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Impact of vanadium ions in barium borate glass

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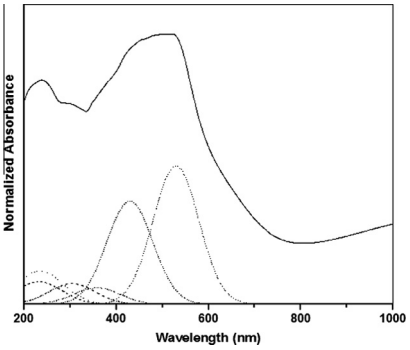
HIGHLIGHTS

- Barium borate glass doped with different vanadium concentrations were prepared.
- FTIR spectra were measured to investigate present structural groups.
- UV/Vis. was employed to study effect of vanadium doping on the optical energy gap.
- ESR spectra was used to confirm state of vanadium ions and confirm UV/Vis. data.

GRAPHICAL ABSTRACT



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ABSTRACT

Combined optical and infrared spectral measurements of prepared barium borate glasses containing different concentrations of V_2O_5 were carried out. Vanadium containing glasses exhibit extended UV–visible (UV/Vis.) bands when compared with base binary borate glass. UV/Vis. spectrum shows the presence of an unsymmetrical strong UV broad band centered at 214 nm attributed to the presence of unavoidable trace iron impurities within the raw materials used for the preparation of such glass.

The calculated direct and indirect optical band gaps are found to decrease with increasing the vanadium content (2.9:137 for indirect and 3.99:2.01 for direct transition). This change was discussed in terms of structural changes in the glass network. Infrared absorption spectra of the glasses reveal the appearance of both triangular and tetrahedral borate units. Electron spin resonance analyses indicate the presence of unpaired species in sufficient quantity to be identified and to confirm the spectral data.

Introduction

Barium containing glasses are one of the most interesting materials due to their characteristic structural, optical, and electrical properties. These glasses can be used for sulfate bearing high level radioactive liquid waste [1], barrier of plasma display ribs [2], gamma ray shielding materials [3,4], and crown optical glasses [5,6]. Borate glasses are one of the common famous families of glass-forming materials. The ability of boron atoms to present in both trigonal and tetrahedral coordination's with oxygen make the creation of anionic sites that accommodate the modified metal cations [7] beside forming variable borate units (such as diborate, triborate, pentaborate, and pyroborate).

On the other hand, the addition of transition metal oxides such as V_2O_5 in the host borate glasses has gained the semiconducting property and it can be applicable as memory and switching devices [8,9]. Vanadium containing glasses are identified as n-type semiconductors due to the process of electron hopping between vanadium states from V^{4+} to V^{5+} ions. However, these ions may also exist in the glass network as V^{2+} and V^{3+} states depending on the

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concentration and the nature of modifiers, glass formers, size of the ions in the glass structure, condition of melting, etc. [10,11].

This work aims to investigate the base barium borate glass and samples of the same glass composition containing different concentrations of V_2O_5 by combined optical and FT infrared absorption spectral analysis in order to know how the vanadium ions can play a major role on the vibrational and optical properties of such glasses. Also, density and ESR technique measurements were used to supplement the work and confirm the optical studies. These measurements correlate the increase of vanadium concentration to the structural changes in these barium borate glasses.

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, and V_2O_5 was used as such. The chemical compositions of the prepared glasses are given in Table 1.

The accurately weighed batches were melted in platinum crucibles at 1200 °C for 90 min under normal atmospheric condition. 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.

Density measurements

A conventional Archimedes method at room temperature was used to determine the glass densities by weighing the samples in both air (W_A) and weighed in submerged xylene (W_B) (ρ_{xylene} = 0.863 g/cm^3). The density of the glass (ρ) is calculated by the following expression:

$$\rho = \frac{W_A}{W_A - W_B} \times \rho_{xylene}\ (\mathrm{g/cm^3}) \quad (1)$$

The measurements for each sample were repeated three times, and the average was obtained.

UV–visible absorption measurements

Ultraviolet and visible absorption spectra were immediately measured for highly polished glass samples of equal thickness (2 mm ± 0.1 mm) using a recording double beam spectrophotometer (type JASCO corp.v-570, Rel-OO, Japan) covering the range from 190 to 1000 nm with (1 nm) resolution.

Infrared absorption measurements

The FTIR absorption spectra of both the prepared base binary borate glass and the V_2O_5-doped samples were measured at room temperature in the wave number range 4000–400 cm^{-1} by a Fourier transform computerized infrared spectrometer type, Nicolet *iS*10, USA with resolution <0.8 cm^{-1}. The prepared samples as pulverized powder were mixed with KBr in the ratio 1:100 mg (powder: KBr, respectively). The weighed mixtures were subjected under pressure of 5 tons/cm^2 producing clear homogeneous discs. The infrared absorption spectra were measured immediately after preparing the desired discs.

Table 1
Composition of the glasses in mol% and their densities.

Glass	B_2O_3 (mol%)	BaO (mol%)	V_2O_5 (wt%)	Density, ρ (g/cm^3) ±0.02
V0	55	45	0	3.97
V1	55	42.5	2.5	3.85
V2	55	40	5	3.74
V3	55	37.5	7.5	3.62

Electron spin resonance measurements

Electron spin resonance spectra were recorded at room temperature on an ESR spectrometer (Bruker, E 500; Germany) operating at 9.808 GHz and using 100 GHz field modulation. The magnetic field was scanned from 480 to 6480 Gauss. The ESR measurements were taken for glass as an evidence for the optical spectral data and confirmation of the state of vanadium ions containing unpaired electrons.

Results and discussion

Density

Table 1 shows the density dependence on the glass composition. It is clearly seen that the density values are decreased with increasing V_2O_5 content. Furthermore, the introduction of one molecule of BaO into borate matrix converts BO_3 units into BO_4 units [12]. Also the base glass has barium content 45 mol% which means that the large number of NBOs is reached as early discussed. Hence the addition of V_2O_5 content into barium borate glass is to cause more disorder in the structure and make it more opened. The density values as shown in Table 1 are varied from 3.97 g/cm^3 (for the base glass) to 3.62 g/cm^3 (for the highest V_2O_5 content) that are in good agreement when compared with the previous reported results [12,13].

FTIR results

Fig. 1 shows the infrared absorption spectra of the base and vanadium containing barium borate glasses. The observed

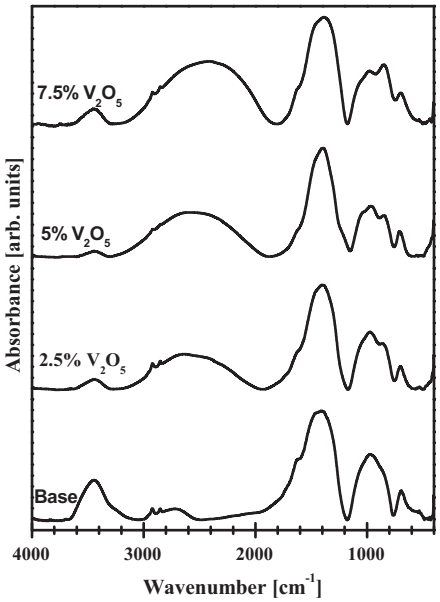

Fig. 1. FT infrared absorption spectra of $BaO–B_2O_3$: V_2O_5 glasses.