The CTE was obtained using dilatometry between -30 and 70°C with a TMA8140 (Rigaku) dilatometer. The density was measured using the Archimedes method. The Young’s modulus was measured using an ultrasonic pulse method with a USN-50 (Japan Kurautkramer) device. The flexural strength was measured using a four-point bending method with a UTA-5KN instrument (Orientech) at room temperature. The size of flexure bars was 4 mm \( \times \) 3 mm \( \times \) 30 mm, and surfaces for rupture were polished using #320 SiC grit.

The crystalline phases developed on reheating the parent glasses were identified using powder X-ray diffraction using a Rint2500 (Rigaku) diffractometer. The SEM analysis was performed using a S-800 (HITACHI) to observe the microstructures of the glass-ceramics after etching the samples with 5% HF for 5–10 min.

3. Results

3.1 Crystalline phases and CTEs of the glass-ceramics

The glass compositions and the properties of the glass-ceramics investigated in this section are summarized in Table 3. The reference samples (Ref), mentioned in the section 2.1 is also shown in the table. For samples A–C, only the K\(_2\)O/Na\(_2\)O ratio in the parent glass was varied to see how those affect to the crystalline phases precipitated in the glass and change the CTEs of the glass-ceramics.

Table 4. Chemical compositions and properties of glass-ceramics containing different amount of nucleating agents

| D  | E  | F  | G  | H  | I  | J  |
|----|----|----|----|----|----|----|
| Composition of crystal components (mol \%) | SiO\(_2\) | 54 | Al\(_2\)O\(_3\) | 25 | Na\(_2\)O | 7 | K\(_2\)O | 14 |
| Composition of other components (mol \%) | MgO | 3 | TiO\(_2\) | 6.8 | ZrO\(_2\) | 1 |
| Properties of glass-ceramics | Density (g/cm\(^3\)) | 2.68 | 2.68 | 2.69 | 2.70 | 2.65 | 2.68 | 2.70 |
| CTE (\(\times 10^{-7}/\)°C) | 112 | 110 | 111 | 108 | 112 | 110 | 109 |
| Young’s Modulus (GPa) | 92 | 93 | 93 | 93 | 93 | 92 | 93 |
| Light Scattering constant (10\(^5\)m\(^3\)) | 1.51 | 0.80 | 0.85 | 1.09 | 0.47 | 0.65 | 1.99 |

Fig. 1. Heat-treatment schedule for crystallization.

Fig. 2. XRD patterns of glass-ceramics sample A, B, and C.
the JCPDS 12-0198. On the other hand, for the sample C (K$_2$O/Na$_2$O = 0.75/0.25 in the parent glass), the main peak was observed at 2$\theta = 28.94^\circ$ ($d = 3.085\ \text{Å}$), and the three peaks associated to $d = 4.015\ \text{Å}$, $d = 3.350\ \text{Å}$, and $d = 2.954\ \text{Å}$ in JCPDS 12-0198 almost disappeared. Thus, it was observed that the crystalline phases changed depending on the K$_2$O/Na$_2$O ratio in the parent glasses. The CTEs of the glass-ceramics increased from $105 \times 10^{-7}/\circ\ C$ (sample A) to $112 \times 10^{-7}/\circ\ C$ (sample C) as shown in Table 3.

3.2 Effect of nucleating agents on the transparency of the glass-ceramics

The glass compositions and the properties of the glass-ceramics investigated in this section are summarized in Table 4. For samples D-J, only the amount of TiO$_2$ and ZrO$_2$ were varied to see how those affect to the transparencies and the microstructures of the glass-ceramics.

Typical internal transmittance curves (sample E, J, and H) are shown in Fig. 3. When these curves were analyzed according to the procedure described in 2.3, straight lines were obtained as shown in Fig. 4. Therefore, transmittance losses of these glass-ceramics were confirmed to be due to Rayleigh light scattering. The constants $C$ in the Eq. (3) for glass-ceramic are shown in Table 4.

Figure 5 and 6 shows the light scattering constant $C$ as a function of the concentrations of TiO$_2$ and ZrO$_2$, respectively. The light scattering constant $C$ shows a minimum at a TiO$_2$ concentration of 8 mol\% (Fig. 5). On the other hand, the light scattering constant $C$ increased with increase of ZrO$_2$ concentration (Fig. 6).

SEM images of the microstructures of the glass-ceramics containing different amount of TiO$_2$ (sample D, E, and G) and different amount of ZrO$_2$ (sample H and J) are shown in Figs. 7 and 8, respectively. It was observed that the microstructures of the glass-ceramics became finer when more TiO$_2$ or ZrO$_2$ were added into the parent glasses.

3.3 Mechanical strength of the glass-ceramics

Since the highest transparency along with high Young’s modulus over 90 GPa was obtained in the sample H, four-point bending test was performed for this sample. The monolithic glassy material in the same application (WMS-02) was also tested under the same condition as a comparison. The results are shown in Fig. 9. The average strength of the glass-ceramic H was 84 MPa, whereas that of WMS-02 was 63 MPa. Therefore, glass-ceramic materials can be preferable for the application of BPF substrates, particularly when aiming to narrow the band-pass of the filter where higher toughness and Young’s modulus are required when increasing the thickness of the dielectric layers.

4. Discussion

4.1 Crystalline phases, mechanical and thermal properties of the glass-ceramics

As mentioned in the previous section, the average mechanical strength of the glass-ceramic (sample H) was 1.3 times higher than that of the glass material (WMS-02). Since the SEM observation revealed that glass-ceramics are composed of fine-grained crystalline phases, more energy should be required for
the fracture of the sample H as compared with the monolithic glassy material. That is the one of the reason why glass-ceramics are advantageous in terms of mechanical strength.

As shown in the XRD patterns (Fig. 2), the main peak of the crystals shifted to lower angle as the content of K2O increased in the parent glasses. According to the card data, the main peak of nepheline is assigned to the (202) plane with $d = 3.027$ Å (JCPDS 09-0338, $K_2O/Na_2O = 0.375/0.625$) and $d = 3.069$ Å (JCPDS 12-0198, $K_2O/Na_2O = 0.7/0.3$). The cell parameters described in these cards are $a = 10.060$ Å, $c = 8.417$ Å (JCPDS 09-0338, $K_2O/Na_2O = 0.375/0.625$) and $a = 10.237$ Å, $c = 8.508$ Å (JCPDS 12-0198, $K_2O/Na_2O = 0.7/0.3$), respectively. On the other hand, the main peak of kalsilite is assigned to the (102) plane with $d = 3.12$ Å associated with cell parameters of $a = 5.159$ Å, $c = 8.703$ Å (JCPDS 11-0579). Both nepheline and kalsilite have similar tridymite-type open three-dimensional network structure (hexagonal system, space group $P6_3$). However, a parameter of kalsilite is almost half of that of nepheline. Because the open spaces of the framework in nepheline are larger for Na ion, the framework is distorted depending on the K/Na ratio due to their difference of the ionic radius. Therefore it is reasonable that kalsilite, containing only potassium as alkali ion, has lower distortion of the framework and higher symmetry of the structure, hence smaller structural unit cell compared to that of nepheline. In Fig. 10, $d$-values and cell parameters were plotted as a function of the $K_2O$ ratio in the crystal. Note that the cell parameter $a$ of kalsilite is plotted as doubled value of 5.159 Å as mentioned above.

As can be seen in Fig. 10, $d$-value, cell parameter $a$ and $c$ increases when the $K_2O$ ratio of the crystal increases. When the measured $d$-values of the crystals in the glass-ceramics (3.020 Å for the sample A, 3.062 Å for the sample B, and 3.085 Å for the sample C) were referred in this figure, $K_2O$ ratio is estimated to be ~0.3, 0.65, and 0.85, respectively. From these observations,
solid-solutions of nepheline-kalsilite with different K₂O ratio precipitated in glass-ceramics in this study. It should be mentioned that in Fig. 2, it is also observed that the intensities of the three diffraction peaks associated to \( d = 4.015 \text{Å}, d = 3.350 \text{Å}, \) and \( d = 2.954 \text{Å} \) almost disappeared in the sample C. Since these diffraction peaks are absent in pure kalsilite (JCPDS 11-0579), the crystal structure precipitated in the sample C seems to be rather close to kalsilite than nepheline. Since the CTEs of the glass-ceramics sample A–C increased from A to C, it is suggested that CTEs of the glass-ceramics can be controlled by K₂O ratio of the parent glass composition owing to the change of the CTEs of nepheline–kalsilite solid-solutions.

4.2 Effect of nucleating agents on the transparency of the glass-ceramics

In the glass-ceramic materials, a smaller particle size is beneficial for suppressing light scattering and to obtain high transparency. Therefore, one can expect that with the addition of more nucleating agent, more nuclei precipitate on which the main crystals grow, eventually making the crystal size smaller and the glass-ceramics more transparent. In fact, SEM observation did reveal that the microstructure of the glass-ceramics becomes finer as the concentration of TiO₂ increases, as shown in Fig. 7. However, if we see the dependence of the transparency on TiO₂ concentration (sample D, E, F and G), it was found that the light scattering constant \( C \) shows a minimum at a TiO₂ concentration of 8 mol % (Fig. 5). TiO₂ is known to increase the refractive index of the glass, because the Ti ion has a large polarization. The refractive indices of nepheline and kalsilite crystals are 1.526–1.546 and 1.532–1.543 respectively. Since TiO₂ in the parent glass is enriched in the glassy phase after the crystallization, the refractive index of the glass is supposed to be higher than that of the crystals. Therefore, increased light scattering above a TiO₂ concentration of 8 mol % is attributed to the larger difference between the refractive indices of the glass matrix and the crystals. When we see the ZrO₂ concentration dependence on light scattering behavior of the glass-ceramics (sample E, H, I, and J), we find that the light scattering increases as the amount of ZrO₂ increases, even though the crystal size decreases (Figs. 6 and 8). Since the Zr ion also has a large polarization and is known to increase the refractive index of the glass, the light scattering increased for the same reason as in the case of TiO₂ additions. Thus, to obtain glass-ceramics with good transparency, it is important to optimize the amount of nucleating agent considering both crystal size and refractive index matching between the glass matrix and crystals to minimize light scattering. The highest transparency was obtained in a TiO₂ concentration of 8 mol % without addition of ZrO₂ in this study.

5. Conclusions

The chemical composition of nepheline glass-ceramic was designed to satisfy the properties required for the band-pass filter applications in WDM systems. The following conclusions were obtained:

- When the K₂O ratio of the parent glass compositions was high, the solid-solution of nepheline–kalsilite with high ratio of K₂O precipitated in the glass as a main crystalline phase, and the glass-ceramics with high CTE were obtained.
- The glass-ceramics with high transparency was obtained by adding the moderate concentration of TiO₂ (8 mol %) and no ZrO₂ into the parent glass as the nucleating agents.
- The strength of the glass-ceramics with the suitable CTE and transparency was verified to be higher than that of monolithic glassy material in the same application.

References

1) H. Takahashi, *Appl. Opt.*, 34, 667–675 (1995).
2) Japanese Patent 3243474.
3) Japanese Patent 3399883.
4) P. W. McMillan, Glass-ceramics, Academic Press (1979) pp. 162–188.
5) Z. Strnad, Glass-Ceramic Materials, Elsevier (1985) pp. 185–190.
6) G. H. Beall and D. A. Duke, *J. Mater. Sci.*, 4, 340–352 (1969).
7) G. H. Beall, *Rev. Solid State Sci.*, 3, 333–354 (1989).
8) D. A. Duke, J. F. MacDowell and B. R. Karstetter, *J. Am. Ceram. Soc.*, 50, 67–74 (1967).
9) D. A. Duke, J. E. Megles, Jr., J. F. MacDowell and H. F. Bopp, *J. Am. Ceram. Soc.*, 51, 98–102 (1968).
10) Japanese Patent 1483641.
11) W. A. Deer, R. A. Howie and J. Zussman, An introduction to the rock-forming minerals, second edition, Pearson Education Limited (1992) pp. 473–485.
12) Z. Strnad, Glass-Ceramic Materials, Elsevier (1985) pp. 85–101.
13) H. Scholz, “Glass Nature, Structure, and Properties”, Springer-Verlag (1991) p. 224.
14) Appen’s coefficient, “Hajime Garasu Wo Tsukuruhito no Tameni”, Uchidaroukakuho, 92.