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Fabrication and optical characterizations of lead calcium titanate borosilicate glasses

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ABSTRACT

Different glass samples were prepared in the system $59[(Pb_xCa_{1-x})O{\cdot}TiO_2]$-$40[2SiO_2{\cdot}B_2O_3]$-$1Fe_2O_3$ ($0 \le x \le 0.7$) employing a rapid melt-quenching technique. The IR structural and optical properties were evaluated using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and ultraviolet-visible (UV–VIS) spectroscopy. The amorphous nature of the glass samples were confirmed using XRD and SEM analysis. The Archimedes principle was used to calculate the density of all glass samples. The density increased with decrease in CaO content and the trend of molar volume reciprocal to the density. The band gap energy of the prepared glass samples are in the range of 1.25–2.37 eV and decrease with an increase in the concentrations of PbO.

1. Introduction

A material may be classified as crystalline, polycrystalline, amorphous, non-crystalline or glassy depending on the arrangement of atoms or molecules. Thus, glass is a non-crystalline solid possessing irregular periodic arrangement of group of atoms, molecules or ions and they broadly fall into the category of amorphous materials [1]. Consequently, glass can be defined as an inorganic product of fusion that has cooled to a solid state condition without prior crystallizing [2]. Glass exhibits the properties of super cooled liquids above the glass transition temperature, T_g where as it maintains the liquid structure in solid form below T_g. Glasses possess a few unique properties similar to that of ceramics for certain specific applications. The role of glass is significant in the field of science and engineering as they are easy to cast, proves beneficial from production-cost point of view and some of its properties are best suited in the field of architectural, electronics, telecommunications, aerospace industries, shielding and absorption of radiation and nuclear waste disposal.

Due to the existence of wide variety of glasses, the classification becomes extremely difficult as rapid developments in glass manufacturing and fabrication processes lead to creation of new and innovative glasses [3]. The borosilicate glasses are most widely used due to their scientific and technological importance over different oxide glasses such as SiO_2, B_2O_3, P_2O_5 and TeO_2 as they exhibit high chemical resistance, superior electrical shielding capability, high degree of optical transparency and low thermal expansion coefficient and can be used at elevated temperatures [4]. The transition metal oxides viz. V_2O_5, Fe_2O_3, MoO_3 and WO_3 can be incorporated into the borosilicate glasses to make it a semiconducting glass which could be the future base amorphous semiconductors and ionic materials. Elements such as Ti, V, Cr, Fe, Co, Ni and W can exist in more than one valence states in glasses whose insertion into oxide glasses exhibit remarkable electrical properties [5]. Kaewkhao et al. [6] have studied the structural, optical and magnetic properties of borosilicate glass system doped with iron oxide. Most researchers has been recognised the Fe_2O_3 as one of the most potential candidate for the improvement of electrical, optical and magnetic properties [5–10]. Moreover, Marghaa et al. [11] have reported that Fe_2O_3 has the potential applications and can be used as a photocatalyst and a photo electrode due to its strong absorptivity in the visible range, along with its low cost, abundance and narrow band gap, Eg ≈ 2.2 eV. They have also proposed that Fe_2O_3 cannot be used by itself due to the position of the valence band of Fe_2O_3 and so it is to be used with other semiconductors such as TiO_2. Hence, they studied a binary mixed oxide TiO_2-Fe_2O_3 which shows an increased photo catalytic activity for dichloroacetic acid destruction at 450 nm. Ibrahim et al. [12] also confirmed from the FTIR study that BO_3 group gets converted into BO_4 group with the addition of iron oxide which is clear from the shifting of bands and change in intensity. The formation of more non-bridging oxygen (NBO's) and an increase in bond length of the borate structural unit with an increase in PbO was reported by Saddeek et al. [13] which in turn increases the density, refractive index, polarisability and optical basicity of the studied glass system

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xPbO–R$Na_2B_4O_7$–(100-R-x)CAS (0.49CaO,0.21Al_2O_3, 0.3SiO_2) with $0 \leq x \leq 50$ and $50 \leq R \leq 75$ mol%. They also observed that there is a decrease in optical band gap with an increase in PbO content due to replacement of B—O and Si—O bonds (high strength) with a low strength Pb—O bond. Saini et al. [14] have observed that the glass transition temperature, T_g, decreases with an increase in PbO concentration which is due to the concentration of BO_4 and formation of NBO's in lead borate and borosilicate glasses. The PbO also changes its role from a glass modifier to glass former and containing covalent bond of Pb—O with increasing mol% of PbO in lead borosilicate glasses. This ensures a dominant role of PbO_4 and PbO_3 in reconstructing the network of borosilicate glasses by forming Pb—O—Si, Pb—O—Pb and Pb—O—B bonds [15]. Kumar et al. [16] reported that TiO_2 acts as a nucleating agent and promote the crystallization for efficient conversion of glasses into their corresponding glass ceramics which can be used in non-linear optical devices such as ultrafast switch and power limiter. It also acts as an n-type semiconductor by losing oxygen when heated in low oxygen/hydrogen pressure [17].

In the present research work, the main aim has been focussed on the synthesis of bulk and transparent glasses with their structural, physical and optical properties using different characterization techniques like XRD, SEM, FTIR, Raman and UV–VIS spectroscopy which are useful in identifying a variety of phases and unstructured array of atoms/molecules present in the glasses.

2. Experimental procedure

2.1. Glass preparation

For the present research work, a series of glasses in the system $59[(Pb_xCa_{1-x})O{\cdot}TiO_2]$-$40[2SiO_2{\cdot}B_2O_3]$-$1Fe_2O_3$ $(0 \leq x \leq 0.7)$ were prepared by using high purity chemicals viz. PbO (Himedia, 98%), CaO (Himedia, 95%), TiO_2 (Himedia, 99%), SiO_2 (Himedia, 99.5%), H_3BO_3 (Himedia, 99.5%) and Fe_2O_3 (Himedia, 98%). The proper amount of the raw materials were evaluated which were then properly weighed and mixed in a mortar and pestle using acetone medium and finally dried the powder. The dried powder of 25 g batches was melted in a high grade alumina crucible at 1400 °C using a programmable electric furnace @ 5 °C/min. In order to ensure the attainment of homogeneous mixing, the glass melt was kept hold on 1400 °C for ~ 30 min. Thereafter, the homogenised melt was quenched quickly pouring it onto an aluminium mould and pressing it with a thick aluminium plate followed by annealing in a preheated muffle furnace at 400 °C for 3 h to remove the stresses produced in it due to rapid cooling of the glass melt. Finally, the bulk and transparent glass was taken out from the muffle furnace at room temperature. Recently, similar synthesis processes has been reported by Gautam et al. [18–24] in detail.

2.2. Density and molar volume measurements

The density of the prepared glass samples were experimentally calculated by using the Archimedes principle which uses the law of physics related to displacement of liquid. The liquid medium used in this experiment was double distilled water to avoid contamination. A weighing digital balance of readability up to 0.0001 mg was used to measure the density at room temperature. The density of a glass sample was determined by averaging the densities of three samples of the same glass. A random error in the density measurement was found as ± 0.02%. Thus, the densities (ρ) and molar volumes (V_M) of the glass samples were determined using the following formula [15,25,26]:

$$\rho = \frac{W_2\text{-}W_1}{(W_4\text{-}W_1)\text{-}(W_3\text{-}W_2)}\rho_w \quad (1)$$

where, ρ = density (g/cm^3), ρ_w = density of distilled water 1 g/cm^3, W_1 = weight of empty specific gravity bottle (g), W_2 = weight of specific gravity bottle with sample (g), W_3 = weight of specific gravity bottle with sample and distilled water (g), W_4 = weight of specific gravity bottle with distilled water (g).

$$V_M = \frac{\sum X_i M_i}{\rho} \quad (2)$$

where, M_i is the molecular weight of the ith component and X_i is the molar fraction of the ith component.

2.3. X-ray diffraction measurements (XRD)

XRD is a unique analytical technique used for phase identification, unit cell dimension determination; and can also be employed for distinction between amorphous and crystalline nature of the materials. XRD analysis of the powdered glass samples ~~were~~ was carried out using Rigaku Miniflex-II x-ray diffractometer by means of Cu-Kα radiation (λ = 1.54056 Å) with step size of 0.02° over the 2θ range varying from 20° to 80°.

2.4. Fourier transforms infrared spectroscopy (FTIR)

FTIR technique provides valuable information about materials at their molecular level. It uses Fourier transform (a mathematical process) to convert the raw data into the actual spectrum. It computes, at which wavelength a sample absorbs or transmits infrared radiation. The FTIR spectra of the prepared glass samples were recorded by using Perkin Elmer; spectrum 100 spectrophotometer in the wavenumber range of 400–4000 cm^{-1} at room temperature. The samples for recording the FTIR spectra have been prepared by mixing the powdered glass sample (~2 mg) with potassium bromide (KBr) ~300 mg into an agate mortar and followed by making it into pellets by pressing in a hydraulic press machine and drying these pellets in an oven at 100 °C for 30 min to remove the moisture.

2.5. Raman spectroscopy

Raman spectroscopy is being widely used to detect the vibrational modes of molecular or microstructural units and also to acquire information about the composition and arrangement of materials. It is similar to Infrared spectroscopy (IR) in which IR bands arise from a change in the dipole moment of a molecule due to an interaction of light with the molecule of the material, whereas Raman bands arise from a change in the polarizability of the molecule due to the same interaction. The Raman spectra of the powdered glass samples were obtained by Micro Raman set up (Renishaw, UK). This set up was equipped with grating 1800 lines/mm and used powdered glass samples in the wave number range from 30 to 1000 cm^{-1}. For collecting the scatter at 1800 lines/mm with the help of scattering geometry, an Olympus (model MX-50) A/T was attached with the spectrometer to focus laser light into the sample. An excitation source of Ar^+ laser having wavelength of the order 15.4 nm was used, a software GRAM-32 was also used for the data collection.

2.6. UV–VIS spectrophotometer

UV–Visible spectrophotometer is one of the most frequently used techniques to measure the amount of ultraviolet or visible radiation absorbed by a substance. It is simple, quick, reasonably precise and applicable to small quantities of material. UV–VIS spectroscopy was recorded at room temperature from powdered glass samples using UV–VIS spectrophotometer (Shimadzu, UV–2450). It measures the percentage of radiation in ultraviolet (200–400 nm) and visible (400–800 nm) regions that were absorbed at different wavelengths within the regions. Light of these wavelengths excite the electrons in the atomic/molecular ground state to higher energy levels giving rise to an absorbance at wavelength specific to each molecule. Optical energy band gap, E_g, were determined by using Davis and Mott plots relation