Crystallization and Electrical Properties of $Ba_2TiSi_2O_8$ Glass-Ceramics from K_2O-BaO-TiO_2-SiO_2 System

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Abstract

Dielectric properties of glass-ceramics with fresnoite(Ba2TiSi208) crystals have been investigated in xK20-(33.3-x)BaO-16.7TiO2-50SiO2 ($0 \leq x \leq 20$mol%) glasses. The glassy nature was analyzed by differential thermal analyses and glass-ceramics was variable and controllable by the processing parameters like time and temperature. Dielectric constant was measured over a temperature from 125K to 425K at frequencies form 100Hz to 1MHz, and laid in the range 16-10. Piezoelectirc constant d33 was measured using a YE2703A d33meter and changed from 5.9 to 4.8pCN-1 with x contents. The spontaneous polarization Ps estimated from the hysteresis at ±1.2kV was ~0.3μC/cm2 at room temperature.

1. Introduction

According to ASTM definition, glass is an inorganic product of fusion which has been cooled to a rigid condition without crystallization. A glass obtained by cooling a liquid below its freezing point has unique characteristics such as transparency, pore free body and multicomponent system etc. Besides, the glass has high homogeneity because it is prepared by reaction between molecules. Glass-ceramics are ceramic materials formed through the controlled nucleation and crystallization of glass. Glass are melted, fabricated to shape, and thermally converted to a predominatly crystalline ceramics. The basis of controlled crystallization lies in efficient nucleation that allow the development of fine, randomly oriented grain generally without voids, microcracks or other porosity. These advantages of glass-ceramics have been exploited in the electronics industry for a variety of application.

Recently, glass-ceramics with well known ferroelectric crystalline phase in glassy matrix have been investigated and developed. Such glass-ceramics compared with sintered ceramics, offers following advantages: dielectric constant is nearly independent of temperature; the properties can be considerably altered by varying the type of crystal and its size; and the materials can be obtained relatively easily and cheaply. In addition,

the glass-ceramics has superior thermal, mechanical and chemical stability since its uniformity of crystal phase.

Among the number of glass-ceramics, the fresnoite($Ba_2TiSi_2O_8$) glass-ceramics has been attracting considerable attention because of showing excellent piezoelectric property and looking promise for surface acoustic wave(SAW) devices. However, the chemical composition of glass-ceramics examined in the previous studies was limited, and there is not enough report verifying experimental evidence that fresnoite is predicted to be a ferroelectric.

In this study, therefore, we prepared the glass-ceramics with fresnoite crystals in xK_2O-(33.3-x)BaO-16.7TiO_2-50SiO_2 ($0 \leq x \leq 20$mol%) by controlled nucleation and crystallization of glasses and evaluated its electrical properties.

2. Experiments

The glass compositions in study were xK_2O-(33.3-x)BaO-16.7TiO_2-50SiO_2 ($0 \leq x \leq 20$mol%) (here after denoted BTS, 10KBTS, 20KBTS) which slightly modified from the stochiometric compositions corresponding to $Ba_2TiSi_2O_8$ crystals. All the glasses were prepared from reagent grade K_2CO_3, $BaCO_3$, TiO_2 and SiO_2. Well mixed batches calculated to yield 50g of glass were melted in the platinum crucibles for 1hour at 1500 ℃ and then quenched by pouring on the cold iron plate. Thermal properties such as glass transition, Tg, and crystallization peak, Tp, were examined by a differential thermal analysis (TG-DTA, TG8110, Rigaku). The crystalline phase obtained by heat treatment was examined by x-ray diffraction analysis (Cu Kα radiation) (XRD, XD-D1, Shimadzu) at room temperature. Scanning electron microscope (SEM, JSM-5200, Jeol) analysis was used for microstructural investigation. The capacitance of the glass and glass-ceramics which were polished on both sides and silver painted to form electrodes was measured on Impedance Analyzer (LCR meter, Model 4274 and Model 4275, Hewlett-Packard, Palo Alto, CA) at a frequency of 100Hz~1MHz and at 125K~425K. Piezoelectric constant d_{33} was measured using a YE2730A d_{33} Meter(APC, Products. Inc.,), and hysteresis measurement was made on glass-ceramics fresnoite disk at room temperature using a dc voltage amplifier(Modle 609E-6) and RT66A(Radiant co.).

3. Results

The glass formation of the glass with the xK_2O-(33.3-x)BaO-16.7TiO_2-50SiO_2($0 \leq x \leq 20$ mol%) system was confirmed by the visual observation, and the glass fabrication was rather easier with increasing of K_2O contents. Fig. 1 shows the values of Tg and Tx for BTS, 10KBTS, 20KBTS samples. The temperature of glass transition and crystallization moves to the low temperature area with the increase of K_2O contents. The precipitation of microcrystalline $Ba_2TiSi_2O_8$ phase on direct heat treatment at 840 ℃, 745 ℃, 720 ℃, and 680 ℃ for 1h was confirmed by XRD and shown in Fig. 2. Intense Brag peaks, attributable to

$Ba_2TiSi_2O_8$ phase was identified with JCPDS card (22-0513). In the crystal phases, K_2O contents were not effect on the formation of new crystals and decreased the crystallization temperature from 840 °C to 680 °C. The 33.3KTS, K_2O has replaced to BaO, was excluded from this study because the glass reacted strongly with moisture in air due to lot of K_2O content and the target crystal was not confirmed.

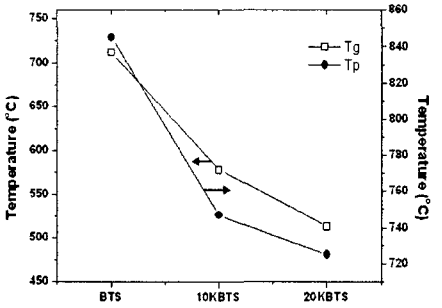

Fig. 1. Compositional dependence of glass transition and crystallization temperature of the glasses

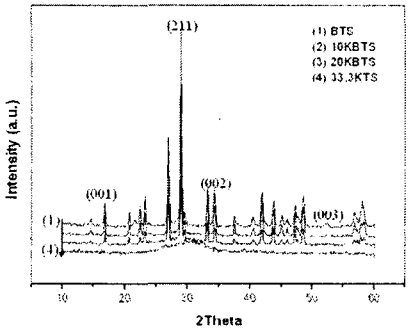

Fig. 2. XRD patterns of the xK_2O-(33.3-x)BaO-16.7TiO_2-50SiO_2 glasses

The shape of crystals observed by SEM are presented in Fig.3. The crystals have ellipsoidal shape[1] and grow normal to glass, as shown in the photographs. This crystal was observed at all the glass-ceramics, and the number of crystals and their sizes continuously increased with heat treatment time and temperature indication simultaneous crystals nucleation and growth.

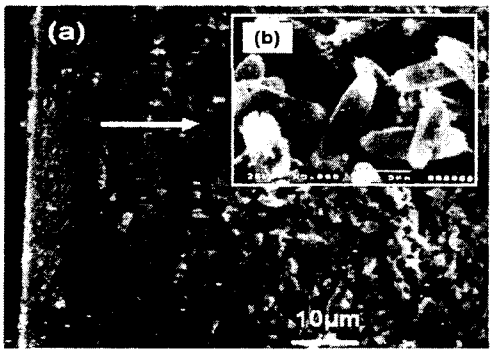

Fig.3. Photos of the fresnoite crystal observed at heat treated glass-ceramics
(a) photos of the cross section (fractured and HF-etched surface) of the BTS samples after heat treatment,
(b)crystal shape of fresnoite

For dielectric, heat treated discs of 15mm diameter and 3mm thickness were lightly polished and electroded with silver paste and then sintered at 600℃. The measured dielectric constant and loss were shown in Fig. 4. The variation of dielectric constant and loss lie in the range 10-14 and below 0.1. This figure shows that the dielectric constant decreased due to decreasing of amount of $Ba_2TiSi_2O_8$ phase according to increasing the K_2O content and the loss increased. Both the dielectric constant and losses increased as the temperature is raised and temperature dependence becoming less marked at higher frequencies as known in general trend. At lower frequencies, furthermore, the dielectric loss increases with temperature because of the increasing contribution from ionic mobility. At all the glass-ceramics, the increasing curve at around 135℃ was observed in both dielectric constant and loss. The curve in the dielectric constant at 135℃ was known as a major phase of $Ba_2TiSi_2O_8$.

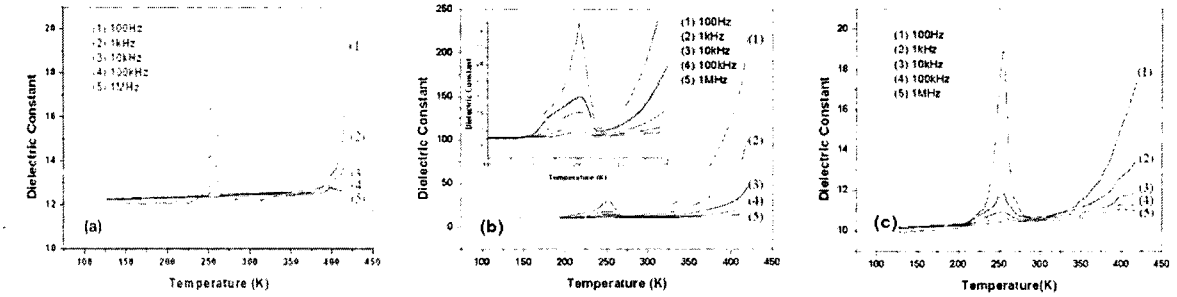

Fig. 4. Dielectric constant of (a)BTS, (b)10KBTS, and (c)20KBTS glass-ceramics according to the temperature and frequency.

Piezoelectric coefficients measured in glass-ceramics were shown in Fig. 5. The measured d_{33} coefficient was decreased with increasing K_2O contents for those glass-ceramics. L.E. Cross et al. reported piezoelectric property of $Ba_2TiSi_2O_8$ prepared in $2SiO_2$-BaO-TiO_2 and 2BaO-TiO_2-$3SiO_2$ glass lie in the range 2~3, 7 respectively. The result of this experimental lies between above-mentioned result and the value of single crystal (3.8).

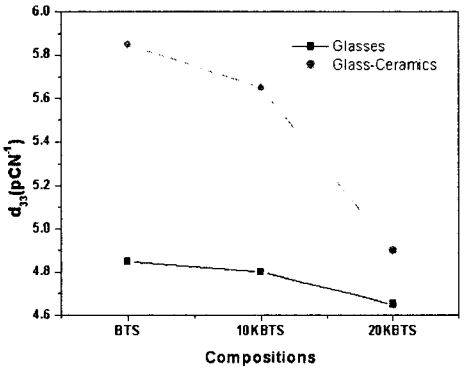

Fig. 5. Magnitude of d_{33} in BTS, 10KBTS, and 20KBTS glass-ceramics.

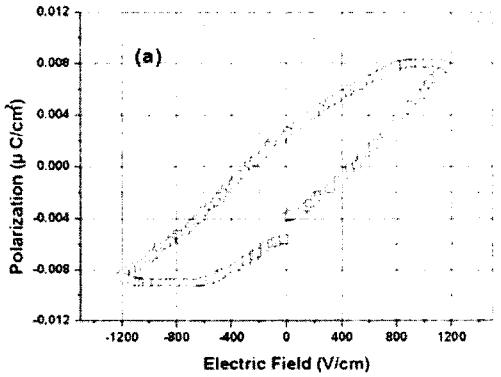

Fig. 6. P-E hysteresis loof of 10KBTS(b) glass-ceramic with a maximum field of ±1.2kV at room temperature

Fig. 6 shows the results of hysteresis measurements were made at dc on a glass ceramics disk, 13mm diameter and 1mm thick, sintered at 1000℃ for 1hr at room temperature with powders heat treated at 745℃ for 24hr. The results of P-E curve demonstrate that fresnoite crystal belongs to ferroelectric materials.

4. Conclusion

We prepared the glass-ceramics containing fresnoite($Ba_2TiSi_2O_8$) crystals in $x$$K_2O$-(33.3-$x$)BaO-16.7$TiO_2-50SiO_2$ ($0 \leq x \leq 20$mol%) glasses by heat treatment method and evaluated the its electrical properties. The temperature of glass transition and crystallization moves to the low temperature with x, and ΔT was found to increase with x content. $Ba_2TiSi_2O_8$ phase with ellipsoidal shape was identified with JCPDS card in all compositions. The dielectric constant decrease and loss increased with K_2O content. The curve change known as a major phase $Ba_2TiSi_2O_8$ of are observed in the dielectric constant and loss. Piezoelectirc constant d_{33} was decreased with K_2O contents and the results of P-E curve

demonstrate that fresnoite crystal belongs to ferroelectric materials.

References

[1] M.H.Lewis, London New York: *Chapman and Hall*, pp. 272-273.
[2] Y. Takahashi, K. Saitoh, Y. Benino, T. Fujiwara, and T.Komatsu, *J. Ceram. Soc. Jpn.*, Vol.112, pp. S1168-S1172, [5] 2004.
[3] J. Gopalakrishnan, K. Ramesha, K. K. Rangan, ans S. Pandey, *J. Solid State Chem*, Vol. 148, pp. 75-80 1999.
[4] Takahashi, Y., Benino, Y., Fujiwara, T. and Komatsu, T., *Jpn. J. Appl. Phys*, Vol. 41, pp.1455-1458, 2002.
[5] Y. Takahashi, K. Saitoh, T. Fujiwara, and T. Komatsu, *Appl. Phys. Lett.* Vol. 81 [2], pp. 223-225, 2002.
[6] Y. Takahashi, K. Saitoh, Y. Benino, T. Fujiwara, and T. Komatsu, *J. Appl. Phys.*, Vol.95, pp.3503-3508, 2004.
[7] T. Hoche, C. Russel, and W. Newmann, *Solid State Comm.* Vol. 110, pp. 651-656, 1999.
[8] A. halliyal, A.S.Bhalla, R.E. Newnham, L.E. Cross, *J. Mat. Sci.* Vol. 16 pp. 1023-1028, 1981.
[9] M.C. Foster, D.J. Arbogast, R.M. Nielson, P.Photinos and S.C. Abrahams, *J. Appl. Phys.* Vol 85 [4], pp. 2299-2303 1999.