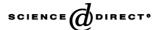
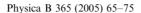


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The role of V₂O₅ in the modification of structural, optical and electrical properties of vanadium barium borate glasses

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Abstract

Vanadium barium borate glasses were prepared by a normal melt quench technique. The infrared spectra of these $V_2O_5 \cdot BaO \cdot B_2O_3$ glasses were recorded over a continuous spectral range (400–4000 cm⁻¹) in an attempt to study their structure systematically. The conversion from three- to four-fold coordinated boron took place. The fundamental absorption edge for all the glasses was analyzed in terms of the theory proposed by Davis and Mott. The position of the absorption edge and hence the value of the optical band gap was found to depend on the semiconducting glass composition. The absorption in these glasses is believed to be associated with indirect transitions. The origin of the Urbach energy is associated with phonon-assisted indirect transitions. The theoretical optical basicity has been calculated and is correlated with a change in the optical band gap. The variation in density and molar volume with composition has been investigated in terms of the structural modifications that take place in the glass matrix on addition of V_2O_5 . The DC electrical conductivity as function of the V_2O_5 :BaO and the V_2O_5 :BaO3 ratio has been measured. The change in conductivity and activation energy with composition indicates that the conduction process varies from ionic to polaronic.

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1. Introduction

Semiconducting glasses can be generally divided into two groups, chalcogenide glasses and oxide

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glasses containing transition metal ions such as Fe, Co, V, etc. Transition metal oxide glasses have been frequently studied from both a chemical and physical point of view in order to better understand the transport mechanism in these semiconductors [1–3]. Electronic transport is only observed in these materials if the transition metal ion is present in two distinct oxidation states [1].

Amorphous vanadium pentaoxide has attracted attention in recent years because of its potential use as cathode material in solid-state devices. Direct current (DC) conductivity of vanadium oxide glasses in which V₂O₅ is associated with other glass formers such as TeO2, P2O5, As2O3 has been extensively studied. These studies have shown that the "small polaron" model can be used to describe the electronic transport phenomena in these materials. Studies on glasses containing B₂O₃ and V₂O₅ are very few. These glasses have their potential applications as optical and electrical memory switching, cathode materials for making solid-state devices and optical fiber [4,5]. In the present work, effect of addition of V₂O₅ in glasses has been studied in order to characterize the geometry of structural units of the glass network with the help of infrared (IR) spectra and the changes caused by the V₂O₅ content on optical, physical and electrical properties in barium borate glasses. These types of glasses exhibit mixed electronic (via electrons hopping along V⁴⁺-O-V⁵⁺ paths) and ionic (via Ba²⁺ ions) conductivity. Glasses with such mixed electrical conductivity attract scientific interest because of potential applications as solid electrolytes in electrochemical devices such as batteries, chemical sensors and smart windows [6].

2. Experimental

The glasses with the composition $xV_2O_5 \cdot (40-x)BaO \cdot 60B_2O_3$ (Series I) and $xV_2O_5 \cdot (60-x)B_2O_3 \cdot 40BaO$ (Series II) with x = 0, 4, 8, 12, 16, 20 mol%, were synthesized by direct melting of the corresponding oxides. The glass samples were obtained by a classical quenching technique described in earlier communication [7] and were finely polished to a thickness of 0.5–1.5 mm for the measurements of various properties.

The IR transmission spectra of various glasses were recorded at room temperature using KBr pellet technique on a Shimadzu FTIR-8001 PC spectrophotometer in the range 400–4000 cm⁻¹. For this powdered glass samples were thoroughly mixed with dry KBr in a ratio of 1:20 and the

pellets were formed under a pressure of 7–8 tons. The resolution was 5 cm⁻¹.

The optical absorption spectra were recorded in the wavelength range 350–1000 nm at room temperature using Perkin Elmer UV/VIS spectrometer (Lambda 20).

The density (D) of the glasses was determined at room temperature using Archimede's method with xylene as the buoyant liquid and the molar volume $(V_{\rm M})$ of each glass sample was also calculated [7]. These values are precise to $\pm 0.5\%$.

For measuring DC conductivity (σ), disks of thickness about 1 mm were coated with silver paint to serve as electrodes. A constant voltage was applied and the current was measured using Keithley 6485 Picoammeter in the temperature range 373–573 K. The relative error in the measurement of σ and activation energy is $\pm 1\%$.

3. Results

3.1. IR transmission spectra

The IR transmission spectra for different values of x for both the series is shown respectively in Figs. 1(a) and (b) over the range 400–4000 cm⁻¹. The spectra were also recorded in the range 400–1100 cm⁻¹ for more clarity (Figs. 2(a) and (b)). It is observed that the IR spectra of these glasses arise largely from the modified borate networks. The structure of the boron oxide glass is made up of a random network of BO₃ triangles. A certain fraction of six membered (boroxol) rings is also present [8]. From these figure, it is seen that the vibrational modes of the borate network are mainly active in three IR spectral regions, which are similar to those reported by several workers [9–11].

The IR spectra of these glasses show eight to nine absorption peaks. These peaks are sharp, medium and broad. The broad bands are exhibited in the oxide spectra, most probably due to the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical scattering from powder samples.

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