Journal of Non-Crystalline Solids 376 (2013) 117–125

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

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

Preparation and electrical conductivity of novel vanadate borate glass system containing graphene oxide

R.V. Barde, S.A. Waghuley *

Department of Engineering Physics, H.V.P.M. College of Engineering & Technology, Amravati 444 605, India

ARTICLE INFO

Article history:
Received 19 March 2013
Received in revised form 3 May 2013
Available online 16 June 2013

Keywords:
Glasses;
Graphene oxide;
Electrical properties;
Vanadate borate glasses

ABSTRACT

The novel vanadate borate glass samples with general formula $60V_2O_5$–$5P_2O_5$–(35-x) B_2O_3–xGO, x = 0.5, 1, 2, 3 and 4 mol% were prepared by melt-quenching method. Graphene oxide (GO) was synthesized using the electrochemical exfoliation. The prepared samples were analyzed by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscope, transmission electron microscope and thermo gravimetric-differential thermal analysis. The DC conductivity of samples was found to be in the range of 10^{-2} to 10^{-6} S cm^{-1}. The activation energies were found to be in the range of 0.47–0.17 eV. The physical studies such as density and molar volume have been investigated. The density of these glasses increases with increasing GO content. The ionic transference number of mobile ions has been estimated by DC polarization method and the results reveal that the charge transport is predominately due to ions.

1. Introduction

Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms packed in a honeycomb crystal lattice. It is the mother element of some carbon allotropes, including graphite, carbon nano tubes, and fullerenes [1,2]. The graphene is the thinnest material, which exhibits excellent electrical conductivity, mechanical flexibility, optical transparency, thermal conductivity, and low coefficient of thermal expansion behavior [3–8]. It has a special electronic structure, which gives it electronic properties such as the anomalous quantum Hall effect [9] and high carrier mobility at relatively high charge carrier concentrations at room temperature [3,10]. Graphene is expected to play an important role in the fabrication of nano-electronic and bio-electronic devices in the near future [2]. Graphene is also capable of replacing metal conductors in electronic and electrical devices due to its excellent electrical conductivity and mechanical flexibility [11–13].

Graphene can replace chemically unstable and brittle indium tin oxide in flexible displays and touch screens [14–16]. The molecular level doping of graphene via charge transfer between electron donor and acceptor molecules gives rise to significant changes in the electronic structure of graphene [17–19]. The successful synthesis of chemically modified graphene such as graphene oxide (GO) [3] arose intense research interests due to their distinctive extremely high mechanical and transport properties such as elasticity [20] and large thermal conductivity [21] respectively. Hwang et al. [22] reported the preparation of graphene sheets from highly oriented pyrolytic graphite through mechanical cleavage in order to investigate their responses to chemical vapor sensing.

Conducting glasses has attracted much interest in the field of solid-state chemistry and materials science. Vanadium pentoxide is known to have a structure composed of VO_5 pyramids. The vanadate based glasses show semiconducting behavior, which is due to electron hopping between V^{4+} and V^{5+} ions existing in the structure of the glass [23]. Though various vanadium ion doped glass systems have been investigated, most of them are restricted to structural studies. Hence, there is a scope still to investigate the influence of vanadium ions on alkali fluoro alkaline earth borate glasses, through dielectric properties [24]. The study of dielectric parameters with the help of spectroscopic properties will cover the way to understand more about the structural environment of the glass network [25–28].

B_2O_3 glasses are found to be very interesting amorphous materials, which possess the specific structure and physical properties for advance applications. In these glasses, two groups of bands are obtained: (i) due to trigonal BO_3 and (ii) due to the tetrahedral BO_4 units. By the addition of transition metal ions to the borate glasses, they would exhibit specific physical properties [29,30].

The aim of this work is to prepare the glass system $60V_2O_5$–$5P_2O_5$–(35-x) B_2O_3–xGO, x = 0.5, 1, 2, 3 and 4 mol% to analyze AC and DC electrical, thermal and physical properties. The graphene oxide was synthesized by electrochemical exfoliation of graphite using silver as a cathodic electrode. The characterization techniques, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), transmission electron microscope (TEM) and thermo gravimetric-differential thermal analysis (TG-DTA) are employed to study the structural and morphological properties of graphene and glass samples.

* Corresponding author. Tel.: +91 9423124882.
E-mail address: sandeepwaghuley@sgbau.ac.in (S.A. Waghuley).

0022-3093/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnoncrysol.2013.05.034

2. Experimental

2.1. Synthesis of graphene oxide (GO)

GO was synthesized by using the electrochemical exfoliation, in which the graphite flake was employed as an anode and source of graphene. The silver electrode was used as a cathodic electrode. This process severely damages the honeycomb lattices of graphene [31]. The graphite flake and silver electrode were inserted into the ionic solution with the separation of 5 cm. The ionic solution was prepared by taking 4.8 g of sulfuric acid (SD fine, 99.99%) diluted in 100 mL of double distilled water. The electrochemical exfoliation process was carried out by DC bias arrangement (10 V). All of this electrochemical exfoliation experiment was performed at room temperature. The exfoliated GO was collected through cellulose nitrate filter paper and washed with double distilled water. The obtained powder was dried at 100 °C for 10 h. The electrochemical exfoliation of graphite is displayed in Fig. 1.

2.2. Sample preparation

The glasses of the compositions of $60V_2O_5$–$5P_2O_5$–(35-x) B_2O_3–xGO, x = 0.5,1, 2, 3 and 4 mol%, were prepared by a conventional melt-quenching method. The AR grade (SD fine, India) chemicals were used in this investigation, which were weighed and mixed together. This mixture was homogenized and melted in silica crucible in a furnace at 900 °C for 3 h and the melt was stirred to remove CO_2. After melting, the mixture was poured out onto a nonmagnetic stainless steel plate so that the sheet sample had a thickness of about 3 mm. To avoid internal strains, the sample was annealed at 200 °C for 1 h.

2.3. Material characterizations

The sample was characterized by using XRD, FTIR, SEM, TEM and TG-DTA techniques. The XRD pattern of powder sample was recorded on XRD Philips PW 1830 using CuK_α radiation ($\lambda = 1.54$ Å) in the range of 20°–60°. The FTIR spectrum was recorded on Shimadzu (Model-8201) spectrophotometer. The FTIR was taken in the KBr medium at room temperature in the region of 4000–400 cm^{-1} at scan rate 16. The structure, morphology and grain size of the samples were observed using SEM (JEOL JSM-6360), TEM (JEOL-1200ex). The TG-DTA was carried out on Shimadzu DTG-60 h thermal analyzer under nitrogen flow at the heating rate of 10 °C/min. The temperature of the sample was varied from room temperature to 600 °C. For the electrical measurements, the samples were polished and conducting silver paste was deposited on both sides of the samples. Measurements of DC conductivity as a function of temperature, for all samples were made by a two-probe technique in the temperature range of 303–473 K.

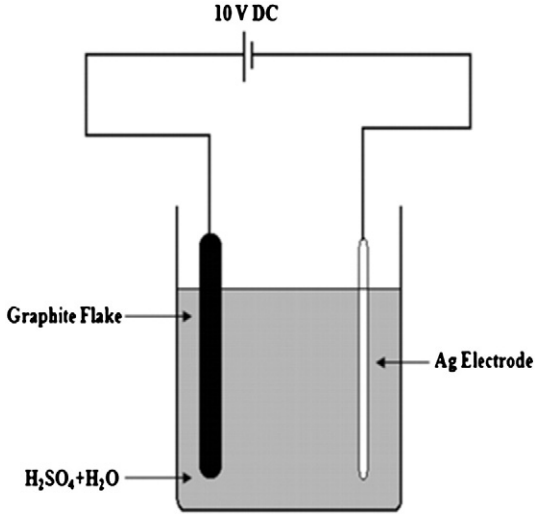

Fig. 1. Scheme of electrochemical exfoliation of graphite.

The temperature dependence of AC conductivity (σ) and dielectric constant (ε′) were measured by using LCR meter, Agilent Technologies, Singapore. The Z and θ were obtained directly from the impedance meter. The values of Z′ and Z″ were computed from |Z| cosθ and |Z| sinθ, respectively. The capacitance (C) and the resistance (R) were read directly from the LCR meter, hence the real and imaginary parts of the dielectric constant (ε′ and ε″) can be obtained. The measurements were performed in a frequency region of 20 Hz to 1 MHz and a temperature range of 303–473 K. The electrical modulus was studied for all compositions.

For ionic transference number measurement the samples were polished and graphite electrode (blocking electrode) was deposited on both sides of the samples. The sample was held between the sample holders. The sample holder was provided with spring-mechanical pressure to ensure good electrical contact. A constant voltage (DC) of 6 V was applied to the sample. The measurement was performed at room temperature. The total ionic (t_{ion}) and electronic (t_{ele}) transference number were calculated from Eqs. (1) and (2) [32–35].

$$t_{ion} = \frac{I_i - I_f}{I_i} \tag{1}$$

$$t_{ele} = 100 - t_{ion} \tag{2}$$

where I_i is initial value of current at the start and I_f is current on reaching saturation.

2.4. Density measurements

The density of the glass bits free of air bubbles and crack was determined at room temperature through Archimedes principle, by using xylene ($\rho = 0.863$ g/cm^3). The density was estimated by using Eq. (3)

$$\rho = \left(\frac{W_a}{W_a - W_l}\right) \times \rho_l \tag{3}$$

where ρ is the density of the sample, W_a is the weight of the sample in air, W_l is the weight of the sample fully immersed in xylene and ρ_l is the density of the xylene.

The molar volume V_m was calculated from Eq. (4) [36–40].

$$V_m = \frac{M_T}{\rho} \tag{4}$$

where M_T is the molecular weight of the glass calculated by multiplying x times the molecular weights of the various constituents.

The oxygen packing density (OPD) was determined from Eq. (5) [41],

$$D_0 = \left(\frac{\rho}{M_T}\right) \times \text{ number of oxygen atoms per formula unit} \tag{5}$$

3. Result and discussion

3.1. XRD analysis

Fig. 2 depicts the XRD patterns of the $60V_2O_5$–$5P_2O_5$–(35-x) B_2O_3–xGO, x = 0.5,1, 2, 3 and 4 mol%, including pure GO pointed out the formation of glasses and GO, respectively. There was no characteristic peak, which corresponds to any crystalline phase, and therefore it can be inferred that the obtained samples are amorphous. The amorphous