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

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Synopsis

Succeeding to 60[Ba,Sr]TiO_3-10Al_2O_3-30SiO_2 glass-ceramics reported in our previous paper[1], another type of ferroelectric glass-ceramics was elaborated by the controlled growth of $Ba_{1-x}Ca_xTiO_3$ crystal particles in the glass system 60[$Ba_{1-y}Ca_y$]TiO_3-10Al_2O_3-30SiO_2 ($0.0 \leq y \leq 0.25$) in molar basis. Analysis of crystal phases by X-ray diffraction revealed that Ca content in the crystal phase of $Ba_{1-x}Ca_xTiO_3$ increased with increasing amount of CaO in glass up to y=0.125, and the composition of $Ba_{1-x}Ca_xTiO_3$ solid solution was restricted by x=0.225. Curie points(T_c) of the present glass-ceramics were independent of the composition of $Ba_{1-x}Ca_xTiO_3$, however temperature coefficients of ε were lowered by the addition of increasing amount of CaO. Frequency dependencies of dielectric constant and loss tangent were examined in the frequency range from 1 k to 1 M Hz.

1. Introduction

As well known, the dielectric properties of a sintered $BaTiO_3$ body around room temperature are usually improved by the addition of particular oxides. SrO acts as the 'shifter', which shifts its Curie point(T_c) to lower temperature by the formation of $Ba_{1-x}Sr_xTiO_3$ solid solution. While, CaO acts as the 'depresser', which causes the lower

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temperature coefficient of ε by the formation of $Ba_{1-x}Ca_xTiO_3$ solid solution[2). In the previous paper, authors reported the preparation of the glass-ceramics in the system $60[Ba_{1-y}Sr_y]TiO_3$-$10Al_2O_3$-$30SiO_2$, and its dielectric properties. It was clarified that SrO added in the glass acted as the 'shifter' of ferroelectric glass-ceramics.

Succeeding to $60[Ba,Sr]TiO_3$-$10Al_2O_3$-$30SiO_2$ glass-ceramics, glass-ceramics in the system $[Ba,Ca]TiO_3$-Al_2O_3-SiO_2 were studied. If the solid solution of $Ba_{1-x}Ca_xTiO_3$ could be grown in the glass matrix, a useful ferroelectric materials with high dielectric constant(ε) and low temperature coefficient of ε could be prepared. The present experiments were conducted to confirm such prediction and a new glass-ceramics with crystalline phase of $Ba_{1-x}Ca_xTiO_3$ was successfully elaborated in the system $60[Ba_{1-y}Ca_y]TiO_3$-$10Al_2O_3$-$30SiO_2$.

This paper describes the preparation of the glass-ceramics, the analysis of crystalline phases grown by the heat-treatment, the determination of the composition of $Ba_{1-x}Ca_xTiO_3$ solid solution and the dielectric properties of the present glass-ceramics.

2. Experimental

Reagent grade chemicals of $BaCO_3$, $CaCO_3$, TiO_2, Al_2O_3 and SiO_2 were used as raw materials. These chemicals were mixed to obtain glasses with composition shown in Table 1 and the mixtures were melted in a Pt crucible at 1400°C for 2 hr in an electric furnace. During melting, glass melt was stirred by a Pt rod. Melts were then poured on a stainless steel plate and disc samples of 20mm in diameter and 2mm thickness were obtained by cutting and polishing. Samples were then heat-treated to grow crystal phase for 1 hr at 1100°C.

Table 1 Glass composition studied

Sample	$60[Ba_{1-y}Ca_y]TiO_3$-$10Al_2O_3$-$30SiO_2$ (mol%)
BC-0	y=0.0
BC-1	=0.083
BC-2	=0.100
BC-3	=0.125
BC-4	=0.167
BC-5	=0.250

X-ray powder diffraction analysis was performed by an X-ray diffractometer and microstructure was examined by a Scanning Electron Microscope. Dielectric properties were measured by an Impedance Analyzer.

3. Experimental Results and Discussion

1) Differential thermal analysis

DTA curves for some glass samples were shown in Fig.1. Three exothermic peaks were observed, a sharp peak around 830°C and two broad peaks around 930°C and 1020°C. All of those exothermic peaks were due to the crystallization of glasses. The sharp exothermic peak around 830°C shifts to higher temperature with increasing content of CaO in glasses.

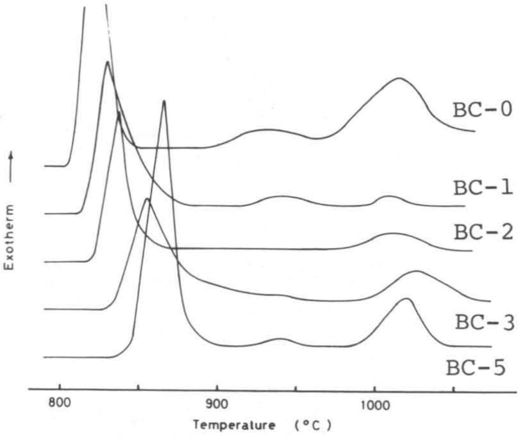

Fig.1 DTA curves of test glasses.

2) Microstructure of glass-ceramics

Scanning electron micrographs are shown in Fig.2. Microstructures were similar for all samples heat-treated at 1100°C for 1hr ,and $Ba_{1-x}Ca_xTiO_3$ were almost uniform in size(≃0.2μm in diam.).

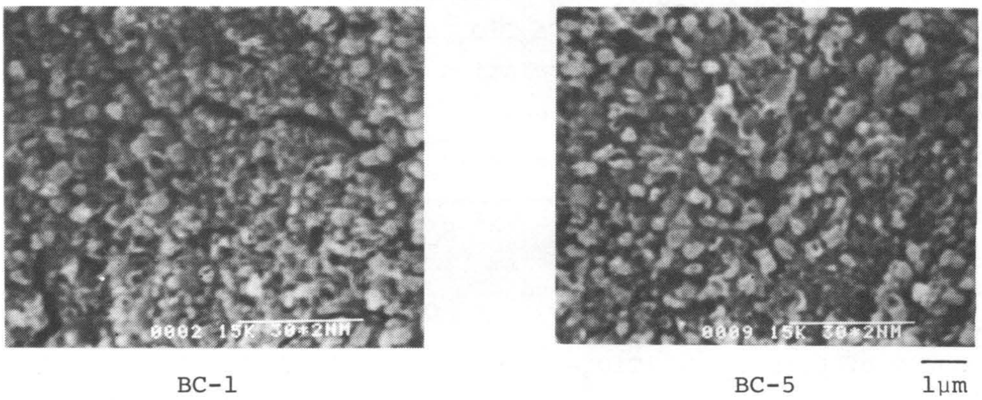

Fig.2 Fracture surfaces of glasses heat-treated at 1100°C for 1 hr

3) Crystalline phases grown at 1100°C

(1) Crystalline phases grown in BC-0~5 $(0.0 \leq y \leq 0.25)$

X-ray diffraction patterns of glasses heat-treated at 1100°C for 1 hr were shown in Fig.3 a),b),c). Main crystal phase was $Ba_{1-x}Ca_xTiO_3$ which peaks shifted to higher angle with increasing content of CaO in glass. Other two crystal phases were identified as β-$BaSi_2O_5$ and β-$BaAl_2Si_2O_8$. Observed crystal phases were similar to those observed on 60[Ba,Sr]TiO_3-10Al_2O_3-30SiO_2 glass-ceramics.

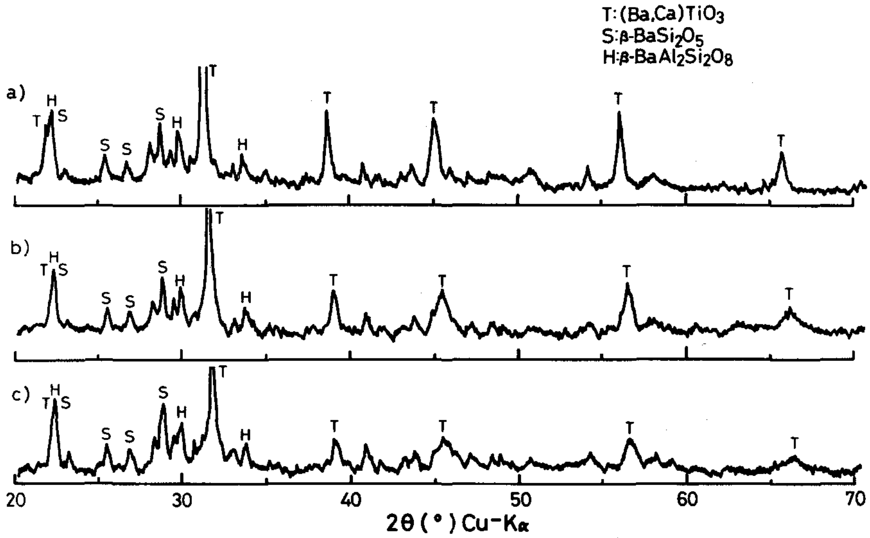

Fig.3 X-ray diffraction patterns of BC-0,-1,-5 glasses heat-treated at 1100°C for 1 hr a) BC-0, b) BC-1, c) BC-5

(2) Composition of $Ba_{1-x}Ca_xTiO_3$ solid solution

The compositions of $Ba_{1-x}Ca_xTiO_3$ grown by the heat-treatment were calculated with the following relation between $\sqrt[3]{a^2\cdot c}$ and x in the same manner as decribed in the previous paper[1,3].

$$x = \frac{\sqrt[3]{a^2\cdot c}_{BaTiO_3} - \sqrt[3]{a^2\cdot c}_{Ba_{1-x}Ca_xTiO_3}}{\sqrt[3]{a^2\cdot c}_{BaTiO_3} - \sqrt[3]{a^2\cdot c}_{CaTiO_3}}$$

Where, $\sqrt[3]{a^2\cdot c}$ was calculated using d_{111} and d_{211}. The relation between y of $60[Ba_{1-y}Ca_y]TiO_3$-10 Al_2O_3-30SiO_2 glasses are shown in Fig.4. It was clarified that Ca in the glass preferentially transferred into $BaTiO_3$ crystal in the composition range of $0.0\leq y\leq 0.125$ during the heat-treatment, however even further addition of Ca to the glass didn't allow to form $Ba_{1-x}Ca_xTiO_3$ beyond x=0.225. Above result coinsides with that of solid state reaction between $BaTiO_3$ and $CaTiO_3$.

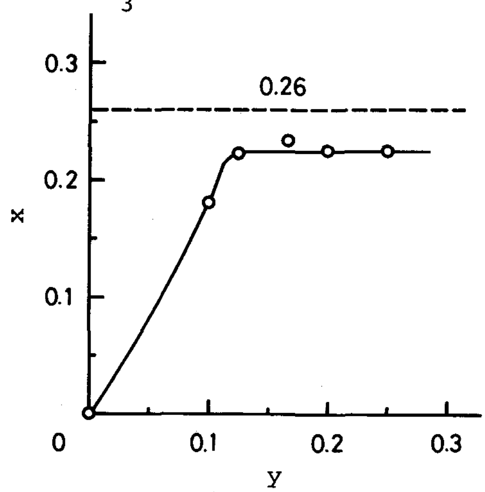

Fig.4 Relation between y of $60[Ba_{1-y}Ca_y]TiO_3$-10Al_2O_3-30SiO_2 glasses and x of $Ba_{1-x}Ca_xTiO_3$

The phase diagram of $BaTiO_3$-$CaTiO_3$ determined by DeVries and Roy[4] indicates that the formation of $Ba_{1-x}Ca_xTiO_3$ solid solution was restricted in the composition range from x=0.0 to x=0.26. Similarly, the composition of $Ba_{1-x}Ca_xTiO_3$ solid solution in the present glass-ceramics was restricted in the range up to x=0.225.

4) Dielectric properties

(1) Dielectric constant(ε)

Temperature dependence of ε for the samples crystallized at 1100°C for 1 hr are shown in Fig.5. The figure indicates that T_c is independent of CaO content in $Ba_{1-x}Ca_xTiO_3$, however ε at T_c decreases with increasing amount of CaO in glasses. The decrease of ε at T_c with y is caused by the formation of $Ba_{1-x}Ca_xTiO_3$. The compositional dependence of ε at T_c may be taken for the product of two factors, namely volume fraction of $Ba_{1-x}Ca_xTiO_3$ in the sample and its ε. From the result of X-ray diffraction, the amount of crystal grown in the glass decreases with increasing amount of CaO, and it has been known that ε of $Ba_{1-x}Ca_xTiO_3$ decreases with increasing x.

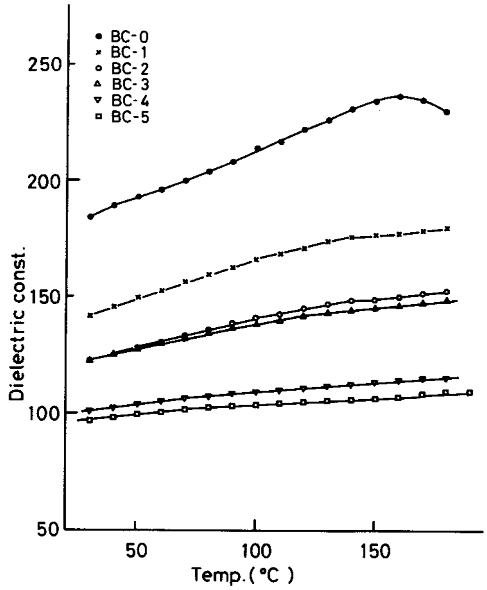

Fig.5 Temperature dependence of ε for the test glasses heat-treated at 1100°C for 1 hr

Thus, the product of above two factors indicates to depress ε with the increase of CaO amount. Above results indicate that CaO in the present glass-ceramics plays a role as 'depresser'.

(2) Frequency dependencies of ε and $\tan\delta$

Frequency dependence of ε of the present glass-ceramics are shown in Fig.6. In the frequency range from 1 k to 1 M Hz, ε decreases with increasing frequency. Fig.7 shows the frequency dependence of $\tan\delta$ in the same range. Loss tangent of the crystallized glass gradually increases with increasing frequency, the same trend is observed on the sintered ferroelectric ceramics. Comparatively high values of $\tan\delta$ may be caused by the surperposition of glassy matrix with high $\tan\delta$.

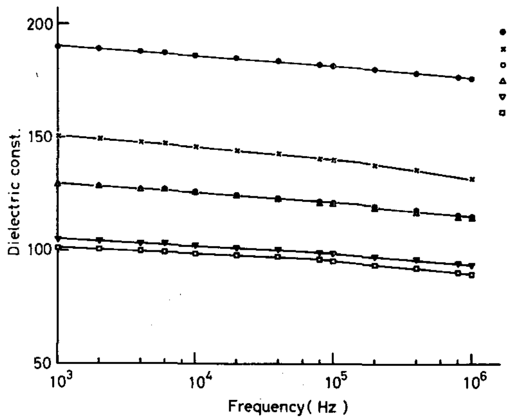

Fig.6 Frequency dependence of ε of test glasses heat-treated at 1100°C for 1 hr

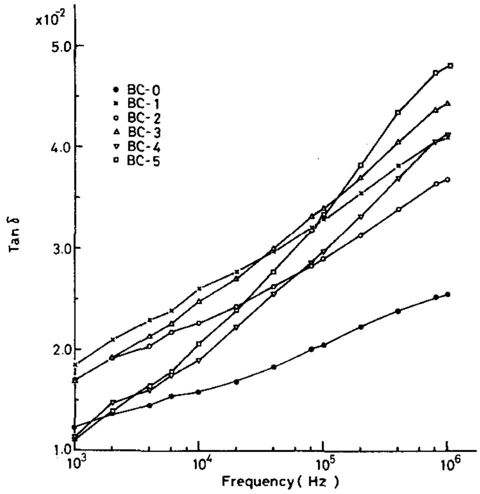

Fig.7 Frequency dependence of tanδ of test glasses heat-treated at 1100°C for 1 hr

4. Conclusion

Succeeding to a series of $60[Ba,Sr]TiO_3$-$10Al_2O_3$-$30SiO_2$ glass-ceramics, another type of glasses with the composition $60[Ba_{1-y}Ca_y]TiO_3$-$10Al_2O_3$-$30SiO_2$ were prepared and were heat-treated at 1100°C for 1 hr. Crystal phases grown in the glass-ceramics were analized, temperature and frequency dependence of ε and tanδ were measured. Following results were obtained.

1) A glass-ceramics with comparatively low temperature coefficient of ε was successfully obtained, which consisted of $Ba_{1-x}Ca_xTiO_3$ as main crystal phase.
2) β-$BaSi_2O_5$ and β-$BaAl_2Si_2O_8$ were grown as coexisting crystal phases by the heat-treatment at 1100°C for 1 hr.
3) Ca in the glass preferentially transferred into $BaTiO_3$ crystal in the composition range where y is less than 0.125, however even further addition of Ca to the glass didn't allow to form $Ba_{1-x}Ca_xTiO_3$ beyond x=0.225.
4) Curie points (T_c) of glass-ceramics were independent of the composition of $Ba_{1-x}Ca_xTiO_3$. While, ε decreased with increasing amount of CaO. Above fact indicates that CaO acts as the 'depresser' in the same manner as sintered ceramics.
5) In the range from 1 k to 1 M Hz, frequency dependencies of

tanδ for the present glass-ceramics showed the same trend as those of sintered ceramics.

References

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