Journal of Non-Crystalline Solids 385 (2014) 175–180

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Structure and chemical property studies of some vanadium boro-phosphate glasses containing iron

A.M. Fayad [a,*], A.B.H. Osman [b], A.G. Mostafa [c], F.A. Moustaffa [a,1]

[a] Glass Research Department, National Research Center, Cairo, Egypt
[b] Faculty of Education, Suez Canal University, Arish, Egypt
[c] Physics Department, Faculty of Science, Azhar University, Nasr City, Cairo, Egypt

ARTICLE INFO

Article history:
Received 30 September 2013
Received in revised form 8 November 2013
Available online 15 December 2013

Keywords:
Vanadium boro-phosphate;
Iron oxide;
X-ray investigation;
Infrared spectroscopy;
Chemical durability

ABSTRACT

The structure and chemical properties of some vanadium boro-phosphate glasses of composition $25V_2O_5$ $(40 - x)P_2O_5$ xB_2O_3 $20Na_2O$ $15Fe_2O_3$ where $x = 0, 10, \ldots, 40$ mol% containing iron oxide were thoroughly investigated, under the effect of replacing P_2O_5 by B_2O_3 in the glass network. These samples were structurally studied using X-ray, IR spectroscopy which reveals complex FTIR consisting of extended characteristic vibrational bands which are specific for phosphate groups as a main constituent but with the sharing of some vibrations due to the borate groups beside FeO_4, FeO_6 and VO_5 units. The density, molar volume calculations and chemical durability were all studied and the results were discussed.

1. Introduction

Pure V_2O_5–P_2O_5 glasses are found to be moisture sensitive and poorly conducting. The replacement of P_2O_5 by various metal oxides like Sb_2O_3, Bi_2O_3 etc., in different amounts, is found to improve the stability of the glasses under ambient conditions and modify their conductivity [1]. In general, phosphate glasses have a wide range of technical applications [2,3] because of their large thermal expansion coefficient and low melting temperature compared with borate or silicate glasses. However, it is well known that pure phosphate glasses are sensitive to moisture since the P – O linkages present in them, which are not bonded to cations, can react with moisture to form phosphoric acid, which spoils/reduces the durability of the material. It has been demonstrated that the addition of various oxides such as B_2O_3, SiO_2 and especially Fe_2O_3 to a phosphate network improves the chemical durability as well as the thermal and mechanical stability of pure phosphate glass [4,5]. Structural modifications brought about by such additives have been studied by Infrared and NMR techniques. Bhargava and Condrate [6] and Sharma and Dube [7], based on infrared studies of V_2O_5–P_2O_5 and V_2O_5–B_2O_3 glasses respectively, have identified the different vibrational modes corresponding to V – O, B – O, P – O etc. associated with different structural units present in the glass. Based on NMR spectroscopy [8] both BO_3 and BO_4 structural units were present in the glass structure. The fraction of BO_4 units in the glasses was also found out in this study, which is an important parameter in the context of improvement of durability of these glasses. The presence of BO_3 and BO_4 structural units affects the chemical bonding with the phosphate tetrahedra, which becomes important in determining the chemical durability of these glasses. So boro-phosphate glasses have interesting structural networks due to the presence of borate, phosphate and boro-phosphate units and have been used in a variety of applications [9].

Glasses with high concentrations of transition metals are interesting because of their semi-conducting properties [10–14]. Electronic conduction can indeed occur through the electronic transfer from the low to high-valence states. Glasses doped with transition metals also attract much attention because of their memorizing and photo-conducting properties [15–17]. In particular, iron phosphate glasses behave as typical semi-conducting oxide glasses and exhibit unusually good chemical durability [18].

In the present study, we have investigated the effect of boron addition on the structure and properties of several studied phosphate glasses in a systematic way by means of infrared spectroscopy. Chemical durability and density of the boron doped vanadium phosphate glasses containing iron were also measured.

2. Experimental

2.1. Glass preparation

Eight compositions of vanadium boro-phosphate glasses containing iron oxide in $25V_2O_5$ $(40 - x)P_2O_5$ xB_2O_3 $20Na_2O$ $15Fe_2O_3$ where $x = 0, 10, 15, 20, 25, 30, 35, 40$ mol% series were prepared using high purity powder of Na_2CO_3 (99.5%), H_3BO_3 (99.98%), $NH_4H_2PO_4$ (99.99%) and Fe_2O_3. The weighed batches were melted in platinum crucibles in an electric furnace regulated at 500 °C for 1 h to evaporate ammonia and water.

* Corresponding author. Tel.: +20 1001574646.
E-mail address: amirafayad@gmail.com (A.M. Fayad).
[1] Tel.: +20 1001574646.

0022-3093/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnoncrysol.2013.11.018

The furnace was then raised to 1200 °C gradually for complete melting to obtain bubble free samples. The melts were rotated to achieve acceptable homogeneity and then poured into stainless steel molds with the required dimensions. The prepared samples were immediately transferred to an annealing muffle furnace regulated at 400 °C. The annealing furnace was switched off after 1 h and left to cool at a rate of 30 °C/h to room temperature.

2.2. X-ray diffraction measurements

The amorphous state of some studied glasses was checked by X-ray diffraction spectra recorded in Bruker D_8 ADVANCE diffractometer, with secondary monochromatic Cu Kα radiation ($\lambda = 1.54181$) and applied voltage of 40 kV and 30 mA anode current.

2.3. FTIR absorption spectral measurements

Fourier transform infrared absorption spectra of the glasses were obtained with FTIR spectrometer (Perkin Elmer spectrometer, model RTX). Powdered glass samples (2 mg) were mixed with KBr powder (200 mg) and pressed with 5 t/cm^2 to form thin transparent disks. Infrared absorption spectra within the range of 4000–400 cm^{-1} were recorded immediately after the preparation of the disks.

2.4. Density measurements and molar volume calculations

The density of glasses was determined by the Archimedes' method, and the density was calculated from the formula

$$\rho = [a/(a-b)] \times 0.86$$

ρ is the density of the glass sample; a is the weight of the glass sample in air; b is the weight of the glass sample in xylene; and 0.86 is the density of xylene.

2.5. Chemical durability measurements

The selected glass samples were immersed in distilled water, 0.1 N HCl and 0.1 N NaOH to study the effect of composition and the time of immersion. The weight loss in g/cm^2 was calculated for all the studied glasses.

3. Results

3.1. X-ray diffraction analysis

X-ray diffraction investigation of the studied glasses reveals no diffraction peaks or lines or any crystalline phases, and the results as shown in Fig. 1 indicate that the samples prepared were of high quality amorphous or noncrystalline glasses.

3.2. Infrared absorption spectra measurements

Infrared spectra recorded from 4000 to 400 cm^{-1} for the representative samples having a fixed composition of V_2O_5 and Fe_2O_3 but varying amounts of P_2O_5 and B_2O_3 are shown in Fig. 2. The infrared spectrum of the base glass (0 B_2O_3) is also included for comparison. There are eight absorption bands in the infrared spectrum of the base glass observed at 450, 520, 630, 750,920, 995, 1025 and 3350 cm^{-1}. It is observed that the addition of B_2O_3 causes some changes in the infrared spectra summarized in the following:

1. The observed absorption bands at 450, 520, 630 cm^{-1} are slightly changed in their intensities and broadening with increasing B_2O_3 content.
2. The intensity of the absorption band observed at 750 cm^{-1} in the base glass disappeared as the B_2O_3 content increases. A similar variation is observed for the absorption band at 920 cm^{-1}.
3. In addition, for B_2O_3 contents above 15% there is a new band observed at 845 cm^{-1} in the infrared spectra of the studied glasses.
4. The intensity of the absorption band at 1025 cm^{-1} increases and this band shifts to 1178 cm^{-1} with the addition of B_2O_3.
5. Also, for B_2O_3 contents above 15% there is a new absorption band observed at 1430 cm^{-1} which turned to a broad band with two maxima at 1465 and 1300 cm^{-1} when B_2O_3 content was increased above 25% in the infrared spectra of the studied glasses.

3.3. Density measurements and molar volume calculations

The density of the glass samples was determined by the Archimedes' method. The molar volume of the glasses (V_m) has been calculated from density measurements by using the equation:

$$V_m\left(\text{in cm}^{-3}\text{ mol}^{-1}\right) = M/d$$

where M is the molecular mass, and d is the density of the glasses.

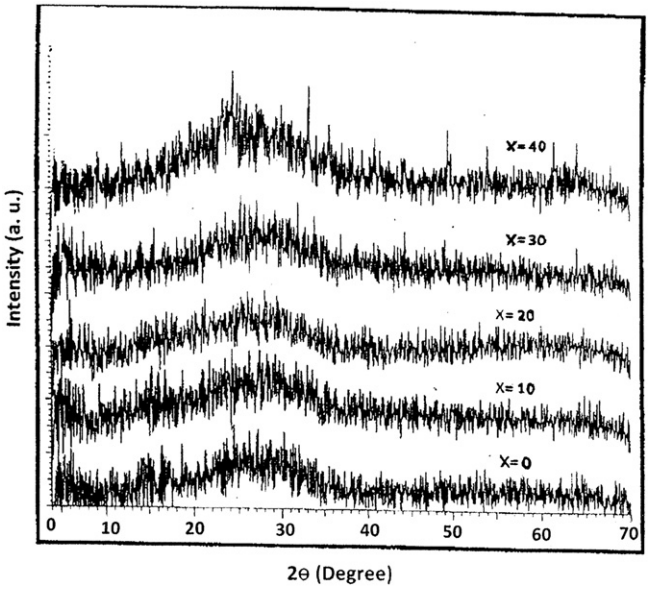

Fig. 1. XRD patterns for a number of boro-phosphate glasses of composition $25V_2O_5$ (40 − x) P_2O_5.xB_2O_3.20Na_2O.15Fe_2O_3 with x = 0, 10, 20, 30, 40.

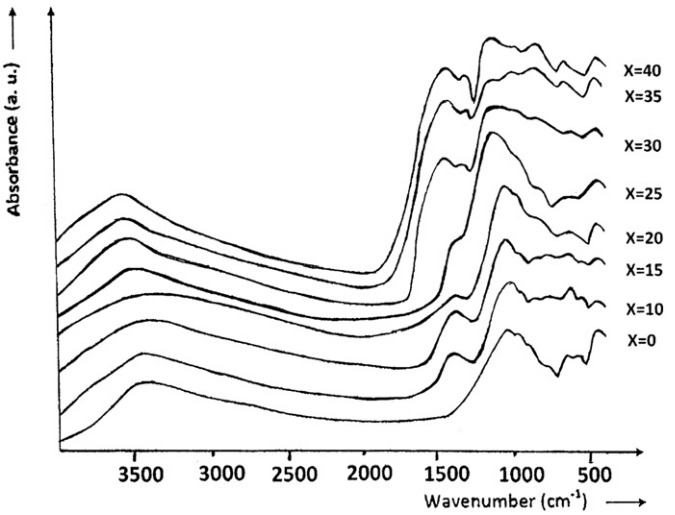

Fig. 2. Infrared absorption spectra for a number of boro-phosphate glasses of composition $25V_2O_5$ (40 − x) P_2O_5.xB_2O_3.20Na_2O.15Fe_2O_3 with x = 0, 10, …, 40.