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Effect of WO_3 on structural and optical properties of CeO_2–PbO–B_2O_3 glasses

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A R T I C L E I N F O

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Pure and WO_3 doped CeO_2–PbO–B_2O_3 glasses are prepared by the melt-quench technique. The structural and optical analyses of glasses are carried out by XRD, FTIR, density and UV–vis spectroscopic measurement techniques. FTIR analysis indicates the transformation of structural units of BO_3 into BO_4 with W–O–W vibration and the presence of WO_4 and WO_6 units observed with increase in WO_3 contents. Decrease in band gap for CeO_2–PbO–B_2O_3 glasses from 2.89 to 2.30 eV and for WO_3 doped glasses from 2.89 to 1.95 eV has been observed and discussed. This decrease in band gap with WO_3 doping approaches to semiconductor behavior. It shows that the presence of WO_3 in the glass samples causes more compaction of the borate network due to the formation of BO_4 groups and the presence of WO_4 and WO_6 groups, which result in a decrease in the optical band gap energy and increase in the density.

1. Introduction

In the modern world of technology, glass material plays an important role. Among oxide glasses, borate glasses have been subjected to a number of infrared studies due to their structural peculiarities. B_2O_3 is a basic glass former because of its higher bond strength, low cation size, small heat of fusion and valency of +3. In borate glasses, B^{3+} ions are triangularly coordinated by oxygen to form glass easily and are often used as dielectric and insulating material. It is also believed that borate glass provides a good shielding against IR radiations.

Cerium doped glasses are used in various practical applications of these materials such as laser active media, radiation protection of fiber optic materials and scintillation materials [1–4]. Recently, Ce^{3+} ions doped high density scintillators have attracted great attention due to quick development of high energy nuclear physics and electromagnetic energy devices. In doped form, ceria is of interest as a material for solid oxide fuel cells because of its relatively high oxygen ion conductivity [5]. It is transparent for visible light and it can absorb ultraviolet radiation; so it is a prospective alternative of zinc oxide and titanium dioxide in sunscreens/UV blocking devices, as it has lower photocatalytic activity. Cerium oxide has γ-radiation sensing, alumina/cerium oxide nano-composite electrolyte for solid oxide fuel cell applications and carbon monoxide gas-sensing properties [6–8] .

WO_3 and MoO_3 are two transition metal oxides, which do not form glasses by themselves but do so readily in combination with other glass formers like B_2O_3. Tungsten trioxide is a wide band gap semiconductor metallic oxide, and it is well known for its interesting optical properties, which are important in solid state micro-batteries, optical smart window, display devices and gas sensors [9–13]. Tungsten ions are well known for their unusual influence on optical and electrochemical properties of glasses for the simple reason that the oxides of tungsten participate in glass network with different structural units like WO_4 and WO_6 [14–16] . Tungsten oxide containing glasses are of great interest because they can exhibit unusual electrochromic or photosensitive properties related to the ability of tungsten atoms to exhibit various oxidation states (W^{6+}, W^{5+} or W^{4+}).

The purpose of this work is to examine the effect of WO_3 on the structural properties and optical band gap of CeO_2–PbO–B_2O_3 glasses and will be used for future applications.

2. Experimental procedure

2.1. Sample preparation

Glass samples of compositions $x\mathrm{WO_3}$–$x\mathrm{CeO_2}$–$(30-x)$ PbO–$(70-x)$ B_2O_3 and $x\mathrm{CeO_2}$–$(30-x)$ PbO–70B_2O_3 with x varying from 2% to 10% mole fraction are prepared by melt-quench technique. The raw materials of lead oxide (PbO), tungsten oxide (WO_3), cerium oxide (CeO_2) and boric oxide (B_2O_3) in appropriate amounts are mixed together and melted in silica crucible at temperature range of 1000 °C for 60 min until a bubble free liquid was formed. The melt is then poured into a preheated steel mould and annealed at temperature of 380 °C for 1 h to avoid breaking of the samples by residual internal strains. The obtained samples are ground with different grades of silica carbide and polished with cerium oxide in order to obtain maximum flatness. The nominal composition of the prepared glasses is given in Table 1.

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Table 1
Nominal composition (mole fraction), density and energy band gap of the glass samples.

Glass	WO_3 (%)	CeO_2 (%)	PbO (%)	B_2O_3 (%)	Density, D (g/cm^3)	Optical band gap, E_{opt} (eV)
c00	0	0	30	70	3.11	2.89
c11	0	2	28	70	3.34	2.60
c22	0	4	26	70	3.44	2.45
c33	0	6	24	70	3.51	2.43
c44	0	8	22	70	3.58	2.35
c55	0	10	20	70	3.99	2.30
W1	2	2	28	68	3.43	2.60
W2	4	4	26	66	3.48	2.54
W3	6	6	24	64	3.82	2.34
W4	8	8	22	62	3.95	2.21
W5	10	10	20	60	4.13	1.95

The amorphous/crystalline nature of the samples is confirmed by X-ray diffraction (XRD) study using a Pan Analytical X'Pert Pro X-ray diffractometer at the scanning rate of 2°/min and 2θ varied from 5° to 70°.

The density of glass samples at room temperature is measured by the standard principle of Archimedes using a sensitive micro-balance with pure benzene as the immersion fluid.

The optical absorption spectra of polished samples are recorded at room temperature using a UV–vis spectrophotometer (Shimadzu, Japan) in the range 200–800 nm.

The infrared transmission spectra of the CeO_2 and WO_3 doped glasses are measured at room temperature in the wave number range 400–4000 cm^{-1} by a Fourier Transform computerized infrared spectrometer type (Thermo Nicolet 380 spectrometer). The prepared glasses are mixed in the form of fine powder with KBr in the ratio 1:100 mg (glass powder:KBr), respectively. The weighed mixtures are then subjected to a pressure of 150 kg/cm^2 to produce homogeneous pellets. The infrared transmission measurements are measured immediately after preparing the pellets.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction pattern (shown in Fig. 1) of pure and WO_3 doped CeO_2–PbO–B_2O_3 glass samples shows no continuous or discrete sharp peaks but exhibit broad halo, which reflects the characteristics of amorphous glass structure. The absence of long range atomic arrangement is a clear indication of the glassy nature of the samples [17–20].

3.2. Density

The density of prepared CeO_2–PbO–B_2O_3 and WO_3–CeO_2–PbO–B_2O_3 glasses is given in Table 1. Proceeding with results, density of both of the glass systems increases, but it gives large value with the addition of WO_3 contents, which decreases the same percentage of PbO contents in both the series. This is due to the availability of more oxygen from WO_3 that shifts the coordination of BO_3 to BO_4. Further increase in density with incorporation of WO_3 in glasses is due to the formation of WO_4 and WO_6 groups. These groups [WO_6 and WO_4] have higher value of field intensity [1.52] than lead ion.

It has been observed that as WO_3 is added to the glasses, packing fraction is able to achieve a higher value as compared with CeO_2 addition. Hence, density of WO_3–CeO_2–PbO–B_2O_3 glasses has higher value than CeO_2–PbO–B_2O_3 glasses. The addition of WO_3 has modified the borate glass structure by creating more BO_4, WO_4 and WO_6 groups.

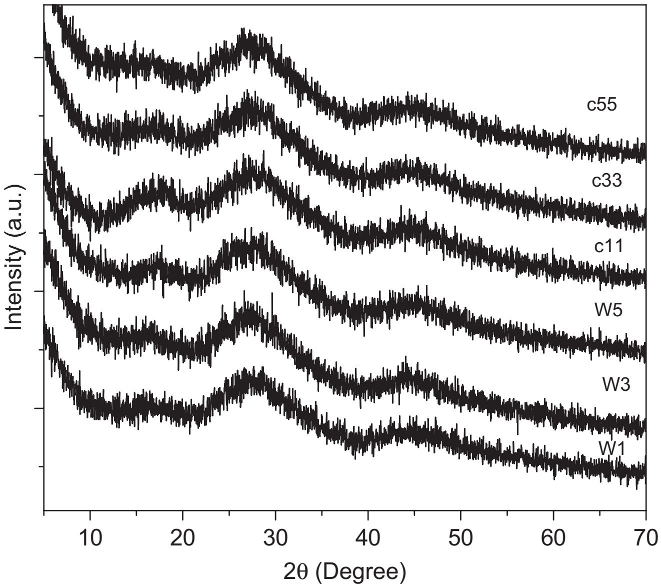

Fig. 1. X-ray diffraction patterns of WO_3 doped and undoped CeO_2–PbO–B_2O_3 glasses.

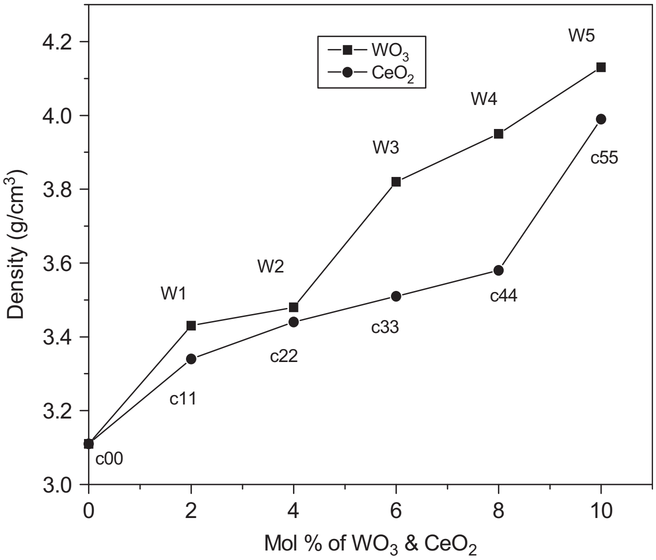

Fig. 2. Density of WO_3 and CeO_2 doped glasses.

The variation in density with WO_3 and CeO_2 contents is shown in Fig. 2. The increase in density reveals the change in the structure of glasses with the increase in oxide contents.