

## K<sub>2</sub>O effect on the crystal structure and crystallization of fresnoite in BaO-TiO<sub>2</sub>-SiO<sub>2</sub> glasses

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To study the K<sub>2</sub>O effect on the crystal structure and crystallization behavior of BaO-TiO<sub>2</sub>-SiO<sub>2</sub> glasses, the glass-ceramics prepared were characterized using X-ray diffraction, Fourier transform infrared spectroscopy (FTIR) and a scanning electron microscope. The results showed that the K<sub>2</sub>O contents did not effect the formation of new crystals but increased the lattice constant. Combined with XRD data, the FT-IR peaks assigned to Ti-O and Si-O vibrations indicate the formation of the fresnoite (Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub>) phase. The crystal shape and crystallization tendency of Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> crystals by the K<sub>2</sub>O content were also discussed.

**Key words:** Glass-ceramics, Fresnoite (Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub>), Surface crystallization, Crystal growth.

### Introduction

Glasses are considered optically isotropic media due to the lack of periodicity, and therefore, theoretically they have a limitation for second harmonic generation (SHG). However, recently, many observations of SHG in glassy materials have been reported [1]. These materials belong to two main groups depending on the mechanism originating the SHG. The first group is formed by poled glasses [2-4] by exposure to an appropriate external excitation field, the second one is formed by nanostructured glasses (NG) i.e. transparent or slightly opalescent crystals. The latter is determined by the growth of nano- or micro-crystallites of ferroelectric or other highly polarizable phases [5-14]. Currently, a number of glass-ceramics comprising some well known ferroelectric crystalline phases in glassy matrices have been investigated and developed. i.e.  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> [5, 6], LaBGeO<sub>5</sub> [7, 8], LiNbO<sub>3</sub> [9], BaTiO<sub>3</sub> [10], KNbO<sub>3</sub> [11, 12], KTiPO<sub>4</sub> [13, 14]. Although many types of glass samples have appeared one after another, a large optical non-linearity has not been achieved in those materials.

Takahashi et al. [15, 16] have developed transparent surface-crystallized glasses consisting of a fresnoite structure (33.3BaO-16.7TiO<sub>2</sub>-50SiO<sub>2</sub>, 33.3BaO-16.7TiO<sub>2</sub>-50GeO<sub>2</sub>) and have found that they exhibit an extremely large  $d_{33}$  value ( $\sim 10$  pm/V), comparable to LN(LiNbO<sub>3</sub>) single crystals. Unfortunately, however, it is difficult to obtain glasses having compositions close to the BTS stoichiometry by conventional melt quenching techniques due to fact that these glasses show high tendency to

devitrification and a poor glass forming ability [17].

Currently we are trying to overcome this problem by replacement of BaO by K<sub>2</sub>O. In this study, the K<sub>2</sub>O effect on the crystal structure and crystallization tendency were investigated in  $x$ K<sub>2</sub>O-(33.3- $x$ )BaO-16.7TiO<sub>2</sub>-50SiO<sub>2</sub> (mol%) with fresnoite crystals by replacement of BaO by K<sub>2</sub>O.

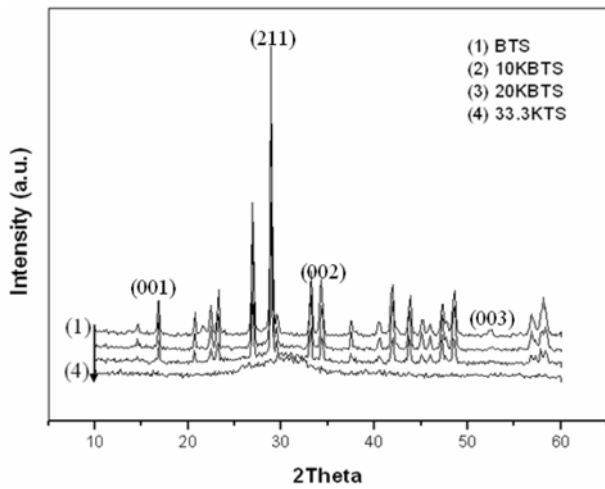
### Experimental procedure

The glass compositions studied were  $x$ K<sub>2</sub>O-(33.3- $x$ )BaO-16.7TiO<sub>2</sub>-50SiO<sub>2</sub> ( $0 \leq x \leq 33.3$  mol%) (here after denoted BTS, 10KBTS, 20KBTS, 33.3KTS) which modified away from the stoichiometric composition corresponding to Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> crystals. All the glasses were prepared from reagent grade K<sub>2</sub>CO<sub>3</sub>, BaCO<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>. Well mixed batches calculated to yield 50 g of glass were melted in platinum crucibles for 1 hour at 1500 °C and then quenched by pouring onto an iron plate. The crystalline phase in the samples obtained by heat treatment, the lattice deformation (%) and lattice constants were examined by X-ray diffraction analysis (Cu K $\alpha$  radiation) at room temperature. Scanning electron microscope (SEM) analysis was used for micro structural characterization. Fractured surfaces of heat-treated samples etched with 1% HF for 20 s were used for SEM observation. Fourier transform infrared spectra (FT-IR) were used in the frequency range 2000-400 cm<sup>-1</sup> with the glass-ceramic pellets dispersed in KBr.

### Results and Discussion

The precipitation of the microcrystalline Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> phase on direct heat treatment at 840 °C, 745 °C, 720 °C, and 680 °C for 1 h was confirmed by XRD and shown in Fig. 1. Intense Bragg peaks, attributable to the

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**Fig. 1.** XRD patterns of glass-ceramics based on the  $x\text{K}_2\text{O}-(33.3-x)\text{BaO}-16.7\text{TiO}_2-50\text{SiO}_2$ . Each sample was heated at each crystallization temperature (840 °C, 745 °C, 720 °C, and 680 °C) for 1 hour.

Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> phase were identified with a JCPDS card (22-0513). In the crystalline phases, the K<sub>2</sub>O content did not effect the formation of new crystals but decreased the crystallization temperature from 840 °C to 680 °C. The 33.3KTS, K<sub>2</sub>O has replaced BaO, was excluded from this study because the glass reacted strongly with moisture in air due to the high K<sub>2</sub>O content and the target crystal was not confirmed.

To analyse the lattice deformation according to the K<sub>2</sub>O content, the fullwidth at half maximum (FWHM) and deviations  $\Delta(2\theta)$  of peak positions from the XRD data of the three glass-ceramics were calculated by the equation as follows [18]:

$$\varepsilon(\psi, \varphi) = \Delta(2\theta)(\psi, \varphi) / 2 \tan(\theta_0)$$

Here,  $\varepsilon(\psi, \varphi)$  is the deformation of the corresponding planes,  $\Delta(2\theta)$  is the deviation of the peak position, and  $\theta_0$  is the standard diffraction angle, respectively. The deformation of the lattice on different planes were calculated and are listed in Table 1. It can be seen from this table that the full-widths of half maximum were approximately from 0.391° to 0.344°, indicating that

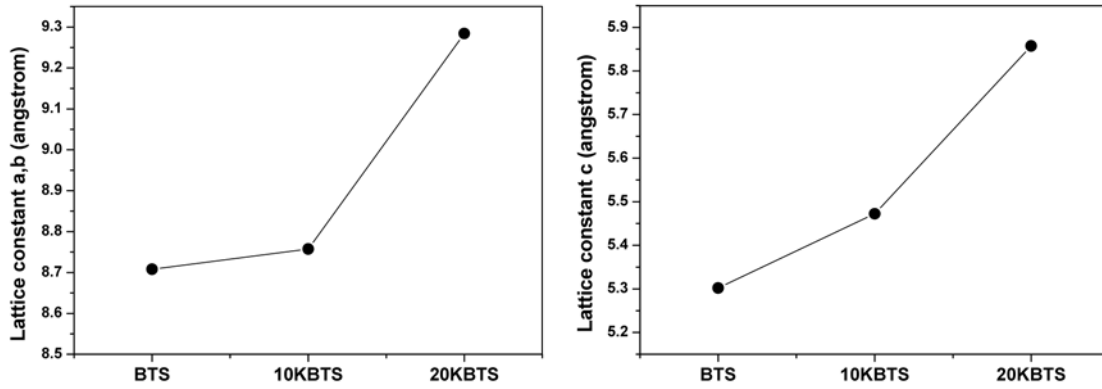
the sizes of crystals in samples of the glass-ceramics increased slightly with increasing K<sub>2</sub>O content. The deviation range of peak positions for the three glass-ceramics varied from 0.024- 0.141° to 0.034-0.155°. In the present study, we showed that the lattice deformation from XRD data is based on internal stress because the deformation comes from mismatch between the thermal expansion coefficient of the glass and crystal phase, and a larger deformation meant that the crystals were subjected to a bigger stress. Hence, it was proposed that deformation was due to the internal stress between the glass and crystal or crystals. Also it seemed that the deformation could be raised by the lattice distortion caused by the increasing replacement for Ba<sup>2+</sup> of K<sup>+</sup>.

Figure 2 shows that the lattice constant of the a,b,c-axes in glass-ceramics increased with increasing K<sub>2</sub>O content. The lattice constant of BTS glass-ceramics was compared with that of Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> powder in the JCPDS file and the lattice constant of glass-ceramics prepared is higher than given in the JCPDS card. This result means that BTS glass-ceramics also have some deformation or strain caused by glass making or heat treatment. Such a deformation is increased with the addition of K<sub>2</sub>O in the glass. We suggest that the K ions (0.227 nm) in the glass might form a non-bridging bonds to oxygen, easily movable ions in glasses, which decreased the thermal properties. Thus, the increase of lattice constants may be due to compression in the crystallized glasses that were compressed due to the density and thermal expansion difference between the crystal and glass matrix. It can also be expected that the lattice deformation for crystallies from BTS glass-ceramics with free K<sub>2</sub>O is smaller than that of the 20KBTS glass-ceramics.

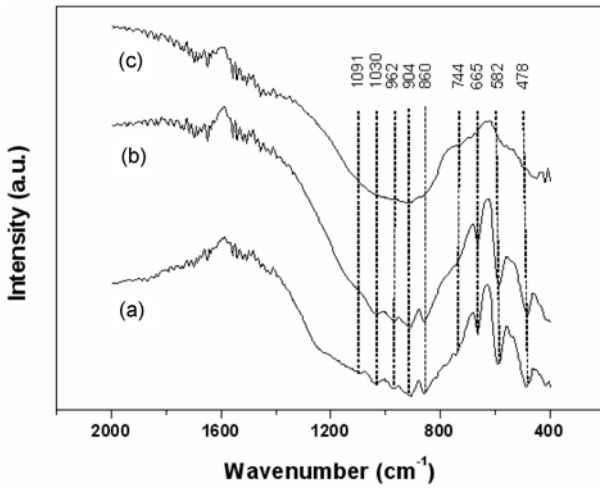
Fresnoite is believed to be a silicate mineral with a specific [TiO<sub>5</sub>] pyramid and layered [Si<sub>2</sub>O<sub>7</sub>] structure. Figure 3 shows the FT-IR spectra of BTS, 10KBTS and 20KBTS glass-ceramics. As the replacement by K<sub>2</sub>O increased from 0 to 20 mole%, all the peaks became gradually weaker. The peak intensity of Fig. 3a is higher than that of Fig. 3b containing 10 mole% K<sub>2</sub>O. In the case of Fig. 3c, although the sample was crystallized

**Table 1.** The analysis of lattice deformation from XRD data

| Compositions<br>(Main Phase)                                  | Standard 2 $\theta$<br>(deg.) | Measured 2 $\theta$<br>(deg.) | $\Delta(2\theta)$<br>(deg.) | FWHM<br>(deg.) | Deformation (%) |
|---------------------------------------------------------------|-------------------------------|-------------------------------|-----------------------------|----------------|-----------------|
| BTS<br>(Ba <sub>2</sub> TiSi <sub>2</sub> O <sub>8</sub> )    | 29.00                         | 28.927                        | 0.073                       | 0.347          | 0.141           |
|                                                               | 26.99                         | 26.928                        | 0.062                       | 0.349          | 0.129           |
|                                                               | 33.19                         | 33.176                        | 0.014                       | 0.354          | 0.023           |
| 10KBTS<br>(Ba <sub>2</sub> TiSi <sub>2</sub> O <sub>8</sub> ) | 29.00                         | 28.927                        | 0.073                       | 0.344          | 0.141           |
|                                                               | 26.99                         | 26.928                        | 0.062                       | 0.344          | 0.129           |
|                                                               | 33.19                         | 33.176                        | 0.014                       | 0.363          | 0.023           |
| 20KBTS<br>(Ba <sub>2</sub> TiSi <sub>2</sub> O <sub>8</sub> ) | 29.00                         | 28.920                        | 0.08                        | 0.359          | 0.155           |
|                                                               | 26.99                         | 26.920                        | 0.07                        | 0.391          | 0.146           |
|                                                               | 33.19                         | 33.170                        | 0.02                        | 0.371          | 0.034           |



**Fig. 2.** The lattice constant of a,b,c-axis of the Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> as a function of the substituted K<sub>2</sub>O content in the xK<sub>2</sub>O-(33.3-x)BaO-16.7TiO<sub>2</sub>-50SiO<sub>2</sub> glass. The lattice constants of Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> powder from JCPDS are 8.5291 and 5.2110, respectively.



**Fig. 3.** FTIR spectra of glass-ceramics crystallized at their crystallization temperatures. BTS, (b) 10KBTS, (c) 20KBTS

by heat treatment, the peak intensity is very weak. In the wave number region of 400-1200 cm<sup>-1</sup>, nine peaks at 478, 582, 665, 744, 860, 904, 962, 1030, and 1091 cm<sup>-1</sup> were observed which indicated that the glasses transformed into a crystalline state.

Table 2 lists the IR vibration peaks of different modes in Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub>. The IR bands of vibration in modes of [Si-O] bonds mainly emerge in the range of 1200-800 and 600-400 cm<sup>-1</sup>, while the IR bands of vibration of [Ti-O] bonds occur in the range of 900-400 cm<sup>-1</sup> [18, 19]. According to the above analysis, the strong absorption at 890-900 cm<sup>-1</sup>, as seen Fig. 3, is assigned to the Si-O structure in glass-ceramics similar to the isolated [SiO<sub>4</sub>]. The symmetric vibration of Si-O-Si stretching of [Si<sub>2</sub>O<sub>7</sub>] leads to an IR peak at 582 cm<sup>-1</sup> and the symmetric stretching of Ti-O bonds

emerged at 744 and 860 cm<sup>-1</sup>. Therefore, the IR spectra shown in Fig. 3, show peaks at 582, 744 and 860 cm<sup>-1</sup>, which means the glass-ceramics containing different K<sub>2</sub>O level possess a similar structure of Si-O and Ti-O groups.

To further study the K<sub>2</sub>O effect in glass-ceramics, the full width of half maximum (FWHM) for the (001), (002) and (003) diffraction peaks and the diffraction intensity ratio I(002)/I(211) are plotted in Fig. 4. As shown in Fig. 4 the order of measured FWHM of the diffraction peaks corresponding to the (001), (002), (003) planes was changed when BaO was replaced by K<sub>2</sub>O. Besides, the FWHM of all diffraction peaks decreases as the temperature increases, and it is obvious that the crystals grow at elevated temperatures. The amount of c-axis oriented Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> also decreases with increasing temperature.

The shape and size of crystals observed by SEM are presented in Fig. 5. The crystals have an ellipsoidal shape [20] as shown in the micrographs. These crystals were observed in all the glass-ceramics, and the number of crystals and their sizes continuously increased with heat treatment time and temperature, indicating simultaneous crystal nucleation and growth.

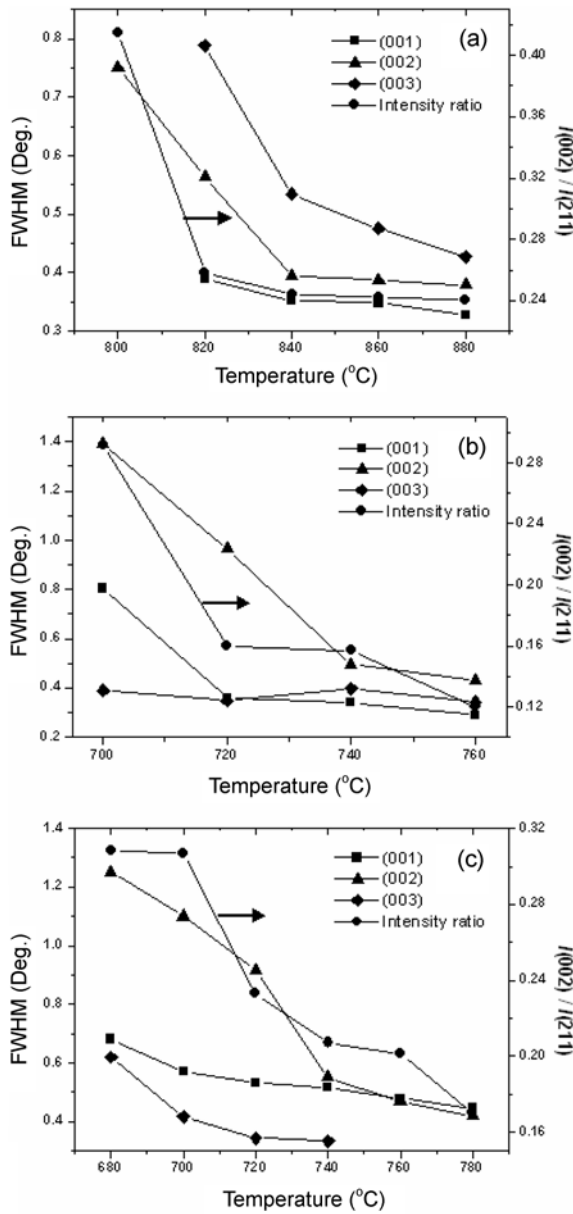
A SEM micrograph of an HF-etched fractured surface of BTS, heat-treated at 840 °C for 84 minutes and then 900 °C for 60minutes is given in Fig. 6. SEM observations indicated the fractured surface showed a loose crystalline (inner) and a dense crystalline (surface) including a glass matrix (seen as a large and dark object). Among the crystalline grains are also the glass matrix (small and dark spots). This result demonstrated that the crystallites are precipitated firstly at the surface and then internally.

The crystals grew normal to the glass surface, as

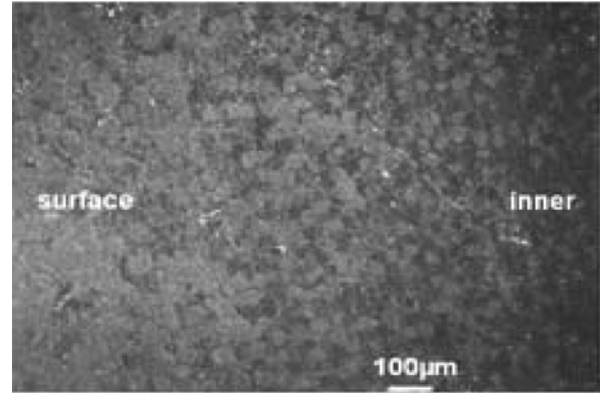
**Table 2.** IR wavenumbers (cm<sup>-1</sup>) for the modes in Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> Crystal

| ν (Ba-O) | δ (Ti-O) | δ (Si-O) | ν (Ti-O) | ν (Si-O-Si) | ν (Ti-O) | ν (Ti-O) | ν (Si-O) |
|----------|----------|----------|----------|-------------|----------|----------|----------|
| 100-300  | 300-400  | 400-550  | 550-650  | 583         | 749      | 860      | 860-1024 |

ν: (symmetrical) stretching vibration; δ: deformation vibrations.



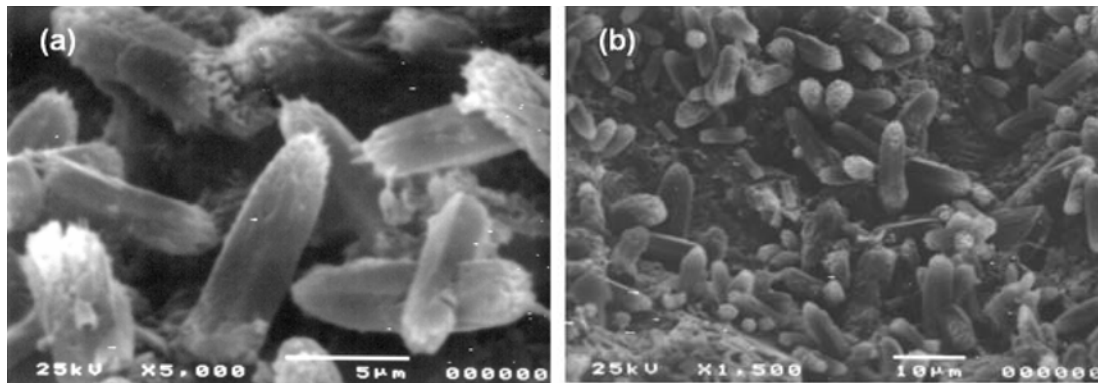
**Fig. 4.** The FWHM(001),(002),(003) and diffraction intensity ratio  $I(002)/I(211)$  of XRD peaks as a function of temperature. (a) BTS, (b) 10KBTS, (c) 20KBTS.



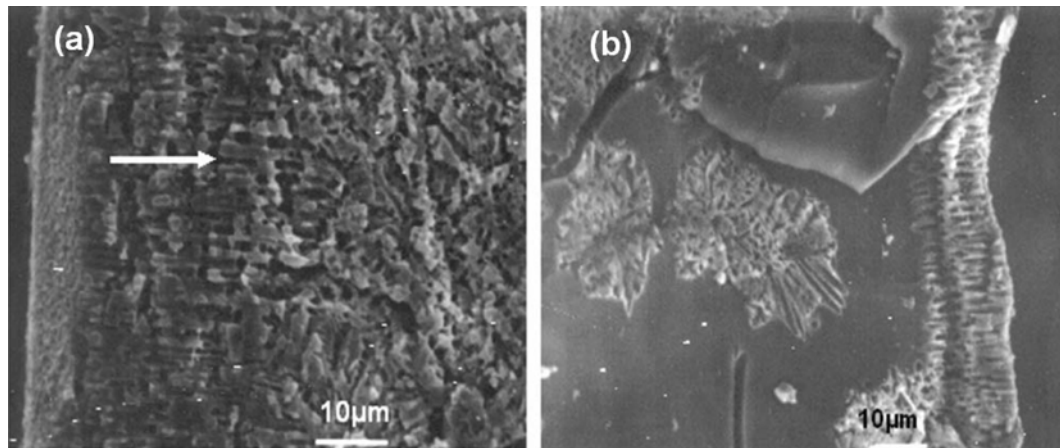
**Fig. 6.** SEM micrograph of an HF-etched fractured face of BTS with two step of heat-treatment at 840 °C for 84 minutes and then at 900 °C for 60 minutes.

shown in Fig. 7 of a cross section of BTS. It is seen from this figure that the ellipsoidal shape crystallites grow straight into the glass until their growth is restricted by crystallites from bulk crystallization [6]. Thus, the direction is the polar direction [001] of Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub>, and the thickening of the layer represents the growth of crystallites in a polar direction. Both micrographs show that the thickness of the well-polar-oriented crystallite layer reaches about 10-30 μm before it contacts clusters of crystallites in the bulk which lack preferred orientation.

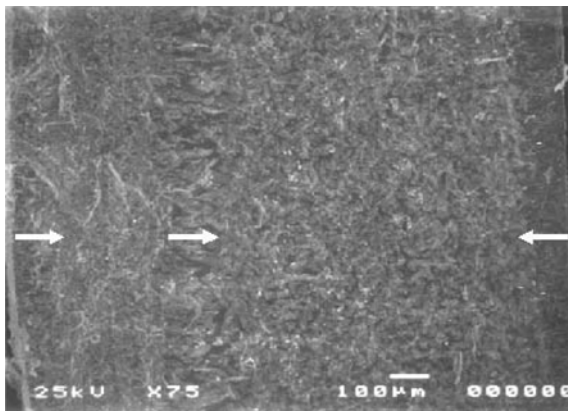
Figure 8 shows a SEM micrograph of a cross section fractured and HF-etched surface of a 10KBTS sample after heat-treatment at 740 °C for 3 h. The arrows indicate the growth direction or polar orientation. As shown in the BST sample, the ellipsoidal shape crystallites grow straight into the glass until their growth is restricted by crystallites from bulk crystallization. Magnified areas of Fig. 8 are shown in Fig. 9. The direction of growth is the polar direction [001] of Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub>, and the thickening of the layer represents the growth of crystallites in a polar direction. The thickness of the well-polar-oriented crystallite layer reaches about ~100 μm before it contacts clusters of crystallites in the bulk which lack preferred orientation. In Fig. 9b, from a



**Fig. 5.** SEM micrographs of the fresnoite crystals observed in heat treated glasses.



**Fig. 7.** SEM micrograph of a cross section (fractured and HF-etched surface) of a BTS sample after heat-treatment at 840 °C for 84 minutes and then at 900 °C for 60 minutes.

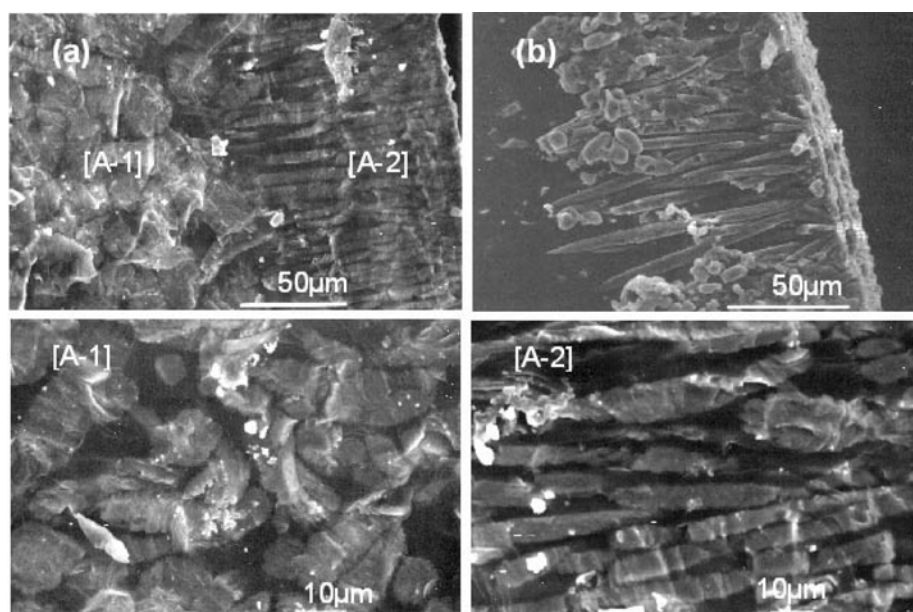


**Fig. 8.** SEM micrograph of a cross section (fractured and HF-etched surface) of a 10KBTS sample after heat-treatment at 740 °C for 3 h.

glass containing 20 mole %  $K_2O$ , we can not observe the bulk crystallization, and this means that the increase of  $K_2O$  content changes the crystallization behavior from bulk to surface crystallization. Even though the thickness of the crystallite layer reaches about  $\sim 100 \mu m$ , the fraction of oriented crystallites was not denser than that of the BTS and 10KBTS samples.

### Conclusions

In this paper, the  $K_2O$  effect on the crystal structure and crystallization of fresnoite in glass was investigated in glass-ceramics based on  $BaO-TiO_2-SiO_2$  glasses. The XRD analysis indicates that the  $K_2O$  has no effect on the formation of the secondary crystal phase, while the lattice deformation and lattice constants of crystals



**Fig. 9.** SEM micrographs of the etched glass-ceramics with (a) 10KBTS and (b) 20KBTS heat treated at 740 °C and 640 °C for 10 h. [A-1] and [A-2] are showing the magnified area of the figure (a).

in Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> glass-ceramics increase with K<sub>2</sub>O content due to the density and thermal expansion differences between the crystals and glass matrix. Also, the crystallinity was enhanced by the crystal growth at elevated temperature. FT-IR spectra show the glass-ceramics containing K<sub>2</sub>O possess a similar structure of fresnoite. Orientated crystals in a polar direction (c-axis) was observed for surface crystallization of BTS, 10KBTS and 20KBTS. In particularly, 20KBTS glass-ceramic showed prominent surface crystallization.

## References

1. A. Aronne, L.E. Depero, V.N. Sigaev, P. Pernice, E. Bontempi, O.V. Akimova, and E. Fanelli, *J. Non-Crystalline Solids* 324 (2003) 208-219.
2. H. Nasu, K. Kurachi, A. Mito, J. Matsuoka, and K. Kamiya, *J. Non-Cryst. Solids* 217 (1997) 182-188.
3. Y. Yamamoto, H. Nasu, T. Hashimoto, and K. Kamiya, *J. Non-Cryst. Solids* 281 (2001) 198-204.
4. T. Fujiwara, S. Matsumoto, M. Ohama, and A.J. Ikushima, *J. Non-Cryst. Solids* 273 (2000) 203-208.
5. Y.H. Kao, Y. Hu, H. Zheng, J.D. Mackenzie, K. Pery, G. Bourhill, and J.W. Perry, *J. Non-Cryst. Solids* 167 (1994) 247-254.
6. Y. Ding, A. Osaka, and Y. Miura, *J. Am. Ceram. Soc.* 77 (1994) 749-752.
7. Y. Takahashi, Y. Benino, V.V. Dimitrov, and T. Komatsu, *J. Appl. Phys.* 89 (2001) 5282-5287.
8. I. Kratochvilova-Hruba, I. Gregora, J. Pokorny, S. Kamba, Z. Zikmund, J. Petzelt, M. Cernansky, V. Studnicka, V.N. Sigaev, and E.N. Smelyanskaya, *J. Non-Cryst. Solids* 290 (2001) 224-230.
9. H.G. Kim, T. Komatsu, R. Sato, and K. Matusita, *J. Non-Cryst. Solids* 162 (1993) 201-204.
10. A. Narazaki, K. Tanaka, and K. Hiro, *J. Mater. Res.* 14 (1999) 3640-3646.
11. K. Narita, Y. Takahashi, Y. Benino, T. Fujiwara, and T. Komatsu, *Optical Materials* 25 (2004) 393-400.
12. N. Tamagawa, Y. Benino, T. Fujiwara, and T. Komatsu, *Optical Communications* 214 (2003) 387-394.
13. V.N. Sigaev, E. Fanelli, P. Pernice, L.E. Depero, P.D. Sarkisov, A. Aronne, E. Bontempi, and S.Yu. Stefanovich, *J. Non-Cryst. Solids* 345&346 (2004) 676-680.
14. V.V. Atuchin, B.I. Kidyarov, and N.V. Pervukhina, *Ceramics International* 30 (2004) 2005-2009.
15. Y. Takahashi, K. Saitoh, Y. Benino, T. Fujiwara, and T. Komatsu, *J. Cera. Soc. Jpn.* 112 (2004) S1168-S1172.
16. Y. Takahashi, Y. Bennio, T. Fujiwara, and T. Komatsu, *J. Appl. Phys.* 95 (2004) 3503-3508.
17. M.V. Shankar and L.B.R. Varma, *J. Non-Crystalline Solids*, 243 (1999) 192-203.
18. M. Zhu, B. Wang, P. Liu, H. Yan, and Z. Ding, *Optical Materials* 23 (2003) 323-326.
19. W. Dai, M. Zhu, Y.D. Hou, H. Wang, H. Yan, M. Shao, X. Chen, and J.B. Xu, *Materials Letter* 58 (2004) 2927-2931.
20. A.A. Cabral, V.M. Fokin, E.D. Zanotto, and C.R. Chinaglia, *J. Non-Cryst. Solids* 330 (2003) 174-186.