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Role of titanium ions on the physical and structural properties of calcium zinc bismuth phosphate glass ceramics

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ABSTRACT

The transparent glass ceramics of composition $10CaF_2$–20ZnO–(15−x)Bi_2O_3–$55P_2O_5$: $x$$TiO_2$ ($0 \le x \le 4$) were prepared by melt quenching followed by heat treatment. The prepared samples were characterized by X-ray diffraction, differential thermal analysis and scanning electron microscopy. These studies have revealed that the samples contain well defined randomly distributed crystalline phases with the complexes of Ti^{4+} and Ti^{3+} ions. Spectroscopic studies viz., optical absorption, electron paramagnetic resonance, Fourier transform infrared and Raman were also carried out on these glass ceramics. The results of optical absorption and electron paramagnetic resonance studies revealed that part of the titanium ions exist in Ti^{3+} state that occupy the tetragonally distorted octahedral sites in the glass ceramic network and these ions are found to increase with an increase in the content of nucleating agent TiO_2. Fourier transform infrared and Raman studies indicating the formation of TiO_6 structural units along with cross linkages viz., P–O–Bi, P–O–Ti. But when TiO_2 is present in the larger quantities, the Π-bond of P = O may be ruptured by TiO_4 structural units which may cause the creation of new non-bridging oxygen ions facilitating the formation of $[TiO_{6/2}]^{2-}$ structural units also. Therefore, the analysis of spectroscopic studies indicating that the glass ceramics contain greater than 2 mol% of TiO_2 is suitable for semi-conducting applications.

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1. Introduction

Glass-ceramics are materials formed through the controlled nucleation and crystallization of glass. Glass-ceramics are also known as vitrocerams, pyrocerams, vitroceramiques and sittals. Glasses are melted, made-up to shape, and thermally converted to a predominantly crystalline ceramic. The basis of controlled internal crystallization lies in efficient nucleation, which allows for the development of fine, randomly oriented grains generally without voids, microcracks, or other porosity [1,2].

Phosphate glasses are technologically important materials because they have a series of attractive advantages over conventional silicate and borate glasses due to their superior properties such as low glass transition and melting temperatures, high thermal expansion coefficient, low preparation temperatures, biocompatibility, low dispersion and relatively high refractive indices [3,4]. The structure of phosphate glasses is composed of an inorganic phosphate network in which PO_4 tetrahedral units are the main building blocks. The tetrahedra can be described in terms of Q^n terminology, where n represents the number of bridging oxygens (BOs) per PO_4 tetrahedron [4].

The addition of ZnO to phosphate glasses is interesting because the ZnO–P_2O_5 systems show unusual changes in correlation between the structural and physical properties (e.g., mass density, refractive index and ultraviolet absorption edge) at the metaphosphate composition [4]. Zinc phosphate glasses have been developed for use as LED light sources [5] and as substrates for optical waveguides written by f-sec lasers [6]. Such glasses also tend to have greater coefficients of thermal expansion with low processing temperatures which make them useful as sealing glasses [7]. A drawback to the use of binary zinc phosphate glasses is their susceptibility to chemical attack because of the ease of hydrolysis of the P–O–Zn bonds [8]. It is known that the incorporation of additional oxides can improve the chemical durability of phosphate glasses; one in particular is the heavy metal based bismuth oxide which has been shown to reduce corrosion rates in aqueous solutions of zinc phosphate glasses, presumably due to the formation of more chemically resistant P–O–Bi bonds. Besides this bismuth based glasses posses the properties viz., high third order non-linear optical susceptibility, high refractive index and high IR transparency. Such properties make them suitable for reflecting windows, layers for optical and opto-electronic devices, thermal and mechanical sensors, optical telecommunication and processing devices, ultra fast optical switches and photonic devices [9].

Addition of calcium fluoride (CaF_2) to heavy metal phosphate glass batches lowers the viscosity of glass melt and there by reduces liquidus temperature to a considerable extent and also makes the glasses more corrosion resistant [10]. Recent research has shown that calcium phosphate glasses which contain titania and fluorine have shown to have

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excellent chemical durability and can have an application as dental filler [11].

In the glass-ceramics system the nucleating agents such as TiO_2, ZrO_2, CaF_2 were used in order to induce bulk crystallization of the phases and reduce the crystallization peak temperature [12]. Among these nucleating agents, even a small amount of TiO_2 showed a remarkable change in the crystallization process and also it is miscible in the molten glass and it induces phase separation during cooling of the melt. TiO_2 also behaves as intermediate network former and contributes to the stabilization of the phosphate network. Thus relatively large glass-forming regions were reported [13,14]. In general, titanium can exhibit two valencies viz., Ti^{4+} and Ti^{3+} in glasses. Among these two mostly observed Ti^{4+} ions participate in the glass network with glass forming position with TiO_4 units, where as Ti^{3+} ions act as only modifier with TiO_6 structural units in the glass matrix and sometimes with comprising trigonal bipyramidal structure of TiO_5 units [3]. Murali Krishna et al. [15] also reported that during the melting process, some of Ti^{4+} ions may convert into Ti^{3+} valence state in certain glass matrices and act as modifiers. Therefore, such variations in the coordination and valence of titanium ions in the glass network produce structural modifications and local-field variations in the glass ceramic structure which influences their potential applications. Some researches [16–18] also reported that titanium doped glasses have much importance because of their possible applications in non-linear optical devices such as ultrafast switch and power limiter 100.

Keeping in view of the above potential applications of zinc bismuth phosphate glasses we are interested in synthesizing the CaF_2–ZnO–Bi_2O_3–P_2O_5 glass ceramics doped with TiO_2 as a nucleating agent and examining the effect of nucleating agent on the spectroscopic properties as they are very sensitive to the oxidation state of TiO_2 and other structural aspects.

2. Experimental

In the present study, the stable and transparent glass ceramics of composition $10CaF_2–20ZnO–(15-x)Bi_2O_3–55P_2O_5: xTiO_2$ ($0 \le x \le 4$) were chosen and prepared by conventional melt quenching and heat treatment process. The detailed compositions (all in mol %) of the prepared glass ceramics are as follows.

T0: $10CaF_2–20ZnO–15Bi_2O_3–55P_2O_5$.
T1: $10CaF_2–20ZnO–14Bi_2O_3–55P_2O_5$: $1TiO_2$.
T2: $10CaF_2–20ZnO–13Bi_2O_3–55P_2O_5$: $2TiO_2$.
T3: $10CaF_2–20ZnO–12Bi_2O_3–55P_2O_5$: $3TiO_2$.
T4: $10CaF_2–20ZnO–11Bi_2O_3–55P_2O_5$: $4TiO_2$.

The batches of 15 g weight containing the proportionate amounts of analytical grade reagents CaF_2 (High media 99.99% pure), ZnO, Bi_2O_3, P_2O_5 and TiO_2 (LOBA, 99.99% pure) were thoroughly mixed in an agate mortar for 40 min and the homogenized mixture melted for 20 min in a thick walled silica (infusil make) crucible at 1300 °C in PID controlled furnace until a bubble free liquid is formed. The molten material was poured on a preheated brass mold at room temperature and subsequently annealed. DTA studies on amorphous samples were carried before the crystallization. The DTA curves of all the samples exhibited exothermic peak between 690 and 710 °C. Based on this observation we have chosen 700 °C for the crystallization treatment of the samples and were heat treated for 36 h. After the heat treatment at above specified temperature, the samples were allowed to cool slowly to room temperature. The titanium free specimen (T0) appeared to be more transparent and it is thick brown in color. Color of the samples was observed to change gradually from thick brown to yellow subsequently yellow to purple color with an increase of TiO_2 from 1 to 4 mol%. The photographs of the heat treated samples are shown in Fig. 1.

These samples were characterized by powder X-ray diffraction (XRD) patterns recorded in the range 10–80^0 of 2θ with an instrument SHIMADZU XRD 7000 Maxima system using the step scan method with Cu-K_α radiation ($\lambda = 1.5406$ Å) operated at 40 kV, 25 mA. The surface morphology of prepared samples was carried out using HITACHI S3700N scanning electron microscope (SEM) to observe the crystallinity of the ceramic samples.

Differential thermal analysis (DTA) of the samples was carried out using SHIMADZU DTG-60 H instrument (to an accuracy of ± 0.1 °C) with a heating rate of 10 °C/min in the temperature range of 200–1300 °C to determine the glass transition and crystalline temperatures. A programmable VIBRA HT density measurement kit was used to determine the densities and molar volumes of samples automatically (with readability 0.001 g/cm^3) by means of Archimedes' principle using O-xylene (99.99% pure) as a buoyant liquid. Using the density and average molecular weight the physical parameters such as titanium ion concentration N_i, polar radius R_P, and inter-titanium ionic distance R_i in the glass ceramics were evaluated.

The samples were then grounded and polished. The optical absorption spectra of the samples (thickness 1 mm) were recorded in the wavelength range of 200–1200 nm up to a resolution of 0.1 nm using JASCO V-670 UV–vis–NIR spectrophotometer. The Fourier transform infrared (FTIR) spectra of prepared glass ceramics were recorded by dispersing the glass powders in KBr with a SHIMADZU FTIR-8400S spectrometer in the range of 400–1400 cm^{-1} with spectral resolution of 0.1 cm^{-1}. Micro-Raman spectra were recorded using a HoribaJobin-Yuon-UV800 Lab RAM HR spectrometer with a 17-mw internal He–Ne laser source of excitation wavelength of 514 nm with a spectral resolution of about ± 0.03 cm^{-1}. The electron paramagnetic resonance (EPR) spectra of titanium doped glass ceramic samples were recorded on JEOL-FE-IX (X-band) EPR spectrometer operating at 9.125 GHz with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT and the microwave power used was 10 mW.

3. Results

3.1. Physical parameters

The density of the titanium free glass-ceramic sample is found to be 4.020 g/cm^3 and observed to decrease gradually with increasing the nucleating agent TiO_2 content in the system. Other physical parameters such as molar volume V_m, titanium ion concentration N_i, mean titanium ion separation R_i, polaron radius R_p of CaF_2–ZnO–Bi_2O_3–P_2O_5: TiO_2 glass-ceramics are evaluated and presented in Table.1.

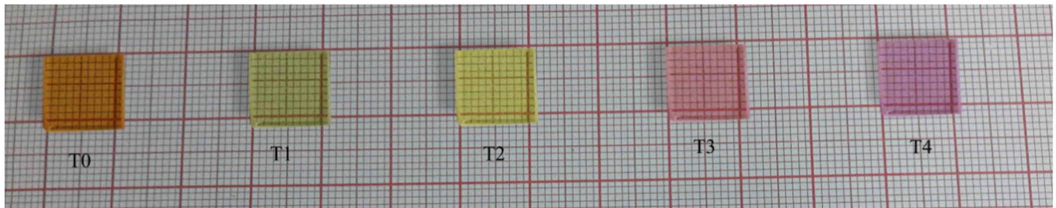

Fig. 1. Photographs of CaF_2–ZnO–Bi_2O_3–P_2O_5: TiO_2 glasses after crystallization.

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