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Titanium oxide doped glass matrices and their spectral properties

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Abstract

A series of Li_2O-PbO-Al_2O_3-B_2O_3-SiO_2 (LPABS) glasses doped with different concentrations of TiO_2 have been synthesized by normal melt quenching method. Differential thermal analysis of the samples indicated increasing glass forming ability with the increasing concentration of TiO_2 in the glass matrix. The prepared glass samples are characterized by X-ray diffraction (XRD), Optical absorption and Fourier transform infrared (FT-IR) spectroscopic techniques respectively. XRD pattern reveals that the titanium doped LPABS glass system is in amorphous nature. The effects of glass composition and melting condition on valence state and coordination geometry of polyvalent Ti ions have been studied by optical absorption spectra. The FT-IR spectra have shown the characteristic spectra of borosilicate glasses.

Key wards: XRD, Optical and FT-IR spectroscopic techniques.

Introduction

Transition metal ions doped glasses have attracted the attention many researchers because of their interesting properties related to spectroscopy and other practical applications like fiber optical communication, memory devices, photo-conducting properties and luminescent solar concentrators [1]. Glass ceramic materials are expected to have several advantages like good mechanical, electrical and thermal properties, high chemical durability with no crack growth inside [2]. Recently, transparent crystallized glasses i.e., composites of crystalline and glassy phases, consisting of nonlinear optical crystals have received much attention and there have been many reports on the fabrication and characterization of such transparent crystallized glasses [3].

Lead oxide (PbO) is the contrast element with the conventional alkali/alkaline earth oxide/halide modifiers which has the tendency to form the stable glasses due to its dual role one as modifier (with PbO_6 structural units) and the other as glass network former both with covalent and ionic bonding with pyramidal units connected in puckered layers. So, the addition of PbO to silicate glasses makes them highly stable against devitrification and chemically inert [4].

Diboran trioxide (B_2O_3) is one of the most important glass forming oxides and has been incorporated into various kinds of glass systems in order to attain the desired physical and chemical properties. Borate glasses have been particular scientific significance for many years. Borate glasses present an ideal case to demonstrate the effectiveness in optical and EPR spectroscopy in glass science in comparison with the other oxide glass forming systems. These glasses are easily melted and are good host for transition metals ions. Hence when glasses are doped with transition metal ions, they will become suitable for many practical applications [5].

Silicate glass plays a significant role in various technically orientated in glass applications. Borosilicate glasses have mixed network formers and combine the advantages of the stability of silicate glass and the higher TM ion solubility of borate glass without producing heavy concentration quenching, and thus are promising candidates for good TM ion hosts to develop highly efficient luminescence materials. The first member of the 3d-TM ions, titanium has been attracting increasing interest in its optical properties, because the addition of titanium dioxide can increase the refractive index, density, transformation temperature and chemical durability of the glass, thereby extending its applications such as optical components, sealing materials, chemically resistant containers, laboratory apparatus, for ampoules, pharmaceutical containers, glass fibers for textile and plastic reinforcement, and other sequestration of radioactive waste [6- 8].

Borosilicate glass, the third major group, it is made mainly of silica (70-80wt %) and boric oxide (7-13wt %) with smaller amounts of the alkalis (Lithium carbonate and potassium oxides) and aluminum oxide. This type of glass has relatively low alkali content and consequently has good chemical durability and thermal shock resistance. As a result it is widely used in the chemical industry, The controlled heat treatment of borosilicate glasses especially those which have domain sizes in sub-optical scale is interesting in controlling and designing the physical properties such as chemical durability, crystal nucleation rates, and high-temperature strength, and is of interest in some natural magmatic systems as well. Due to these interesting physical properties, borosilicate glasses can be used as laser host matrices after doping with rare earth oxides [9].

A large number of commercial glasses are based on alkali borosilicate systems, with a majority of these glasses primarily containing soda instead of any of the other alkali oxides. Most of the commercial glasses, while transparent, are actually phase separated with very fine scale morphology [10].

Alumino borosilicate glasses are well-known due to their low thermal expansion coefficient, high chemical durability, superior biocompatibility and high electrical resistivity. In view of such characteristics these glasses are being widely used in various domains like low cost optical connectors, dielectrics and up-converting optical materials and as sealant materials for solidoxide fuel cells etc. Recently investigated the structural properties of aluminum borosilicate glasses concluded that the ratio of B_2O_3/Al_2O_3 effectively influences the transition temperature of the glass. In general, the presence of Al_2O_3 in the glass matrix makes the glasses more resistant to attack by alkali metal ion like Na^+. This is obviously because of the entering of Al_2O_3 into the glass network with AlO_4 structural units that crosslink the neighboring borate and silicate chains [11].

The addition of TiO_2 to these glasses contributes to improve glass-forming ability, chemical durability and stabilization of the glass structure. TiO_2 has attractive characteristics such as chemical stability and high refractive index, and it is used as a photo catalyst. If oxide semiconductor TiO_2 crystallites are precipitated in glass matrix, TiO_2 glass-ceramic will be a functional optical device, such as photo catalyst or strong scattering media. Thus, several studies of TiO_2 on glass properties have been published. However, only a few reports on effect of TiO_2 in a soda lime borosilicate glass. The aim of the present study is to prepare the TiO_2 doped lithium borosilicate glass with different TiO_2 concentrations and the effect of TiO_2 content on the physical, XRD, FT-IR and optical absorption have been studied.

Experimental details

Glass preparation

The investigated glasses have been prepared by mixing appropriate quantities from the reagent materials are synthesized in this study by a conventional melt-quenching method, are summarized in Table 1. The raw materials are lithium carbonate , lead oxide , aluminum oxide , boric acid, silicon dioxide and Titanium dioxide are used analar grade with purity of 99.9 %. The stoichiometric compositions of the materials (10 g) are melting in air in silica crucibles in an electric furnace at temperature 1200^0C for 20 min until a bubble free liquid is formed. At the end of the melting process in order to obtain homogeneous and the melts are poured on brass plates and annealed at a temperature (T_g - 400^0C) for12 h and cooled slowly to release the thermal stress associated with these glasses during the quenching process. The glass matrix is obtained transparent and colorless. The samples are then ground and optically polished. In this procedure high melting temperature was employed due the high melting points of the PbO, B_2O_3, SiO_2, TiO_2 and Al_2O_3. Additionally, the addition of Al_2O_3 to silicate melts increases the viscosity although the addition of alkali oxides promotes the opposite behavior. The decrease from melt temperature to pour temperature permitted adjusting the viscosity, to obtain bubble free transparent glasses with high homogeneity.

Table. 1 LPABS, Li_2O-PbO-Al_2O_3- B_2O_3- SiO2-xTiO2 glasses composition

Li_2O	PbO	Al_2O_3	B_2O_3	SiO_2	$xTiO_2$
20	10	5	40	25	0
20	10	4.7	40	25	0.3
20	10	4.4	40	25	0.6
20	10	4.1	40	25	0.9

Characterization techniques

The X-ray powder diffraction pattern of prepared undoped and titanium doped glass samples are recorded using on XRD-6100 SHIMADZU X-Ray diffract meter in the scanning range of 10-80^0 (2θ) using Cu K_α radiation having a wavelength of 1.5406 Å at room temperature. The optical UV-Visible absorption spectra of prepared glass samples are recorded using Shimadzu UV-VIS-Spectrophotomètre in the wavelength region of 200-1200 nm.

Results and discussion

XRD Spectra:

The XRD patterns of the glass samples are shown in Fig. 1. The two broaden diffraction lines reveal the amorphous of un-doped and titanium doped glass samples. Each pattern exhibits a broad diffuse scattering especially at low angles, instead of crystal-line peaks, confirming a long range structural disorder characteristic of amorphous network [12].

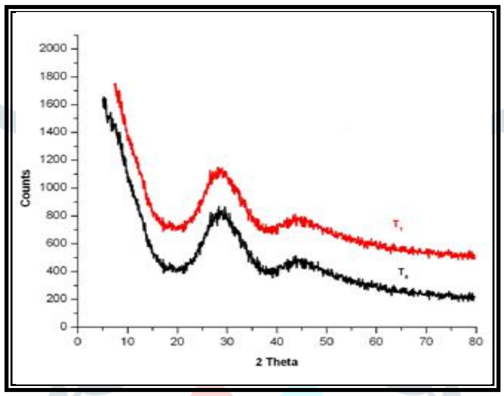

Fig. 1 X-ray diffraction patterns of undoped and TiO_2 doped LPABS glasses

FT-IR Spectra:

FT-IR and Raman spectroscopy are complimentary methods to XRD investigations for studying the structural changes in LPABS glasses [13]. The region of FT-IR spectra (**Fig. 2**) between 1000 cm^{-1} and 1300 cm^{-1} is mainly associated with an asymmetric stretching mode of Si –O- Si. The band near 800 cm^{-1} could be identified as symmetric stretching Si- O- Si vibration, and, finally, the band near 460 cm^{-1} measured in diffuse reflectance in this experiment should be assigned to Si –O-Si bending vibrations [14,15]. It is well known that the effect of introduction of alkali oxides into B_2O_3 glass is the conversion of sp^2 planar BO_3 units into more stable sp^3 tetrahedral BO_4 units, it may be also create non-bridging oxygen (NBO). Each BO_4 unit is linked to two such other units, and one oxygen from each unit with a metal ion and the structure leads to the formation of long tetrahedron chains. The second group of bands is attributed to such BO_4 units whereas the first group of bands is identified as being due to the stretching relaxation of the B–O bond of the trigonal BO_3 units and the band at 715 cm^{-1} is due to the bending of B–O linkages in the borate network [16, 17]. Here the ear-lier studies on the IR spectra of various other glasses containing TiO_2 indicate the presence of a irrational band at about 720 cm^{-1} which is attributed to the vibrations of TiO_4 groups [18]. In this region, the band due to vibrations of AlO_4 structural units is also ex-pected. The irrational band due to AlO_6 structural units is located at about 452 cm^{-1} in this region the band due to Si−O−Si rocking motion is also reported. Hence the linkages of the type Al−O−Si is predictable in the glass network [19].

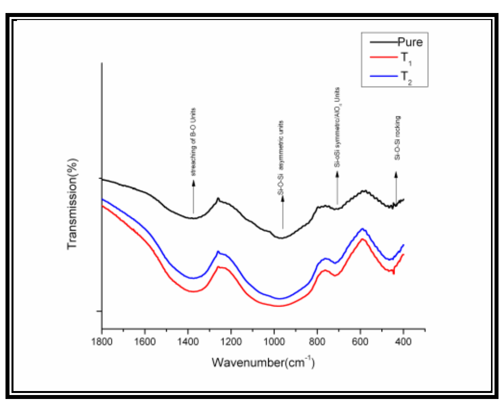

Fig. 2 FT-IR Spectra of TiO_2 doped LPABS glasses

UV-Absorption Spectra:

The absorption spectra of LPABS doped with TiO_2 glasses recorded at room temperature in the wavelength region 300-2000 nm [20]. The absorption edge is observed at 317 nm for the glass ceramic sample to exhibit blue spectral shifted with increase the concentration of TiO_2 is as shown in **Fig. 4.** [21]**.** The Spectrum of glass exhibited two weak bands at about 519 nm and 695 nm .These bands are due to $^2B_{2g}\rightarrow{}^2B_{1g}$ (519 nm) and $^2B_{2g}\rightarrow{}^2A_{1g}$ (695 nm) transitions [22-24]. Ti^{3+} ions give a visible absorption band in the range 510 nm-640 nm change transfer transition between ligand oxygen atoms and Ti^{3+} or Ti^{4+} occur in the ultraviolet region .Our graph produces no color in sodium borosilicate glass [25,26]. The band gap of the prepared glass matrix is 3.9 to 4.0 eV is as shown in **Fig. 3**.

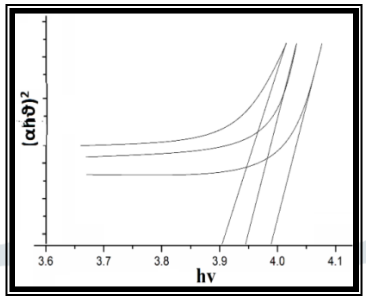

Fig. 3 Direct band gap of TiO_2 doped LPABS glasses

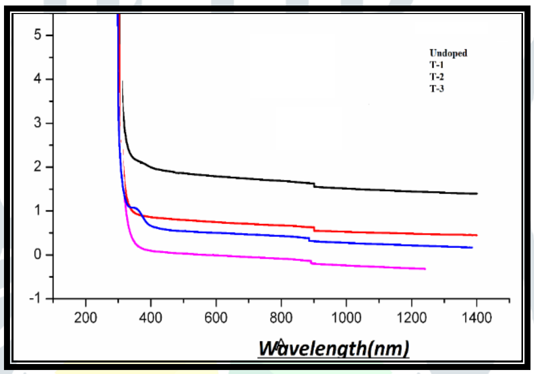

Fig. 4 Optical absorption spectra of TiO_2 doped LPABS glasses

Table. 2 Data on optical absorption spectra of Tio_2 doped LPABS glasses

Glass sample	$^2B_{2g}\rightarrow{}^2B_1$(cm^{-1})	$^2B_{2g}\rightarrow{}^2B_1$(nm)	$^2B_{2g}\rightarrow{}^2A_{1g}$ (cm^{-1})	$^2B_{2g}\rightarrow{}^2A_{1g}$ (nm)
T_1	0.001923	520	0.001349	741
T_2	0.001923	520	0.001349	741
T_3	0.001926	519	0.001351	740

Conclusions

XRD patterns glass system confirm a long range structural disorder characteristic of amorphous network frame. FT-IR spectra observed vibrational modes are in good agreement with the other reported inorganic template glass materials, From UV-Vis spectra the band gap energies are calculated.

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