Materials Research Express

PAPER

Fabrication of lead-bismuth titanate borosilicate glass ceramics and dielectric characteristics doped with GNP

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Keywords: XRD, DTA, PbTiO3, SEM, dielectric behavior

Abstract

Different compositions (\(x\)) of lead-bismuth titanate borosilicate (PBTB) glasses have been synthesized using a conventional melt-quenching method in the compound \(55(Pb_xBi_{1-x})TiO_3\)–44[2SiO_2·B_2O_3], (\(x = 0.0, 0.3, 0.5, 0.7\) and 1.0) mixed with 1 mol \% of graphene nanoplatelets (GNPs). XRD analysis exhibited the synthesis of clear PBTB glasses which confirmed the amorphous nature. Synthesized glasses have been converted into glass-ceramics (GCs) using a differential thermal analysis (DTA) results to understand the crystallization mechanism. XRD results described the crystalline behavior of GC samples and distinct phase formation. The surface morphology of the GCs was analyzed using a scanning electron microscope (SEM). Energy dispersive X-ray analysis (EDAX) have been also performed to verify the elemental composition of the GC sample, PBTG0.5735 F \((x = 0.5)\). The variation in relative dielectric constant \((\varepsilon_r)\) and dissipation factor \((D)\) by increasing temperatures was obtained at different frequencies. The GC sample PBTG1.0746 F \((x = 1.0)\) showed a maximum value of dielectric constant among all glass ceramic samples.

1. Introduction

Glasses are not limited to the ornamental resources, it was distorted from the window panels, household glassware as well as laboratory wares [1]. Recently, glasses find the numerous applications in different fields such as optical instruments, electrical transmission, optical fibre, radiation shielding, electrochemical, electronic and electro-optic devices etc [2, 3]. Different constituents can be used based on the manufacturing process and end-use of the product. For example, silica and boric acid used as glass former while lead oxide and bismuth oxides used as a heavy metal oxides for many applications [4, 5]. These oxide glasses has attracted much attention of the researchers for their outstanding infrared transmission in comparison to the conventional glasses for numerous applications like ultra-fast optical switches, and photonic devices [6–9].

The formation of liquid, crystals and glasses may be explained from the schematic volume-temperature curves as shown in figure 1. It revealed a slow cooling process leads to crystal nuclei formation and crystallization. If the cooling rate is so fast, then the structure of supercooled fluid state becomes rigid and forms a glass. Crystallization is the solidification of a highly structured form of atoms or molecules; this is the process in which glasses are transformed from a non-crystalline state to a crystalline state at elevated temperature [10], which explained in figure 2. The heating rate, temperature and duration of the holding periods are most important due to glass transition temperature \((T_g)\) may be superior for a rapid slope rate or inferior for a lower slope rate. During the crystallization of the glass to GC, change in dimension takes place [11]. The low density of GCs shows that they can be applied for the significant parts of an airplane structure and protective coating for metals [12].

Previously, various oxide glasses were fabricated by melt quenching technique doped with different dopants such as \(La_2O_3\), \(Fe_2O_3\), and \(Cr_2O_3\) for the enhancement of the crystallization and dielectric behaviors [13–15].
However, the GNPs was not used much as a dopant for the synthesis of perovskite glass and glass ceramics. Thus, owing to the exceptional properties of graphene such as high current density, high electron mobility at room temperature, high thermal conductivity and large surface area it is widely being used for several device applications [16–18]. Herczog and Stookey [19] were first to attempt the controlled crystallization of lead titanate (PbTiO₃) and they were successfully crystallized from the investigated glassy system SiO₂-Al₂O₃-TiO₂-PbO. PbTiO₃ glass and GCs showed their distinct properties such as structural, optical and dielectric behaviors [20]. These properties of PbTiO₃ glassy material attract for pyroelectric, electro-optical and nonlinear optical applications [21, 22]. Perovskite titanate

Figure 1. Schematic volume-temperature curves for the formation of liquid, crystal and glass [7–9].

Figure 2. Formation of glasses and heat treatment schedule for the preparation of glass ceramics: (a) casting stage, (b) rapid cooling, (c) annealing, (d) cooling down to room temperature, (e) heating the glass from room temperature, (f) nucleation, (g) increasing temperature, (h) crystallization and (i) cooling down to room temperature [10].
such as PbTiO₃ without any dopant was being studied by Bergeron [23]. Later on, Martin [24] observed that during heating of the glass PbO-TiO₂-SiO₂-B₂O₃, a secondary phase of PbTiO₃ was precipitated and then transformed into other secondary phases with further heating. Besides that, Kokubo et al [25] raised several issues to manage the suitable dielectric properties of PbTiO₃ GCs for their special demands. Consequently, Kokubo and Tashiro [26] have been reported a new glass forming region, grain size as well as T dependent high εᵣ. They also reported a spontaneous distortion within crystal grains of transparent PbTiO₃ GCs that precipitated in a glassy compound PbO-TiO₂-Al₂O₃-SiO₂. Literature showed various information are accessible on lead titanate glasses [27–37].

Based on graphene composites, various research articles have been reported. Many of them used graphene sheets which are produced from graphite oxide (GO) or graphite intercalation compounds (GIC). The main reasons for using GO and GIC, they showed high electrical conductivities, Young’s modulus and high chemical stability [38–40]. However, GNPs and graphene nanoribbons (GNRs) exhibit numerous interesting properties such as high electrical conductivities, Young’s modulus, linear monochromatic optical contrast, and electronic band gaps [41–44]. Therefore, due to these interesting properties, GNPs has been used to synthesize various glass and glass ceramic compounds.

Several considerable efforts have been made by the researchers to improve the εᵣ. However, the dissipation factor is still quite high. Synthesis and structural behaviors with effective εᵣ and less D are still of critical interest. Furthermore, to date, the studies have not been performed on PBTB glasses with the inclusion of GNPs. Therefore, we can optimize the compositional distribution with GNPs as an additive and their proper concentration to achieve the high εᵣ with low D for high storage applications. Thus, the current research was carried out to describe the glassy compound [(PbₓBi₁₋ₓ)TiO₃·][2SiO₂·B₂O₃]·[GNPs] with varying content of Pb/Bi to understand the crystallization mechanism, surface morphology and dielectric behaviors through optimized parameters.

2. Methods

2.1. Chemicals and synthesis of the glasses

Stoichiometric amounts of high purity AR grade chemicals of PbO (Himedia, 99% purity), Bi₂O₃ (Himedia, 99.5% purity), TiO₂ (Himedia, 99% purity), SiO₂ (Himedia, 99.5% purity), H₂BO₃ (Himedia, 99.5% purity), and GNPs (Reinstе, 99% purity) were used. The well weighed raw materials were mixed in acetone medium using an agate mortar-pestle to obtain the homogenous mixing; powder was dried in a muffle furnace at 100 °C for half an hour. The ~20 gm of the glass batches were poured into an alumina crucible which kept in an electric furnace. The glass melt was kept at 1300 °C with a heating @ 5 °C min⁻¹ for 30 min soaking time. The glass melt then quenched by pouring into a brass mould and pressed by an aluminum slab and then quickly moved inside a preheated programmable furnace at 400 °C for 3 h to remove the residual stresses. Eventually, the glasses were obtained at room temperature (RT) and taken out from the furnace for further characterizations. The investigated glass compositions, glass sample codes, melting temperature, casting temperature, appearance and color of the glasses in the compound 55[(PbₓBi₁₋ₓ)TiO₃·][2SiO₂·B₂O₃]·[GNPs] are listed in table 1.

2.2. Thermal analysis

For the DTA measurements, the coarse powdered glass samples of ~20 mg was used by employing a ‘Perkin Elmer Thermal Analysis’ within temperature range from 200 °C–900 °C given a heating @ 5 °C min⁻¹. The sintered kaolin was taken as reference material. Based on DTA results the various glass samples were devitrified into glass-ceramics using a controlled heat treatment schedule. During the crystallization the nucleation and growth started at crystallization temperature which is completed within the prescribed soaking time. The crystalline phases of the glass ceramic samples were recognized for indexing of each XRD peak comparing with standard JCPDS files.

2.3. Volumetric measurements

Density of the synthesized glass and GCs were estimated by employing the Archimedes principle [45]. Double distilled water was used to avoid the contamination. Density measurements were repeated three times for each sample to get statistically reliable results and the average values were taken respectively. Various values of the density of glass, and GC samples were calculated using the relation [46]:

\[
\rho = \frac{W_A \rho_L}{W_A - W_L}
\]

ρᵣ is representing the density of double distilled water at RT, Wₐ and Wₐ are the weight of the samples in liquid and air.
| S. No. | Investigated glass compositions | Glass samples code | Melting temperature (°C) | Casting temperature (°C) | Appearance | Color of the glasses |
|--------|--------------------------------|--------------------|--------------------------|--------------------------|------------|---------------------|
| 1.     | 55[(Pb_xBi_{1-x})TiO_3]-44[2SiO_2:B_2O_3] doped with 1 mol % of GNPs | BTG0.0             | 1200                     | 1300                     | Transparent | Light Brown         |
| 2.     | 55[(Pb_xBi_{1-x})TiO_3]-44[2SiO_2:B_2O_3] doped with 1 mol % of GNPs | PBTG0.3            | 1200                     | 1300                     | Transparent | Light Brown         |
| 3.     | 55[(Pb_xBi_{1-x})TiO_3]-44[2SiO_2:B_2O_3] doped with 1 mol % of GNPs | PBTG0.5            | 1200                     | 1300                     | Transparent | Light Brown         |
| 4.     | 55[(Pb_xBi_{1-x})TiO_3]-44[2SiO_2:B_2O_3] doped with 1 mol % of GNPs | PBTG0.7            | 1200                     | 1300                     | Transparent | Dark Brown          |
| 5.     | 55[(Pb_xBi_{1-x})TiO_3]-44[2SiO_2:B_2O_3] doped with 1 mol % of GNPs | PTG1.0             | 1200                     | 1300                     | Transparent | Dark Brown          |
The molar volumes, $V_M$, were also calculated with the help of density values from equation (1) and then substituted in the following relation [47]:

$$ V_M = \frac{aM_X + bM_Y + cM_Z}{\rho} $$

(2)

where, $a$, $b$, and $c$ are the mole percent of the components X, Y and Z; and $M_X$, $M_Y$ and $M_Z$ are respective molecular weights.

2.4. XRD and phase identifications

A Rigaku Ultima-IV diffractometer was used within 2θ range of 20–80° and a scanning rate of 2°/min. All XRD peaks were recognized analogous to the utmost peak containing (h k l) values and marked properly for the identification of crystalline phases for each GC sample. The crystallite size was calculated by using Debye-Scherer formula [48].

$$ \text{Crystallite size, } t_{DS} = \frac{K\lambda}{\beta. \cos \theta} $$

(3)

where, $K$ (0.94) reveals a shape factor, $\lambda$ represents Cu-K$_\alpha$ line having the wavelength (1.54 Å), $\beta$ indicates the FWHM and $\theta$ represents the Bragg’s angle.

2.5. Morphological study

For the recording of SEM images the surface of GC samples was polished successively on a thick and flat glass plate using different grades of SiC having mesh numbers 120, 600, 800 respectively. Further, samples were polished via different grades emery papers. To achieve the smooth finish, GCs were finally polished using a soft cloth with diamond paste having the particle size from 1 to 6 μm with a Hifin fluid ‘OS’. For the enhancement of the surface features the well-polished GCs were etched for 45 s with a solution (30 % nitric acid and 20 % hydrofluoric acid) to record the desired morphology. The etched GCs have been washed entirely by using double distilled water for eliminating the redundant wreckage from the surface and dried in an electric oven at 100 °C for half an hour to eradicate the water content from them. Preparation of the samples for SEM examination using JEOL (JEC-3000FC) Auto Fine Coater, palladium thin films spread over the etched surface of the GCs by using sputtering technique for avoiding the charge accumulation. Finally, GCs have been examined to study the morphology of the crystalline phase using a SEM (JSM-7610F, JEOL Ltd, Japan). The etched and dried GCs have been fixed at the copper stubs with conducting tape. Thus, the various SEM images were captured at desired magnification. The grain size was determine by employing a linear intercept method.

2.6. EDAX analysis

The characterization capabilities of EDAX are extremely outstanding to determine the chemical constituents [49]. The EDAX of palladium-coated GCs was used for qualitative and quantitative analysis. EDAX spectra were recorded by scanning a selected area of the sample to determine the average elemental composition. Later the electron beam was focused on the SEM image and an average EDAX pattern of a tentative GC sample was recorded.

2.7. Dielectric measurements

The both surfaces of GCs have been polished successively on a flat glass plate with special grades of SiC powders of grade number 120, 600 and 800 respectively. Further, GCs have been polished with the help of various emery papers 0/0, 1/0, 2/0, 3/0 and 4/0 respectively. Finally, the GC samples were polished by a smooth blazer cloth and using diamond paste of the atomic size 1–6 μm with Hifin fluid ‘OS’ for attaining the shining at the surfaces. GCs have been electroded using a fine silver paste on the polished surfaces and then cured at 450 °C for 10 min. The samples were mounted in the sample holder and placed inside a programmable muffle furnace. The sample holder was attached by an LCR Meter (Wayne Kerr 6500 P, UK). The various dielectric parameters, capacitance (C) and dielectric loss (D) were recorded at different frequencies (20 Hz–10 MHz) within temperature range from RT to 600 °C. The values of the relative dielectric constant, $\varepsilon_r$, were estimated by using the formula [50]:

$$ \varepsilon_r = \frac{C \times d}{\varepsilon_0 A} $$

(4)

where, ‘C’ is a measured capacitance; $\varepsilon_0$ is representing permittivity of the free space (a constant $8.854 \times 10^{-12}$ F m$^{-1}$); $d$ is the thickness of the sample (mm) and $A$ represents area of the sample (mm$^2$). Thus, the values of $\varepsilon_r$ and D have been plotted as a function of T at preferred frequencies for showing the variation in $\varepsilon_r$.
with temperature and frequency \( f \) of the applied electric field. Values of the dissipation factor were noted directly from the high-frequency LCR meter or determined by given relation below:

\[
D = \frac{G}{\omega C}
\]

where, \( \omega = 2\pi f \); \( f \) represents the frequency while \( G \) be the conductance.

3. Results and discussion

3.1. XRD study of glass samples

XRD analysis was performed to confirm the glassy (non-crystalline) behavior of PBTB glasses added with one mol percent of GNPs. The XRD patterns of the tentative glass samples BTG0.0, PBTG0.5 and PTG1.0 are depicted in figures 3(a)–(c) respectively. The figure exhibited broad peaks, which indicates that the tiny array of structural order uniqueness of the synthesized amorphous glassy material. Thus, the lack of jagged crystalline peaks divulged, that each of glass sample is noncrystalline in nature i.e. amorphous.

3.2. Volumetric analysis

The densities with molar volumes for PBTB, glass and GCs are scheduled in table 2. The density has been found in the range of 1.39–2.23 gm cm\(^{-3}\) for glass samples, while 1.44–2.25 gm cm\(^{-3}\) for the GC samples. It is observed that the enhancement in density for glass and GCs with increasing concentration of lead oxide and which is probably owing to rise in non-bridging oxygen (NBO) and may be ascribed to the substitution of less density material (\( \text{Bi}_2\text{O}_3, 8.90 \text{ gm cm}^{-3} \)) through a large density material (\( \text{PbO}, 9.53 \text{ gm cm}^{-3} \)). Hence, density of the Pb rich glass, PTG1.0 have been noticed highest (2.23 gm cm\(^{-3}\)) although this was noticed lowest, (1.39 gm cm\(^{-3}\)) in Bi-rich glass sample, BTG0.0. The densities of GC samples were found to be greater than the densities of its parent glasses. The density of PBTB glass and GCs doped with 1 mol % of GNPs were found to be less as compared to the density of PbT borosilicate glass and GC samples doped \( \text{La}_2\text{O}_3/\text{CeO}_2 \) [51–53]. This is the cause of the less density of GNPs (0.2–0.4 gm cm\(^{-3}\)), whereas the standard density of \( \text{La}_2\text{O}_3 \) and \( \text{CeO}_2 \) is 6.51 and 7.22 gm cm\(^{-3}\) respectively. The alteration in the values of density and \( V_M \) for different mol percentage of PbO for PBT borosilicate glass and GCs were depicted in figures 4(a), (b). The \( V_M \) decreases from 189.95 to 63.21 cm\(^3\) mol\(^{-1}\) for the entire range of the glass sample while for GC samples it decreased from 183.35 to 62.65 cm\(^3\) mol\(^{-1}\) with enhancing the content of PbO. The decrement in \( V_M \) endows available space which was diminishing all over the glassy matrix due to the growth of NBO [54]. It is also perceived that density and \( V_M \) of PBTB glass and GCs revealed a linear response with increasing amount of PbO.
3.3. Differential thermal analysis

DTA curves of various synthesized glass samples BTG0.0, PBTG0.3, PBTG0.5, PBTG0.7 and PTG1.0 are shown in figures 5(a)–(e) respectively. The DTA results were explored in the temperature range of 200 °C–900 °C. In all the glass samples, two separate exothermic peaks were observed for their crystallization from glass to GCs. The glass transition temperature, Tg and two distinct exothermic peaks Tc1, Tc2, were clearly observed at different temperatures. The first exothermic peak, Tc1 is sharp and mainly responsible for the major phase formation of bismuth titanium oxide and lead titanate (Bi2Ti2O7/PbTiO3) during the crystallization of the glasses whereas second exothermic peak, Tc2 is due to the formation of other secondary phases. Glass samples code, heating rate, holding time, Tg and Tc of the various PBTB glass samples have been enlisted in table 3. It is clear from table 3 that the glass transition temperature, Tg and crystallization exothermic peaks Tc1, Tc2 for all glass samples are increased with increasing concentration of PbO in the glassy compound. However, it should be decreased with increasing the ‘x’ due to the less viscous nature of the lead-rich glassy melts. Therefore, this reverse trend might be due to the addition of 1 mol % of GNPs. There are specific trends observed in the values of Tg and Tc, it is increasing with rising the content of PbO. This may be owing to the reduction in viscosity of glass melt by raising the amount of PbO in the glasses. Moreover, it is also observed that the Tc strongly affected by the doping concentration of GNPs due to the very high melting points of GNPs. The GNPs acts as an efficient nucleating mediator during heat treatment of PBTB glasses and also enhances the Tc of glass samples. It was also observed that the Tc for Pb rich glasses is greater than all the Bi-rich glasses. The first Tc1 (exothermic peak) was marked for each glass sample within temperature range 716 °C–746 °C. Based on the first Tc1, PBTB glasses doped with one mol percent of GNPs were converted into GCs by given a suitable heat treatment in the specified temperature range to explore the possibility of crystalline phase in the glassy matrix.

3.4. Crystallization behavior of the GC samples

The XRD results of various PBTB GC samples BTG0.0 716 F, PBTG0.3 722 F, PBTG0.5 735 F, PBTG0.7 740 F and PTG1.0 746 F were depicted in figures 6(a)–(e) respectively. XRD results for all the GC samples have been
Table 2. Glass compositions, density and molar volume of various glass and glass ceramics with their samples code in the system 55[(Pb₅Bi₁₋₅)TiO₃]-44[2SiO₂B₂O₃]-1GNPs.

| PbO | Bi₂O₃ | TiO₂ | SiO₂ | B₂O₃ | GNPs | Glass samples code | Density (gm/cm³) | Molar volume (cm³/mol) | Glass ceramic samples code | Density (gm/cm³) | Molar volume (cm³/mol) |
|-----|-------|------|------|------|------|-------------------|-----------------|------------------------|-------------------------|-----------------|-----------------------|
| 0.0 | 46.95 | 8.05 | 21.72| 22.28| 1    | BTG0.0           | 1.39            | 189.95                 | BTG0.0716 F           | 1.44            | 183.35                |
| 7.85| 37.87 | 9.28 | 21.72| 22.28| 1    | PBTG0.3          | 1.56            | 153.99                 | PBTG0.3722 F          | 1.61            | 149.20                |
| 14.57|30.11 |10.32 |21.72 |22.28 |1    | PBTG0.5          | 1.82            | 120.82                 | PBTG0.5735 F          | 1.89            | 116.34                |
| 22.99|20.37 |11.64 |21.72 |22.28 |1    | PBTG0.7          | 1.97            | 98.66                  | PBTG0.7740 F          | 2.01            | 96.69                 |
| 40.61|0    |14.39 |21.72 |22.28 |1    | PTG1.0           | 2.23            | 63.21                  | PTG1.0746 F          | 2.25            | 62.65                 |
indexed with standard JCPDS card numbers 32–0118, 74–2495 and 030401 showed the major crystalline phases of Bi$_2$Ti$_2$O$_7$/PbTiO$_3$ along with minor phase of GNPs. XRD patterns of GC samples BTG0.0716 F and PBTG0.3722 F have been displayed in figures 6(a), (b). XRD results of these GCs are almost comparable with each other, merely a slight disparity was observed in their crystallite size and the phase formation. The lead free GC sample (x = 0.0) showed a major phase of Bi$_2$Ti$_2$O$_7$ along with a minor phase of cubic crystal (lattice parameters a = b = c = 20.68 Å) and the crystallites size analogous to high-intensity peaks are 43.71 and 47.66 nm respectively. Figure 6(c) shows the XRD pattern of GC sample PBTG0.5735 F and depicts Bi$_2$Ti$_2$O$_7$ as a main phase with the minor phase of lead titanium oxide, PbTiO$_3$ as well as GNPs. The GC sample PBTG0.7740 F with x = 0.7 was specified an appropriate heat treatment at 740 °C for 4 h soaking time and the XRD pattern is shown in figure 6(d). This XRD pattern shows the reverse crystallization behavior of the GC sample PBTG0.5735 F. The crystalline structure of the GC sample PBTG0.7740 F shows the improved crystallinity and has been changed from cubic to tetragonal crystal structure. The PbTiO$_3$ was found to be a major crystalline phase with tetragonal crystal structure while Bi$_2$Ti$_2$O$_7$ and GNPs were found as the secondary phases. Figure 6(e) shows the XRD pattern of bismuth free lead titanate borosilicate GC sample PTG1.0746 F (x = 1). In this GC sample PTG1.0746 F, only the major phase development of PbTiO$_3$ and the minor phase of GNPs were observed with a tetragonal crystal structure and having lattice parameters, a = b = 3.90 Å and c = 4.15 Å. The GC samples code, crystallite size, lattice parameters, crystalline structure and the formation of phase of

**Table 3.** Glass samples code, heating rate, holding time, glass transition temperature and crystallization temperature of various glass samples in the system 55 [(Pb$_x$Bi$_{1-x}$)TiO$_3$]-44[2SiO$_2$-B$_2$O$_3$]-1GNPs.

| Glass samples code | Heating rate (°C min$^{-1}$) | Holding time (hours) | Glass transition temperature T$_g$ (°C) | Crystallization temperature T$_c1$ (°C) | T$_c2$ (°C) |
|--------------------|-----------------------------|----------------------|---------------------------------------|----------------------------------------|------------|
| BTG0.0             | 5                           | 4                    | 616                                   | 716                                    | 756        |
| PBTG0.3            | 5                           | 4                    | 624                                   | 722                                    | 759        |
| PBTG0.5            | 5                           | 4                    | 693                                   | 735                                    | 823        |
| PBTG0.7            | 5                           | 4                    | 696                                   | 740                                    | 827        |
| PTG1.0             | 5                           | 4                    | 698                                   | 746                                    | 831        |
PBTB GCs were enlisted in table 4. The average crystallite sizes related with high-intensity peaks were determined and found to be 26.08 nm and 89.32 nm for the GC samples PTG1.0746 F and PBTG0.5735 F respectively. The variations in the values of various parameters for the different compositions of GC samples in the glassy compound $\text{Pb}_{x}\text{Bi}_{1-x}\text{Ti}_2\text{O}_7-44\text{SiO}_2\cdot\text{B}_2\text{O}_3-1\text{GNPs}$ have been shown in figures 7(a), (b).

3.5. Surface morphological analysis

The SEM micrographs of all the GC samples BTG0.0716 F, PBTG0.3722 F, PBTG0.5735 F, PBTG0.7740 F and PTG1.0746 F are depicted in figures 8(a)–(e) respectively. Figure 8(a) reveals the SEM micrograph of the GC sample BTG0.0716 F. The microstructure of this GC sample shows a large amount of residual glass was present inside the sample after the crystallization process. This may be due to the low crystallization temperature or less soaking time. It is also observed from this micrograph that the grains of $\text{Bi}_2\text{Ti}_2\text{O}_7$ are well dispersed all over glassy matrix. The average grain size of this GC sample was found to be 429 nm. Further, from figure 8(b), it is observed that when the crystallization temperature is increased, it shows better crystallization and the crystallites shows the uniform distribution of grains that appears to be cubic and very dense inside the glassy matrix of the GC sample PBTG0.3722 F. Further, the major and minor phase formation of $\text{Bi}_2\text{Ti}_2\text{O}_7$ and $\text{PbTiO}_3$ were found with the average grain size of 462 nm. These results were further verified with the help of XRD results of the GC sample PBTG0.3722 F that crystallized at 722 °C for 4 h duration (figure 8(b)). The SEM micrograph of GC sample PBTG0.5735 F revealed randomly oriented and elongated grains of the $\text{Bi}_2\text{Ti}_2\text{O}_7$ as a main crystalline phase with a minor phase of $\text{PbTiO}_3$ (figure 8(c)). The average grain size for this micrograph was found to be the order of 925 nm. Figure 8(d) shows the well evolved and directionally oriented grains of the major crystalline phase of $\text{PbTiO}_3$ with some residual glassy phase of the GC sample PBTG0.7740 F. The crystallization of this GC...
Table 4. Glass ceramic samples code, crystallite size, grain size, lattice parameters, crystal structure, phase formation, dielectric constant and dissipation factor of various glass ceramic samples in the system 55\((Pb_xBi_{1-x})TiO_3\)-44\(2SiO_2\cdotB_2O_3\)–1GNPs.

| Glass ceramic samples code | Crystallite size (nm) | Grain size (nm) | Lattice parameters (Å) | Crystal structure | Phase formation | Dielectric constant, \(\varepsilon_r\) | Dissipation factor, D |
|----------------------------|-----------------------|-----------------|------------------------|-------------------|----------------|------------------------|---------------------|
|                            |                       |                 | a b c                   |                   |                | 100 Hz | 10 MHz | 100 Hz | 10 MHz |
| BTG0.0716 F                | 43.71                 | 429             | 20.68 20.68 20.68       | Cubic             | Bi_2Ti_2O_7 + GNPs | 201    | 61     | 1.00  | 0.01   |
| PBTG0.3722 F              | 47.66                 | 462             | 20.69 20.69 20.69       | Cubic             | Bi_2Ti_2O_7 + PbTiO_3 + GNPs | 369    | 50     | 0.73  | 0.01   |
| PBTG0.5735 F              | 89.32                 | 925             | 20.71 20.71 20.71       | Cubic             | Bi_2Ti_2O_7 + PbTiO_3 + GNPs | 576    | 46     | 1.75  | 0.01   |
| PBTG0.7740 F              | 72.47                 | 670             | 3.94 3.94 4.19          | Tetragonal        | PbTiO_3 + Bi_2Ti_2O_3 + GNPs | 689    | 62     | 1.78  | 0.01   |
| PTG1.0746 F               | 26.08                 | 616             | 3.90 3.90 4.15          | Tetragonal        | PbTiO_3 + GNPs | 820    | 66     | 2.49  | 0.01   |
sample was perceived better than the GC sample PBTG0.5735 F. The secondary phase formation of Bi$_2$Ti$_2$O$_7$ in the residual glassy matrix has been also noticed in the micrograph of the GC sample PBTG0.7740 F, which is also well consistent with its XRD results as depicted in figure 6(d). Figure 8(e) reveals that the morphology of grains distribution was found to be changed for bismuth free GC sample PTG1.0746 F and the amount of secondary phase was completely absent. The measured average grain sizes from the SEM micrographs for various GC samples have been listed in table 4.

3.6. EDAX study
The EDAX were carried out to understanding the chemistry of average elemental distribution within the crystallites of various constituents in different phases (major/minor) of GC samples. Understanding of this may also help us to analyze the influence of dopants on dielectric behaviors of the GC samples. The EDAX spectra of a tentative GC sample PBTG0.5735 F with $x = 0.5$, crystallized at 735 °C for 4 h and corresponding SEM micrographs are shown in figure 9. The GCs have complex microstructures and the characteristics depend on the controlled heat treatment process. From the SEM micrograph, it is noticed that the crystallites of Bi$_2$Ti$_2$O$_7$ are entirely grown in the glassy matrix as a major crystalline phase and showed the excellent nucleation as well as crystal growth of the GC sample. The average grain size for this micrograph was found to be the order of 925 nm. It is also observed from the EDAX spectra of GC sample PBTG0.5735 F that well-resolved peaks corresponding...
to different elements, Pb, Bi, O, Ti, Si and C were present and confirmed the synthesis of PBTB glasses with the presence of dopant, GNPs in the form of carbon (C). It confirms that the carbon ions present during the crystallization of glasses and changes the dielectric behavior of GC samples. The EDAX spectra of the average of the whole selected region show the high-intensity peak of Pb, O and Bi, which confirmed the presence of major constituents of lead and bismuth oxides. No any unwanted peak of irrelevant element/impurity was present in the EDAX spectra for this GC sample.

3.7. Dielectric characteristics
The dielectric behaviors of synthesized GC samples depend on different aspects viz. crystallization process, environment and content of the crystalline phases, crystallite sizes, morphology and crystal clamping etc [55]. The deviations of $\varepsilon_r$, dissipation factor (D) with variation of temperature at preferred frequencies between 100 Hz, - 10 MHz for various GC samples in the glass compound 55[(Pb$_x$Bi$_{1-x}$)TiO$_3$]-44[2SiO$_2$.B$_2$O$_3$]-1GNPs are shown in figures 10(a)–(j) respectively. These GC samples showed the elevated value of $\varepsilon_r$ with addition of 1 mol % of GNPs due to space charge polarization at semiconducting grains and insulating grain boundaries because of the semiconducting PbTiO$_3$ crystallites were bounded through insulating residual glass matrix for

Figure 8. Scanning electron micrographs of glass–ceramic samples (a) BTG0.0716 F, (b) PBTG0.3722 F, (c) PBTG0.5735 F, (d) PBTG0.7740 F and (e) PTG1.0746 F.
GC sample PTG1.0746 F. Moreover, the electric charge stuck at the boundary of crystal-glass interface and hence induces an interfacial polarization. Therefore, GC sample attains the effective values of dielectric constant in comparison to the rest GCs \[^{[56]}\]. At lower frequencies, the values of \(\varepsilon_r\) for all the GC samples were initially stable up to a fixed temperature, 150 °C and afterwards, it rises rapidly with increasing the temperature. However, the effect of temperature variation was lesser at higher frequencies and showed approximately stable trend with respect to temperature and exhibited temperature independent performance. The motive after this drift might be due to the dipole oscillation on the application of an external electric field, the enormous magnitudes of \(\varepsilon_r\) with low frequencies has been recognized as the potential of dipoles to follow the applied field. With increasing the \(f\), \(\varepsilon_r\) decreases since dipole start sheathing the electric field. Finally, with increase in the frequency, dipole does not succeed to track the field and for this reason, \(\varepsilon_r\) achieve a stable value at excessive frequencies. The variations of \(\varepsilon_r\) and dissipation factor showed almost similar trends for all the GC samples.

The values of \(\varepsilon_r\) and dissipation factor of all GC samples were enlisted in table 4. At 100 Hz, the observed minimum value of \(\varepsilon_r\) and D are found to be 201 and 1.0 respectively for the GC sample BTG0.0716 F (figures 10(a), (b)). The low \(\varepsilon_r\) may be because of vast content of glass phase exist inside the lead-free GC sample BTG0.0716 F \[^{[57]}\]. The \(\varepsilon_r\) for GC samples were increased from 201 to 820 with an increasing concentration of PbO from \(x = 0.0\) to \(x = 1.0\) because the GNPs enhanced the crystallization behavior of GC samples. GC samples revealed an increase in the values of \(\varepsilon_r\) because of the interfacial polarization. Moreover, it is also increasing from the conductivity variation between diverse phase as well as the interface of lingering glass and crystalline phase \[^{[58]}\]. The value of \(\varepsilon_r\) at 100 Hz of the GC sample PTG1.0746 F was 820 and the value of the maximum dielectric loss was found to be 2.49 (figures 10(i), (j)). The reason behind the large value of dielectric constant at low frequencies (<1 kHz) might be attributed to the unlimited charge buildup at boundaries of the crystallites and residual glassy phase inside the interfacial Maxwell-Wagner polarization as well as space-charge polarization at electrodes \[^{[59]}\]. This is also due to the good crystallization behavior and single phase formation of PbTiO\(_3\) in the bismuth free GC sample PTG1.0746 F that has been well consistent with the XRD results.

4. Conclusions

Different homogeneous, transparent colored and bulk glasses in lead-bismuth titanate borosilicate glassy compound have been fabricated through a simple melt-quenching technique. XRD analysis recognizes the noncrystalline behavior of synthesized glass samples. DTA results reveal two distinct exothermic peaks, \(T_{c1}\) and \(T_{c2}\) at different temperatures corresponding to their crystallization of the glass to GCs. The crystallization temperatures of the present glassy compound were strongly affected by the doping concentration of GNPs due to the very high melting points and large surface area. The GNPs doped PBT borosilicate glass and GCs revealed the less density and pretty good dielectric properties, which are significantly useful for various optical applications.
Figure 10. Variations of dielectric constant, $\varepsilon_r$ and dissipation factor, D with temperature at different frequencies for the various glass-ceramic samples (a), (b) BTG0.0716 F, (c), (d) PBTG0.3722 F, (e), (f) PBTG0.5735 F, (g), (h) PBTG0.7740 F, and (i), (j) PTG1.0746 F respectively.
and semiconducting devices. XRD analysis of PBT borosilicate GCs showing structural changes i.e. cubic to tetragonal and depends on the ratio of PbO/Bi₂O₃ as well as heat treatment schedules. Micrographs of the prepared GC samples show the distinct morphology of the crystallites by varying content of PbO/Bi₂O₃. The values of εᵣ of Pb rich GC samples were higher than the Bi-rich GCs. The εᵣ was observed highest for Bi free GC sample, PTG1.0746 F and the value of D was minimum for the GC sample PBTG0.3722 F at 100 Hz. Moreover, the increased εᵣ is because of the interfacial polarization on semiconducting crystallites and insulating crystallites borders of tetragonal phase of PbTiO₃. Thus, it is concluded that the inclusion of GNPs improved the growth of crystallites throughout the crystallization process and decreases the values of the dissipation factor. This shows that the doping of 1 mol % GNPs is suitable for good crystallization of the glasses.

Acknowledgments

The author is thankfully recognized to the Council of Scientific and Industrial Research–Human Resource Development Group, CSIR Complex, Pusa, New Delhi (India) for providing the financial help under ‘Senior Research Fellowship’ no. 09/107(0380)/2016-EMR-I (Ach. No. 124250/2 KI 5 /1). The authors are also conveying a sincere thanks to Centre of ESUP Scheme Government for extending the powder XRD facility at the Department of Physics, University of Lucknow. C. R. Gautam admiringly acknowledged to the Science and Engineering Research Board, Department of Science and Technology (SERB-DST) New Delhi, India for providing the monetary support under Empowerment and Equity Opportunities for Excellence in Science (File No. EEQ/2018/000647) as a major research project.

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