Journal of Non-Crystalline Solids 371–372 (2013) 22–27

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

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

Studies of (90-x) $P_2O_5 - xB_2O_3 - 10Fe_2O_3$ glasses by Mossbauer effect and impedance spectroscopy methods

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ARTICLE INFO

Article history:
Received 30 January 2013
Received in revised form 26 March 2013
Available online 8 May 2013

Keywords:
Oxide glasses;
Mossbauer Effect;
Impedance spectroscopy

ABSTRACT

Glass systems of composition (90-x) $P_2O_5 + xB_2O_3 + 10Fe_2O_3$ (x = 0 mol.%, 10 mol.%, 20 mol.%, 30 mol.%, 40 mol.%) were prepared using normal melt-quench technique. The Mossbauer Effect has been used intensively to help investigate the structure and bonding of oxide glasses. The Mössbauer spectra indicate the presence of iron (II) and iron (III) in tetrahedral or octahedral coordination. The dependence of electrical data was analyzed in the frame work of the impedance Cole–Cole plot in a frequency range from 5 Hz to 19.5 MHz at room temperature. Constant-phase elements (CPE) are used in equivalent electrical circuits for the fitting of experimental impedance data.

The frequency dependence of the electric conductivity was found to follow a simple power law behavior, in accordance with the relation $\sigma(f) = \sigma(0) + Af^{s}$, where **s** is smaller than 1. The thermal activation energies for the electronic conduction were estimated on the basis of the Arrhenius plots.

1. Introduction

Due to their potential applications in various domains of modern technology, glasses containing transition-metal oxides have been the subject of intensive investigations [1–5] or example, the glasses containing transition metal ion such as Fe_2O_3 are used in electrochemical, electronic and electro-optic devices [6]. The simultaneous presence of two glass formers such as P_2O_5 and B_2O_3 is expected not only to improve the conduction characteristics but also the stability of phosphate glasses [7–9].

Nuclear gamma resonance spectroscopy, also known as Mossbauer spectroscopy, is a technique that probes transitions between the nuclear ground state and a low-lying nuclear excited state. The nucleus most amenable to Mossbauer spectroscopy is ^{57}Fe, and ^{57}Fe Mossbauer spectroscopy provides detailed information about the chemical environment and electronic structure of iron [10].

Mossbauer effect spectroscopy has the advantage of being able to probe the structure of materials containing Fe on the atomic scale. Besides, it has advantages over the conventional XRD method because it is more sensitive to identify amorphous and crystalline phases too. Moreover, the Mössbauer spectroscopy can also differentiate some phases which could not be identified by XRD. Therefore, this technique can be used successfully to study the crystallization process in amorphous alloys [11,12]. Infrared spectroscopy has been extensively employed over the years to investigate the structure of glasses. Infrared spectroscopy is a unique and powerful technique for characterization of the structure of local arrangements in the glasses [13,14].

Borate glasses have been the subject of numerous infrared due to their structural peculiarities. Recently, the study of oxide glasses has received considerable attention due to their structural characteristics. In borate glasses, B_2O_3 is a basic glass former because of its higher bond strength, lower cation size, smaller heat of fusion and trivalency of boron [15]. In borate glasses B^{3+} ions are triangularly coordinate by oxygen, form glasses readily [16,17].

It is found that the triva-lent ions can take two different coordination sites, i.e., either tetrahedral or octahedral sites in glasses. The addition of iron to borate glass makes it electrically semiconducting [18]. A general condition for the semiconducting behavior is the coexistence of transition metal ions in more than one valence state, for instance Fe^{2+} and Fe^{3+}, so that conduction can take place by a transfer of electrons from low to high valence ions [19–21].

Charge transport in these glasses is usually considered in terms of small-polaron hopping model [22].

The main aim of this work is to correlate the electric conduction with new glasses systems based on $Fe_2O_3 - P_2O_5 - B_2O_3$ doped with various concentrations of B_2O_3. A melt is studied by impedance spectroscopy at room temperature over a wide frequency from 5 Hz to 19.5 MHz. Evidence of the presence of microclusters of iron ions in studies of the glass matrix were provided by Mössbauer spectroscopy.

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0022-3093/$ – see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.jnoncrysol.2013.04.002

2. Experimental

Glasses of (90-x) P_2O_5 + xB_2O_3 + 10Fe_2O_3 (x = 0 mol.%, 10 mol.%, 20 mol.%, 30 mol.%, 40 mol.%) system was prepared using pure reagent grade chemicals, B_2O_3, $NH_4H_2PO_4$ and Fe_2O_3 in suitable proportions. The Components were mixed into (m = 2 ± 0.014)g batches with a mortar and pestle, and melted in sintered corundum crucibles in an electric furnace. The mixtures were introduced directly at 1200 °C in the pre-heated furnace. After 1 h the molten materials were quenched to room temperature by pouring those on stainless-steel were plates. The samples were transferred to an annealing furnace and held at 450 °C for 30 min.

The Archimedes method was employed to determine the glass density, ρ, using toluene (ρ_t = 0.653 g/cm^3 at 25 °C) as an immersion liquid according to the following equation:

$$\rho = \frac{\rho_t(W_a - W_{al})}{[(W_a - W_t) + (W_{tl} - W_{al})]} \quad (1)$$

Where, W_a is the weight of the glass in air, W_t is the weight of the glass in toluene and W_{a1}, W_{t1} are the weights of the suspended thread in the air and toluene, respectively. The molecular volume, V_m of each glass was calculated using this equation: $V_m = M/\rho$, where, M is the molecular weight of glass components.

The glassy nature of the samples, was confirmed by XRD studies using D5000 Siemens Diffractometer with Cu–K_α line of a wavelength λ = 1.5406 Å at a scanning rate of 1°/min. And 2θ was varied from low angle to 70°.

IR-spectra of (90-x) P_2O_5 + xB_2O_3 + 10Fe_2O_3 (x = 0 mol.%, 10 mol.%, 15 mol.%, 20 mol.%, 30 mol.%, 40 mol.%) were recorded at room temperature using a Nicolet Magna-750 Fourier-spectrometer in the wave number range 300–1600 cm^{-1}. Powdered samples for data collection were mixed with KBr and pressed into pellets. The spectra were measured immediately after preparing the desired disks.

The Mossbauer spectra were obtained at room temperature on a spectrometer (ASA 600) which used a room temperature 50 mCi cobalt-57 source embedded in a rhodium matrix. The spectrometer was calibrated at 23 °C with a-iron foil and the line width of the a-iron spectrum was 0.27 mm/s. Mossbauer absorbers of an approximate thickness of 140 mg/cm^2 were prepared using 200 mesh powders. The Mossbauer spectra were fitted with broadened paramagnetic Lorentzian doublets. This fitting method has been proved to give reliable hyperfine parameters [23]. Details of this fitting procedure have been discussed previously [24].

Impedance spectroscopy measurements were carried at room temperature using an Impedance/Gain Phase Analyzer Solar-tron 1260 in the 5Hz to 19.5 MHz frequency range. For these measurements, gold electrodes were evaporated onto opposite sides of the glasses. The sample has the form of a disk with (d = 0.84 cm) diameter and (e = 3 mm) thickness, on which gold electrodes were deposited by thermal evaporation in vacuum.

The DC conductivity (σ_{DC}) measurements were carried out by using a Keithely electrometer (Model 617) in the temperature range of 625–1250 K and. Silver paste electrodes were deposited on both faces of the polished samples. The absence of the barrier layers at the contacts was confirmed by linear I–V characteristics.

3. Results and discussion

3.1. Density and molar volume

Fig. 1 shows the dependence of the density and molar volume of prepared samples of the glass system (90-x) P_2O_5 + xB_2O_3 + 10Fe_2O_3 noted by: PBF0 (x = 0 %mol), PBF1 (x = 10 %mol), PBF2 (x = 20 %mol), PBF3 (x = 30 %mol), PBF4 (x = 40 %mol), where x on the B_2O_3 content and the associated uncertainties is $\Delta(B_2O_3) = x.\frac{\Delta m}{m}$,

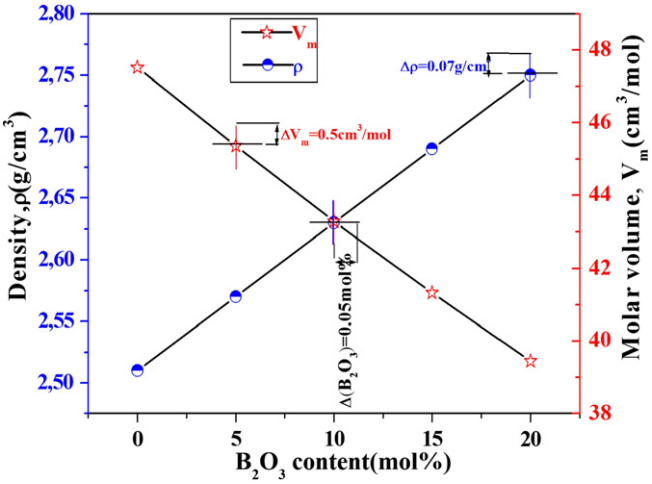

Fig. 1. The dependence of density, ρ (g/cm3) and molar volume, Vm (cm^3 mol^{-1}) of: [(90-x) P_2O_5 + xB_2O_3 + 10Fe_2O_3] glasses, on composition where, x is as indicated. The lines are drawn to guide eyes with percent error in ρ and V_m ± 0.02%.

where Δm = ±0.01 g. This figure indicates that the glass density is monotonically increased while the molar volume decreased as the mol.% of B_2O_3 is gradually increased. The observed decrease in V_m shows that the packing of the coordination polyhedra in the structural network of borophosphate glasses improves with increasing B_2O_3.

Additionally, we have calculated the density and molar volume uncertainties that have been expressed by $\Delta\rho = \rho.\left(\frac{\Delta m}{m} + 2\frac{\Delta d}{d} + \frac{\Delta e}{e}\right)$ and $\Delta V_m = V_m\frac{\Delta\rho}{\rho}$ respectively. The average estimated errors in the density, molar volume and the B_2O_3 content (%) were estimated as ±0.07 g/cm^3, ±0.5 cm^3/mol and ±0.05 mol.% respectively.

3.2. X-ray diffraction studies

The X-ray diffraction patterns of the samples confirm its overall amorphous nature. Fig. 2. shows the X-ray diffraction pattern of the glass sample prepared with x = %, 20 mol. as an example.

3.3. Infrared measurements

The experimental IR spectra of PBF0, PBF1, PBF2, PBF3 glass system with various content of B_2O_3 are presented in Fig. 3.

The low frequency band observed at ~460 cm^{-1} for all samples, is assigned to Fe–O stretching vibration in FeO_6 [25,26]. In addition, for PBF1 one distinguishes the absorption bands near 775 cm^{-1} that are assigned to the asymmetric and symmetric stretching modes of the

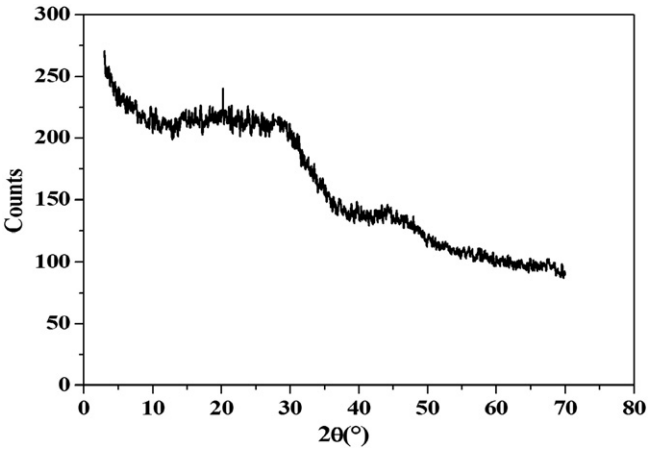

Fig. 2. X-ray diffraction pattern of the sample with x = %, 10 mol.