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Effect of MgO addition on the properties of PbO –TiO_2–B_2O_3 glass and glass–ceramics

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Abstract

Glass samples with composition of $(50-X)$ PbO–X MgO–25 TiO_2–25B_2O_3 (where $X=0$, 5, 10 and 15 mol%) were prepared using conventional quenching technique. The amorphous nature of glass samples were confirmed by XRD. The glass transition temperature, T_g and crystallization temperature T_c were determined from the DTA. It has been observed that the addition of MgO enhances the T_g. The rise in T_g with MgO content may be attributed to the greater field strength of Mg^{2+} cation (as compared to Pb^{2+}) which leads to the formation of stronger bonds. These glass samples were converted to glass–ceramics by following a two-stage heat treatment schedule. It was observed that there was good correlation between the density and CTE results of the glass–ceramics. The XRD results revealed the formation of tetragonal lead titanate as a major crystalline phase in the glass–ceramics. The addition of MgO to the glass contributes to the formation of MgB_4O_7. The dielectric constant for all the glass–ceramic samples was observed to be higher than that of corresponding glass samples. Further, with addition of MgO the room temperature dielectric constant for glass–ceramic samples increases up to 10 mol% of MgO and then decreases for 15 mol%. It has been further observed that the variation of dielectric constant of glass–ceramic samples with MgO content is exactly opposite to the variation of crystallite size of $PbTiO_3$ embedded in the glass ceramic-samples.

Keywords: C. Dielectric properties; D. MgO; Glass–ceramics

1. Introduction

Glass–ceramic processing can be used to form solids with zero porosity, very small crystals and in complex shapes which are not readily obtained by other methods. As a result, the glass–ceramic process appears to be ideal for forming ferroelectric ceramic products. The other unique characteristics, such as no ageing or depoling problems and good stability at high temperature, high-pressure and in harsh environments, make glass ceramics attractive for use in variety of applications. Realizing the advantages of the glass–ceramic process, several attempts have been made to produce glass–ceramics having high permittivity, low dielectric loss, high electrical resistance and high dielectric breakdown strength by precipitating ferroelectric phases such as $BaTiO_3$, $LiTaO_3$, $NaNbO_3$, Pb_5GeO_{11}, $LiNbO_3$, $SrTiO_3$, $KNbO_3$, $K(Na,Nb)O_3$, $Pb(Zr,Ti)O_3$ and $PbTiO_3$ in the glassy matrix.

However, the systematic study of properties of $PbTiO_3$ based glass-ceramics containing MgO has not been reported so far. Hence, in the present work MgO has been added as a modifier in glass matrix with an idea to restrict the volume fraction of residual glass phase and to improve dielectric and thermal properties of $PbTiO_3$ based glass–ceramics.

2. Experimental

Glasses with composition $(50-X)$ PbO–X MgO–25 TiO_2–25 B_2O_3 (where $X=0$, 5, 10 and 15 mol%) were prepared from the high purity ingredients heated in an alumina crucibles at 1373 K–1523 K for 1 h. The melt was homogenized by stirring it before quenching into aluminum mold at room temperature. The resultant glass samples were

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annealed at 573 K for 4 h to remove the residual stresses. T_g and T_c for the glass samples were determined from DTA (Perkin Elmer, DTA7). The conversion of glass samples into glass–ceramics was done using two stage heat treatment (i.e., 733 K for 14 h and 793 K for 14 h). The optimization of nucleation and crystallization schedule has been reported [1] in detail for glass sample $X=0$. The density of glasses and glass–ceramics were measured using Archimedes principle with toluene as immersion liquid. Coefficient of Thermal Expansion (CTE) was measured using Orton Dilatometer (DIL 2010). The XRD patterns of glass and glass–ceramics recorded with Xpert PANalytical diffractometer. The dielectric measurements for different glass and glass–ceramic samples were carried out at different temperatures as a function of frequency by high resolution dielectric analyzer (Novo control systems) over a frequency range 1 mHz–1 MHz. Ferroelectric hysteresis measurements were performed using TF Analyzer 2000 (aixACCT Systems).

3. Results and discussions

All the quenched glass (G) samples were transparent yellow in color. The values of T_g, T_c, CTE and density of glass and glass–ceramics (GC) are given in Table 1.

It may be observed from the Table 1 that with the addition of MgO both the T_g and T_c initially decrease for sample containing 5 mol% MgO and subsequently increase. The increase in T_g with MgO content may be attributed to the greater field strength of Mg^{2+} cation as compared to Pb^{2+} which leads to the formation of stronger bonds (conversion of BO_3 to BO_4 units). It can be also observed from Table 1 that the values of CTE for glass–ceramic samples are lower than those of corresponding glass samples.

It is evident from Table 1 that for glass samples the density (g/cc) increases initially with addition of MgO upto 5 mol% and beyond that it decreases. The increase in density for glass samples may be attributed to the conversion of planar BO_3 units to BO_4 units. The decrease in density for glasses with 15 mol% MgO addition may be due to the replacement of heavier PbO by lighter alkaline earth oxide MgO. Further addition of alkaline earth oxide (MgO) may be creating more non bridging oxygens (NBO) thereby weakening the glass structure. The density of glass–ceramic samples is found to be higher than those of as-annealed glass samples. This is due to the precipitation of crystalline phases in glass matrix, thereby reducing the voids in the glass network while getting converted to glass–ceramic. When the value of density increases for a glass–ceramic sample, it indicates that the structure becomes more rigid and there is a decrease in CTE value as shown in Fig. 1.

The XRD (Fig. 2) analyses show that all the major crystalline peaks of all glass–ceramic samples of this series are identified to be that of tetragonal $PbTiO_3$ phase (JCPDS 06-0452). MgO addition resulted in the formation of minor phase, which is identified as MgB_4O_7 phase (JCPDS 31-0787) using the standard ICDD data. It is also observed that there are few low intensity peaks which are ascribed to lead borate phase (JCPDS 84-2152). Gomaa et al. [2] have also reported the formation of MgB_4O_7 phase, in lead alumino borosilicate glass–ceramics containing magnesium.

The amount of volume fraction of crystalline phase X_c, was calculated by comparison of integral intensities from X-ray diffraction patterns of amorphous and completely crystalline samples as per the method reported by Ilinsky et al. [3]. It can be observed (Fig. 3) that the volume fraction of $PbTiO_3$ crystalline phase decreases with increase in MgO content. This may be attributed to increase in secondary phase (MgB_4O_7) at the cost of $PbTiO_3$ phase.

It can be observed from Fig. 4(a) and (b) that the variation of dielectric constant and dielectric loss for glass–ceramic sample $X=10$ with temperature at fixed frequencies 1, 10, 100 KHz and 1 MHz show nearly constant values upto 300 °C and thereafter show a significant increase. Upto 300 °C, the polarization remains small as the dipoles cannot respond easily to the applied external electric field. After this temperature, the dipoles start responding to the external electric field giving high values of dielectric constant and dielectric loss. Thus, the temperature dependence of dielectric constant and dielectric loss becomes significant above 300 °C. This may be attributed to increased interfacial polarization [4] at higher temperature. Due to this effect the frequency dependence of dielectric constant and dielectric loss show a remarkable dispersion in low frequency region at higher temperatures. Similar results have been observed for all other samples in the present work.

It is found (Fig. 5) that the room temperature dielectric constant for glass–ceramic samples increase up to 10 mol%

Table 1
T_g, T_c, CTE and density of series $(50-X)$ PbO–X MgO–25 TiO_2–25 B_2O_3.

X (MgO mol%)	T_g (K)	T_c (K)	CTE (G) (10^{-6}/K)	CTE (GC) (10^{-6}/K)	ρ (G)	ρ (GC)
0	731	875	8.44	5.21	4.98	5.62
5	723	867	8.25	5.15	5.58	5.90
10	730	873	8.61	5.89	5.39	5.63
15	745	879	8.32	5.63	5.20	5.43

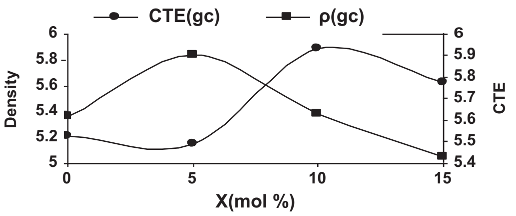

Fig. 1. Variation of density and CTE of glass–ceramics with X (mol%).

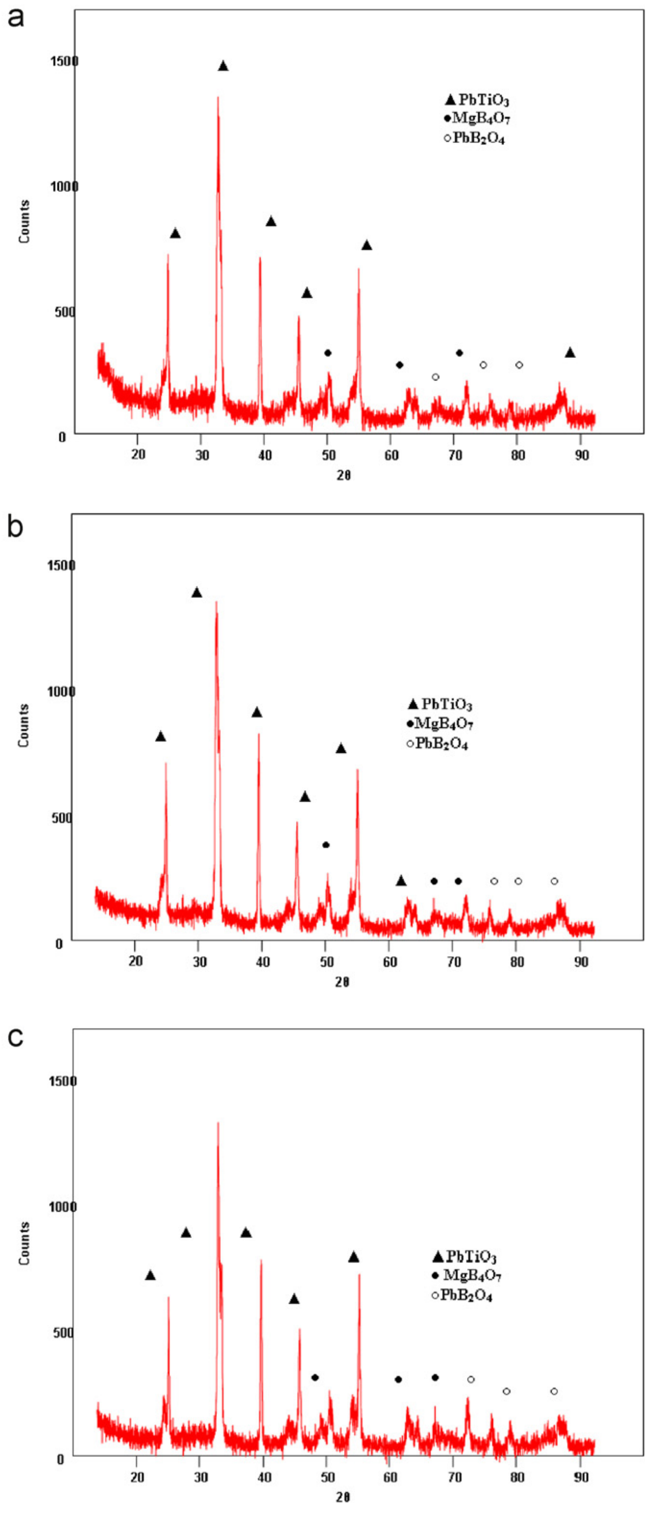

Fig. 2. XRD of glass–ceramic samples with (a) $X=5$ mol%, (b) $X=10$ mol% (c) $X=15$ mol%.

MgO addition and then decreased further addition of 15 mol%. It has been further observed that the variation of room temperature dielectric constant of glass–ceramic samples with MgO content is exactly opposite to variation of crystallite size of $PbTiO_3$ embedded in the glass–ceramic samples as shown in Fig. 5. The crystallite size was

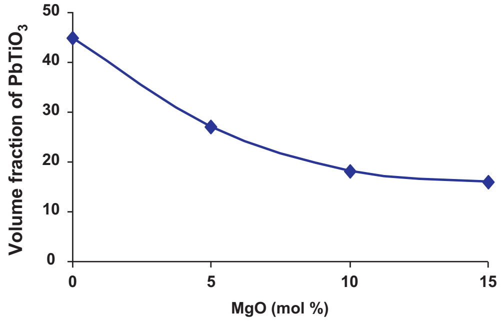

Fig. 3. Variation of volume fraction of $PbTiO_3$ with MgO addition.

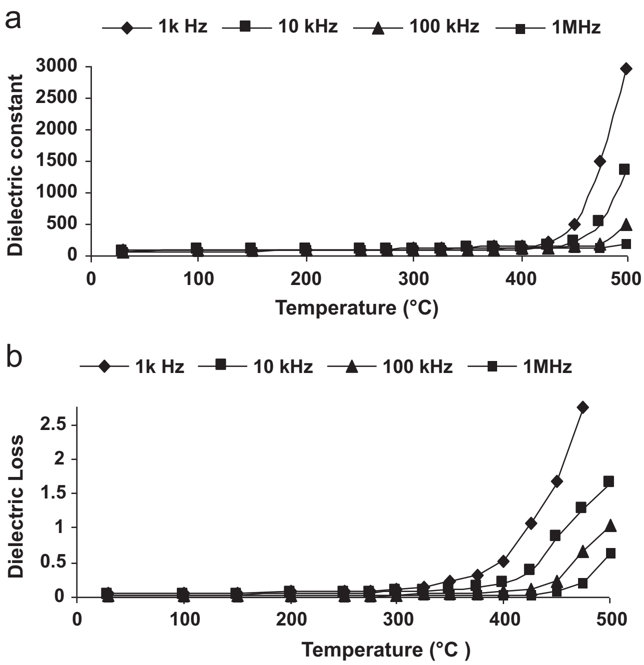

Fig. 4. (a) Variation of dielectric constant with temperature for glass–ceramic $X=10$ at different frequencies, and (b) variation of dielectric loss with temperature for glass–ceramic $X=10$ at different frequencies.

calculated from the XRD patterns using Scherrer's formula. It was observed that smaller the crystal size, higher was the dielectric constant. It has been reported [5] that the smaller the size of crystallite of ferroelectric phase embedded in glass matrix; the higher the dielectric constant. Niyompan et al. [6] have also reported similar results for ferroelectric glass–ceramics in Na_2O–Nb_2O–Al_2O_3–SiO_2 system. It may be noted that several factors such as grain size, its distribution and morphology, secondary phases, crystal clamping and interconnectivity of crystallites in the glass matrix affect the value of dielectric constant.

Observation of a hysteresis loop between polarization and electric field is the true test of the presence of ferroelectricity in a given material. A representive ferroelectric hysteresis loop for glass–ceramic sample $X=5$ is given in Fig. 6.

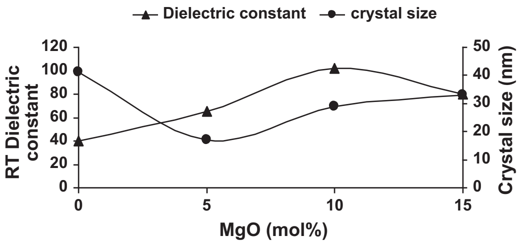

Fig. 5. Variation of room temperature dielectric constant and $PbTiO_3$ crystallite size in glass–ceramics with MgO (mol%).

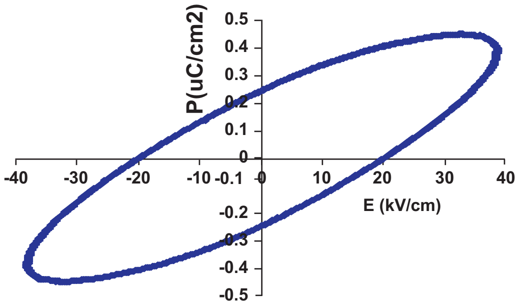

Fig. 6. P–E hysteresis loop for glass–ceramic sample $X=5$ MgO (mol%).

This hysteresis loop shows non saturation. The appearance of non saturated loops may be attributed to high coercivity in lattice structure and microstructure. The high coercivity in lattice structure was caused by a high axial (c/a) ratio. The high coercivity in microstructure was attributed [7] to factors such as volume fraction of crystallites, grain size, position and connection which affect the difficulty of polarization switching during a poling process. All other glass–ceramic samples of the present work also exhibit the similar non saturated hysteresis loops. It has been also reported in the literature [8] that the ceramic–glass interface plays an important role in causing the non saturated hysteresis loops. This phenomenon is believed to be due to interfacial polarization. Since, the dielectric constant and conductivity of glass and ceramic phase is so vastly different, charge tends to build up at the interface and become trapped in the sample. This interfacial polarization may be the cause for the non linear bulky hysteresis loops which is indicative of a lossy ferroelectric system [9].

4. Conclusions

The T_g and T_c initially decrease with the addition of MgO and subsequently increases with increase in the content of MgO. The XRD results revealed the formation of ferroelectric $PbTiO_3$ as major phase and MgB_4O_7 as minor phase in the glass–ceramics. The variation of room temperature dielectric constant of glass–ceramic samples with MgO content is exactly opposite to the variation of crystallite size of $PbTiO_3$ embedded in the glass ceramic samples. The observed hysteresis (P vs. E) loop at room temperature confirmed the ferroelectric nature of these glass–ceramics.

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