UDC：666.266.6

1. Transparency and Mechanical Properties of Glass-Ceramics Including Nepheline-Kalsilite Solid Solution

Motoyuki Hirose*, Tomoyuki Kobayashi* and Kei Maeda*

Nepheline glass-ceramics are known as transparent materials with a high coefficient of thermal expansion (CTE). The Nepheline glass-ceramics have been modified in order to increase mechanical strength and transparency while maintaining the high CTE. By optimizing the composition of solid solutions of Nepheline crystal and the matrix glass and crystallinity, better mechanical properties and transparency have been obtained. It was found that the introduction of Kalsilite improved the transparency of glass-ceramics and the introduction of Celsian was useful for increasing strength with maintaining the high CTE of the glass-ceramics.

1. Introduction

Recently, new applications have appeared for materials with high transparency and high coefficient of thermal expansion (CTE). For example, substrate for band pass filters (BPFs) used for optical telecommunication systems requires materials with such properties. The BPFs consist of more than 100 thin films, whose components are typically SiO_2-Ta_2O_5, on the glass substrate. The center wavelength of light, which transmits the filter, depends on temperature due to change of the refractive index of the films. It is known that this dependence can be compensated by using a substrate with high CTE[1]. Takahashi demonstrated that the suitable CTE of the glass substrate needed for compensating this temperature dependence was $100 \sim 120 \times 10^{-7}$/°C[1]. Besides, the substrate needs to have high Young's modulus and high mechanical strength to avoid warp or failure because of the strong stress generated by the difference of CTE between films and substrate.

Nepheline ($Na_2Al_2Si_2O_8$) glass-ceramics are known to have high transparency and high CTE[2, 3]. **Table 1** shows the composition and properties of typical Nepheline glass-ceramics reported[2]. Scattering constant in this table relates to transparency as mentioned in section 3.1. Since the mechanical properties and the transparency of this glass-ceramic are not as high as the other glass-ceramics for the substrate[4], there might be some limitations for the use of this material in some applications.

It is known that Nepheline crystal can precipitate with other crystals whose compositions are similar to that of Nepheline, such as Kalsilite ($K_2Al_2Si_2O_8$)[5], Celsian ($BaAl_2Si_2O_8$)[6]. But the properties of glass-ceramics containing these three crys-

Table 1　Properties of Typical Nepheline-Kalsilite Glass-Ceramics.

		Sample A
Composition (mol%)	SiO_2	51.2
	Al_2O_3	22.4
	TiO_2	6.8
	Na_2O	14.8
	K_2O	4.8
Density (g/cm^3)		2.64
CTE $_{[-30\sim70°C]}$ (10^{-7}/°C)		105
Young's modulus (GPa)		85
Scattering constant (10^{10}nm^4/mm)		7.15

*Research Center

tals are not well known. The experiments on glass-ceramics containing these crystals were conducted for improving the mechanical properties and transparency of Nepheline glass-ceramics.

2. Experimental

2.1 Preparation of glass-ceramics

The mother glasses whose compositions are shown in **Table 2** and **Table 3** were prepared from reagent grade SiO_2, Al_2O_3, Na_2CO_3, K_2CO_3, $BaCO_3$, TiO_2, ZrO_2, and MgO as the raw materials. Titanium oxide and zirconium oxide were added as nucleating agents. Sulfate (Na_2SO_4) was added to the glass batches as refining agent. The glass batch of 600g was melted in a platinum crucible for 5～6 hours at 1650°C in air using an electrical furnace. The melt was stirred with a platinum stirrer for homogenization and poured onto a carbon plate to form slab sample. The glass sample was heat-treated for crystallization according to the heat schedule shown in **Fig. 1.** The maximum temperature for the heat-treatment was 900°C for 1 hour.

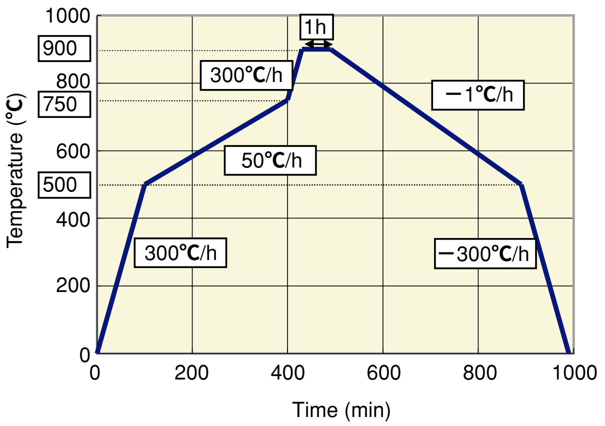

Fig. 1 Heating treatment schedule for crystallization.

2.2 Evaluation of properties and characterizations

Physical properties of glass-ceramics were measured using conventional methods. Density was measured by the Archimedes method. Young's modulus was measured using an ultrasonic pulse method with USN-50 (Japan Kurautkramer). Flexural strength was measured using a four-point bending method with UTA-5KN (Orientech) at room temperature. The size of flexure bars was 4mm×3mm×30mm, and the surface was abraded by #320 SiC grit. CTE was obtained by dilatometer between −30°C～70°C with TMA8140 (Rigaku). Optical absorption was measured for wavelengths between 300 nm to 1600 nm with U-3500 (HITACHI). Internal transmittance eliminating reflection loss was calculated by subtracting absorption spectra measured for two samples with different thickness.

Crystalline phase precipitated on reheating the mother glass was identified using powder X-ray diffraction technique using Rint 2500 (Rigaku). SEM analysis was performed with S-800 (HITACHI) in order to observe the microstructures of glass-ceramics after etching with 5% HF for 5～10 minutes.

3. Results and Discussion

3.1 Effect of potassium

Table 2 shows the compositions and the properties of Nepheline-Kalsilite glass-ceramics. Theoretical crystallinities were calculated by the summation of components of Nepheline-Kalsilite solid solutions These samples have near stoichiometric Nepheline-Kalsilite solid solutions composition with changing only the alkali ratio. Since a small amount of nucleating agents and excess SiO_2 and Al_2O_3 are added, theoretical crystallinity is 77.6% as shown in **Table 2**. **Figure 2** shows the internal transmittance of these glass-ceramics. It was found that the transparency increased with increasing ratio of potassium to sodium. The CTE also increased a little while the Young's modulus changed slightly.

Table 2 Properties of Nepheline-Kalsilite Glass-Ceramics.

		#1	#2	#3
Composition (mol%)	SiO_2	50.6	50.6	50.6
	Al_2O_3	22.2	22.2	22.2
	TiO_2	6.8	6.8	6.8
	ZrO_2	1.0	1.0	1.0
	Na_2O	14.7	9.7	4.9
	K_2O	4.8	9.7	14.6
Theoretical crystallinity (%)		77.6	77.6	77.6
$K_2O/(Na_2O+K_2O)$		0.24	0.50	0.75
Density (g/cm^3)		2.69	2.66	2.64
CTE $_{[-30\sim70℃]}$ (10^{-7}/℃)		105	108	112
Young's modulus (GPa)		88	89	88
Scattering constant ($10^{10}nm^4/mm$)		1.42	0.48	0.29

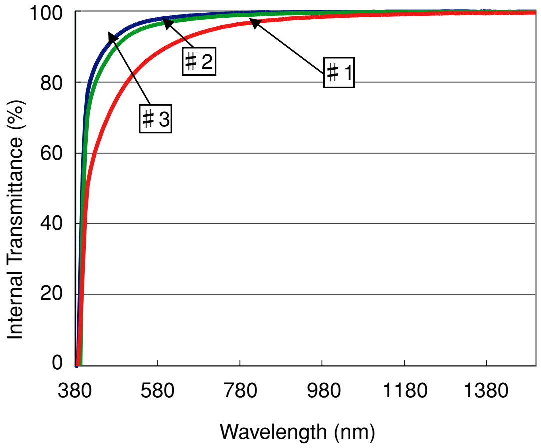

Fig. 2 Internal transmittance of sample #1, #2, #3.

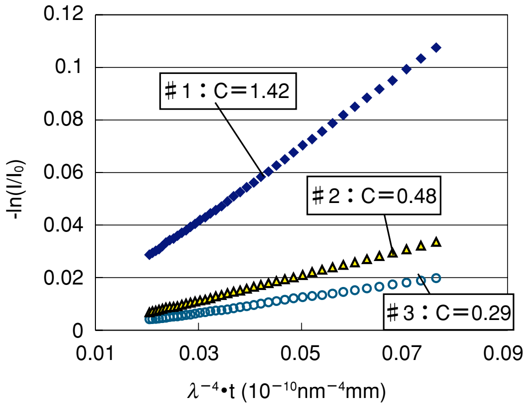

Fig. 3 Internal transmittance vs. λ^{-4}. The slopes of lines (C value) denote scattering constants.

Light scattering in glass-ceramics can be discussed using Rayleigh scattering theory if the particle size is smaller than the wavelength[7]. The scattering factor F is described by the following equation ;

$$I/I_0=\exp(-Ft) \quad (1)$$

$$F=(24\pi^3 n_1^4/\lambda^4)V\cdot NV\cdot\{(n_2^2-n_1^2)/(n_2^2+2n_1^2)\}^2 \quad (2)$$

Where, t is the sample thickness, n_1 is the refractive index of matrix phase, n_2 is the refractive index of particles, V is the particle volume, N is the numerical density of particles and λ is the wavelength of the light. Combining these two equations, the following equation can be obtained ;

$$-\ln(I/I_0)=C\cdot t\cdot\lambda^{-4} \quad (3)$$

Where C represents the scattering constant. Therefore, if the light loss is due to scattering, the straight line should be obtained by plotting the logarithmic internal transmittance and minus fourth power of wavelength according to equation[3]. The results are shown in **Fig. 3**, demonstrating that the transmittance loss is caused by scattering. Moreover, the scattering loss decreased by increasing the ratio of potassium in the glass-ceramics. In order to characterize the reduction of scattering, XRD and SEM analysis were performed for these samples. **Figure 4** shows XRD patterns of these glass-ceramics. It was found that the main peak position shifted to lower angles as we increase ratio of potassium. This is reasonable because the main peak of Kalsilite crystal is located on lower angles than that of Nepheline crystal. Furthermore, it was

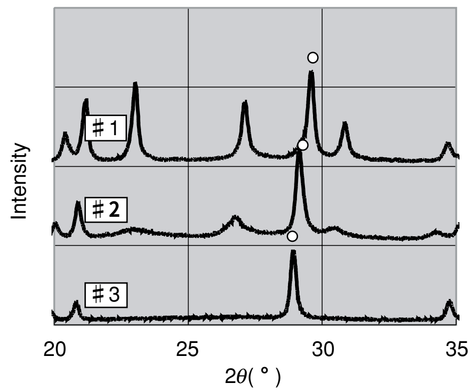

Fig. 4 XRD powder pattern of sample #1, #2, #3. Circles denotes main peak of Nepheline-Kalsilite solid solutions.

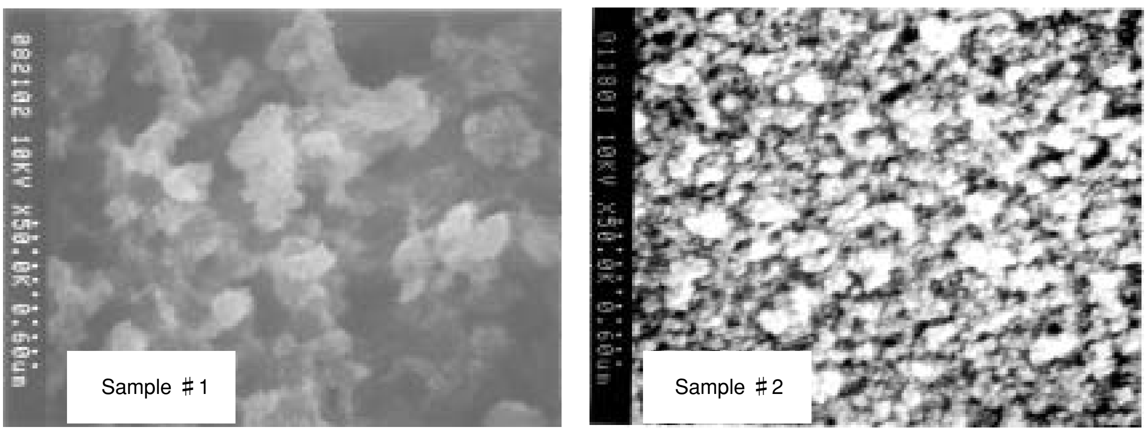

Fig. 5 SEM photograph of microstructures of sample #1 and #2.

found that intensities of the main peaks of them were nearly the same. This suggests that these samples have nearly the same value of crystallinity. **Figure 5** shows microstructures of sample #1 and #2. It was confirmed that the Kalsilite rich glass-ceramics consist of smaller crystals and have homogeneous microstructure. Small crystals have low V in equation[2], and the scattering constant becomes to decrease. As a result, Kalsilite rich glass-ceramics decreased scattering factor, improving the transparency.

3.2 Effect of magnesium and barium

Table 3 shows compositions and properties of Nepheline-Kalsilite glass-ceramics containing magnesium and barium. The crystallinities were calculated by the summation of components of Nepheline-Kalsilite solid solutions and Celsian. Titanium oxide was added as nucleation agents, and a slight amount of SiO_2 and Al_2O_3 were added as residual glass components. Also, a small amount of MgO was added because it is known that MgO increases Young's modulus of glasses as compared to other oxides, such as Na_2O and K_2O[7]. The higher Young's modulus of sample #4, compared to those in **Table 2**, is considered to be due to MgO.

As shown in **Table 3**, the CTE increased with increasing theoretical crystallinity (sample #4 and #5). This is reasonable, because Nepheline- Kalsilite solid solutions have high CTE [135×10^{-7}/℃(20～800℃) : Nepheline-Kalsilite solid solutions with Na_2O : K_2O=59 : 41]. On the other hand, it was found that the CTE did not increase for barium-

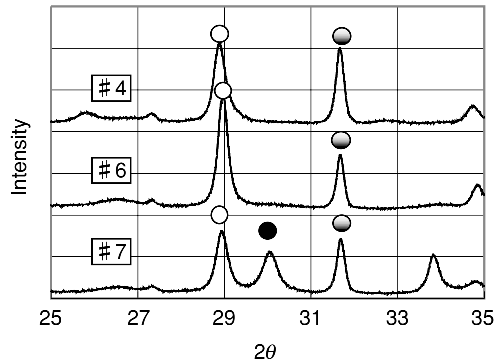

Fig. 6 XRD powder pattern of sample #4, #6 and #7.
○ :Nepheline-Kalsilite solid solution ● :Celsian
◐ : NaCl

containing samples (#6 and #7), even though the theoretical crystallinities of them are also increasing. **Figure 6** shows the result of XRD analysis for these glass-ceramics with adding NaCl as an internal standard. It was found that Celsian precipitated in the sample #7. Therefore, it should be reasonable to consider that the low CTE of the sample #7 is attributed to the precipitation of Celsian having its low CTE [23×10^{-7}/℃(20～100℃)]. On the other hand, the precipitation of Celsian was not observed in the sample #6. And the crystallinity of this glass-ceramics is confirmed to be higher than that of the sample #4 by comparing the relative diffraction intensity of Nepheline-Kalsilite solid solution to NaCl. Besides, it can be observed that the peak position of the solid solution shifts larger angles slightly for the sample #6, as compared with the sample #4. These observations suggest that anoth-

Table 3 Properties of Nepheline-Kalsilite-Celsian Glass-Ceramics (σ denotes standard deviation).

			Sample	#4	#5	#6	#7
Composition (mol%)			SiO_2	47.9	45.9	45.4	45.9
			Al_2O_3	22.6	22.6	22.3	21.6
			MgO	3.0	3.0	3.0	3.0
			BaO	0.0	0.0	3.0	6.0
			TiO_2	8.0	8.0	8.0	8.0
			Na_2O	6.2	6.9	6.1	5.2
			K_2O	12.4	13.7	12.2	10.4
Theoretical crystallinity(%)				74.2	82.2	85.2	86.2
Density (g/cm^3)				2.65	2.67	2.76	2.85
CTE [−30～70℃] (10^{-7}/℃)				112	125	111	102
Young's modulus (GPa)				92	−	94	−
Bending strength	n			19	−	10	8
	average	(MPa)		83	−	88	92
	σ	(MPa)		10.5	−	8.2	8.0
appearence				transparent	transparent	transparent	opaque
Scattering constant (10^{10}nm^4/mm)				0.47	−	0.30	−

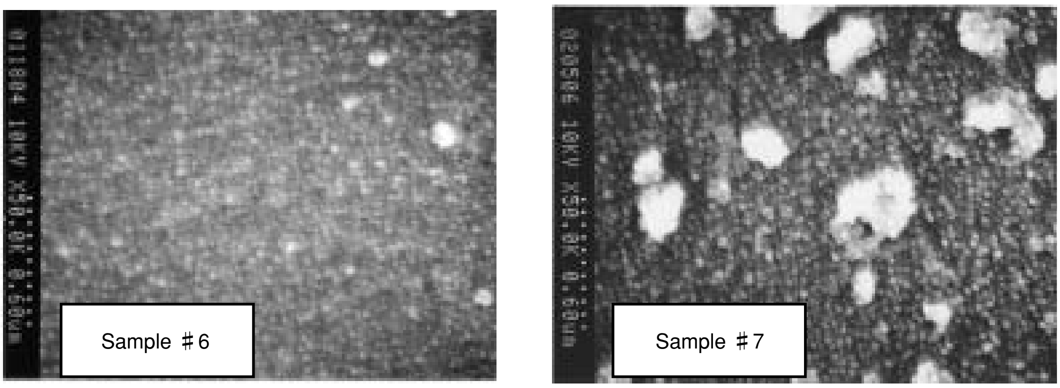

Fig. 7 SEM photograph of microstructures of sample #6 and #7.

er solid solution different from Nepheline-Kalsilite solid solution precipitates in sample #6. The contents of Na_2O and K_2O in sample #6 are almost the same as those in sample #4. So, it is considered that BaO mixes with Nepheline-Kalsilite solid solution in the sample #6.

The strength of the sample #6 and #7 increased as compared with the sample #4. This result seems to be reasonable because the mechanical strength of glass-ceramics increases with increasing crystallinity in general[8]. On the other hand, the transparency was lost for sample #7 as shown in **Table 3**. As seen in SEM image (**Fig. 7**), large particles, which can increase light scattering, precipitate in this glass-ceramics. Combining with the result of XRD, it is considered that these particles are Celsian.

From these results, it was found that the addition of barium was effective to improve the strength by increasing the crystallinity with maintaining the CTE of Nepheline-Kalsilite glass-ceramics, although the excess addition promotes the precipitation of Celsian and reduces the transparency of glass-ceramics.

3.3 Optimizing nuclear agents

Table 4 shows compositions and properties of Nepheline-Kalsilite glass-ceramics containing various TiO_2 contents and ZrO_2 contents. A slight amount of SiO_2, Al_2O_3 and MgO were added as residual glass components. It was found that if ZrO_2 contents were maintained 1 mol%, the scattering constant decreased adding TiO_2 to about 8 mol%, then increased more than about 8 mol% as shown in **Fig. 8**. Also, it was found that if TiO_2 contents were maintained 8 mol% the scattering constant increased by the addition of ZrO_2 as shown in **Fig. 9**. **Figure 10** shows SEM images of sample #8, #9, #12 and #16. It was found that the size of crystals became small with increasing contents of TiO_2 or ZrO_2.

The difference of crystal size as well as of refractive index between glass phase and crystals exerts an influence on the scattering constant. It is known that TiO_2 and ZrO_2 increase refractive index of glasses compared to other oxides such as SiO_2, Al_2O_3 and MgO[7]. It is known that the refractive index of Nepheline crystal is about 1.53 and the Appen's factors of refractive index of TiO_2 and ZrO_2 are about 2.0～2.2. This means that increasing TiO_2 or ZrO_2 contents in the residual glass phase increases scattering constant. As a result, scattering constant increased though the size of crystals became small by the addition of excessive TiO_2 or ZrO_2.

From these results, it was found that the addition of appropriate amount of TiO_2, without ZrO_2, was effective to improve the transparency of glass-ceramics.

Table 4　Properties of Nepheline-Kalsilite-Celsian Glass-Ceramics.

	Sample	#8	#9	#10	#11
Composition (mol%)	SiO_2	48.0	47.4	46.9	46.4
	Al_2O_3	22.6	22.3	22.1	21.8
	MgO	3.0	3.0	3.0	3.0
	TiO_2	6.8	8.0	9.0	10.0
	ZrO_2	1.0	1.0	1.0	1.0
	Na_2O	6.2	6.1	6.0	5.9
	K_2O	12.4	12.2	12.1	11.9
Theoretical crystallinity(%)		74.4	73.2	72.2	71.2
Density (g/cm^3)		2.68	2.68	2.69	2.70
CTE $_{[-30\sim70℃]}$ (10^{-7}/℃)		112	110	111	108
Young's modulus (GPa)		92	93	93	93
Scattering constant ($10^{10}nm^4/mm$)		1.51	0.80	0.85	1.09

	Sample	#12	#13	#14	#15	#16
Composition (mol%)	SiO_2	47.9	47.7	47.5	47.4	47.2
	Al_2O_3	22.6	22.4	22.4	22.3	22.2
	MgO	3.0	3.0	3.0	3.0	3.0
	TiO_2	8.0	8.0	8.0	8.0	8.0
	ZrO_2	0.0	0.5	0.8	1.0	1.4
	Na_2O	6.2	6.1	6.1	6.1	6.1
	K_2O	12.4	12.3	12.3	12.2	12.1
Theoretical crystallinity(%)		74.2	73.7	73.4	73.2	72.8
Density (g/cm^3)		2.65	2.67	2.68	2.68	2.70
CTE $_{[-30\sim70℃]}$ (10^{-7}/℃)		112	111	110	110	109
Young's modulus (GPa)		92	92	93	93	93
Scattering constant ($10^{10}nm^4/mm$)		0.47	0.54	0.65	0.80	1.99

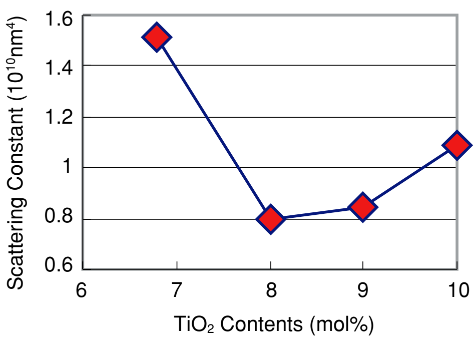

Fig. 8　TiO_2 contents vs. scattering factor (ZrO_2:1mol%).

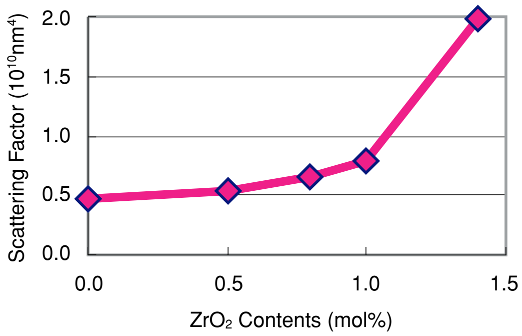

Fig. 9　ZrO_2 contents vs. scattering factor.

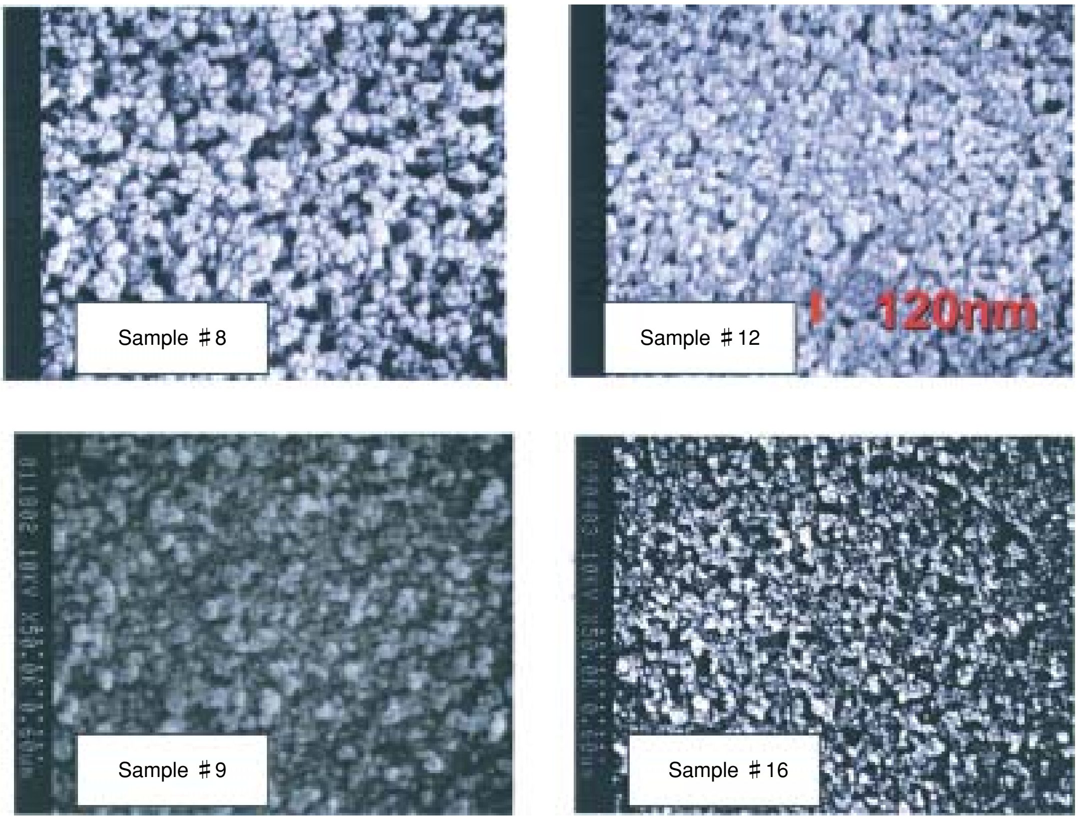

Fig. 10 SEM photograph of microstructures of sample #8, #9, #12 and #16.

4. Conclusion

We investigated the transparency and the mechanical properties of glass-ceramics including Nepheline-Kalsilite solid solution. Then it was found that increasing K_2O and the addition of appropriate amount of TiO_2 without ZrO_2 improved transparency. And then it was found that introduction of MgO was effective for high Young's modulus. Furthermore, it was found that addition of adequate BaO improved strength and could control the CTE. As a result, we could obtain glass-ceramics with high transparency and high mechanical strength under controlling the high CTE.

－References－

(1) H. Takahashi, *Appl. Opt.* **34**, 667-675 (1995).
(2) Duke et al., J. *Am. Ceram. Soc.*, **50**(2), 67 (1967).
(3) S. P. Clark, Jr.," Handbook of Physical Constants revised edition " The Geological Society of America, Inc (1966).
(4) N. Goto, M. Kataoka, *Electronic Parts and Materials* **40**(11), 75 (2001).
(5) J. F. MacDowell, *Ceramic Bulletin* **63**(2), 282 (1984).
(6) S. K. Das et al., *J. Non-cryst. Solids* **38-39**, 730 (1980).
(7) H. Scholze," Glass ", Springer-Verlag, (1990).
(8) Mc. Millan," Glass-Ceramics ", ACADEMIC PRESS, (1964).