J Mater Sci (2008) 43:1265–1269
DOI 10.1007/s10853-007-2213-6

Thermal analysis and phase evolution of ferroelectric $PbTiO_3$ obtained from silicate and borate based glasses

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Received: 10 September 2007 / Accepted: 8 October 2007 / Published online: 4 December 2007

Abstract This article assessed the glass formability for crystallization of lead titanate ($PbTiO_3$) as the primary phase. It was found that silicate-based glasses formed glass as a block without the need for cold splatting, but B_2O_3-based glasses needed to be prepared by cold splatting to retard devitrification. Also, incorporation of BaO was favoured by an increase in the concentration of B_2O_3. DTA showed the crystallization of crystalline phases occurred above glass transition temperature. XRD traces supported the DTA data where the first exothermic peak in each case was presumed to be related to the crystallization of $PbTiO_3$ (PT) phase. XRD also showed the lower c/a ratios compared to pure PT ceramic, which suggested three possibilities for lower values: crystal clamping by the rigid glass matrix, intrinsic size effect and incorporation of impurities in the PT phase.

Introduction

$PbTiO_3$ (PT) is a typical ferroelectric material with the perovskite structure. It undergoes a first-order phase transition, $T_c \sim 490$ °C above which the structure is cubic but below is tetragonal. The large ionic displacements in PT at T_c lead to a particularly large room temperature spontaneous polarization (>53 μC/cm^2), the largest in the perovskite family [1]. PT exhibits large pyroelectric coefficients, low relative permittivity (~100–200) and dielectric properties stable with time, temperature and frequency. These properties make PT an attractive material for pyroelectric and electro-optical applications [2–4]. Undoped PT is difficult to form as a ceramic body due to its large crystal anisotropy (c/a ~1.06) and breaks into pieces on cooling below T_c. This has limited the applications of undoped PT ceramics. The glass-ceramic route, therefore, offers the possibility of fabricating PT without cracking.

Glass-ceramics are polycrystalline solids prepared by the controlled crystallization of glasses [5]. Many glass-ceramics have been investigated for use in the electronic industry due to advantages for preparing complex, large, fine-grained microstructures and pore-free bodies [6]. The applications include, for example [7–13], materials used in substrate applications, dielectric, pyroelectric/piezoelectric and optical devices. New glass forming techniques have led to a wide range of glass forming materials and as a result, new materials for a number of electronic applications are being fabricated. However, due to the limited number of published investigations the development in this area is still slow and a better understanding into the relationships between glass formation, crystallization, microstructure and electrical properties is still required.

Studies relating to nucleation of high-permittivity ferroelectric crystals in glasses have been carried out since the early 1960s. Ferroelectric crystalline phases investigated $SrTiO_3$, $BaTiO_3$, $LiTaO_3$, $LiNbO_3$, $NaNbO_3$, $KNbO_3$, $PbTiO_3$, PZT, $(Pb,Sr,Ba)Nb_2O_6$ [135] and strontium barium niobate (SBN) [14–24].

In this work, a series of glass compositions were melted and glass formation had been assessed for further compositional modification. The crystallization to form $PbTiO_3$

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based glass-ceramics was carried out via thermal treatment following the differential thermal analysis (DTA) data. This work followed closely a glass composition suggested by Shyu and Yang [24] based on PbO–BaO–TiO_2–B_2O_3–Al_2O_3–SiO_2 as a starting point. Their composition was claimed to undergo bulk crystallization to give high volume fraction of $PbTiO_3$ (~40 vol%).

Experimental

Glass batch preparation

For each glass composition (Table 1), the batch was made according to the calculation to give approximately 200 g total weight. This amount was enough to produce a glass block or a thin slab of glass. The appropriate ratios of raw materials (Table 1) were weighed out on a precise balance and mixed by hand.

Glass melting

After rough mixing, the glass batch was transferred to a platinum crucible for melting. Platinum was selected to avoid corrosion of the crucible, which commonly occurs with, e.g. alumina when melting compositions containing lead oxide at high temperatures. Lead (II) oxide, PbO, was not selected as a source of Pb because it evaporates easily above 886 °C and hence leads to lead loss. PbO also increases the possibility of reduction to metallic lead and subsequent reaction with the platinum crucible. Instead, Pb_3O_4 was used as a source of lead, which was assumed to reduce to a +2 oxidation state at the melt temperature.

The melting was carried out in an electric furnace for 2 h at 1,200–1,250 °C depending on the composition using a platinum paddle stirrer after 1 h at ~50 rpm. Stirring was necessary to instil homogeneity into the glass melt.

Glass formation

Two techniques were employed to form clear glass. The first technique involved pouring the melt onto a preheated metal block. The glass block was quickly transferred to a preheated muffle furnace for annealing to reduce internal stresses within the glass block. Annealing was carried out at 500–550 °C for 1 h followed by cooling to room temperature at 3 °C/min. The second technique involved rapid quenching to retard devitrification (uncontrolled crystallization) and ensure clear glass. Quenching was carried out by pouring the melt onto a cold steel plate and then immediately pressing another cold plate onto the glass for 2 s before withdrawing. A thin slab of homogeneous glass was produced in this way.

Differential thermal analysis

Differential thermal analysis (DTA) was used to establish chemical and physical transformation temperatures such as the glass transition temperature (T_g), various crystallization temperatures and melting temperature. In this study, DTA was performed on a Perkin Elmer DTA7 (Boston, USA). For each DTA run, approximately 25 mg of a fine glass powder was filled into a small alumina crucible and heated in air with a heating rate of 10 °C/min against an Al_2O_3 control powder.

X-ray diffraction

X-ray diffraction (XRD) was used to identify phases present in selected glass-ceramic samples. A Philips PW1373 (Holland) diffractometer operated at 40 kV and 30 mA was used. The data were collected in reflection mode at room temperature and scanning was carried out from 10° to 80° with a scan speed of 1°/min and step interval 0.02° using Cu K_α radiation with a wavelength of

Table 1 Glass compositions melted in mol% oxide

Oxide	PbO	BaO	TiO_2	Al_2O_3	B_2O_3	SiO_2
Glass A	39	1	25	9.8	1	24.2
Glass B	30	10	25	9.8	1	24.2
Glass C	20	20	25	9.8	1	24.2
Glass D	39	1	25	9.8	24.2	1
Glass E	39	1	25	5	25	5
Glass F	39	1	25	5	25	5
Glass G	20	20	25	5	25	5
Glass H	20	20	25	5	15	15

$\lambda = 1.5405$ Å. The diffractometer was interfaced with Hiltonbrooks software for data collection. Sample preparation for XRD was carried out on finely ground powders.

Results and discussion

Glass formation

Results of glass formation, appearance and colour are shown in Table 2. Composition A was similar to that proposed by Shyu and Yang [20, 24] and formed a glass without cold splat quenching onto a steel plate. No sagging was observed on cooling. Compositions B and C retained the same silicate concentration as A but the PbO:BaO ratio decreased. However, after melting for 2 h, unreacted batch was still present and it was concluded that these compositions were outside of the glass-forming region. BaO is generally more refractory than PbO, which may account for the lack of glass formability. Composition D is similar to A, except the SiO_2 network has been largely replaced by B_2O_3. The glass melt was consequently more fluid than A at the equivalent temperature and easy to pour. However, pouring into a steel block mould resulted in devitrification and therefore a cold splatting technique was adopted to increase the quench rate and retain an amorphous structure.

Compositions E and F retained the same PbO, BaO and TiO_2 concentrations as A and D but they were composed of a mixture B_2O_3 and SiO_2 network former, in addition to a reduction in the Al_2O_3 content. These two compositions melted readily but required cold splatting to retard devitrification.

Compositions D, E and F demonstrated that B_2O_3 decreased the viscosity of the melt. It was postulated therefore, that more fluid B_2O_3 containing melts could more readily dissolve BaO than the more viscous silicate-based melts. Compositions G and H were therefore produced and, provided that they were cold splatted on casting, formed glass.

Table 2 Glass formation, appearance and colour

Composition	Forming technique	Appearance and colour
A	Casting	Clear glass block, dark yellow/orange
B	N/A*	Unreacted batch
C	N/A	Unreacted batch
D	Quenching	Thin glass slab with some devitrified parts, yellow
E	Quenching	Thin but unclear glass slab, yellow
F	Quenching	Thin but unclear glass slab, yellow
G	Quenching	Thin with some devitrified parts, pale yellow
H	Casting or quenching	Clear glass block or thin slab, pale yellow

* N/A = not applicable

Differential thermal analysis

Figure 1 shows the DTA traces for glasses A, D, E, F, G and H, respectively. Endothermic minima represent the glass transition temperature T_g and exothermic peaks were related to either phase separation or crystallization. In general, glasses with higher SiO_2 rather than B_2O_3 concentration have higher T_g's and no exothermic peaks were observed in any glasses above 800 °C. Glasses A and D both revealed three sharp exothermic peaks, probably related to the crystallization of three different phases. Endothermic peaks at about 1120 °C in glass A and at about 1000 °C in glass D were related to the melting point of the glass (T_m) and/or one of the crystalline phases.

Five exothermic peaks were observed for Glass E whereas Glass F showed only one sharp peak. DTA traces of glass G and glass H showed at least four different peaks assumed to be associated with four crystallization events. Glass G and H had higher T_g than glass E and F and it was concluded that decreasing the PbO:BaO ratio increased glass transition temperature.

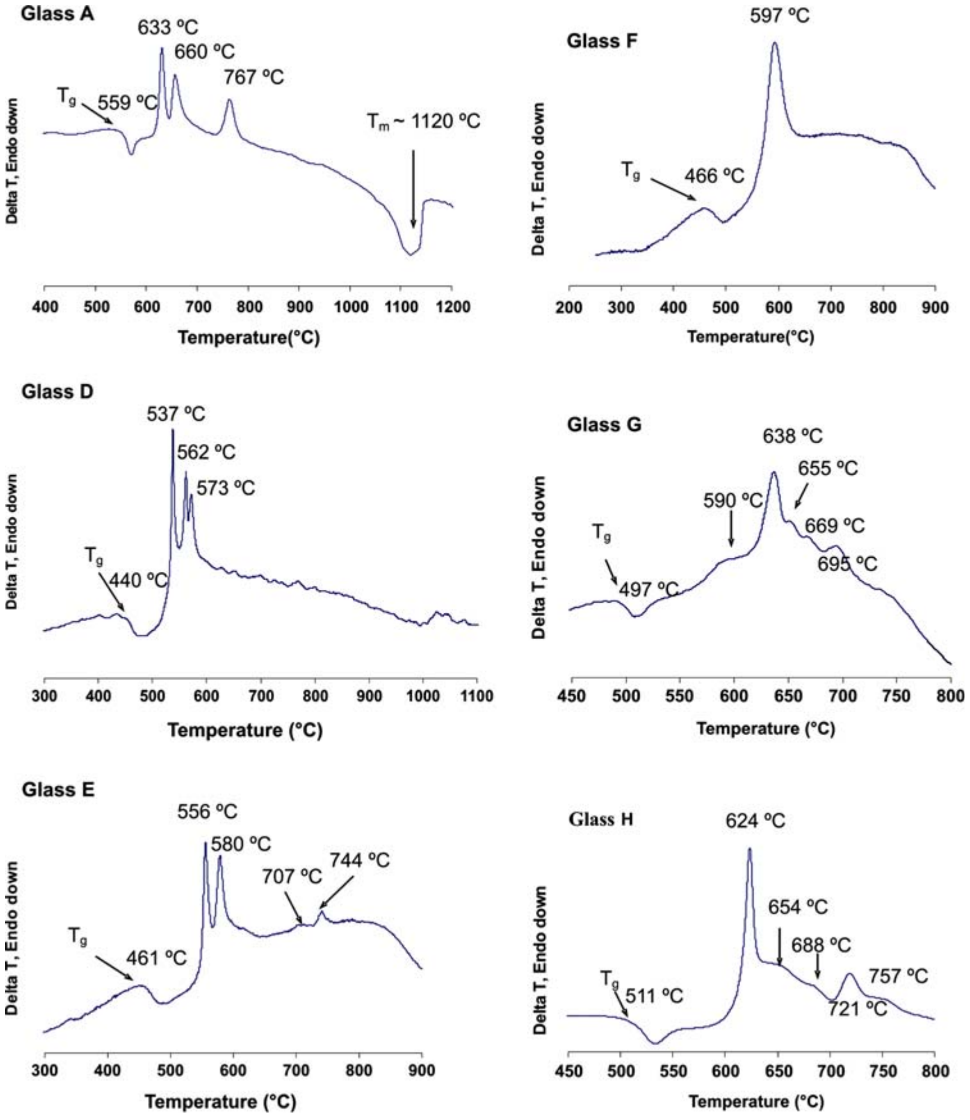
It was evident from the glass melting and DTA data presented in Fig. 1 that the six compositions which successfully formed glasses crystallized readily on heating, giving rise to a large first exotherm at $\sim$530–630 °C, was presumable related to $PbTiO_3$ in each case.

X-ray diffraction

Two glass compositions were selected for XRD (Fig. 2) analysis. The logical choices were glass A, the original silicate-based composition, similar to that suggested by Shyu and Yang [24] and glass D, the lowest T_g composition, in which the network former, SiO_2 in glass A was replaced by B_2O_3.

XRD traces 1 and 2 were for as-annealed glasses A and D, respectively. The broad XRD hump indicates amorphous nature of material. XRD traces of glass A heat-treated at 600 and 900 °C are shown in traces 3 and 4, respectively. PT is the first phase to crystallize at 600 °C. The peaks are characteristic of cubic rather than tetragonal PT since there is no peak splitting of any reflections (c/a $\sim$1.00). As temperature increases, e.g. at 900 °C, separation of the {hh0} and {h00} doublets occurs, characteristic of tetragonal PT. At 900 °C, c/a ratio of PT was 1.052 and an additional phase was found, possibly $PbAl_2Si_2O_8$ (lead

Fig. 1 DTA traces for glasses A, D, E, F, G and H



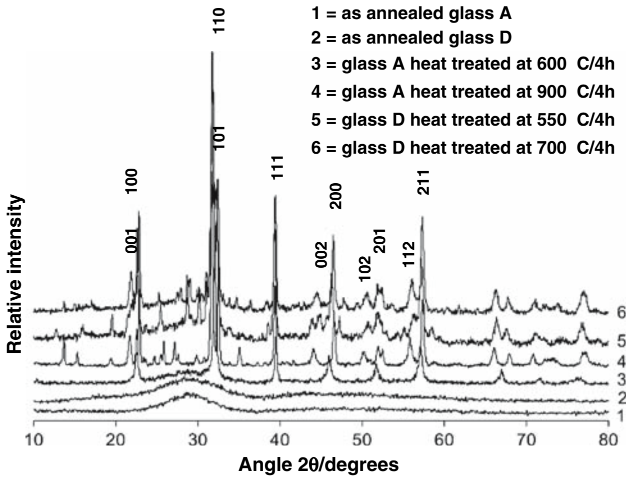


Fig. 2 XRD traces of selected samples: as annealed and heat-treated glasses A and D. Peaks for PT phase were indexed only

aluminium silicate or lead feldspar, JCPDS card No. 25–428).

Although, the XRD data were obtained from isothermal holds and the DTA traces from a heating rate of 10 °C/min, it was reasonable to attribute the exothermic peaks observed in the DTA trace of glass A (Fig. 1) to the crystallization of PT (633 °C), the unknown transient phase (660 °C) and $PbAl_2Si_2O_8$ (767 °C). It should be noted, however, that when sufficient time for crystallization was allowed during isothermal holds, PT crystallized at a lower temperature than observed by DTA.

A c/a ratio ~1.00 in samples heat-treated at 600 °C may be explained either in terms of clamping from the surrounding matrix, finite size effects or the formation of a perovskite solid solution with an intrinsically low c/a ratio [20, 22, 24–28].

XRD traces of glass D heat-treated at 550 and 700 °C are shown in traces 5 and 6, respectively. At 550 °C, PT has tetragonal structure with small c/a ratio of ~ 1.03. As temperature increased to, e.g. 700 °C, the separation of the $\{hh0\}$ and $\{h00\}$ doublets increased slightly to 1.044. The increase in c/a ratio of the borate-based glass-ceramics was not so significant when compared to silicate-based glass-ceramics. At 550 °C, additional peaks were observed and were attributed to a transient phase, which disappeared at 700 °C. This last phase to crystallize was possibly $PbTi_3O_7$ (JCPDS card No. 45–533).

Similar to glass A, in heat-treated glass D it was reasonable to attribute the three exothermic peaks observed in the DTA trace of glass D (Fig. 1) to crystallization of $PbTiO_3$ (537 °C), the transient phase (573 °C) and $PbTi_3O_7$.

Conclusions

The results from glass melting can be summarized as follows:

(1) Silicate-based melts based on the works of Shyu and Yang formed glass as a block without the need for cold splatting.
(2) B_2O_3-based glasses needed to be prepared by cold splatting instead of casting as a block.
(3) Incorporation of BaO was favoured by an increase in the concentration of B_2O_3.

The results from DTA showed that the borate-based glass has the lowest glass transition temperature, T_g and the crystallization of crystalline phases occurred above this temperature. XRD traces supported the DTA data and the first exotherm in each case was presumed to be related to the crystallization of PT phase. XRD also showed the lower c/a ratio compared to pure PT ceramic (1.06), which suggested three possibilities for lower values: crystal clamping by the rigid glass matrix, intrinsic size effect and incorporation of impurities in the PT phase.

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