Crystallization and Analysis of Perovskite Crystals in Ferroelectric-based Glasses

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ABSTRACT

The effects of heat treatment on properties of ferroelectric materials prepared by glass-ceramic route based on two glass compositions with different ratios of glass forming oxides were studied. The compositions were Glass I: 20PbO – 20BaO – 25TiO₂ – 5Al₂O₃ – 15SiO₂ – 15B₂O₃ (mol%) and Glass II: 20PbO – 20BaO – 25TiO₂ – 5Al₂O₃ – 5SiO₂ – 25B₂O₃ (mol%). Both glasses were heat treated at 600, 700 and 800 °C for 8 h to form glass-ceramics. XRD found PbTiO₃ as the primary phase but not BaTiO₃. Ferroelectric PbTiO₃ had tetragonal perovskite structure. Increasing heat treatment temperature resulted in an increase of PbTiO₃ crystal size with an increase of c/a ratio (>1) which indicates the increase in tetragonality of PbTiO₃ phase. XRD also found crystallization of secondary phase(s) in each heat treated glass and analysis by SEM revealed that the phase composition and morphology were different for different glass compositions. The apparent densities of these glass-ceramics were found to increase with increasing heat treatment temperature due to increase amount of crystalline phases. The room temperature dielectric constants of as-annealed glasses were about 20 and increased to values of 30 – 65 for crystallized samples.

Keywords: glass-ceramics, crystallization, x-ray diffraction, electron microscopy.

1. INTRODUCTION

Crystallization of glasses in a controlled way led to a development of polycrystalline solids. These materials are known as glass-ceramics [1] which have been exploited in various applications. In the electronics industry they can be used, for instance, as an insulator for high voltages, substrates for electronic circuits, dielectrics and pyroelectric/piezoelectric devices [2-5]. The main advantage of glass over ceramic materials is the relatively simple methods which can form complex shapes, such as casting and lost wax techniques. They are pore-free and usually have fine-grained microstructures. The properties can be controlled by compositional modification and heat treatment profile [3]. In the case of crystallization of high permittivity ferroelectric phase in glasses, a number of investigations have been
carried out usually concerning \( \text{BaTiO}_3 \) [7, 8], \( \text{NaNbO}_3 \) [9], \( \text{LiNbO}_3 \) [10], \( \text{SrTiO}_3 \) [11], and \( \text{PbTiO}_3 \) [12-16]. To obtain ferroelectric phase as the main crystalline phase, some problems must be overcome such as those related to composition and methods of glass preparation. Network-forming oxides such as \( \text{SiO}_2 \) and \( \text{B}_2\text{O}_3 \) must be of sufficient amounts to ensure glass formability and composition must be carefully chosen to minimize interactions between the desired crystal phase and the residual glass or any other secondary phases [7].

This paper investigates two glass compositions in the \( \text{PbO-BaO-TiO}_2-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3 \) system.

**Glass I**: \( 20\text{PbO} - 20\text{BaO} - 25\text{TiO}_2 - 5\text{Al}_2\text{O}_3 - 15\text{SiO}_2 - 15\text{B}_2\text{O}_3 \) (mol%)

**Glass II**: \( 20\text{PbO} - 20\text{BaO} - 25\text{TiO}_2 - 5\text{Al}_2\text{O}_3 - 5\text{SiO}_2 - 25\text{B}_2\text{O}_3 \) (mol%)

They were successfully melted and cast by Sooksaen and Reaney [17]. The ratio PbO/ BaO was kept constant at 1 and the amounts of \( \text{TiO}_2 \) and \( \text{Al}_2\text{O}_3 \) were kept unchanged. The total mol% of glass-forming oxides, \( \text{B}_2\text{O}_3 \) and \( \text{SiO}_2 \) was kept the same at 30 mol% but their ratios were different. Glass I composed of equal amounts of \( \text{SiO}_2 \) and \( \text{B}_2\text{O}_3 \) where Glass II was mainly borate-based. In this study, crystallization was performed for 8h instead of shorter periods which have been studied previously [3, 15, 17]. It was assumed that longer periods of heat treatment would give less amount of residual glass. XRD was used to study phase evolution and crystal structure of the perovskite phase. Microstructures of heat treated samples were studied by SEM and compared for two different ratios of glass-forming oxides and the results were then correlated with XRD. Measurement of dielectric constants was also performed to relate results with the microstructures observed.

### 2. EXPERIMENTAL

#### 2.1 Glass Preparation

The glass batches (Glass I and Glass II) were roughly mixed from appropriate ratios of \( \text{Pb}_3\text{O}_4, \text{BaCO}_3, \text{TiO}_2, \text{Al}_2\text{O}_3, \text{B}_2\text{O}_3 \) and silica sand, \( \text{SiO}_2 \) (all with purity ≥99%) and then melted in high-grade alumina crucibles. The melting was carried out following the procedures proposed by Sooksaen and Reaney [17]. Glass of each composition was cut into small pieces and ground to smooth surface by an SiC grinding paper (No.P80) to give size ~ 8mm x 8mm x 5mm.

#### 2.2 Glass-ceramics Preparation

Differential Thermal Analysis (DTA) of as-annealed glasses was carried out on an Elmer Perkin DTA7 which was reported previously by Sooksaen and Reaney [17] to locate various thermal transitions. After crystallization temperature range was established from DTA, glass samples were then heat treated for 8 h at 600, 700 and 800°C (following DTA data ref [17]) with a heating/cooling rate 5°C/min.

#### 2.3 X-Ray Diffraction

X-ray Diffraction (XRD) was used to identify phases present in the crystallized glass-ceramics and also study crystal structures of a ferroelectric phase. Samples were analyzed as bulk on a smooth surface. The analysis were performed on a Bruker AXS D8 Discover from \( 10^\circ \) to \( 70^\circ \) 2\( \theta \) with a scan speed of 2\( ^\circ \)/min and step size 0.02\( ^\circ \) using Cu K\( _\alpha \) radiation with a wavelength of \( \lambda = 1.5406 \) Å. The samples were calibrated to account for misalignment. Software WinXpow Version 2.10A was used to refine lattice parameters of the perovskite phase from XRD patterns.

#### 2.4 Apparent Density

As-annealed glasses and heat treated samples were calculated for apparent densities and averaged and the densities were assumed...
to be 100% of theoretical density since they contained no porosity. The measurements were carried out on a Mettler Toledo precision balance using Archimedes method.

2.5 Microstructure

Glass-ceramic samples were cold mounted by epoxy resin. Surface grinding was carried out using SiC grinding paper (P1200) followed by polishing to a mirror finish using 1 mm alumina slurry. Chemical etching was required to reveal surface microstructures where the etchant used composed of concentrated HF (50%) 15 ml, concentrated HNO₃ (70%) 5 ml and deionized water 80 ml. Etching was carried out at room temperature for 90 seconds. Samples were then gold coated by a Cressing Sputter Coater 108 before analysis by Scanning Electron Microscope (SEM). Analysis was carried out using a Camscan SEM with EDAX link, operated at 10 – 20 kV. Backscattered electron (BE) mode was used to reveal microstructures and see qualitative changes in composition at the sample surface.

2.6 Dielectric Constant

The as-annealed and the crystallized glasses were ground to smooth surface using SiC grinding paper (P1200) and cleaned then electroded with high purity silver paint (SPI) on the top and bottom faces. The dielectric measurements were conducted by Hioki 3522-50 LCR HiTESTER (Japan) at room temperature and at frequency of 1 kHz.

3. RESULTS AND DISCUSSION

XRD patterns of as-annealed Glass I and heat treated samples at 600, 700 and 800°C are shown in Figure 1. As-annealed glass showed broad peak characteristic of amorphous materials. At 600°C, PbTiO₃ was the main phase that crystallized out from Glass I. There was no evidence of ferroelectric BaTiO₃ formation. This agreed with the previous studies concerning systems based on borate glass. Bhargava et al. [8] studied the crystallization of BaO-TiO₂-B₂O₃ glasses and found a strong chemical affinity between barium and boron to form compounds of

![Figure 1. XRD traces of as-annealed and heat treated Glass I BaAl₂Si₂O₈ (▲) and unidentified phase (●).](image-url)
the type BaO-B$_2$O$_3$ and BaO-TiO$_2$-B$_2$O$_3$ which suggests that substitution of PbO with BaO is unlikely to give BaTiO$_3$ in B$_2$O$_3$-based compositions. However, there are only a few studies based on compositions of silicate glasses [14-18]. Substitution of SiO$_2$ for B$_2$O$_3$ as a glass former may also permit the formation of solid solution (Pb,Ba)TiO$_3$ by reducing the affinity between barium and boron [3, 17, 18]. Therefore, solid solution formation should not be excluded. The first second phase that crystallized out alongside at 600°C was possibly barium feldspar, BaAl$_2$Si$_2$O$_8$ (●), PDF card No.28-124. This second phase seemed to dissolve as heat treatment temperature was raised. Heat treatment at 700°C found an evolution of unidentified phase (●) which remained up to 800°C. This phase could be a compound of the type BaO-B$_2$O$_3$ and BaO-TiO$_2$-B$_2$O$_3$ as mentioned earlier.

XRD patterns of as-annealed Glass II and heat treated samples at 600, 700 and 800°C are shown in Figure 2. This as-annealed glass also showed amorphous nature (broad XRD peak). At 600°C, PbTiO$_3$ was the main phase that crystallized out from Glass II. There was still no evidence of ferroelectric BaTiO$_3$ formation although solid solution should not be excluded. There was also crystallization of an unidentified phase (●) at 600°C and this phase remained upon heat treatment to 800°C. Heat treatment at 700°C and above also led to the formation of third phase possibly BaTiB$_2$O$_6$ (●), PDF card No.35-825.

As far as the crystal structure of perovskite phase was concerned, XRD peaks were refined against tetragonal structure of PbTiO$_3$. Heat treatment at 600°C and above showed an increase in peak splitting of the {h00} and {hh0}, leading to an increase in tetragonality of the perovskite phase. Figure 3 shows enlarged XRD traces of {hh0} peak splitting as a function of heat treatment temperature for heat treated Glass I and Glass II. It can be seen that the splitting has increased.

**Figure 2.** XRD traces of as-annealed and heat treated Glass II Unidentified phase (●) and BaTiB$_2$O$_6$ (●).
Figure 3. Enlarged XRD traces showing \{hh0\} peak splitting as a function of heat treatment temperature (a) heat treated Glass I and (b) heat treated Glass II.

**Table 1.** Lattice parameters, unit cell volume and c/a ratio for the perovskite phase in heat treated Glass I.

<table>
<thead>
<tr>
<th>Cell parameters</th>
<th>Heat treated Glass I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600 °C/8h</td>
</tr>
<tr>
<td>a /Å</td>
<td>3.9298(19)</td>
</tr>
<tr>
<td>c /Å</td>
<td>4.069(3)</td>
</tr>
<tr>
<td>unit cell volume (a^3c) /Å³</td>
<td>62.84(5)</td>
</tr>
<tr>
<td>c/a</td>
<td>1.035</td>
</tr>
</tbody>
</table>

**Table 2.** Lattice parameters, unit cell volume and c/a ratio for the perovskite phase in heat treated Glass II.

<table>
<thead>
<tr>
<th>Cell parameters</th>
<th>Heat treated Glass I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600 °C/8h</td>
</tr>
<tr>
<td>a /Å</td>
<td>3.9264(15)</td>
</tr>
<tr>
<td>c /Å</td>
<td>4.0737(21)</td>
</tr>
<tr>
<td>unit cell volume (a^3c) /Å³</td>
<td>62.80(4)</td>
</tr>
<tr>
<td>c/a</td>
<td>1.038</td>
</tr>
</tbody>
</table>
upon increasing heat treatment temperature. Refined lattice parameters, unit cell volume and $c/a$ ratio for the perovskite phase of heat treated Glasses I and II are shown in Tables 1 and 2, respectively. In general, the $c/a$ ratio and the unit cell volume increased with increasing heat treatment temperature, until values of 1.049 and 63.25 Å³ and 1.050 and 62.88 Å³ were attained for glass-ceramics I and II, respectively. An increase in the unit cell volume with increasing $c/a$ ratio in the tetragonal phase supports previous studies on lead titanate ceramics \[19, 21\]. The effect of the ratio of glass-forming oxides on the $c/a$ ratio between the two glass-ceramic compositions was, however, not significant and therefore difficult to compare.

Following previous studies on ferroelectric based glass-ceramics, crystal clamping by residual glass is responsible for reduced $c/a$ ratio where Grossman and Isard \[13\] first found a slight increase in the $c/a$ ratio by XRD after leaching in acid for 2 h. Another factor that may have reduced the $c/a$ ratio of ferroelectric PbTiO$_3$ is the effect of impurities that form solid solution within the ferroelectric phase such as Ba and Al. Further transmission electron microscopy analysis and impedance study are required to detect solid solution \[3\].

The apparent densities of the as-annealed Glass I and Glass II were 4.87(±0.01) and 4.79 (±0.01) g.cm$^{-3}$, respectively but in general increased with increasing heat treatment temperature, (see Figure 4). The increase in density may be due to sample shrinkage driven by an increase in the volume fraction of crystalline as opposed to glassy phase(s). When compared the two heat treated compositions with different ratios of glass-forming oxides it was found that at 800°C the density of heat treated Glass II dropped below heat treated glass I. The reason for the decrease was so far not known but may be related to type and volume fraction of crystalline phases.

Microstructural analyses of heat treated Glasses I and II are shown in Figures 5 and 6, respectively. Chemical etching during sample preparation was sufficient to discern microstructures. However, heat treatment at 600°C for each glass revealed large amount of residual glass within the resolution of a Camscan SEM. Although, residual glass resulted in

![Figure 4. Density of heat treated Glasses I and II for 8h from 600°C to 800°C.](image-url)
unclear images, it was presumed that crystals dispersed within a glassy matrix which had been etched away.

It can be seen under backscattered electron mode that Glass I heat treated at 600°C (Figure 5a) showed three different contrasts possibly from different crystal types and residual glass. These were shown as dark region, light region and needle-like crystals. Qualitative chemical analysis by energy dispersive x-ray spectroscopy, EDS (not shown), revealed dark region of rounded crystals composing mainly of Pb and Ti which are responsible for the main ferroelectric phase. Although EDS analysis within the resolution of SEM found other small peaks such as Si, Al and Ba, it could be attributed to contamination from surroundings due to large spot size of electron beam. Because of small crystal sizes, transmission electron microscope would be helpful to study in more detail of the phase composition in glass-ceramics. The size of ferroelectric crystals varies from 0.3 – 1 μm where the needle-like crystals were about 1 μm in length. Light region could have been either residual glass or the first second phase found in XRD.

In Glass I heat treated at 700 and 800°C (Figures 5b and 5c) the ferroelectric crystals and needle-like crystals only increased slightly in size and length. The largest crystal detected had size just above 2 mm.

Glass II heat treated at 600, 700 and 800°C (Figures 6a, 6b and 6c) generally showed

![Figure 5](image_url)

**Figure 5.** Back scattered electron (BE) images of Glass I heat treated 8h (a) 600°C, (b) 700°C and (c) 800°C.
only one contrast under electron backscattered mode. It was difficult to discern whether it was the main ferroelectric phase or second phase(s) because EDS analysis (not shown) revealed similar traces and also difficult to avoid contamination from surroundings. The correlation to XRD data was then difficult to be made. Residual glass was observed mainly on samples heat treated at 600 °C due to incomplete surface etching. Although the crystal types were difficult to distinguish in these glass-ceramic samples, it was possible to mention that the size of crystal increased with increasing heat treatment temperature which varies from 0.5 – 2 μm.

For as-annealed glasses the values of room temperature dielectric constant at 1 kHz were measured to be 20 (±2) and 21 (±2) for Glass I and Glass II, respectively. Figure 7 shows the dielectric constant, $\varepsilon_r$, at 1 kHz as a function of heat treatment temperature for crystallized Glass I and Glass II. The dielectric constants increased after crystallization for 8 h, indicating that crystalline phase(s) especially the presence of ferroelectric phase as opposed to glassy phase [3, 15, 22] had an effect of raising dielectric constant values. In Glass I, the dielectric constant increased from 20 for as-annealed glass to 56 when heat treated at 600°C and continued rising to 65 at 700°C. This increase may have come from the increased amount of ferroelectric PbTiO$_3$ phase as observed by SEM (Figure 5). Above 700°C, however, the dielectric constant decreased to 45. This drop may be due to the presence of needle-like second phase which has dielectric constant value smaller than that of a ferroelectric phase. From SEM (Figure 5) it was observed that the amount of this second phase seemed to increase with
Figure 7. Dielectric constant (at 1 kHz) as a function of heat treatment temperature for crystallized Glass I and Glass II.

In Glass II, the dielectric constant increased from 21 for as-annealed glass to 29, 40 and 64 when heat treated at 600, 700 and 800°C respectively. In this composition the dielectric constant has a trend to increase with increasing heat treatment temperature. However, when comparing the two crystallized compositions it was found that the borate-based composition (Glass II) generally had the dielectric constant value lower than that of Glass I ($\text{SiO}_2/\text{B}_2\text{O}_3$ ratio = 1) especially at heat treatment temperature below 700°C. This smaller value may be due to various effects such as types and amounts of crystalline phases and residual glass, crystal sizes, crystal clamping effect, heterogeneity in glass-ceramics and space charge effects arising from residual glasses [3, 13, 15, 22, 23]. So far, studies related to dielectric properties in glass-ceramics have shown various results with no definite conclusions due to the effects mentioned above.

4. CONCLUSIONS

Heat treatment of Glass I and Glass II for 8 h at 600, 700 and 800°C resulted in crystallization of glass-ceramics whose main phase was perovskite PbTiO$_3$ with tetragonal structure. The $c/a$ ratio and unit cell volume of the perovskite phase increased with increasing heat treatment temperature indicating the increase in tetragonality. Secondary phases that crystallized out from the two glass compositions were different in both phase composition and morphology as a result of different ratio of glass-forming oxides ($\text{SiO}_2/\text{B}_2\text{O}_3$). Densities of crystallized samples of both compositions were higher than the parent glasses. The increase in density with heat treatment temperature was due to the increase of crystalline as opposed to glassy phase/s. The room temperature dielectric constants at 1 kHz of as-annealed glasses were about 20 and the values increased for crystallized samples and varied in the range of 30 – 65. The increase in dielectric constant was mainly due to the presence of ferroelectric phase as opposed to residual glass phase.

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