Preparation and Dielectric Properties of [Ba, Ca] TiO$_3$-Al$_2$O$_3$-SiO$_2$ Glass-Ceramics

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Synopsis

Succeeding to 60[Ba,Sr]TiO$_3$-10Al$_2$O$_3$-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$_x$TiO$_3$ crystal particles in the glass system 60[Ba$_{1-y}$Ca$_y$]TiO$_3$-10Al$_2$O$_3$-30SiO$_2$ (0.0\textless{}y\textless{}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$_x$TiO$_3$ increased with increasing amount of CaO in glass up to y=0.125, and the composition of Ba$_{1-x}$Ca$_x$TiO$_3$ 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$_x$TiO$_3$, however temperature coefficients of $\varepsilon$ 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 kHz to 1 MHz.

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$_x$TiO$_3$ solid solution. While, CaO acts as the 'depresser', which causes the lower...
temperature coefficient of $\varepsilon$ by the formation of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ solid solution$^2$). In the previous paper, authors reported the preparation of the glass-ceramics in the system $60[\text{Ba}_{1-y}\text{Sr}_y]\text{TiO}_3-10\text{Al}_2\text{O}_3-30\text{SiO}_2$, and its dielectric properties. It was clarified that SrO added in the glass acted as the 'shifter' of ferroelectric glass-ceramics.

Succeeding to $60[\text{Ba},\text{Sr}]\text{TiO}_3-10\text{Al}_2\text{O}_3-30\text{SiO}_2$ glass-ceramics, glass-ceramics in the system $[\text{Ba,Ca}]\text{TiO}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ were studied. If the solid solution of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ could be grown in the glass matrix, a useful ferroelectric materials with high dielectric constant($\varepsilon$) and low temperature coefficient of $\varepsilon$ could be prepared. The present experiments were conducted to confirm such prediction and a new glass-ceramics with crystalline phase of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ was successfully elaborated in the system $60[\text{Ba}_{1-y}\text{Ca}_y]\text{TiO}_3-10\text{Al}_2\text{O}_3-30\text{SiO}_2$.

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 $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ solid solution and the dielectric properties of the present glass-ceramics.

2. Experimental

Reagent grade chemicals of $\text{BaCO}_3$, $\text{CaCO}_3$, $\text{TiO}_2$, $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ 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 $1400^\circ\text{C}$ 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 $1100^\circ\text{C}$.

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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$60[\text{Ba}_{1-y}\text{Ca}_y]\text{TiO}_3-10\text{Al}_2\text{O}_3-30\text{SiO}_2$ (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-0</td>
<td>$y=0.0$</td>
</tr>
<tr>
<td>BC-1</td>
<td>$=0.083$</td>
</tr>
<tr>
<td>BC-2</td>
<td>$=0.100$</td>
</tr>
<tr>
<td>BC-3</td>
<td>$=0.125$</td>
</tr>
<tr>
<td>BC-4</td>
<td>$=0.167$</td>
</tr>
<tr>
<td>BC-5</td>
<td>$=0.250$</td>
</tr>
</tbody>
</table>
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.

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 1 hr, and $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ were almost uniform in size ($\approx 0.2 \mu\text{m}$ in diam.).

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 $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ which peaks shifted to higher angle with increasing content of CaO in glass. Other two crystal phases were identified as $\beta$-$\text{BaSi}_2\text{O}_5$ and $\beta$-$\text{BaAl}_2\text{Si}_2\text{O}_8$. Observed crystal phases were similar to those observed on 60$\text{[Ba,Sr]TiO}_3$-10$\text{Al}_2\text{O}_3$-30$\text{SiO}_2$ 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 \( \frac{1}{a^2}c \) and x in the same manner as described in the previous paper 1, 3.

\[
x = \frac{\frac{1}{a^2}c_{BaTiO_3} - \frac{1}{a^2}c_{Ba_{1-x}Ca_xTiO_3}}{\frac{1}{a^2}c_{BaTiO_3} - \frac{1}{a^2}c_{CaTiO_3}}
\]

Where, \( \frac{1}{a^2}c \) was calculated using \( d_{111} \) and \( d_{211} \). The relation between y of 60[Ba_{1-y}Ca_y]TiO_3-10Al_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 coincides with that of solid state Fig. 4 Relation between y of 60[Ba reaction between BaTiO_3 and CaTiO_3 \( \cdot \left(1-\frac{1}{y} \right) \) 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 indicates that the formation of Ba$_{1-x}$Ca$_x$TiO$_3$ solid solution was restricted in the composition range from $x=0.0$ to $x=0.26$. Similarly, the composition of Ba$_{1-x}$Ca$_x$TiO$_3$ solid solution in the present glass-ceramics was restricted in the range up to $x=0.225$.

4) Dielectric properties

(1) Dielectric constant ($\varepsilon$)

Temperature dependence of $\varepsilon$ 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$_x$TiO$_3$, however $\varepsilon$ at $T_c$ decreases with increasing amount of CaO in glasses. The decrease of $\varepsilon$ at $T_c$ with $y$ is caused by the formation of Ba$_{1-x}$Ca$_x$TiO$_3$. The compositional dependence of $\varepsilon$ at $T_c$ may be taken for the product of two factors, namely volume fraction of Ba$_{1-x}$Ca$_x$TiO$_3$ in the sample and its $\varepsilon$. 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 $\varepsilon$ of Ba$_{1-x}$Ca$_x$TiO$_3$ decreases with increasing $x$. Thus, the product of above two factors indicates to depress $\varepsilon$ 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 $\varepsilon$ and tan$\delta$

Frequency dependence of $\varepsilon$ of the present glass-ceramics are shown in Fig.6. In the frequency range from 1 kHz to 1 MHz, $\varepsilon$ 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 $\varepsilon$ of test glasses heat-treated at 1100°C for 1 hr

Fig. 7 Frequency dependence of $\tan\delta$ test glasses heat-treated at 1100°C for 1 hr

4. Conclusion

Succeeding to a series of 60[Ba,Sr]TiO$_3$-10Al$_2$O$_3$-30SiO$_2$ glass-ceramics, another type of glasses with the composition 60[Ba$_{1-y}$Ca$_y$]TiO$_3$-10Al$_2$O$_3$-30SiO$_2$ were prepared and were heat-treated at 1100°C for 1 hr. Crystal phases grown in the glass-ceramics were analyzed, temperature and frequency dependence of $\varepsilon$ and $\tan\delta$ were measured. Following results were obtained.

1) A glass-ceramics with comparatively low temperature coefficient of $\varepsilon$ was successfully obtained, which consisted of Ba$_{1-x}$Ca$_x$TiO$_3$ as main crystal phase.

2) $\beta$-BaSi$_2$O$_5$ and $\beta$-BaAl$_2$Si$_2$O$_8$ 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$_x$TiO$_3$ beyond $x=0.225$.

4) Curie points ($T_C$) of glass-ceramics were independent of the composition of Ba$_{1-x}$Ca$_x$TiO$_3$. While, $\varepsilon$ 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
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...tanδ for the present glass-ceramics showed the same trend as those of sintered ceramics.

References