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Preparation and Dielectric Properties of [Ba,Sr]TiO_3-Al_2O_3-SiO_2 Glass-Ceramics

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Synopsis

A series of ferroelectric glass-ceramics was elaborated by the controlled growth of $Ba_{1-x}Sr_xTiO_3$ crystal particles in the glass system 60[$Ba_{1-y}Sr_y$]TiO_3-10Al_2O_3-30SiO_2($0 \leqq y \leqq 0.2$) in molar basis. Analysis of crystal phases by X-ray diffraction revealed that Sr content in $Ba_{1-x}Sr_xTiO_3$ increased with increasing content of SrO in glasses by its preferential transfer into the crystal phase, and the appropriate temperature for the crystal growth was 1100°C. Curie temperatures of glass-ceramics shifted to lower temperature with increasing SrO content in the crystal and comparatively high dielectric constant was obtained at room temperature for a glass-ceramics with y=0.2. Frequency dependences of dielectric constant and loss tangent were examined in the frequency range from 1 K to 1 M Hz.

1. Introduction

Glass-ceramics is a material fabricated by controlled growth of crystalline phase in a glassy matrix and its properties reflect those of the crystalline phase. Ferroelectric materials can be prepared by growing ferroelectric crystalline phase in a glass article. Many investigations were carried out to develop ferroelectric glass-ceramics in the various compositional systems, such as BaO-TiO_2-Al_2O_3-SiO_2[1-4],

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$SrO-TiO_2-Al_2O_3-SiO_2$[5,6], $PbO-TiO_2-Al_2O_3-SiO_2$[7] and $Na_2O-Nb_2O_5-SiO_2$[8]. Some of above systems are practically utilized as dielectric materials in condensers or other applications.

Barium titanate,[$BaTiO_3$], is a representative ferroelectric material and has been extensively studied as sintered ceramics[9,10] and glass-ceramics. The dielectric property of sintered $BaTiO_3$ at around room temperature is usually improved by addition of oxides such as SrO,CaO, ZnO and ZrO_2, which shift its Curie points, T_c, to lower temperature by the formation of solid solutions, e.g. $Ba_{1-x}Sr_xTiO_3$. Thus, if the solid solution of $Ba_{1-x}Sr_xTiO_3$ can be grown in glassy matrix, then a useful ferroelectric material can be prepared with high dielectric constant, ε , and low temperature coefficient of ε at around room temperature. The present experiments were conducted to confirm above prediction and a new glass-ceramics with crystalline phase of $Ba_{1-x}Sr_xTiO_3$ was successfully elaborated in the system $60[Ba_{1-y}Sr_y]TiO_3-10Al_2O_3-30SiO_2$.

This paper describes preparation of the glass-ceramics, analyis of crystalline phases grown at various temperatures, determination of the composition of $Ba_{1-x}Sr_xTiO_3$ solid solution and dielectric properties of the present glass-ceramics.

2. Experimental

Reagent grade chemicals of $BaCO_3$, $SrCO_3$, TiO_2,Al_2O_3 and SiO_2 were used as raw materials. These chemicals were mixed to obtain glasses with compositions shown in Table 1 and the mixtures were melted in Pt crucible at 1400°C for 2 hr in an electric furnace. During melting, glass melts were stirred by Pt rod. Melts were then poured on a stainless steel plate and disc samples of 20 mm in diameter and 2 mm thick were obtained by cutting and polishing. Samples were then heat-treated to grow crystal phase for 1 hr at various temperatures ranging from 760° to 1200°C.

Table 1 Glass composition studied

Sample	$60[Ba_{1-y}Sr_y]TiO_3-10Al_2O_3-30SiO_2$ (mol %)
BS-0	y=0
BS-1	=0.067
BS-2	=0.1
BS-3	=0.125
BS-4	=0.167
BS-5	=0.2

X-ray diffraction analysis was performed by X-ray diffractometer and microstructure was examined by Scanning Electron Microscope.

Dielectric properties were measured by Impedance Analizer.

3. Experimental Results and Discussion

3-1. Differential thermal analysis

DTA curves for some glass samples are shown in Fig.1. Three exothermic peaks are observed, a sharp peak at around 830°C and two broad peaks at around 930° and 1030°C. All of those exothermic peaks are due to the crystallization of glasses. The sharp exothermic peak at around 830°C shifts to higher temperature with increasing content of SrO in glasses.

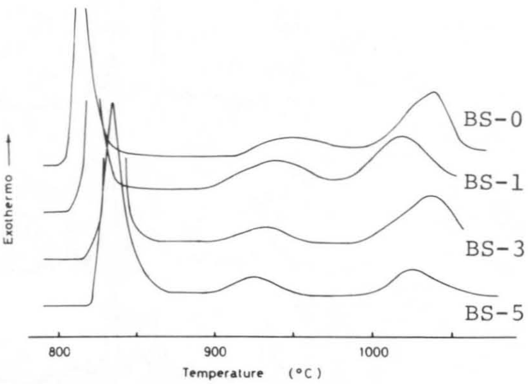
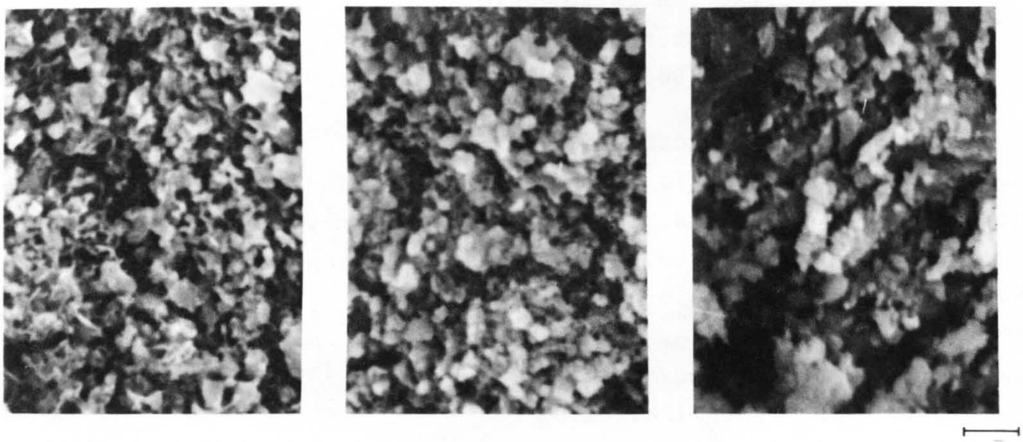


Fig.1 DTA curves of test glasses.

3-2. Microstructures of glass-ceramics

Scanning electron micrographs are shown in Fig.2. Microstructures are similar for all samples heat-treated at 1100°C for 1 hr and $Ba_{1-x}Sr_xTiO_3$ grains are almost uniform in size(0.2 μm in diam.).



BS-1 BS-3 BS-5 1 μm

Fig.2 Fracture surfaces of glasses heat-treated at 1100°C for 1 hr.

3-3 Crystalline phases grown at various temperatures

(1) Crystal phases grown in BS-0(y=0) glass

X-ray diffraction patterns are shown in Fig.3 (a)-(e). No significant diffraction peaks are observed for the sample heat-treated at 760 °C, and two crystal phases appear for the sample heat-treated at 800°C

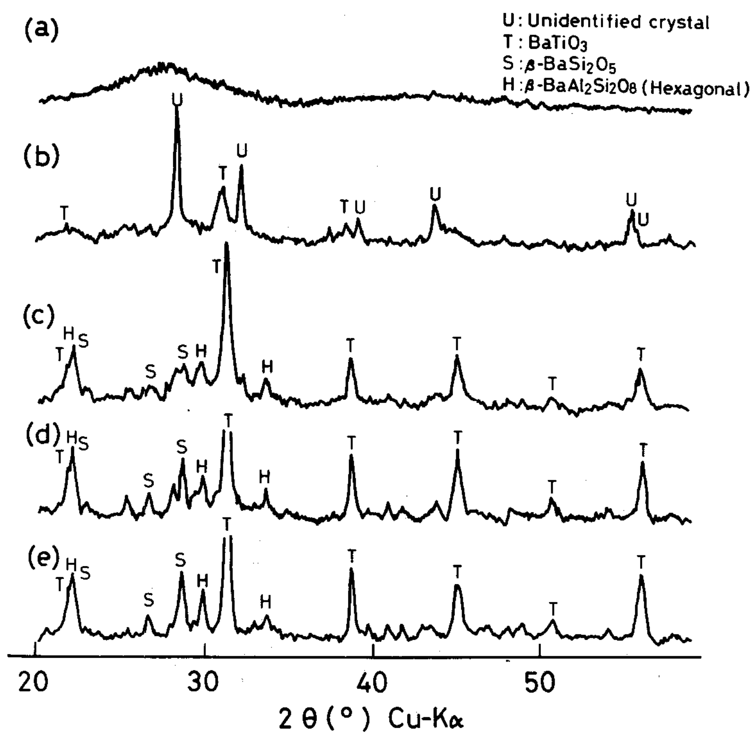


Fig.3 X-ray diffraction patterns of BS-0 glass heat-treated at various temperatures for 1 hr.
(a) 760°C, (b) 800°C, (c) 900°C, (d) 1000°C, (e) 1200°C

, one is $BaTiO_3$ and another is unidentified. Analysis of the unidentified peaks, assuming it to be a hexagonal crystal, yields its lattice parameters of a=5.543 Å and c=8.220 Å, which is close to those of hexagonal benitoite-type crystal ($BaTiSi_3O_9$:a=5.50 Å, c=8.32 Å)[4], as shown in Table 2. In addition, the fact that the diffraction peaks of the benitoite-type crystal disappear when the sample surface is abraded, implies the crystal growth at the surface of glass. Main crystal phases grown in the glass heat-treated at 900°C or higher are identified as $BaTiO_3$, β-$BaSi_2O_5$ and β-$BaAl_2Si_2O_8$ (Fig.3 (c)-(e)).

Table 2 Indexing of the unidentified crystal powder pattern as a hexagonal lattice.

d(obs.)(Å)	I/I_0(%)	$1/d(obs.)^2$	$1/d(cal.)^2$	(hkl)
3.1372	33	0.1016	0.1016	(102)
2.7715	21	0.1302	0.1300	(110)
2.3382	5	0.1829	0.1752	(200)
2.2981	7	0.1893	0.1883	(112)
2.0691	10	0.2336	0.2315	(202)
1.6529	9	0.3660	0.3660	(114)
1.6474	5	0.3685	0.3700	(005)

a=5.543 Å, c=8.220 Å

(2) Crystal phases grown in BS-1-5 (y=0.067-0.2) glasses

It is recognized that three identified crystal phases appear in these glasses when they are heat-treated in the temperature range from 900° and 1200°C. X-ray diffraction patterns of glasses heat-treated at 1100°C for 1 hr are shown in Fig.4 (a)-(c). Two crystal phases observed are β-$BaSi_2O_5$ and β-$BaAl_2Si_2O_8$, another is $Ba_{1-x}Sr_xTiO_3$ which peaks shift to higher angles with increasing content of SrO in glass. That is, $Ba_{1-x}Sr_xTiO_3$ solid solution, β-$BaSi_2O_5$ and β-$BaAl_2Si_2O_8$ are grown by the heat-treatment at higher temperature.

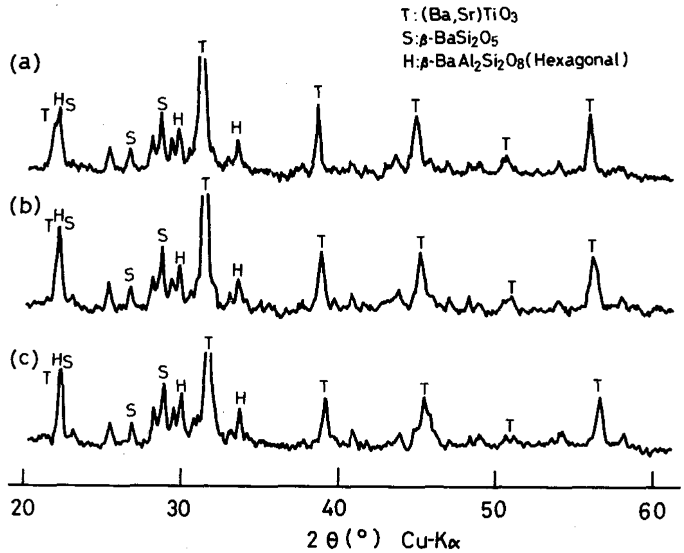


Fig.4 X-ray diffraction patterns of BS-0,-2,-5 glasses heat-treated at 1100°C for 1 hr. (a) BS-0, (b) BS-2, (c) BS-5

(3) Composition of $Ba_{1-x}Sr_xTiO_3$ solid solution

The phase diagram of the system $BaTiO_3$-$SrTiO_3$ was determined by Basmajian and Devries[11]. They indicated that the solid solution of $BaTiO_3$ was formed in full composition range of the system and $\sqrt[3]{a^2c}$ decreased with increasing amount of $SrTiO_3$. Based on their results, present authors calculated the composition of $Ba_{1-x}Sr_xTiO_3$ as follows.

$$X = \frac{\sqrt[3]{a^2 \cdot c}_{BaTiO_3} - \sqrt[3]{a^2 \cdot c}_{Ba_{1-x}Sr_xTiO_3}}{\sqrt[3]{a^2 \cdot c}_{BaTiO_3} - \sqrt[3]{a^2 \cdot c}_{SrTiO_3}}$$

Where, $\sqrt[3]{a^2c}$ was calculated using the d-values, d_{111} and d_{211}.

$$a^2=\frac{3d_{111}^2 - d_{211}^2}{d_{111}^2 - d_{211}^2}$$

$$c^2=\frac{0.6(d_{211}\cdot d_{111})^2}{d_{211}^2 - 0.4d_{111}^2}$$

The relationship between y(Sr/Sr+Ba) in the glasses and x(Sr/Sr+Ba) in the crystal indicates that Sr in the glass preferentially transfers into the $BaTiO_3$ during heat-treatment (Fig.5).

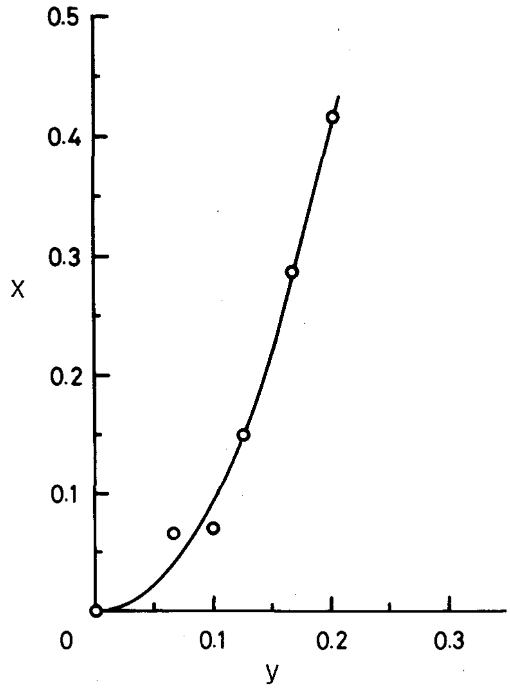


Fig.5 Plot of x in $Ba_{1-x}Sr_xTiO_3$ vs. y in $60[Ba_{1-y}Sr_y]TiO_3-10Al_2O_3-30SiO_2$ glasses heat-treated at 1100°C for 1 hr.

3-4 Dielectric properties

(1) Dielectric constant, ε

Temperature dependence of ε of the samples crystallized at 1100°C for 1 hr are shown in Fig.6. The figure indicates that T_c decreases with increasing content of SrO in the glasses, and ε at T_c seems to have a minimum(at y=0.125), that is ε at T_c decreases with increasing amount of SrO in glass($0\leq y\leq 0.125$). Beyond y=0.125, it conversely increases($0.125<y\leq 0.2$). The decrease of T_c with y is caused by the formation of $Ba_{1-x}Sr_xTiO_3$. The compositional dependence of ε at T_c may be taken for the product of two factors, amount of $Ba_{1-x}Sr_xTiO_3$ in sample and its ε .

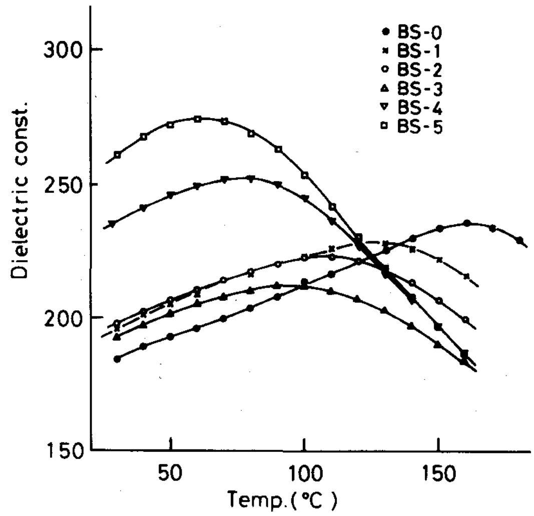


Fig.6 Temperature dependence of ε for test glasses heat-treated at 1100°C for 1 hr.

Amount of crystal grown in the glass increases with increasing amount of SrO, and ε at T_c of $Ba_{1-x}Sr_xTiO_3$ decreases with increasing of x. Consequently, the product of these factors is likely to give above non-linear relation.

Values of ε obtained in the present work are lower than that of the glass-ceramics in the system of $BaTiO_3$(ε=500) obtained by Kokubo et al.[2]. This is due to smaller particle size and smaller amount of crystal, which results from the suppression of crystal growth by higher content of SiO_2 in the present glass.

(2) Curie point, T_c

T_c of the crystallized BS-0 glass is 160°C, which is higher than the T_c of $BaTiO_3$, 120°C. Generally, T_c of crystal shifts by impurities , applied stress and grain size of crystal. In the present work, no impurity is contained in $BaTiO_3$ crystal grown in BS-0 glass and applied stress to the crystal particles is very small because its tetragonality, represented as c/a ratio, is 1.015, which is almost identical to that of $BaTiO_3$ single crystal. The shift of T_c in this case is likely to be the result of small particle size(0.2 μm in diam.). Ulrich and Smoke[13] obtained T_c of 150°C for $BaTiO_3$ prepared by the heat-treatment of spray welded glassy $BaTiO_3$. They considered that the shift of T_c is attributed to small grain size, 0.2-0.5 μm.

(3) Variation of ε and tanδ with frequency

Variations of ε with frequency are shown in Fig.7. In frequency range from 1 K Hz to 1 M Hz, ε decreases with increasing frequency.

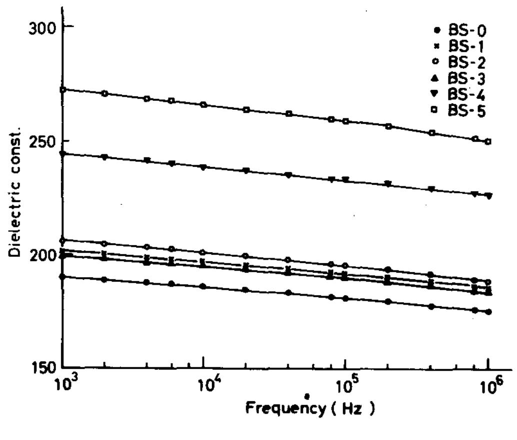


Fig.7 Frequency dependence of ε of test glasses heat-treated at 1100°C for 1 hr.

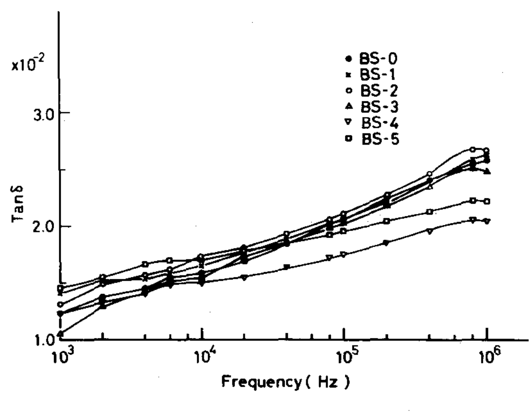


Fig.8 Frequency dependence of tanδ of test glasses heat-treated at 1100°C for 1 hr.

Fig.8 shows variation of tanδ with frequency in the same range. Loss tangent of the crystallized glass slightly increases with increasing frequency, the same trend is observed in sintered ferroelectric ceramics. Comparatively high values of tanδ is caused by the superposition of glassy matrix with high tanδ.

4. Conclusion

In order to obtain glass-ceramics with T_c at comparatively low temperature, a series of glass were prepared and they were heat-treated for crystallization. Glass composition in the present work was the system $60[Ba_{1-y}Sr_y]TiO_3-10Al_2O_3-30SiO_2$ $(0 \leqq y \leqq 0.2)$, and heat-treatments were carried out at temperature ranging from 760° to 1200°C. Variation of ε and tanδ were measured as a function of frequency in the range from 1 K Hz to 1 M Hz. Following results were obtained.

1). A glass-ceramic with comparatively low T_c of 60°C is successfully elaborated, which contain $Ba_{1-x}Sr_xTiO_3$ solid solution as main crystal phase.
2). In the glass with y=0, crystal phases of $BaTiO_3$, β-$BaSi_2O_5$ and β-$BaAl_2Si_2O_8$ are grown by heat-treatment above 900°C, and in glasses with $0<y \leqq 0.2$ three phases of $Ba_{1-x}Sr_xTiO_3$, β-$BaSi_2O_5$ and β-$BaAl_2Si_2O_8$.
3). It is recognized that SrO in the glass preferentially transfers into $BaTiO_3$ during heat-treatment.
4). T_c of glass-ceramics, where ε shows maximum, reduce with increasing content of SrO, that is, y. This is due to the growth of $Ba_{1-x}Sr_xTiO_3$, the composition of which depends upon SrO content in glass.
5). ε at T_c have non-linear relation with x showing the minimum at y=0.125. It is assumed that the non-linear relation comes out as the product of two factors, namely, increase of $Ba_{1-x}Sr_xTiO_3$ amount and decrease of its ε.
6) In the range from 1 K Hz to 1 M Hz, frequency dependence of ε and tanδ for the present glass-ceramic show the same trend as that of sintered ferroelectric ceramics.

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