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Effect of 3d-transition metal doping on the shielding behavior of barium borate glasses: A spectroscopic study

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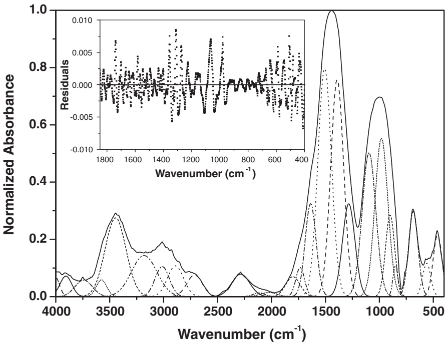
HIGHLIGHTS

- Base barium borate glass and glasses with minor transition metal doping were prepared.
- FTIR and UV–Vis. absorption were measured before and after gamma irradiation.
- UV optical data reveals some different changes that related to composition.
- FTIR shows minor variation which are interpreted and discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

UV–visible and FT infrared spectra were measured for prepared samples before and after gamma irradiation. Base undoped barium borate glass of the basic composition (BaO 40%–B_2O_3 60 mol.%) reveals strong charge transfer UV absorption bands which are related to unavoidable trace iron impurities (Fe^{3+}) within the chemical raw materials. 3d transition metal (TM)-doped glasses exhibit extra characteristic absorption bands due to each TM in its specific valence or coordinate state. The optical spectra show that TM ions favor generally the presence in the high valence or tetrahedral coordination state in barium borate host glass.

Infrared absorption bands of all prepared glasses reveal the appearance of both triangular BO_3 units and tetrahedral BO_4 units within their characteristic vibrational modes and the TM-ions cause minor effects because of the low doping level introduced (0.2%).

Gamma irradiation of the undoped barium borate glass increases the intensity of the UV absorption together with the generation of an induced broad visible band at about 580 nm. These changes are correlated with suggested photochemical reactions of trace iron impurities together with the generation of positive hole center (BHC or OHC) within the visible region through generated electrons and positive holes during the irradiation process.

Introduction

Glasses doped with 3d transition metal ions gained importance because of interesting spectroscopic and electrical properties exhibited by them and their suitability for various glass filters, solid state lasers, solar energy converters, plasma display panels and in a number of electronic devices [1–4].

Borate glasses are promising candidates as good hosts for transition metal ions because of their rich chemistry involving the ability of boron to change easily its coordination with oxygens between three and four. The formation of such wide range of anio-

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nic environments with three and four coordinated borons could coordinate the modifying metal cation and hence affect the local environments around transition metal ions. Optical and infrared spectroscopy is accepted to be very sensitive research methods for the characterization of the spectral variations within borate glasses containing TM ions [5].

Recent studies on spectroscopic properties of 3d-transition metal ions in lithium borate glass [5] and sodium borate glass [6] have indicated that these 3d TM ions exhibit mainly the high valence or tetrahedral coordination states in such host alkali borate glasses. Also, these spectral studies have shown that some 3d transition metal ions exhibit shielding behavior towards the effects of progressive gamma irradiation. A further recent work includes spectral studies on 3d-transation metal ions in high lead borate glass [7] and the same conclusion has been reached on this type of host glass containing heavy metal lead oxide (PbO) instead of Na_2O or Li_2O.

The study of radiation-induced defect centers in glass has been renewed as an interesting subject of investigation during the last two decades [8–11]. Such studies can help in justifying the suitability of glasses for radiation dosimetry applications, radiation shielding candidates or even for encapsulation of radioactive wastes [12–14]. The action of gamma-rays irradiation on glasses is accepted [8] to produce secondary electrons which lose excess energy on collision within the glass network. Such excited electrons travel through the glass network and are finally trapped, thus forming color centers. The trapping sites may be nonbridging oxygens, trace impurities including transition metal ions and even any constitutional cations or anions can share in this process and thus all glass constituents can be expected to affect the radiation induced defects [8].

This work aims to study combined optical (UV–Vis.) and FT infrared absorption spectra of prepared undoped binary barium borate glass of the composition (mol%) BaO 40%–B_2O_3 60% together with samples of the same nominal composition but containing additional 0.2% of one oxide of the 3d transition metals (Ti → Cu) before gamma irradiation. The same combined spectroscopic measurements were repeated after the glasses were gamma irradiated with a dose of 8 Mrad (8×10^4 Gy). It is expected to characterize the induced defects generated from the base barium borate glass and the 3d-TMs doped samples.

Experimental details

Preparation of glasses

The glasses were prepared from chemically pure and fine-grained grade materials including orthoboric acid for B_2O_3, anhydrous heavy barium carbonate for BaO supplied by Rasayan Lab., Mumbai, India, and the 3d transition metal oxides TiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3, CoO, NiO and CuO were introduced separately as additional 0.2% was supplied by Sigma–Aldrich Company.

Melting was carried out at 1200 °C for 90 min under normal atmospheric condition in platinum crucibles. The crucibles were rotated at intervals to promote homogeneity to the melts. After complete melting and homogenizing, the melts were cast into warmed stainless steel molds of the required dimensions. The prepared glassy samples were carefully and immediately transferred to a muffle furnace regulated at 420 °C for annealing. The muffle with the samples inside was left to cool after 1 h to room temperature at a rate of 30 °C/h.

Ultraviolet and visible absorption spectra were measured for highly polished glass samples of equal thickness (2 mm ± 0.1 mm) before and immediately after gamma irradiation using a recording double beam spectrophotometer (type JASCO corp.v-570, Rel-OO, Japan) covering the range from 190 to 1000 nm.

The FTIR absorption spectra of both the prepared parent glasses and the TM-doped samples were measured at room temperature in the wave number range 400–4000 cm^{-1} by a Fourier transform computerized infrared spectrometer type, Nicolet *iS*10, USA. The prepared samples as pulverized powder were mixed with KBr in the ratio 1:100 mg (powder: KBr, respectively). The weighed mixtures were then subjected to a pressure of 5 $tons/cm^2$ to produce clear homogeneous discs. The infrared absorption spectra were measured immediately after preparing the desired discs and the same measurements were repeated after gamma irradiation with a dose of 8 Mrad.

A ^{60}Co gamma cell (2000 Ci) was used as a γ-ray source with a dose rate of 1.5 Gy/s (150 rad/s) at a temperature of 30 °C. The investigated glass samples were subjected to the same gamma dose every time. Using a Fricke dosimeter, the absorbed dose in water was utilized in terms of dose in glass. No cavity theory correction was made. Each glass sample was subjected to a final gamma dose of 8×10^4 Gy (8 Mrad).

Results

Optical absorption spectrum of undoped barium borate glass

Fig. 1 illustrates the UV–visible absorption spectrum of the base barium borate glass before irradiation. The spectrum is observed to consist of strong ultraviolet absorption extending from 200 to about 400 nm and revealing three small peaks at about 235, 320 and 360 nm while no visible bands could be identified. On gamma irradiation, the UV absorption increases in intensity and is accompanied by the resolution of an additional induced broad visible band centered at about 580 nm.

Optical absorption spectra of 3d transition metal ions-doped glasses

Fig. 2 illustrates the UV–Vis. absorption spectra of 3d TM ions-doped (0.2%) barium borate glasses before and after gamma irradiation and the results can be summarized as follows;

(a) Titanium doped glass

This TiO_2-doped glass spectrum exhibits strong charge transfer ultraviolet absorption extending from 200 to about 400 nm and revealing three peaks at 235, 320 and 340 but with no visible bands. On gamma irradiation, the UV absorption decreases in intensity and the visible spectrum, reveals the resolution of an induced broad visible band centered at 580 nm.

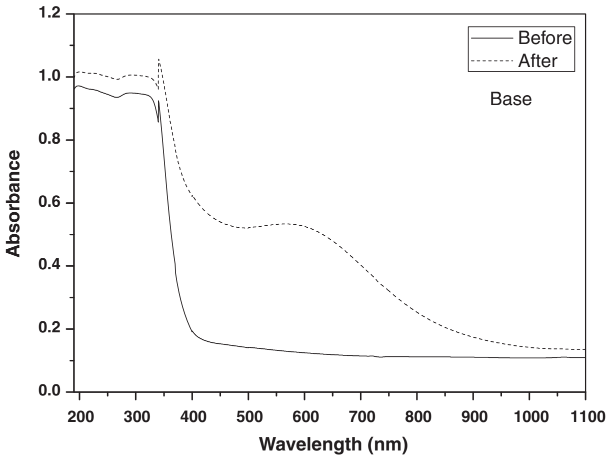

Fig. 1. UV–Vis. absorption spectra of barium borate glass before and after gamma irradiation.