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ORIGINAL ARTICLES

Crystallization, Optical And Electrical Properties Of Lead Barium Titanate Based Sodium Borate Glass

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ABSTRACT

The effect of heat treatment on the properties of ferroelectric lead barium titanate based sodium borate glass of the composition 0.5PbO - 0.5BaO- 1.0TiO_2 - 0.5 $Na_2B_4O_7$ have been investigated using DTA, XRD analysis, optical and electrical measurements. Deferential thermal analysis was measured for the present glass ceramic sample and revealed that there were more than one phase in the glass ceramic network. The glass was next heat treated at 650 ^oC for 2h and then 750 ^oC for 8 hours. The present glass ceramic sample was crystallized after heat treated for 8h, at 750 ^oC. The tetragonal perovskite ferroelectric Ba-$PbTiO_3$ phase have been shown in the XRD pattern for the crystallized glass ceramic as the primary phase with particle size 21.3 nm. The secondary phases were shown for Pb_3O_4 and $PbTiO_3$. The electrical properties were investigated for both the glass as quenched and the glass ceramic after heat treatment. It was found that the electrical conductivity showed a considerable increase after heat treatment at 650 ^oC as a result of the growth of small grains within the amorphous network. Ferroelectric Curie's temperature was identified at 310 ^oC. Heat treatment at higher temperature 750 ^oC and longer time 8h leads to fully crystallization for the present glass sample and decreasing electrical conductivity. Such decrease in conductivity was attributed to the formation of larger grains surrounded by interfacial regions causing reducing of the electronic paths. The mechanism of conductivity was suggested to be small polaron hopping (SPH) mechanism. The optical energy gap was calculated and equal 2.82 eV when r = 2 which corresponds to indirect optical transition.

Key words: *$PbBaTiO_3$, glass, glass-ceramic, Dc and Ac electrical conductivity, Optical energy gap.*

Introduction

The ferroelectric and piezoelectric properties of $BaTiO_3$-$PbTiO_3$ ceramics material have attracted much attention in the development of many devices and applications such as capacitors, electro-optic devices, ferroelectric thin films memories, radio communication filters and thermal switches(Kim *et al*., 2007; Lines *et al*., 1977). It is known that crystallization of glasses under a controlled conditions leads to the formation of polycrystalline solids with better properties known as glass ceramics. These materials exhibit a large change in dielectric constant with an applied dc electric field Dou Zhang *et al*., (2010). Therefore many researches have been carried out to develop pore-free glass ceramics containing $BaTiO_3$ - $PbTiO_3$ and $NaNbO_3$ and they still under investigation (Mori *et al*., 2006; Sahu *et al*., 2004; Sahu *et al*. 2006; Thakur, *et al*., 2003). To prepare such materials with the ferroelectric phase as the main phase, the composition and methods of glass preparation must be controlled. Sufficient amounts of forming oxides such as SiO_2, B_2O_3 must be added to ensure glass formability and the composition must be carefully chosen to minimize interactions between the desired crystal phase and the residual glass or any other secondary phase Herzog (1964). Generally the glass former should be added to overcome the high cooling rate and to lower the melting temperature Al-Assiri *et al*., (2009); where $BaTiO_3$ crystal melts at 1618 ^oC and it is hard to attain a high cooling rate that is necessary to make glass Glass *et al*., (1977). There is a great interest in the study of the ferroelectric properties of $BaTiO_3$ in a glassy matrix or glass ceramics as nanocrystals, which are attractive for pyro-electric, piezoelectric and electro-optic Al-Assiri *et al*., (2009). It was observed that ferroelectricity is to exist in a glassy material containing transition metal oxides (TMO) in Bi_2O_3- CuO- PbO based glass (Bahgat *et al*., 2001; Bahgat *et al*., 2002; Bahgat., 2003). The doping of PbO in $Ba_{0.7}$ $Sr_{.3}TiO_3$ thin film could increase the Curie temperature Sun *et al*., (2004); and the further increase of lead ratio of the composition ($Ba_{0.25}$ $Pb_{0.25}$) $Sr_{.5}TiO_3$ could enhanced the tunability and induce the diffuse phase transition of BPST thin film Xia *et al*., (2006). Both $BaTiO_3$ and $PbTiO_3$ based glass former possess ferroelectric behavior Pel`aiz *et al.,* (2009). On the other hand crystallization of such materials could lead to the development of polycrystalline solids with good properties. Such glass ceramic materials are usually composed of one or more crystalline phases distributed in the glassy matrix Chiang Mai (2008). In this paper an equal ratio (0.5/0.5) of barium oxide and lead oxide was mixed in the presence of titanate oxide to prepare glass ceramic

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material with borax as a glass former. The obtained glass ceramic was heat treated at 650 ^oC for 1h and 750 ^oC for 8 hours, respectively. The crystallization was performed at 750 ^oC when the sample was heated for the longer period. It was mentioned that the longer time of heat treatment, would give less amount of residual glass.

2. Experimental procedure:

Appropriate amounts of PbO-BaO-TiO_2-$Na_2B_4O_7$ with the ratio 0.5:0.5:1.0:0.5 (purity of all 99.9%) were roughly mixed in agate mortar and then melted in porcelain crucible in air at 1200 ^oC for about 30 min. The melt was stirred to ensure complete mixing, then poured on a copper plate and immediately quenched. A yellowish transparent sheet of glass was formed. Conducting silver paste was applied on the both flat surfaces for carrying out the electrical measurements. Differential thermal analysis (DTA) for the glass sample was performed by Schinadzu – DSC-16 using Al_2O_3 powder as a reference material. The heating rate was 10 ^oC/min. X-ray diffraction pattern for both the resulting perovskite glass-ceramic sample and the crystallized one were measured and recorded using X'Pert PRO MPD, Philips, Eindhoven, Netherlands, with $Cuk_{\alpha 1}$ radiation (λ=1.5406 A^o). The obtained X-ray diffraction pattern was measured in the 2θ range from 10 to 80 degree. The sample was polished to obtain glass discs for optical measurements as well.

Results and Discussion

3.1. Differential thermal analysis (DTA):

Fig 1. illustrates DTA curve for the glass ceramic sample. The endothermic peak at 556 ^oC is attributed to the change in specific heat which occur at the glass transition range. The onset temperature of this endothermic dip is usually referred to the glass transition temperature(T_g), while the minimum temperature is attributed to the softening point (T_s). The exothermic peaks at 589 ^oC, 607 ^oC and 624 ^oC are attributed to the glass crystallization temperatures T_{c1}, T_{c2} and T_{c3}. The glass crystallization peaks in the DTA plot indicates the presence of more than one phase in the glass ceramic net work. The nucleation temperature (T_N) of the glass sample is generally located between T_g and T_s and it could be calculated as :

$$T_N = \frac{T_g + T_S}{2} \quad \textbf{(1)}$$

The results are recorded in table 1.

3.2 X-ray diffraction analysis and crystallization results:

The glass ceramic sample was heat treated according to the DTA results.

Fig. 2-a. illustrates the X-ray pattern for the glass sample as quenched demonstrating the glassy state for the present sample and Fig. 2-b after heat treatment for 2h at 650 ^oC. This pattern contains a number of diffraction peaks corresponding to a crystalline phase super composed with a wide helo, which indicates the growth of small crystallites in the glass matrix. Further heat treated at 750 ^oC for 8 hours leads to the fully crystallization of the present glass ceramic as shown in Fig. 2-c. Such glass ceramic materials are usually composed of one or more crystalline phases distributed in the glassy matrix, therefore X-ray diffraction pattern are used to identify phases present in the crystallized glass ceramic and also study crystal structure of a ferroelectric phase Chiang Mai (2008). It can be seen from Fig.1-c that the ferroelectric tetragonal perovskite phase of $BaPbTiO_3$ is the main phase according to JCPDS 74-2492 card with lattice parameters a = 3.977A^o and c = 4.042 A^o. The two secondary phases were attributed to Pb_3O_4 and $PbTiO_3$ respectively (JCPDS 85-0859 and 78-029 cards). The average particle size D of the precipitated $BaPbTiO_3$ phase were calculated according to Sherrerss's formula Lou *et al*., (1997):

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

Where k ≈ 1, λ is the wavelength of $Cuk_{\alpha 1}$ radiation, θ is the Bragg angle of the XRD peak and β represents the full width of half maximum of the diffraction peak (in radians). The average particle size D was found to be equal 21.3 nm.

3.3 Optical properties:

The optical transmition spectra of the glass sample in the wavelength range from 300- 1100 nm is shown in Fig.3. the glass sample shows a strong absorption in the UV region while it shows a good transparency in the visible region. The absorption coefficient, $\alpha(\upsilon)$, in amorphous materials obeys Tauc equation,(Tauc):

$$\alpha(\upsilon) = const\left[\frac{(h\upsilon - E_{opt})^r}{h\upsilon}\right] \quad (3)$$

Where hυ is the photon energy, E_{opt} the optical energy gap and the exponent ***r*** = 1/2 or 3/2 for direct transition depends on whether the transition is allowed or forbidden, and ***r*** = 2 or 3 for allowed and forbidden indirect transitions respectively. In the present work according to Tauc equation, the optical energy gap could be measured from the extrapolation of the linear region of the $(\alpha h\upsilon)^{1/2}$ vs hυ plot as shown in Fig. 4. which corresponds to indirect optical transition with energy gap 2.82 eV. The width of the tails of the localized states E_t within the optical band gap is calculated by the extrapolation of the linear part of the lnα vs. photon energy curve in Fig. 5. It was suggested that the optical absorption in solids appears by the mechanism of coupling of the electric field of the incident radiation to the dipole moment in the material and the consequent transfer of energy Hogarth (1983). According to Stevals (1953); the absorption edge in oxide glasses are due to the transition of an electron belonging to an oxygen ion to an excited state, therefore the more weakly these electrons are bound (NBO), the more easily absorption occurs. Addition of alkali earth element above 15%mole percent will cause a shift in the fundamental absorption edge towards the longer wavelength region Shajo Sebastian *et al*.,(2004). It was found that increasing Na_2O concentration in borate glasses, boron transforms from three fold to four fold coordinated state and Na^+ ions possess the electroneutrality to the four- fold boron Zagar *et al*.,(1971). Further addition of alkali oxide leads to breaking of the bridging bonds of oxygen atom and formation of non-bridging oxygen ions leading to increasing the conductivity.

Table 1: Some important physical parameters of 0.5PbO-0.5BaO-1.0TiO_2-0.5 $Na_2B_4O_7$ glass ceramic.

Tg (^oC) glass transition temperature	466
T_s (^oC) dilatometeric softening point	559
T_N (^oC) nucleation temp.	512.5
T_{c1}(^oC) first Cryst. temp.	589
T_{c1}(^oC) second Cryst. temp.	607
T_{c1}(^oC) third Cryst. temp.	624
Particle size D (nm)	21.3
W_{dc} (eV) activation energy	1.27
E_{op} (eV) optical energy gap	2.82
σ_o ($S.m^{-1}$)	$8.1x10^4$

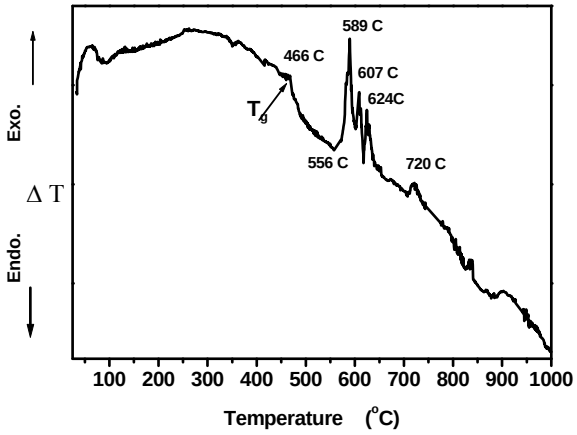

Fig. 1: DTA plot of glass specimen.

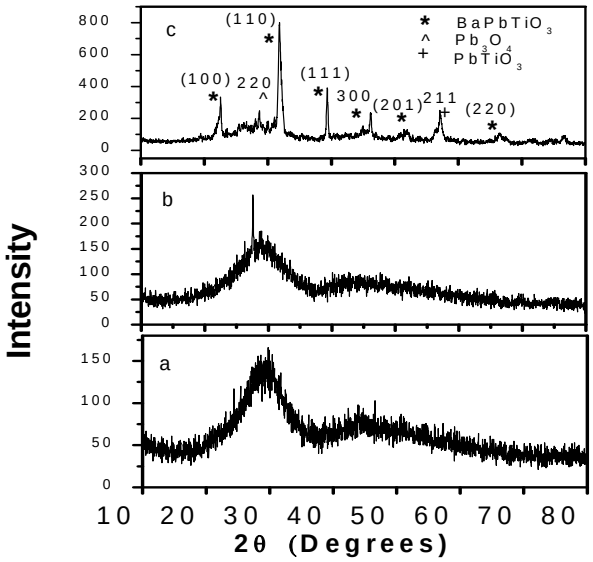

Fig. 2: XRD pattern of 0.5PbO-0.5BaO-1.0TiO_2-0.5 Na_2 B_4 O_7 glass ceramic. a- glass as cast. b- glass after heat treatment for 1h at 650 ^oC. c- glass after heat treatment for 8h at 750 ^oC

3.4 *Electrical properties:*

Dc and ac conductivity measurements for the present glass sample as quenched are illustrated in Fig.6. Dc conductivity of the glass as quenched shows linear dependent on temperature up to a critical temperature $\theta_D/2$ (θ_D is Debye temperature), then the curve deviates from linearity at low temperatures. The activation energy W of conduction at high temperatures is well investigated according to Arrheneous formula Mott (1968):

$$\sigma = \sigma_o \exp(-W/kT) \quad (4)$$

where σ_o is the pre-exponential factor (room temperature conductivity) and k is Boltzmann constant. The obtained value of σ_o was $8.1x10^4$ $S.m^{-1}$ in the range of the almost universal value (10^4 to 10^5 $S.m^{-1}$) Mott *et al.,* (1971). The activation energy was calculated from the slope of the dc curve at high temperatures. It is clear that the activation energy changes with temperature which give feature to the SPH mechanism Mott (1968). However, as shown in Fig. 6, the glass sample exhibits a frequency dependent conductivity of the type Hogarth (1983).

$$\sigma_{ac}(\omega) = A\,\omega^S$$

where A is the constant of temperature dependence and s is the frequency exponent which is less than or equal one. Fig.7 illustrates the dependent of frequency exponent, s, on temperature, it is clear that s is inversely proportional to the temperature which indicates that the mechanism of conductivity is by hopping process. Ac conductivity was measured at fixed frequency 10 kHz for the glass as quenched and the glass after heat treatment as shown in Fig. 8. It was found that electrical conductivity showed a considerable enhancement after heat treatment for 2h at 650 ^oC, while the activation energy decreased. Such behavior is attributed to the growth of nanocrystals as reported in the XRD and formation of effective interface region "conduction tissue" between nanocrystals and the glass matrix named conduction paths Garbarczyk *et al.,*(2006). Further heat treatment at 750 ^oC leads to crystallization and a decrease of the electrical conductivity. This phenomena was explained on the basis of formation of large grains and disappearing of the glassy phase and reduction of the conduction tissue (electronic paths). On the other hand the dependence of dielectric permittivity on temperature of the present heat treated glass sample is illustrated in Fig. 9. Application of Curie's law; $1/\varepsilon` = C/T\text{-}T_o$ was applied and is illustrated in Fig. 9b as well for the glass sample after heating for two hours at 650 ^oC. It is observed from the figure that the ferroelectric peak of $PbBaTiO_3$ is reduced to a small hump at 310 ^oC, in good agreement to previously reported data on the ferroelectric behavior of comparable sample Lai *et al.,*(1994). This partial masking may be attributed to the effect of substitution of Na atoms in the glass network and the effect of its ionic character on the ferroelectric characteristics.

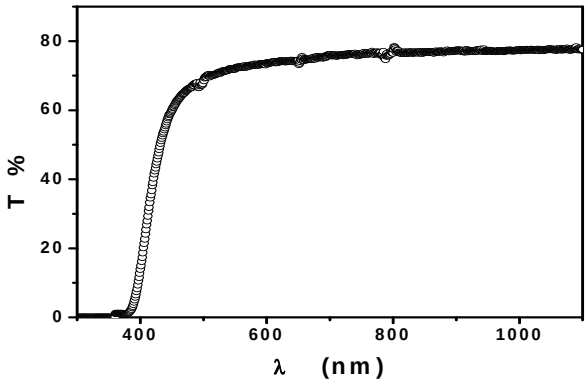

Fig. 3: Optical transmission as a function of wavelength for 0.5PbO-0.5BaO-1.0TiO_2-0.5 Na_2 B_4 O_7 glass.

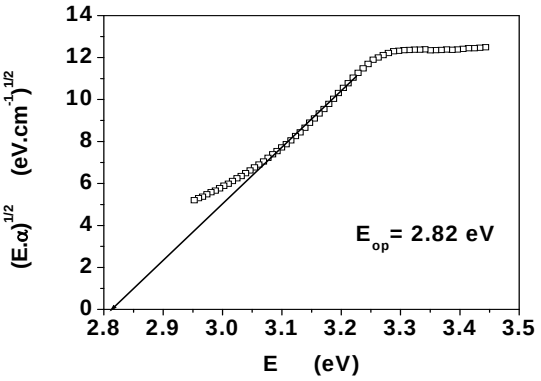

Fig. 4: $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plot for 0.5PbO-0.5BaO-1.0TiO_2-0.5$Na_2B_4O_7$ glass.

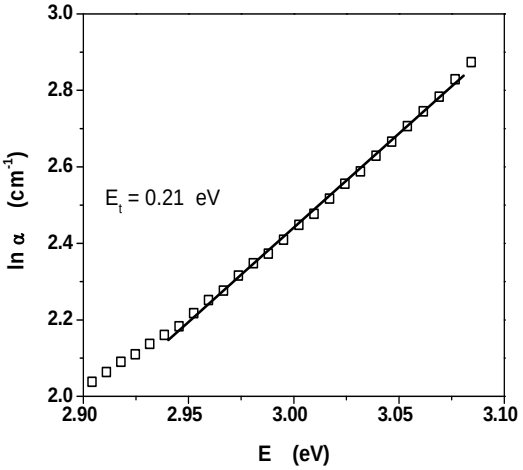

Fig. 5: ln α vs. photon energy for 5PbO-0.5BaO-1.0TiO_2-0.5 $Na_2B_4O_7$ glass.

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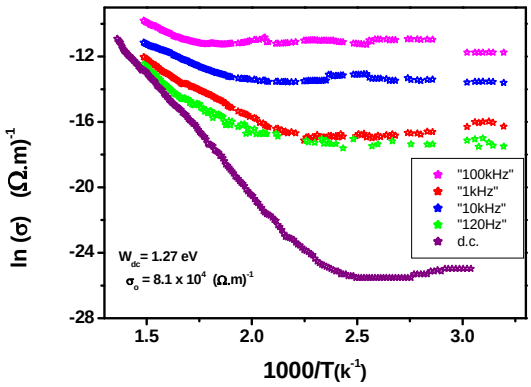

Fig. 6: Dc and ac conductivity for the as quenched glass sample.

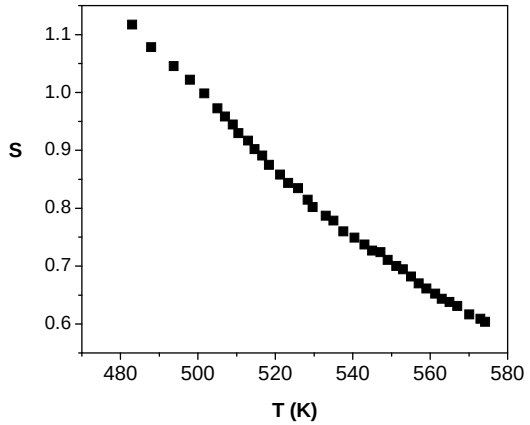

Fig. 7: Exponent factor s as a function of temperature for the present glass.

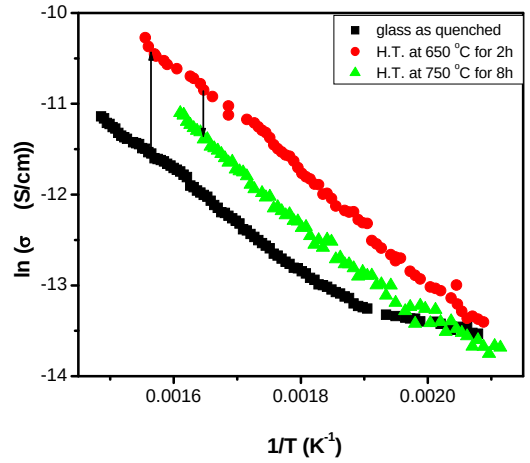

Fig. 8: ln σ as a function of 1/T for 5PbO-0.5BaO-1.0TiO_2-0.5 $Na_2B_4O_7$ glass at a fixed frequency of 10 kHz. The arrows are a guide to the eye showing the general trend.

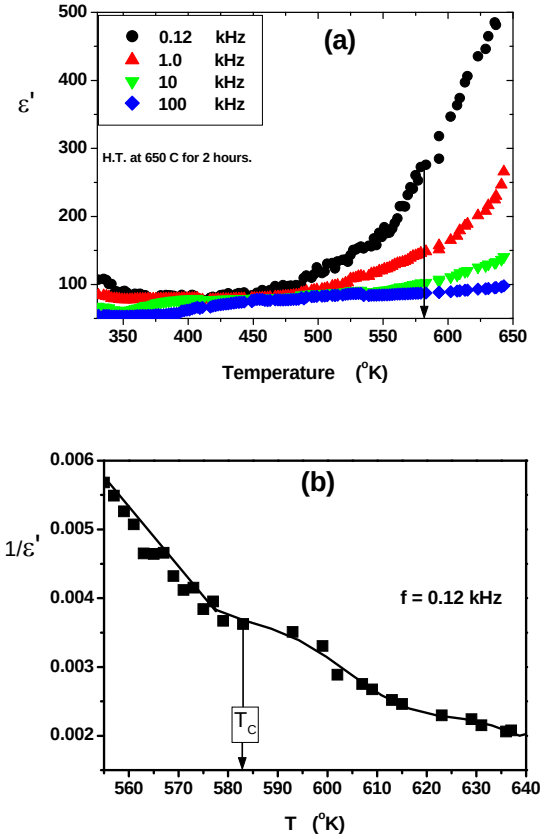

Fig. 9: (a) Dielectric permittivity of the heat treated glass at 650 C for two hours. (b) Application of Curie's law on the dielectric permittivity data at 0.12 kHz. The inserted arrow shows the position of the Curie's temperature.

4. Conclusion:

Fabrications methods of glass under control enhanced the formation of glass ceramic materials with better properties. DTA, XRD, optical and electrical properties were investigated and measured. DTA and XRD results showed the presence of more than one phase in the glass matrix. The electrical conductivity of the glass ceramic was increased by heat treatment at 650 ^{o}C and then decreased by heat treatment for 8h at 750 ^{o}C to fully crystallization for the glass sample. This behavior was explained on the basis of the core-shell model (conduction tissues). The electrical conductivity at high temperature could be explained by small polaron hopping (SPH) model. The ferroelectric behavior of $PbBaTiO_3$was partially masked as due to the effect of substitution of Na atoms by Ba and Pb atoms. Curie's temperature was observed at 310 ^{o}C. The optical energy gap was measured indicating indirect optical transition with energy gap 2.82 eV. The small values of the dielectric permittivity gives rise to various applications.

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