Crystallization of (Ca,Sr,Ba)O-Al_2O_3-SiO_2-Ta_2O_5 System Glasses.

Koichiro Tsuzuku* and Hiroshi Kishi
R&D Center, Taiyo Yuden Co., Ltd., 5607-2, Nakamuroda, Haruna-machi, Gunma-gun, 370-3347, JAPAN

Seiichi Taruta and Nobuo Takusagawa
Shinshu University, 500 Wakasato, Nagano, 380-8553, JAPAN

The crystallization and the resultant dielectric properties for the (Ca,Sr,Ba)O-Al_2O_3-SiO_2-Ta_2O_5 glass systems were examined to develop new glass-ceramics as dielectrics. The samples, which containing Ta_2O_5 in the range of 0-17.1 mol%, were prepared by conventional melt-quench method. Obtained glasses were milled under 44μm in size, pelleted into disks and sintered at 1000°C for 2hr in air atmosphere. The rod-like particles of a few μm in length, micro particles of about 0.1-0.5μm in size and needle-like particles of about 0.5 in length were precipitated in the sintered samples and the number of the micro particles increased and of the rod like particles decreased with increasing Ta_2O_5 content. The major precipitated phases were identified as $BaAl_2Si_2O_8$s.s., $CaTa_2O_6$s.s.and $SrTa_4O_{11}$s.s. by XRD method. The amount of $CaTa_2O_6$s.s. and $SrTa_4O_{11}$s.s. phases precipitated in the sintered samples were increased with increasing Ta_2O_5 content, and also the dielectric constant increased from 7 to 17, and the TCD changed from +100ppm/°C to -150ppm/°C.

Introduction

The dielectric properties of glass-ceramics can be controlled by the composition of precipitated crystalline phases. The relationships between precipitated phases and dielectric properties on glass-ceramics were already reported in previous papers and the most of precipitated phases reported in those papers were titanate crystals (1-5). It is expected as new dielectrics, if the dielectric properties of glass ceramics are controllable by the composition of precipitated phases except titanate. Therefore, the crystallization and the resultant dielectric properties for the (Ca,Sr,Ba)O-Al_2O_3-SiO_2-Ta_2O_5 glass systems were examined to develop new glass-ceramics as dielectrics.

Experimental procedure

Preparation of Samples

The samples having chemical composition of $0.4(Ca_{0.2},Sr_{0.5},Ba_{0.3})O + 0.1Al_2O_3 + 0.5SiO_2+xTa_2O_5$ as shown in Table 1 were examined. The x-value, Ta_2O_5 content, was changed in the range of 0 – 17.1 mol% (here after T0–T17). Raw materials mixture was melted in an alumina crucible at 1600°C or 1650°C and the melt was cast on an iron plate. Clear glass was obtained for the sample T0–T11 and partially crystallization occurred for T17. Obtained glass samples were milled under 44 μm in

Table 1 Chemical compositions for the samples T0-T17.

	mol ratio						melting temperature
	CaO	SrO	BaO	Al_2O_3	SiO_2	Ta_2O_5	
T0	7.3	20.0	11.3	9.4	52.0	0.0	1600
T1	7.3	20.0	11.3	9.4	52.0	1.0	1600
T2	7.3	20.0	11.3	9.4	52.0	2.0	1600
T3	7.3	20.0	11.3	9.4	52.0	3.0	1600
T4	7.3	20.0	11.3	9.4	52.0	3.9	1600
T5	7.3	20.0	11.3	9.4	52.0	4.9	1600
T6	7.3	20.0	11.3	9.4	52.0	5.9	1600
T7	7.3	20.0	11.3	9.4	52.0	6.8	1600
T9	7.3	20.0	11.3	9.4	52.0	8.6	1650
T11	7.3	20.0	11.3	9.4	52.0	11.4	1650
T17	7.3	20.0	11.3	9.4	52.0	17.1	1650

size. Those glass powders were pelletted into disks (10 mm in diameter and 1 mm in thickness) and these specimens were sintered at 1000°C for 2 hr in air atmosphere. Heating and cooling rate of sintering process were 5°C/min. The fractured surface of sintered specimen was chemically etched with 0.5 vol% HF solution for observation of microstructures.

Characterization of samples

Glass transition temperatures (Tg), temperatures at the onset of crystallization exo-therm (Tc) and melting temperature (Tm) of the glass samples were examined with Differential Scanning Calorimeter (DSC: Seiko Ins. Inc., DSC320) at the heating rate of 200°C/min. Precipitated crystalline phases in the sintered samples were examined with X-ray diffraction meter (XRD: Rigaku, RINT2500) and microstructures of sintered samples were observed with scanning electron microscope (SEM: Hitachi, S-4000). Dielectric properties of sintered samples were measured using Ag electrode and LCR meter (HP, 4284A) at temperatures ranging from -55°C to +125°C.

Results and discussion

Crystallization temperature and precipitated phases

The glass transition temperature (Tg) increased form 759°C to 838°C with increasing x value, while crystallization temperature increased from 1010°C (T0) to 1087°C (T6) then decreased to 1026°C (T17) as shown in Fig. 1.

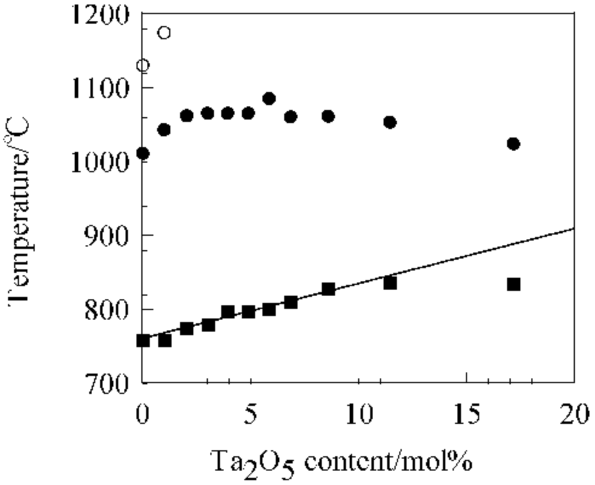


Fig.1 . Tg and Tcp of sintered samples depending on Ta_2O_5 content.

■: Tg, ●: Tcp1, ○: Tcp2.

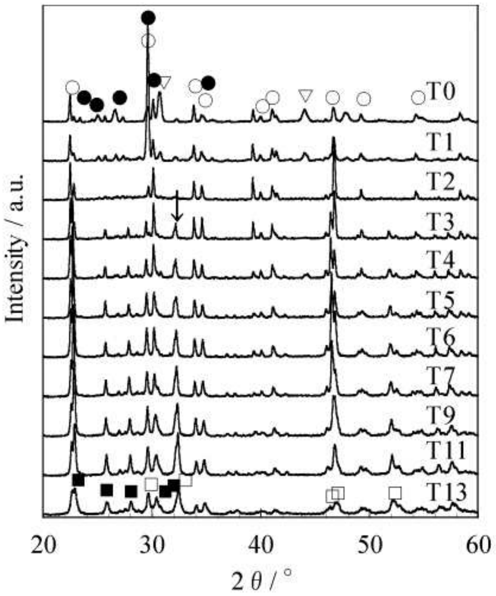
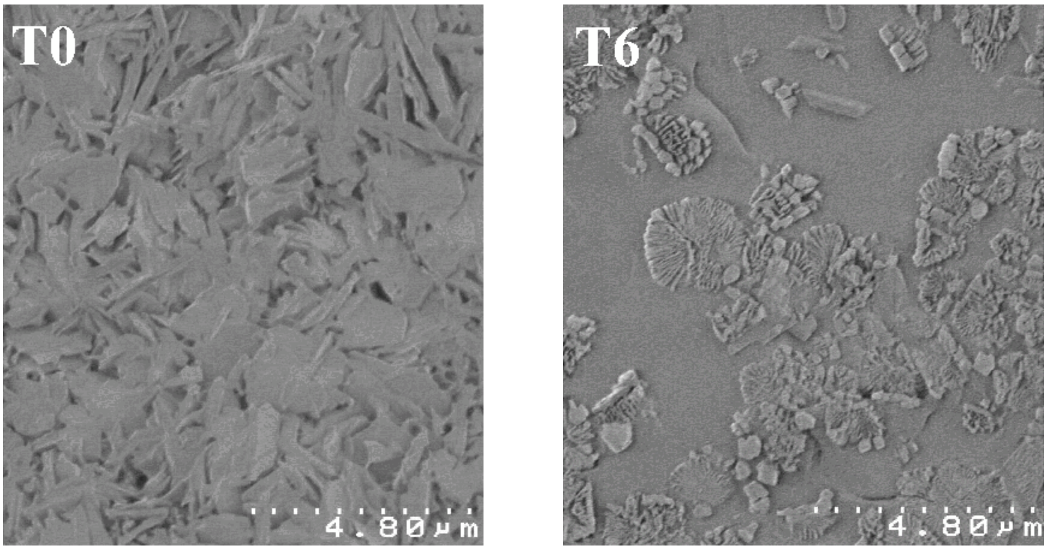


Fig.2. XRD patterns of the samples sintered at 1000℃.
○:h-AS, ●:m-AS, □:CT2, ■:ST4, ▽:$SrTiO_3$

XRD patterns for the sintered samples T0–T17 were shown in Fig. 2. $BaAl_2Si_2O_8$ phase precipitated in the whole samples as major phase and $CaTa_2O_6$ phase and $SrTa_4O_{11}$ phase precipitated in the sample T3-T17 and peak intensity of diffraction of $CaTa_2O_6$ and $SrTa_4O_{11}$ increased with increasing x value. However, there are differences between observed data and those of JCPDS cards for $BaAl_2Si_2O_8$, $CaTa_2O_6$ and $SrTa_4O_{11}$ phases. Those differences probably shows that Ca and Sr substituted for a part of Ba in $BaAl_2Si_2O_8$ phase, Sr and Ba substituted for a part of Ca in $CaTa_2O_6$ phase and Ca and Ba substituted for a part of $SrTa_4O_{11}$phase. These facts means that these precipitated phases were solid-solutions such as $(Ca,Sr,Ba)Al_2Si_2O_8$ (hare after AS), $(Ca,Sr,Ba)Ta_2O_6$ (hare after CT2) and $(Ca,Sr,Ba)Ta_4O_{11}$ (hare after ST4).

Microstructure of sintered samples

The SEM micro-photographs for the chemically etched fracture surfaces of sintered samples T0, T6 and T11 are shown in Fig. 3.



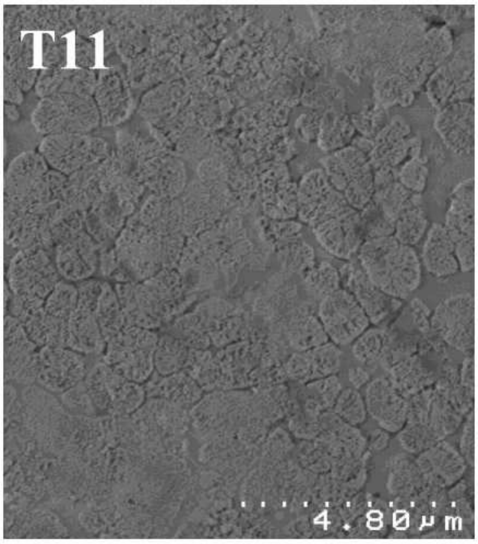


Fig.3. SEM photographs of the fractured and chemically-etched samples.

For the sample T17 no sintering was occurred, because for this composition glass phase was not obtained in this study. Larger number of rod-like particles of about 2-4μm in length and about 0.5μm in width and particles of about a few μm in size were observed for the samples T0. Those particles are regarded as AS because AS phase which having the hexagonal or monoclinic structure precipitated in the sample T0 as major phase and hexagonal $BaAl_2Si_2O_8$ phase grow having flake shape (6). Needle-like particles of about 0.5μm in length with dendritic arrangement, smaller particles of about 0.2-0.5μm in size and few number of rod-like particles of about 2μm in length and about 0.2μm in width were observed for the sample T6. Larger number of micro particles of less than 0.1μm in size with spherically agglomerated was observed for the sample T11. The number of the micro particles increased and of the rod-like particles decreased with increasing Ta_2O_5 content.

Dielectric properties

The dielectric constant and TCD of the sintered samples are shown in Fig. 4.

The dielectric constant slightly increased from 7.6 to 16.9 and TCD changed from 86 to -147ppm/°C with increase x value. However, small deviation between the expected line and observed value of the dielectric constant at the sample T17 was observed. This deviation was owing to non-dense microstructure of sample having large amount of pores. Furthermore, the deviation of TCD at the samples T1 and T2 were owing to the precipitated phase changed from hexagonal-$(Ca,Sr,Ba)Al_2Si_2O_8$ (h-AS) phase to monoclinic-$(Ca,Sr,Ba)Al_2Si_2O_8$ (m-AS) phase. The relationship between the dielectric properties of samples and the diffraction peak area of 32.5° corresponding to CT2 and ST4 was shown in Fig. 5.

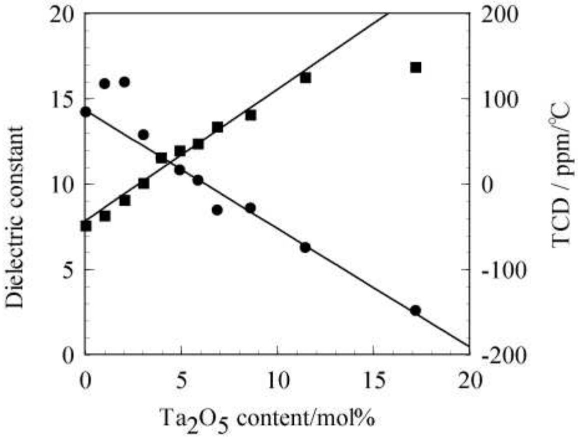


Fig. 4. Dielectric constant and TCD of the samples depending on Ta_2O_5 content.
■: Dielectric constant, ●: TCD.

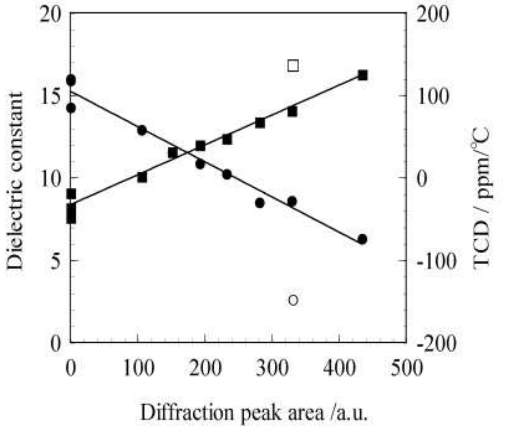


Fig. 5. Dielectric constant and TCD versus diffraction peak area at 32.5° on XRD pattern of sintered samples.
■: Dielectric constant, ●: TCD, Open simbols were the data of the sample T17 which could not sintered.

The observed linear relationships were probably shows that the dielectric properties of the crystallized samples depend on the volume of precipitated CT2 and ST4 phases in the samples.

Conclusion

The crystallization of sample glasses and dielectric properties of those crystallized samples having chemical composition of (Ca,Sr,Ba)O-Al_2O_3-SiO_2+xTa_2O_5 were studied. The linear relationships between the dielectric properties of crystallized samples and the diffraction peak area of precipitated CT2 and ST4 phases in the samples were observed. From the mentioned above, the dielectric properties of sample in which CT2 and ST4 phase precipitated is able to control of the volume of those phases which depend on Ta_2O_5 content of the samples. The crystallized glass-ceramics precipitated CT2 and ST4 phases having comparatively high dielectric constant and controllable TCD value in wide range were able to expect as the new dielectrics.

---

[1] Halliyal, A., Bhalla, A. S., Newnham, R. E. and Cross, L. E., *Glass and Glass-Ceramics*, ed. Lewis, M. H., Chapman and Hall, 1989, pp.272-315.

[2] Kokubo, T., Nagao, H. and Tashiro, M., Crystallization of PbO-TiO_2-Al_2O_3-SiO_2 Glasses and Dielectric Properties of their Crystallized Products, *Yogyo-Kyokai-Shi*, 1969, **77**, 9, 293.

[3] Hayashi, H., Nishioka, Y. and Okamoto, Y., Fabrication of Diopside Ceramics by Densification and Crystallization of Glsass Compacts and Their Dielectric Properties, *J. Ceram. Soc. Jpn.*, 1990, **98**, 8, 801.

[4] Tuzuku, K., Taruta, S., Takusagawa, N. & Kishi, H., Crystalline Phases and Dielectric Properties of Crystallized Glasses in the (Ca,Sr,Ba)O-Al_2O_3-SiO_2-TiO_2 System, *J. Ceram. Soc. Jpn.*, 1999, **107**, 733.

[5] Tsuzuku, K., Taruta, S., Takusagawa, N. & Kishi, H., Dielectric properties of sintered materials prepared from glass-ZrO_2-$SrTiO_3$ mixtures, *J. Mat. Sci.:Mat. in Elect.*, 2000, **11**, 419.

[6] Liu, C., Komarneni, S. & Roy, R., Crystallization and Seeding Effect in $BaAl_2Si_2O_8$ Gels, *J. Am. Ceram. Soc.*, 1995, **78**, 9, 2521.