Preparation, Optical and Dielectric Properties of $(Pb_xBi_{1-x})TiO_3$ ($0.0 \leq x \leq 1.0$) Borosilicate Glass and Glass Ceramics Doped with La_2O_3, CeO_2 and Graphene Nanoplatlets

Chapter 1 introduces the processing of glass and glass ceramics, properties as well as their important applications.

Chapter 2 deals with the literature review of the earlier work done in the field of glass and glass ceramics; in particular, lead titanate, strontium titanate, lead strontium titanate and lead calcium titanate glass ceramics. Since the processing of glass ceramics offers several advantages over conventional solid state sintering method, it is desirable to obtain the required crystallites by controlled crystallization of glasses. Earlier attempts have been made by various researchers and scientists in the field of glass and glass ceramics, which are highlighted in this chapter. This chapter was also focused on brief discussions of optical, crystallization as well as dielectric behaviors of the glass and glass ceramics respectively.

Chapter 3 highlights the aim of the present research work. Although several studies on the synthesis, optical, crystallization and dielectric behaviors of glass and glass ceramics containing crystalline phases such as $PbTiO_3$, $SrTiO_3$, $(Pb,Sr)TiO_3$ and $(Pb,Ca)TiO_3$ have been reported but till date, no detailed investigations were observed on lead bismuth titanate borosilicate glass system in the literature to the best of our knowledge. Therefore, the main aims of the present investigations are to explore the possibility of bismuth substitution for the lead in lead titanate borosilicate glassy matrix. The search for easy glass forming system and its subsequent crystallization to give a desired solid solution perovskite phase was also studied. The effects of the addition of several dopants such as La_2O_3, CeO_2 and graphene nanoplatelets (GNPs) on structural, optical, crystallization and dielectric behaviors of lead bismuth titanate borosilicate glass and glass ceramics is also desirable for our study.

Chapter 4 deals with the experimental techniques which have been used to synthesize and characterized the glasses as well as glass ceramics in the present investigations. In order to achieve the set goal, there are three different glassy systems were optimized for our investigations that are prepared in several compositions by melt quenching technique. The optimized three glass systems are as follows:

1. $55[(Pb_xBi_{1-x})TiO_3]$ $-44[2SiO_2.B_2O_3]$$-1La_2O_3$; (0.0 ⍰ x ⍰ 1.0)

2. $55[(Pb_xBi_{1-x})TiO_3]$ $-44[2SiO_2.B_2O_3]$$-1CeO_2$; (0.0 ⍰ x ⍰ 1.0)

3. $55[(Pb_xBi_{1-x})TiO_3]$ $-44[2SiO_2.B_2O_3]$-1GNPs ; (0.0 ⍰ x ⍰ 1.0)

The synthesized glasses were characterized by infrared (IR) spectroscopy, Raman spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and contact angle measurements. To determine the glass transition temperature, T_g, crystallization temperature, T_c, melting temperature, T_m and the nature of the reaction kinematics, differential thermal analysis (DTA) measurements were carried out on the synthesized glasses. Therefore, on the basis of DTA results, glasses were subjected to different heat treatment schedules for the crystallization of glasses to glass ceramics. Density of the glass and glass ceramic samples were determined by the liquid displacement method. The crystalline phase, crystal structure and crystallite size of the resulting glass ceramics were identified with the help of powder X-ray diffraction (XRD). Scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX) of polished and chemically etched surfaces of the glass ceramic samples were recorded for studying the surface morphology and phase formation. Dielectric characteristics of the glass ceramic samples were studied by measuring capacitance, C and dissipation factor, D as a function of temperature at a few selected frequencies using LCR meter. X-ray absorption spectroscopy (XAS) measurements in transmission mode were carried out to confirm the high value of absorption coefficient. XAS measures the energy dependent fine structure of the X-ray absorption coefficients near the absorption edge of a particular element.

Chapter 5 contains the preparation, structural, optical, crystallization, microstructural and dielectric behaviors of lead bismuth titanate borosilicate glass and glass ceramic system $55[(Pb_xBi_{1-x})TiO_3]-44[2SiO_2.B_2O_3]-1La_2O_3$ within the compositions range of $0.0 \leq x \leq 1.0$. The bulk transparent glasses were successfully prepared by conventional melt quenching technique. For the study of structural information in the borosilicate network, the synthesized glasses were characterized by IR and Raman spectroscopy. The optical properties were studied by using UV-Vis spectroscopy. The optical band gap energy of various glass samples were calculated by Davis and Motts plots. The contact angle revealed the hydrophilic behavior and chemical heterogeneity of the observed solid surface for all the glass samples. DTA was carried out for investigations of crystallization kinematics. Variations of density and molar volume of glass and glass ceramic samples with the doping concentration of PbO were also discussed. Powder XRD patterns of glass ceramic samples confirmed the major formation of $Bi_2Ti_2O_7$ / $Pb_3Bi_4Ti_6O_{21}$ / $PbTiO_3$ as the crystalline phase. The microstructural studies were carried out with the help of SEM micrographs followed by EDAX for studying the surface morphology, phase formation as well as analysis of crystal growth, densification and elemental analysis. The high value of dielectric constant, ε_r is attributed to space charge polarization at crystal glass interface. The lead free glass and glass ceramic samples exhibit excellent XAS properties and are a promising material for the application of X-rays radiations protection. During heat treatment of the glasses, La_2O_3 serves as a nucleating agent for the perovskite crystalline phase and also acts as donor dopant. It makes the semiconducting nature of lead bismuth titanate borosilicate glass ceramics.

Chapter 6 described the studies on the preparation, structural, optical, crystallization, microstructural and dielectric behaviors of lead bismuth titanate borosilicate glass and glass ceramic system $55[(Pb_xBi_{1-x})TiO_3]-44[2SiO_2.B_2O_3]-1CeO_2$ with compositions ($0.0 \leq x \leq 1.0$). This chapter deals the similar studies of lead bismuth titanate borosilicate glass and glass ceramics as compared with chapter 5 but chapter 6 covers the studies with doping of 1 mol percent of CeO_2 in place of one mol percent of La_2O_3. **Chapter 7** focused on the studies of the preparation, structural, optical, crystallization, microstructural and dielectric behaviors of lead bismuth titanate borosilicate glass and glass ceramic system $55[(Pb_xBi_{1-x})TiO_3]-44[2SiO_2.B_2O_3]-1GNPs$ with compositions ($0.0 \leq x \leq 1.0$). This chapter also deals with the similar studies of lead bismuth titanate borosilicate glass and glass ceramics as compared with chapter 5. Chapter 7 covers the studies of lead bismuth titanate borosilicate glass and glass ceramics with 1 mol percent of GNPs in place of 1 mol percent of La_2O_3. However, a new investigation i.e. solid state nuclear magnetic resonance spectroscopy was also carried out for the GNPs doped lead bismuth titanate borosilicate glass samples

Chapter 8 contains a brief summary of the present investigations and an overview of lead bismuth titanate borosilicate glass and glass ceramics with different dopants La_2O_3, CeO_2 and GNPs respectively. Finally, the **Appendix** contains detailed descriptions of the standard JCPDS data with different phases for the presently studied glass ceramic systems.