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Optical and FT Infrared spectral studies of vanadium ions in cadmium borate glass and effects of gamma irradiation

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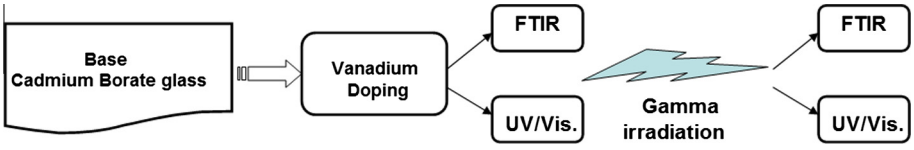
HIGHLIGHTS

- Base cadmium borate glass and glasses doped with different content of V_2O_5.
- FTIR and UV–Vis. absorption measured before and after gamma irradiation.
- UV optical data reveals some different changes that are related to vanadium ions and irradiation.
- FTIR spectra show minor variations on the combined vibrational units which are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Combined optical and infrared absorption spectra of V_2O_5-doped cadmium borate glasses were investigated before and after gamma irradiation with a dose of 8 Mrad (=8×10^4 Gy). The undoped base cadmium borate glass reveals a spectrum consisting of strong charge transfer UV absorption bands which are related to the presence of unavoidable contaminated trace iron impurities (mainly Fe^{3+}). The V_2O_5-doped glasses reveal an extra band at 380 nm and the high V_2O_5-content glass also shows a further band at about 420 nm. The observed optical spectrum indicates the presence of vanadium ions mainly in the pentavalent state (d^0 configuration). The surplus band at 420 nm shows that some trivalent vanadium ions are identified at high V_2O_5 content. The optical spectra of the glasses after gamma irradiation show small decrease of the intensity of the UV absorption which are interpreted by assuming the transformation of some Fe^{3+} ions by photochemical reactions with the presence of high content (45 mol%) of heavy massive CdO causing some shielding behavior.

FT infrared absorption spectra of the glasses show vibrational bands due to collective presence of triangular and tetrahedral borate groups in their specific wavenumbers. The FTIR spectra are observed to be slightly affected by both the V_2O_5-dopants being present in modifying low percent or gamma irradiation due to the presence of high content heavy CdO.

Introduction

Borate glasses are special type of best known glass forming systems. They find various applications including dielectric and insulating material, shielding candidate against irradiation and in burial of radioactive wastes together with recent interest as biomaterial [1–5]. Borate glasses possess distinct chemical importance involving the ability of boron atom to change its coordination with oxygen between three and four providing a

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range of various structural groups (e.g. diborate, triborate, tetraborate, pentaborate etc.) which possess different structures [6,7].

Vanadium as one of the 3d transition metals exhibits distinct behavior in which it can exist in glass in three different ionic valence states, namely V^{3+}, V^{4+} and V^{5+} [8–11]. Trivalent vanadium ions exist in distorted octahedral coordination with oxygens and show characteristic absorption bands at 350–400 nm, 580–680 nm and a third possible band in UV region originating from electron transfer within vanadium ion itself [12]. Tetravalent vanadium ions are assumed to exist as vanadyl (VO^{2+}) ions and exhibit four characteristic four weak peaks at 420 nm, 760–860 nm, 1000 nm and a possible UV band [8,11,12]. Pentavalent vanadium ions correspond to the d^0 configuration and will not give rise to any d–d transitions but give a characteristic band at 380 nm [8,12,13], Bishay [13] and Friebele [14] have agreed that most glasses acquire radiation-induced defects when subjected to ionizing radiation which may give rise to optical and/or electron spin resonance absorption bands. Transition metal (TM) ions have been assumed to compete with intrinsic defects and some of them capture negative electrons or positive holes causing changes in their valencies through photochemical reactions during the exposure to successive gamma irradiation. Also, some of the 3d TM ions show some shielding behavior and their spectral curves did not show any variations with continuous irradiation and remain parallel to their original spectra before irradiation [9,11,15,16].

The main objective of this study was to investigate combined optical and FT infrared spectral measurements of undoped and V_2O_5-doped cadmium borate glasses. The same collective spectral studies were repeated after gamma irradiation with a dose of 8 Mrad = 8×10^4 Gy to study the states of vanadium in relation to the structure of base cadmium borate glass.

Experimental details

Preparation of glass

The studied glasses were prepared using chemically pure grade orthoboric acid (H_3BO_4) for B_2O_3 and cadmium carbonate for CdO and vanadium pentoxide V_2O_5 was added as such with different successive percents. All V_2O_5 additions are in weight percent of the original batch and added overweight. All the weighed batches were melted in platinum crucibles at 1100 °C for 2 h. The crucibles containing the melts were rotated several times to reach acceptable homogeneity. The melts were cast in slightly preheated stainless steel molds to the required dimensions and the prepared specimens were immediately transferred for annealing in a muffle furnace adjusted at 400 °C. The muffle was left to cool after 1 h to room temperature at a rate of 20 °C h^{-1} (see Table 1).

Irradiation facility

A ^{60}Co gamma cell (2000 Ci) was used as a gamma ray source with a dose rate of 1.5 Gys^{-1} (150 rad s^{-1}) at a temperature of 30 °C. The investigated glasses were subjected to the same gamma dose every time.

Table 1
Chemical composition of the studied glasses.

Glass	B_2O_3 (mol%)	CdO (mol%)	V_2O_5 Add wt%
G0	55	45	0.0
G1	55	45	0.1
G2	55	45	0.2
G3	55	45	4.0
G4	55	45	5.0

UV/Vis. absorption spectra measurements

The optical UV/Vis. absorption spectra before and after gamma irradiation were measured at room temperature in the range of 190–900 nm using a computerized recording spectrophotometer (type JASCO V/630) Japan. Polished samples of equal thickness (2 ± 0.1 mm) were used in these measurements. The measurements were repeated twice to confirm the positions of the peaks.

Infrared absorption measurements

FTIR absorption spectra of the prepared samples were measured at room temperature in the wavelength range 400–4000 cm^{-1} by a Fourier Transform infrared spectrometer (Nicolet *i*10). The powdered glass samples were mixed with KBr in the ratio 1:100 glass powder: KBr, respectively. The mixtures were then subjected to a pressure of 5 tons/cm^2 to produce clear homogeneous discs. The IR measurements were carried out immediately after preparing the discs. The same measurements were repeated after subjecting the glass to a gamma dose of 8 Mrad.

Results and discussion

Optical absorption spectra of undoped and V_2O_5-doped glasses

Figs. 1a and 1b illustrates the UV/Vis. absorption of the studied glasses before and after gamma irradiation. The undoped base cadmium borate glass reveals before irradiation strong UV absorption with two peaks at 240 and 310 nm and no visible absorption bands are observed. Such strong UV absorption bands are accepted by various scientists [18–24] to originate from unavoidable trace iron impurities (mainly Fe^{3+} ions) contaminated within the raw materials used for the preparation of the glasses. Earlier, Sigel and Ginther [17] and Cook and Mader [18] identified strong UV absorption bands in various commercial glasses and they related them to unavoidable trace (Fe^{3+} ions) iron impurities. Duffy [20] assumed that certain ions (e.g. Fe^{3+}, Cr^{6+}, etc.) exhibit strong UV absorption bands which are related to electron transfer mechanism and such strong charge transfer bands are identified even if the trace ions are present in the ppm level.

Moncke and Ehrt [21] and El Batal et al. [22–24] have separately identified strong UV absorption bands in various undoped phosphate, borosilicate and borate glasses and they have attributed that these strong charge transfer UV bands are related to trace iron impurities (mainly Fe^{3+} ions) within the chemicals used for the preparations of such various glasses.

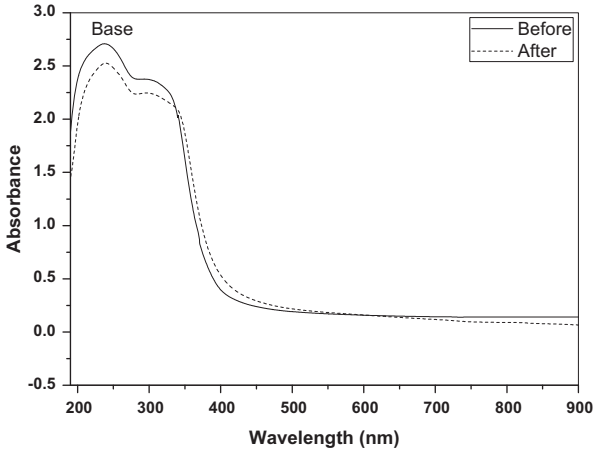

Fig. 1a. Optical absorption spectra of undoped binary cadmium borate glass before and after gamma irradiation.