Synthesis and Characterization of Bismuth Borate-Barium Titanate Glass Ceramics

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Abstract

Objectives: In the present investigation, transparent novel glass embedded with ferroic matrix was prepared by melt-quenching method. Among all the glasses, selective glass ceramic is also prepared. Optical and electrical measurements were carried out on the samples. Methods: We have prepared the transparent glass composition of (100-x)[0.55Bi$_2$O$_3$-0.30B$_2$O$_3$-0.15TiO$_2$]+xBaTiO$_3$ with x=0, 10, 20, 30, 40, 50 wt.%. Appropriate amounts of reactant mixture were well mixed in agate mortar and melted in a porcelain crucible. The composition is quickly quenched by pouring on pre-heated stainless-steel plate and pressed with another plate. Differential Thermal Analysis was made on the glasses. Detailed optical absorption and impedance measurements were made on the said above glass matrix. Findings: From the XRD spectra, amorphous and crystalline nature was established on the glass and glass ceramic sample. Optical absorption spectra show that with increasing the BaTiO$_3$ in the glass matrix, it results into structural compactness by means of non-bridging oxygen. The results are consistent with the oxygen packing density values. Impedance spectroscopic plots have shown broad peaks and therefore these materials are being considered as special type multicomponent glass ceramics. Disorder nature of the samples was also discussed with the help of dc-conductivity plots. Among all the samples, 60-BBT-40BT has shown broad spectroscopic peak. Therefore, this sample was annealed at 700°C, and the XRD pattern resembles with Bi$_4$Ti$_3$O$_{12}$ Aurivillius phase, instead of BaTiO$_3$ phase. Detailed impedance measurements were also made on the glass ceramic. Novelty: Dielectric ceramic-glass are being used to fabricate energy storage capacitors; however, further studies are needed in order to improve pore-free microstructures. In view of this, transparent glass matrices are embedded with ferroic materials namely BaTiO$_3$ and the combined optical and electrical results would be useful for future promising optoelectronic materials by means of one-to-many applications.

Keywords: Ferroelectric; glassceramics; optical absorption; impedance; dielectric; FTIR
1 Introduction

Ferroelectric materials have attracted much attention due to its domain characteristic feature and temperature dependent macroscopic properties such as phase transition, coupling properties etc. In addition, ferroic materials form an essential subgroup of functional or smart materials whose physical properties are sensitive and changes with the external conditions such as temperature, pressure, electric, and magnetic fields. The most important and striking feature of ferroic material is its spontaneous polarization (the material possesses’ polarization without any applied electric field). Due to the fact of this, these substances are considered to be high-energy–density materials (to store and release energy). Finally, in a well-regulated manner, one can make these materials as highly useful sensors and actuators[1,2]. Recent reports on phosphate–lithium, sodium borate silicate embedded with chromium oxide glasses and cadmium lead phosphate glasses have shown interesting radiation/neutron shielding applications[3–6]. Among all the ferroelectric perovskite oxides, BaTiO$_3$ is the most investigated material in the last few decades because of its intrinsic ferroelectric properties, they have shown promising applications in the fields of electroceramics, especially in microelectronic, dielectric and multilayer capacitors, ultrasonic transducers, positive temperature coefficient (PTC) resistors, pyroelectric infrared sensors etc. It is a known fact that the borosilicate glasses have strong network and easily can be doped with any oxide materials[7,8]. In addition, multiferroic materials belonging to the Aurivillius family have shown high coupling (magnetolectric) coefficient[9]. Another important material of Aurivillius family is Bi$_4$Ti$_3$O$_{12}$. It is a well-known Ferroelectric Random-Access Material (FRAM). In addition, Bi$_4$Ti$_3$O$_{12}$ has higher transition temperature and above the phase transition temperature ($T_c$~$675^\circ$C) it turns from orthorhombic to tetragonal[10].

Ferroelectric glass ceramics exhibit unusual ferroelectric properties owing to the fact of its ceramic–glassy nature. Due to its characteristic nature of energy-storage applications, many Indian researchers have been concentrating in this direction[11,12].

Glass matrices are being prepared by means of solid-state route, sol-gel, hydrothermal route etc. However, it is difficult to choose the above-mentioned process due to many constraints involved in the reaction process. Recently many researchers have concentrated on BiFeO$_3$, Pb-based, Bi$_2$O$_3$ and Fe$_2$O$_3$ glasses[13–17]. Bismuth based glass ceramics are used in the fabrication of electronic and semiconducting devices. However, further improvements are needed to prepare pore free microstructures. In addition, very few reports are available on electrical studies on glass ceramics. Keeping in view of importance of ferroelectric glass ceramics and to improve pore free microstructure, a systemic study on combined optical and electrical is needed in this direction.

In the present investigation, we are focusing on the BaTiO$_3$ based glass-samples. Prior to the BT preparation, we have fabricated Bi$_2$O$_3$–Ba$_2$O$_3$–TiO$_2$ (BBT) glass matrix, and embedded with BaTiO$_3$ (BT) by using the following composition (100–x) BBT-x BT (with x=0, 10, 20, 30, 40, 50 wt. %). It should be noted that Bi$_2$O$_3$ is very suitable for both network modifiers as well as network former. Therefore, high concentration of Bi$_2$O$_3$ is chosen in the present glass matrix composition. Moreover, recent reports revealed that the glass-ceramics have lower sintering temperature, compared to ceramics[11]. Among the entire glass samples, selective glass sample was crushed into powder and pressed into a pellet. The pellet glass ceramic sample was annealed at 700${^\circ}$C for 2 hours. Impedance measurements were made on all the samples and the results were discussed.

2 Methodology

Keeping in view of aforementioned importance, in the present study we have prepared transparent glass-materials. The ferroic-glass materials were prepared by melt–quenching method and the chosen composition is: (100–x) [0.55Bi$_2$O$_3$–0.30 B$_2$O$_3$–0.15TiO$_2$] +xBaTiO$_3$ (with x= 0, 10, 20, 30, 40, 50 wt %). Appropriate amounts of Bi$_2$O$_3$, B$_2$O$_3$, TiO$_2$ and BaTiO$_3$ are well mixed in agate mortar and melted in a porcelain crucible for half-an-hour at 1100–1200$^\circ$C depending on the BaTiO$_3$ concentration and then quickly quenched by pouring onto pre-heated stainless-steel plate and pressed with another plate (both maintained at 100$^\circ$C). The glass transition temperature is obtained from TGA analysis. The glass transition ($T_g$) and crystallization temperature ($T_c$) were found to be 450$^\circ$C and 525$^\circ$C respectively.

X-ray diffraction (XRD) peaks are recorded on the glass ceramics samples, using Pan Analytic X’pert plus diffractometer. The Cu-Kα (1.54 Å) radiation is used and scanned in the range 10$^\circ$ ≤ 2θ ≤ 80$^\circ$ with a speed of 2$^\circ$/min. Densities of the glass ceramics are measured using Archimedes principle using xylene (density 0.87 gm/cm$^3$) as liquid media. Scanning electron micrographs of these samples are obtained with ZEISS EVO18 (special edition). Oxford system Energy Dispersive Spectroscopy (EDS) attached to the electron microscope is used for obtaining the EDS spectra. Fourier transform infrared (FTIR) spectra were recorded using FTIR-8400S Shimadzu. FTIR Spectra were obtained in the range of 400-2000 cm$^{-1}$. Optical absorption spectra were recorded using UV 3092 UV-VIS spectrometer. Differential Thermal Analysis (DTA) was carried out from room temperature to 1000 $^\circ$C at a rate of 10$^\circ$C/min, using DTG-60 Shimadzu. Among all the glass samples, 60BBT-40 BT glass was crushed into powder and pressed into a cylindrical pellet. Detailed impedance spectroscopic studies were also made on the glasses as well as glass ceramic sample, using Autolab (PGSTAT-30) Impedance analyzer. Prior to the electrical measurements,
silver paste was coated on both sides of the glass/ceramic pellets (or disks) for good electrical contact.

3 Results and Discussion

The XRD patterns shown in Figure 1, exemplifies the amorphous nature of the sample. The data presented in the Figure 1, reveal that the prepared glass samples have amorphous nature. Scattering observed at low Bragg angles, indicates disorder-lattice and this is being attributed to the amorphous characteristic nature of the glass. The crystalline nature of BT is not appeared in these samples. In the present study, the quenched samples have shown the amorphous nature, in spite of adding ferroelectric phase. However, the glass composition 60-BBT-40BT, annealed at 700°C for 2 hours, has shown crystalline phase (Figure 1 g). The crystalline Bragg peaks were well-matched with the Bi₄Ti₃O₁₂ Aurivillius (layered perovskite) phase. The matched (h k l) values were mentioned in the Figure 1g. All glass samples were found to be transparent. The pure BBT transparent glass sample is shown in the Inset Figure 1 a. The ceramic pellet, made by the glass composition 60 BBT-40 BT, photograph is also shown as the inset Figure 1 g.

Figure 1 g shows the crystalline phase and this nature is attributed to the ionic conductivity of glass-ceramic matrix. It is a known fact that Aurivillius layer compounds, (Bi₄Ti₃O₁₂) have high ionic conductivity nature, due to the presence of oxygen vacancies. It should remember here that Bi⁺³ alone may not contribute high ionic conductivity in bismuth-based glasses and Bi-based glasses should not be compared with other Pb-based glasses. Moreover, Bi⁺³ groups of ions have lone-pair electronic configuration, and they have two outer most orbits with a closed shell of Pyramidal bonding. The pyramid posses a dipole moment and finally might lead to spontaneous polarization in these materials.

The general formula of BLSF is described as (Aₙ₋₁BₙO₃n+1)²⁻ (Bi₂O₂)²⁺. The perovskite blocks are interleaved with (Bi₂O₂)²⁺ layers. The bismuth ion situated at A-site in the perovskite structure and the ferroelectric properties are mainly attributed to strong covalent bonds of Bi-O. The density and molar volume of transition metal ion concentration (Nᵢ), Polaron radius

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Fig 1. (a-f)XRD patterns of the Glass Composition of 100-xBBT- X BT (x=0,10,20,30,40,50) (g)XRD pattern of the glass composition 50BBT+50BT showing crystalline nature
Density of the samples were calculated from the Archimedes Principle using the relation

\[ \rho = \frac{w_a - w_b}{w_a - w_b} \times \rho_b \]  

(1)

Where \( \rho_b \) - is the density of the reference liquid (xylene=0.865 g/cc) and \( w_a \) & \( w_b \) represent the weight of the glass-ceramic samples measured in air and xylene respectively.

Molar Volume can be calculated by using the formula:

\[ V_m = \frac{M_c}{\rho} \]  

(2)

Is the molecular weight of the glass-ceramic

Transition metal ion concentration (N) can be calculated by using the relation

\[ N = \frac{0.01 \times NA \times \rho}{V_m} \]  

(3)

Where \( NA \) is Avogadro number and \( \rho \) is density and \( V_m \) are molar volume of the samples respectively. Polaron radius of the glass matrix is calculated by using the following formula

\[ r_p = \left( \frac{1}{N} \right)^{\frac{3}{2}} \]  

(4)

The interionic distance of the constituent atoms is calculated by using the formula

\[ r_i = \frac{1}{2} \left( \frac{\pi}{6N} \right)^{\frac{3}{2}} \]  

(5)

Here, \( N \) represents the transition metal ion concentration.

The above said calculation were made and summarized in the Table 1. From the Table 1, the molar volume of the glass materials was found to decrease with increasing the BT concentration in the glass-matrix. The decreasing nature of the molar volume is attributed to conversion from non-bridging oxygen atoms (NBO) to bridging oxygen atoms (BO) in the glass matrix. In TiO\(_6\) octahedral structure, this kind of conversion is predominant in glass materials. The result is consistent with the optical studies of Ni-doped bismuth borate glasses\(^{(19)}\) and lithium phosphate glasses\(^{(20)}\). The interionic distance between titanium is mainly dependent on the concentration of Ti ion. The interionic distance decreases with the increase of Ti concentration\(^{(20)}\).

To extract more information on this, optical measurements were performed on these samples.

The Differential Thermal Analysis (DTA) is shown in Figure 2. The glass transition (\( T_g \)) and crystalline temperature (\( T_c \)) were obtained within the experimental errors. The endothermic and exothermic dips were found at 450\(^{0}\)C and 650\(^{0}\)C respectively. It is also noticed from the plot that \( T_g \) increases with the BT concentration. The increase of \( T_c \) indicates that the coordination nature of glass network former. An increase in \( T_g \), with BT concentration, indicates the bond strength of network former. The difference between \( T_g \) and \( T_c \) is also found to be nearly 200\(^{0}\)C. The large difference between \( T_g \) and \( T_c \) shows that these glass materials are thermally very stable. The thermal stability of these compounds is attributed to the complex structure of the present ferroelectric glasses. In addition, the average interionic separation (\( r_i \)) and polaron radius (\( r_p \)) were calculated and given in the Table 1. From the values it is concluded that strong localized carriers predominate in the conduction process, as \( r_p < r_i \).

Table 1. Depicting the Various Physical parameters- Density, Molar volume,Transition Metal Ion concentration, Polaron Radius, Inter Ionic Distance,Oxygen Packing Density, Optical Band Gap and Urbach Energy of different Glass Compositions

<table>
<thead>
<tr>
<th>SL NO</th>
<th>Sample</th>
<th>Density (( \rho )) gm/cc</th>
<th>Molar Volume (VM) cc/mole</th>
<th>Transition Metal Ion Concentration (Ni) 1020/cc</th>
<th>Polaron Radius (rp) ( A^0 )</th>
<th>Inter Ionic Distance (ri) ( A^0 )</th>
<th>Oxygen Packing Density (OPD) g/atm/l</th>
<th>Eopt eV</th>
<th>Urbach Energy (( \Delta E )) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure BBT</td>
<td>7.5209</td>
<td>40.6014</td>
<td>11.1568 X 1020</td>
<td>9.6416 X 10 -16</td>
<td>3.8849 X 10 -16</td>
<td>197.0375</td>
<td>2.97</td>
<td>0.58</td>
</tr>
</tbody>
</table>

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The FTIR spectra of the present glass materials (100-x ) BBT-x BT, obtained at room temperature in the spectral range of 400-2000 cm\(^{-1}\), is shown in the Figure 3. Peaks observed at 860-869 cm\(^{-1}\) indicates the asymmetric stretching vibrations of Bi-O bonds of [BiO\(_3\)]Units\(^{21,22}\). The peaks associated 500-530 cm\(^{-1}\), shown as inset Figure 3, is assigned to Bi-O bonding of BiO\(_6\)octahedral\(^{23}\). A shift in the peak maxima, observed with increasing the BT-composition, confirm the asymmetric stretching. Peaks appearing near 600 cm\(^{-1}\) clearly indicates Bi-O stretching vibration mode. The peaks at 750 cm\(^{-1}\) are ascribed to the B-O-B linkage network. Peaks appearing near 750 cm\(^{-1}\) are mainly due to the Ti-O-Ti symmetric stretching of TiO\(_4\) units. Band appearing near 1100 cm\(^{-1}\) (IR region) is being attributed to B-O stretching vibrations of BO\(_4\) tetrahedral network\(^{24}\). From the spectra, the peak at 1250 cm\(^{-1}\) is found to increase that with BT content in the glass composition. Peaks observed near 1450 cm\(^{-1}\) is attributed to asymmetric vibrations modes of non-bridging oxygen of B-O-B matrix. Bands assigned ~1549 cm\(^{-1}\) is attributed to B-O asymmetric stretching vibration of BO\(_3\) units in meta-borate, pyro-borate and ortho-borate groups\(^{24}\). Band at 1632 cm\(^{-1}\) is due to metal-hydroxyl ion bonding\(^{11}\). From the overall spectra it is concluded that the presence of BT composition in the glass matrix certainly influencing the glass structure and acts as a network modifier.

Figure 4 shows the optical absorption spectra and Tauc plot. Figure 4 c shows Urbach Energy of the BBT-BT glass samples. From the UV-visible optical spectra, shown in Fig 4(a), the absorption coefficient is calculated by using the following formula:

\[
\alpha = \frac{1}{d} \log \left( \frac{I_0}{I} \right) \tag{6}
\]

The term \(d\) represents thickness of the sample, \(I_0\) and \(I\) represent the intensity of incident and transmitted light beam respectively.

The absorption coefficient is calculated by the following formula:

\[
\alpha \hbar \nu = \left[ B (\hbar \nu - E_g) \right]^2 \tag{7}
\]
The constant \( B \) is independent of energy (E), also known as tilting parameter.

The term \( h\nu \) represent the photon energy and \( \nu \) index constant. The index constant can be 1/3, 1/2, 2, 3 and these values correspond to forbidden, direct allowed, indirect allowed, indirect forbidden respectively. However, in the present case, the index constant \( \nu \) fitted by 1/2, therefore it is concluded that the bands are belong to direct band gap. The variation of \((\alpha h\nu)^{1/2}\) with \( h\nu \), known as Tauc Plot, is shown in Figure 4 b. The values of \( E_g \) were estimated with help of the tau plots (Table 1). The values of \( E_g \) were calculated by extrapolating the linear region of the plot, which touches the X-axis. The optical band energies (\( E_g \)) were found to increase with increasing the BT composition. An increase in optical band gap energy is attributing to the conversion of Non-bridging oxygen's to bridging oxygen atoms. The variation of \( \ln \alpha \) with \( \alpha h\nu \) is shown in Figure 4 c. The Urbach energy was evaluated from the plot and the values are summarized in Table 1.

Fig 3. FTIR spectra of \((100-x)BBT-(x)BT\) (\(x=0,10,20,30,40,50\)) (The peaks associated 500-530 cm\(^{-1}\) shown in inset)

Fig 4. (a) Optical Absorption Spectra of all \((100-x)BBT-(x)BT\) (\(x=0,10,20,30,40,50\)) (b) Tauc plots of the corresponding Glass Samples (c) Ina Vs energy (eV) or Urbach Energy (eV) of all Glass Compositions
The dielectric properties of the glass ceramics can be understood by means of combined impedance and modulus spectroscopic plots. Figure 5 shows the variation of $Z''$ and $M''$ with frequency for all the glass compositions, obtained at 125°C and 200°C respectively. From this plot, it is evident that the broad peaks found to increase with increasing the BT content. In addition, the maximum peak position is also found to shift towards right with increasing the BT-composition. The broad $Z''$ peak also indicates the presence of multiple ions namely Bi, Ti and Ba in the glass matrix. All $Z''$ values were found to merge into single value at higher frequency region. Observing higher $Z''$ values at lower frequencies are being attributed to accumulation of space charges at grain boundary interfaces. Similar results were seen in lead calcium titanate borosilicate glasses. Modulus also known as dielectric modulus which is inversely related to the permittivity ($M''=1/\varepsilon''$; $M''=M'-jM''$ here $M'$ and $M''$ represents real and imaginary part of modulus). Broad spectroscopic peaks observed in the intermediate frequency range clearly confirm the disorder nature of glass-materials. An interesting aspect in the modulus plot is that the $M''$ increases suddenly at higher frequency region and this kind of behavior is mainly due to the increasing the ionic conductivity of the glass samples.

![Figure 5. Variation of $Z''$ (a&b) and $M''$ (c&d) with frequency for all glass compositions at 125°C and 200°C](image)

Figure 6 shows the variation of ac-conductivity with frequency for all glass materials. The data was obtained at different temperatures, mentioned in the plot. From the plot it is clearly seen that the dispersion observed at low frequency region is found to increase with increasing the BT-composition in the BBT-BT glass matrix. From the plot, a sudden change in the conductivity near 125°C is ascribed to the presence of oxygen vacancies. For all compositions, $M''$ approaches to zero at lower frequencies. Dispersion observed at liger frequency region and merging of ac-conductivity into single value at higher frequency is generally attributed to conduction mechanism assisted by short rage mobility of charge carriers.

Figure 7 shows the variation of dc-conductivity, obtained from the ac-conductivity data by extrapolating to 1 Hz frequency with inverse of temperature. From the dc-conductivity plot it is evident that the activation energy increases with the BT-composition. Moreover, the ac-conductivity is found to merge into single value at higher frequency domain. This nature clearly confirms the following hoping mechanism:

$$Ti^{3+} + e^- \rightarrow Ti^4$$

(8)
Fig 6. Variation of ac-conductivity with frequency for all glass compositions

The conductivity data is well fitted into Arrhenius Law and one can obtain activation energy from the slopes of the plots. The activation energy values, calculated from the slope of the dc-conductivity, were mentioned in the Figure 7. It is also evident that the activation energy values were found to be around 1 eV. From this one can speculate that Pure BBT sample has more oxygen vacancies and these vacancies participate in the role of conduction process. Figure 8 shows SEM photographs all the glass samples. From the plot it is evident that the grain size increases with BT-composition in the matrix. From this, one can speculate that BT composition has shown influence on the microstructure. Changes observed in the size, shape and mean crystalline size can also corroborated to the conduction phenomenon, where activation energy is found to increase with the BT composition. Similar results were seen in BT-based cadmium alkali borate glasses, where the glass density was found to increase with the BT composition. From this it is evident that TiO\textsubscript{2} plays glass former\textsuperscript{(23)}.  

Fig 7. The activation energy values from the slope of thc-dc-conductivity for (100-x)BBT- (x)BT (x=0,10,20,30,40,50)

The variation of log $Z''$ with frequency is shown in the Figure 9a. Two distinct slopes observed in Figure 9 b explains about grain and grain boundary contribution of the samples. Figure 9c demonstrates the variation of imaginary part of impedance ($Z''$)
with real part of impedance \(Z'\) (Cole-Cole Plot) at 125° C. Observing an incomplete semicircle, and a spike like behavior at 125° C in the intermediate region is attributed to limited ionic conduction and the blocking capacitance of the sample. The ionic conduction is mainly due to the doubly ionized vacancies. This type of conduction process can be explained by the following Korger-Vink notation.

\[
O_{Qx} \rightarrow V'' + 2e' + 1/2O_2
\]  

(9)

Recent report of Zhao et al\(^{(26)}\) on BaCO\(_3\)-TiO\(_2\)-Al\(_2\)O\(_3\)-SiO\(_2\)-CeO\(_2\) revealed that the molten solution has shown BaTiO\(_3\) (BT) phase at higher temperature (>1200\(^{0}\)C). However, on the contrary, in the present investigation, BBT-glass matrix embedded with BT has shown Bi\(_4\)Ti\(_3\)O\(_{12}\) (an alternative compound of BT). Based on the above reaction (equation 9), the source of conduction is through Ti\(^{4+}\) to Ti\(^{3+}\). The released electrons get trapped at the defects such as \(V_{o''}\). It is also presumed that the conduction in glass ceramic is due to low doubly ionized vacancies (\(V_{o''}\)) and stable oxygen vacancies. The results are consistent with increasing dc-activation energy values of all glasses. A sudden decrease in dc-activation energy of ceramic-glass sample clearly confirms the hopping of electron between the titanium ionic sites.
4 Conclusions

The glasses with the composition (100-x) BBT-xBT, (where x=0, 10, 20, 30, 40, 50 wt. %) were prepared under controlled heat treatment process. Among all the composition, 60BBT-40BT has shown broad spectroscopic peak with lesser relaxation time. It is concluded that there is a decrease in the dipole concentration and moreover the sample has shown crystalline nature of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> phase instead of BT-phase. From the detailed ac-conductivity data and impedance, it can be concluded that excited Ti<sup>4+</sup> ion reduces to Ti<sup>3+</sup> ions by means of electron hopping mechanism. In addition, oxygen vacancies play role in the conduction process. Ac conductivity data follows Jonscher’s power law. Broad asymmetric Z” peaks indicate different relaxation times. Decrease of Z” peak with the composition clearly indicate increase of dipole concentration. The trend of Dc conductivity confirms the mixed transition conductivity of hopping of electron and migration of oxygen vacancies. Thermal analysis also reveals that the stability of the glass compounds is due to bridging of oxygen network. The increasing order nature with BT clearly indicates that the chosen composition makes it a suitable candidate for ferroelectric applications.

References


