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Optical, FT infrared and photoluminescence spectra of CeO_2 – doped Na_2O – ZnO – B_2O_3 host glass and effects of gamma irradiation

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ABSTRACT

Collective optical, FTIR and photoluminescence spectra of prepared (1 → 10) CeO_2 doped Na_2O – ZnO – B_2O_3 glasses have been examined before and after gamma irradiation doses 2 or 9 × 10^4 Gy (2 or 9 Mrad). Optical absorption spectrum of undoped glass reveals distinct UV absorption bands which are correlated with trace impurities of ferric ions. Upon gamma irradiation, the UV bands reveal limited changes accompanied with the generation of an induced visible band which is assumed to be due to (BOHC) or (NBOHC). The CeO_2 – doped glasses show an additional UV band due to Ce^{3+} ions while the absorption for Ce^{4+} ions are assumed to be overlapped by the strong charge transfer absorption due to traces impurities of Fe^{3+} ions. The irradiated CeO_2 – doped glasses reveal no induced visible band due to the efficiency of cerium ions to capture electrons and positive holes during the irradiation. The CeO_2 – doped glasses show a distinct luminescence peak centered at 410 nm after excitation at 308 nm and its intensity increases with the CeO_2. The optical parameters of the band gap energy and Urbach energy are found to change with the CeO_2 content. FTIR spectra of the undoped and CeO_2 – doped glasses are almost similar with minor variations in the intensities of some vibrational bands and they show vibrational modes due to both triangular and tetrahedral borate groups in their specific different wavenumbers. The IR spectra of the irradiated glasses reveal stability with minor variations in the intensities of some bands.

1. Introduction

Borate glasses belong to the three familiar and extensively studied glass families from inorganic vitreous systems and which exhibit numerous commercial applications. Borate glasses differ from silicate and phosphate glasses in being able to exist within their network in two coordination states with oxygens for the basic boron element with variable percents depending on the other partners. Some of the alkali borate glasses possess anomalous behaviors in some of their physical properties [1–4]. The effects of alkali ions in borate glasses are quite different and more complex than their action in silicate or phosphate glasses [1,4]. In the latter two glasses, the addition of alkali oxides leads invariably to the creation of nonbridging oxygens (NBOs) where their concentration increases linearly with the alkali oxide content [2–4]. The addition of alkali oxide to B_2O_3 initiates that some of the triangulary coordinated borons to be progressively transformed to compact or strong tetrahedrally borons until certain percent after which the alkali oxide starts to form nonbridging oxygens like that happened in silicate and phosphate glasses in all their entire compositional ranges. The transformation processes of 3 fold borons to 4 fold coordination only exist till glass network attains some definitive consistency of BO_4 tetrahedral coordination (primarily to appear at 16–20 mol% of alkali oxide) after that any excess of alkali oxides will produce much formation of nonbridging oxygens that resulting in compositional reverse in the trend of some properties [3]. The previous postulation has been accepted by many authors but other authors introduced another assumption for the relation between the chemical composition and changes in physical properties [3].

The introduction of ZnO to alkali borate glasses causes some interesting changes in the chemical and physical properties depending on the way of housing zinc ions in glass. It has been suggested by several authors [5–7] that zinc ions can exist in glasses either as network formers (with tetrahedral coordination as ZnO_4 groups) or exist as modifiers (in octahedral coordination) depending on the availability of alkali oxide to initiate and support the formation of such tetrahedral units. The formed ZnO_4 tetrahedra need to be compensated for the excess negative charge by nearby alkali ions. In such case, the release of alkali ions decreases and such glasses containing ZnO_4 will be more chemically durable and possess better physical properties. The choice of ZnO within the constituents of the studied host glass becomes from the

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ability of such oxide to introduce to this glass to have better optical properties beside their high chemical durability and glasses containing ZnO are considered as special optical materials [7,8].

The addition of 3d transition metal or rare – earths ions to glasses introduces interesting optical and electrical properties which can be examined and evaluated through optical, FTIR, photoluminescence and electrical measurements [9–11]. Cerium belongs to the rare – earths or lanthanides which are known to exhibit almost similar properties because their outermost electronic structures are the same through the screening of the 4f electrons by outer $5s^2 5p^6$ electrons [12–14]. However, cerium ion as one of the lighter group of the lanthanides can exist in glass in both the tetravalent beside the trivalent states and the ratio of each state depends on the condition of melting, composition of the glass including the concentration of cerium ions [15,16].

The objective of this work is to characterize through collective spectral studies (optical, FTIR and photoluminescence) of the prepared glasses derived from the host undoped glass of composition (B_2O_3 60% - Na_2O 12.5% - ZnO 27.5% wt%) together with doped samples containing additional CeO_2 (1, 2.5, 5, 7.5, 10%). The same combined spectral measurements have been repeated after gamma irradiation with two doses (2, 9×10^4 Gy = 2, 9 Mrad). The second aim of this study is to justify the shielding effect of cerium ions upon gamma irradiation as revealed by the combined spectral measurements.

2. Experimental details

2.1. Glass preparation

Glasses from the ternary borate system (B_2O_5 60, Na_2O 12, ZnO 28) in mol% with additions of (1 → 10 in wt%) of CeO_2 were prepared. The batches were obtained from orthoboric acid (H_3BO_3) for B_2O_3, Na_2O was introduced as anhydrous sodium carbonate and both ZnO and CeO_2 were added as such.

The accurately weighed batches were melted in platinum crucibles at 1200 °C for 90 min in SiC heated furnace (Vecstar, UK). The melts were rotated at intervals of 30 min to reach complete mixing and homogeneity. The homogenized melts were poured into stainless steel molds of the required dimensions. The prepared glassy samples were immediately transferred to an annealing muffle furnace regulated at 400 °C. The annealing muffle was switched off after 1 h with the glasses inside and left to cool to room temperature at a rate of 25 °C/h.

2.2. X-ray diffraction analysis

The amorphous nature of the prepared glasses was identified by X-ray diffraction technique. The glass samples were ground and the fine powders were examined using a diffractometer type (Philips PW 1390) adopting Ni-filter and Cu-target. Computer software (Materials studio 4.4 processes) was used to identify any crystalline species after melting.

2.3. Optical absorption spectra measurements

The optical UV–Vis absorption spectra before and after gamma irradiation were measured at room temperature in the range 200 to 1100 nm using a computerized recording spectrophotometer (type T80t, PG Instrument Ltd., England). Highly polished samples of equal thickness [2 ± 0.1 mm] were used in these measurements. The same optical measurements were repeated after gamma irradiation with two doses of 2 and 9×10^4 Gy.

2.4. Photoluminescence spectra measurements

Photoluminescence (PL) measurements were recorded at room temperature under the excitation wavelength 308 nm in the spectral range 200–600 nm using a fluorescence spectrophotometer (type JASCO, FP-6500, JAPAN) equipped with a xenon flash lamp as the excitation light source. The scan speed is 0.15 step $^{-1}$ with a step length of 0.25 nm and slit width 0.2 nm.

2.5. Optical band gap, band tail and refractive index

The electronic band structure in crystalline and non-crystalline materials can be evaluated from the observed absorption edges. The energy band gap values can be determined through the relation given by Mott and Davis [17]:

$$\alpha h\nu = B(h\nu - E_{opt})^n \quad (1)$$

where E_{opt} is the optical energy gap, B is a constant called the band tailing parameter and n is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption.

The Urbach energy (ΔE) values can be calculated from the Urbach's model [18]:

$$\alpha(v) = B\exp\left(\frac{h\nu}{\Delta E}\right) \quad (2)$$

The ΔE values can be obtained from plots drawn between lnα and photon of energy hv by taking the slope at the linear region of the curves and are presented in Table 1.

To determine the refractive index, from the value of E_{opt}, we applied the formula proposed by Dimitrov and Sakka [19] as follows:

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{\frac{E_{opt}}{20}} \quad (3)$$

The refractive index is assumed to be closely related to the atomic weight and coordination number of the cation [20].

2.6. Fourier transform infrared absorption spectra measurements

FTIR measurements of the prepared glasses were carried out at room temperature in the wavenumber range 4000–400 cm^{-1} by a Fourier transform computerized spectrometer type (FTIR – 4600, JASCO Crop., JAPAN). Through the KBr disc technique, glasses in the form of pulverized powder were examined by mixing 2 mg of the powdered samples and 200 mg KBr and the mixtures were subjected to a load of 5 tons/cm^2 in an evocable die to produce clear homogeneous discs. The prepared discs were measured directly.

3. Results

3.1. XRD

X-ray diffraction measurements (Fig. 1) depict the amorphous nature of the prepared glasses and give no evidence of separation or precipitation of any crystalline phase during the melting and annealing process with increasing the content of CeO_2 up to 10%.

Table 1
Optical parameters of the prepared glasses.

Optical parameter	Dose/Gy	CeO_2%					
		0	1	2.5	5	7.5	10
E_{opt} (eV)	0×10^4	3.208	2.194	2.341	2.455	2.666	2.420
± (0.032–0.035)	2×10^4	2.717	2.525	2.334	2.226	2.430	2.187
	9×10^4	2.439	2.315	2.194	2.273	2.296	2.054
ΔE (eV)	0×10^4	0.741	0.735	0.263	0.258	0.520	0.652
± (0.018–0.021)	2×10^4	0.542	0.510	0.493	0.480	0.412	0.362
	9×10^4	0.450	0.568	0.683	0.605	0.531	0.462
n	0×10^4	2.353	2.656	2.601	2.561	2.493	2.573
± (0.004–0.005)	2×10^4	2.477	2.538	2.604	2.664	2.570	2.659
	9×10^4	2.567	2.611	2.656	2.626	2.618	2.713