Solid State Sciences 12 (2010) 1426–1434

Contents lists available at ScienceDirect

Solid State Sciences

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

Spectroscopic, mechanical and magnetic characterization of some bismuth borate glasses containing gadolinium ions

Yasser B. Saddeek [a,*], I.S. Yahia [b], K.A. Aly [a], W. Dobrowolski [c]

[a] Physics Department, Faculty of Science, Al-Azhar University, PO. 71452, Assiut, Egypt
[b] Physics Department, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt
[c] Institute of Physics, Polish Academy of Sciences, Al. Lotnikow, 32/46, 02-668 Warszawa, Poland

ARTICLE INFO

Article history:
Received 18 September 2009
Received in revised form
25 January 2010
Accepted 24 May 2010
Available online 1 June 2010

Keywords:
Borate glasses
Bismuthate glasses
IR
Density
Elastic properties
Magnetic characterization
Entropy change

ABSTRACT

The ultrasonic parameters, the optical parameters along with the IR spectroscopy and magnetic susceptibility studies have been employed to explore the role of Gd_2O_3 in the structure of the glasses $x$$Gd_2O_3$–$60B_2O_3$–$10MoO_3$–(30-$x$)$Bi_2O_3$, with $0 \leq x \leq 7$ mol %. IR analysis indicates that Gd_2O_3 is preferentially incorporated into the borate network-forming BO_4 units. It is assumed that Bi_2O_3 and MoO_3 enter the structure as modifiers in the form of BiO_6 and MoO_6 only. The compositional dependence of the mechanical and the optical parameters are interpreted in terms of the transformation of the structural units BO_3 into BO_4, the increase in the number of bridging oxygen atoms, and the substitution of high bond strength Gd–O, in the place of low bond strength Bi–O bond. The results of the magnetic susceptibility reveal the paramagnetic behavior as described by the Curie-Weiss law and indicating the presence of weak antiferromagnetic exchange interactions between Gd^{3+} ions. The magnetic entropy change of the glasses was determined according to the temperature and magnetic field dependence of magnetization.

1. Introduction

Recently, bismuth borate glasses containing gadolinium ions have attracted a great deal of interest due to their potential applications as fast ion conducting glasses [1], layers for optical and optoelectronic devices [2,3], and thermal sensors [4]. Also, these glasses possess good mechanical resistance [5,6], enhanced the magnetic properties [7–9] and photo-induced non-linear optical properties, which are caused by substantial contribution of anharmonic electron–phonon interactions [10]. The magnetic properties are mainly determined by the gadolinium ion concentration, the distribution of the gadolinium ions in the host glass matrix and their micro-environment [8]. Whereas the local structure of the gadolinium sites seems to be similar in different types of glasses, the correlation between the doping level and clustering depends on the glass type and composition [8,11,12].

Pure Bi_2O_3 glass due to its low field strength and its high polarizability cannot be obtained compared with pure B_2O_3 glass. However, in the presence of very small additions of conventional glass formers, it may build a glass network of [BiO_3] and [BiO_6] polyhedra. With larger additions (e.g., 9…75 mol% B_2O_3), widespread areas of glass formation have been found. Also, it was suggested that Bi_2O_3 can occupy both network-forming and network modifying positions in the borate glasses, and as a result, the physical properties of such glasses exhibit discontinuous changes when the structural role of the cation was switching over in this way [13–17]. The boron atom in borate glasses usually coordinates with either three or four oxygen atoms forming [BO_3] or [BO_4] structural units. These two fundamental units can be arbitrarily combined to form either the so-called super-structure or different B_xO_y structural groups like boroxol ring, pentaborate, tetraborate, diborate groups…etc [18].

Electron paramagnetic resonance EPR and magnetic susceptibility measurements were performed on some gadolinium -containing glasses such as borate, bismuthate, boro-tellurite, germanate, and phosphate. These studies reveal aspects concerning the distribution of the gadolinium ions in the glass matrix and the nature of magnetic interactions between these ions [19–22].

On the basis of the aforementioned aspects, the main goal of this work is to synthesize and extend the available information of the particular family of the glasses $x$$Gd_2O_3$–$60B_2O_3$–$10MoO_3$–(30-$x$)$Bi_2O_3$, with $0 \leq x \leq 7$ mol %. This work was systematically

---

[*] Corresponding author.
E-mail address: ysaddeek@gmail.com (Y.B. Saddeek).

1293-2558/$ – see front matter © 2010 Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.solidstatesciences.2010.05.023

investigated by using FTIR, density, ultrasonic, optical and ac magnetic susceptibility measurements. The concentration of Gd_2O_3 was limited to 7 mol% inside the host glass matrix because the glass formation gets harder beyond this limit. This concentration is the maximum rare earth load in our glasses, without devitrification. The concentration of Gd_2O_3 is in a good agreement with the literature [3,7,13,14,21].

2. Experimental procedures

Glass samples of the formula xGd_2O_3–$60B_2O_3$–$10MoO_3$–$(30\text{-}x)$ Bi_2O_3 vitreous system with $(0 \le x \le 7$ mol%) have been prepared by the well known melt quench technique. Required quantities of Analar grade Bi_2O_3, Gd_2O_3, MoO_3 and H_3BO_3 were mixed together by grinding the mixture repeatedly to obtain a fine powder. B_2O_3 was added in the form of its respective boric acid. The mixtures were melted in porcelain crucibles in an electrically heated furnace under ordinary atmospheric conditions at a temperature of about 1323 K for 0.2 h to homogenize the melt. The glass formed by quenching the melt on a preheated stainless-steel mold was immediately transferred to another furnace where it was annealed at 623 K for 3 h. The obtained glasses were lapped and two opposite sides were polished to be suitable for the use in the ultrasonic velocity measurements. Non-parallelism of the two opposite side faces was less than 0.01°.

X-ray diffraction patterns were recorded to check the non-crystallinity of the prepared glass samples using a Philips X-ray diffractometer PW/1710 with Ni-filtered, Cu-K_a radiation ($\lambda = 1.542$ Å) powered at 40 kV and 30 mA. The patterns (not shown) revealed a broad hump characterizes the amorphous materials and did not reveal any discrete or sharp peaks.

Infrared (IR) spectra for the glass powder were obtained using an IR Fourier spectrophotometer type JASCO, FT/IR–430 (Japan). For this purpose, each sample was mixed with KBr in the proportion of 1:100 (by weight) for 20 min and pressed into a pellet using a hand press. The spectra were recorded in the wavenumber range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}, corrected for dark-current noise, and normalized. The resulted spectra were curving fitted [23] to get quantitative values for the band areas of heavily overlapped bands. The curve fitting procedure is based on a least-squares minimization which in its turn involves entering the values of the wavenumbers of the component bands (determined by deconvolution) and then a program determines the best estimated parameters of the component curves. The program is Origin version 8. The deconvolution process involves several steps: computation of an interferogram of the sample by computing the inverse Fourier-transform of the spectrum, multiplication of the interferogram by a smoothing function and by a function consisting of a Gaussian–Lorentzian band shape, and Fourier-transformation of the modified interferogram. The deconvolution procedure is typically repeated iteratively for best results. At iteration, the line shape is adjusted in an attempt to provide narrower bands without excessive distortion. Therefore, each IR spectra has its characteristic peak positions.

The optical transmittance (T), and reflectance (R) spectra of the glasses, were recorded at room temperature in the wavelength (λ) range of 300–1100 nm using a computerized double beam spectrophotometer, type SHIMADZU UV-2100. The optical constants [16,24] of the glass (in the form of plane parallel slab) such as the refractive index (n) in terms of modified Sellmeier dispersion relation, the extinction coefficient (k), and the absorption coefficient (α) can be evaluated from the measured values of the transmittance (T) and reflectance (R) at normal incidence of light according to the relations:

$$\alpha = \frac{1}{d}\ln\left(\frac{1-R}{T}\right) \tag{1}$$

$$R = \frac{(1-n^2)+k^2}{(1-n^2)+k^2} \tag{2}$$

$$n(\lambda) = A - \frac{B}{\lambda} + \frac{C}{\lambda^2} - \frac{D}{\lambda^3} + \frac{E}{\lambda^4} \tag{3}$$

where A,B,C,D and E are the Sellmeier coefficients, d is the thickness of the sample and $\alpha = 4\pi k/\lambda$.

The density (ρ) of the glass samples was determined using Archimedes technique by using toluene as an immersion fluid. A random error in the density values was found as ±1%. The molar volume (V_m), and the mean atomic volume (V_a), have been determined as M/ρ, and V_m/n, respectively, where M is the molar weight of the glass and n is the number of atoms in the unit formula.

The ultrasonic velocities, longitudinal (ν_L) and shear (ν_T), at room temperature (~300 K) were obtained using the pulse-echo method. In this method, x-cut and y-cut transducers (KARL DEUTSCH) operated at a fundamental frequency 4 MHz along with a digital ultrasonic flaw detector (KARL DEUTSCH Echograph model 1085) were used. The uncertainty in the measurement of the ultrasonic velocity is ±10 m/s. The two velocities besides the density were utilized to determine the elastic moduli and Debye temperature (θ_D). The uncertainty in the elastic moduli is ±0.15 GPa.

The ac susceptibility measurements were carried out in the temperature range of 5–200 K at a frequency 625 Hz with Lake-Shore 7229 ac susceptometer using a mutual inductance bridge with an excitation field $H_{ac} = 5$ Oe. To relate the magnetic susceptibility to atomic properties, the mass magnetic susceptibility was converted into the molar magnetic susceptibility χ_m using: $\chi_m = \chi_g.\ M_w$, where M_w is the molecular weight of the sample.

3. Results

The infrared absorption spectra of the studied glasses as shown in Fig. 1 revealed the existence of three principle (broad) bands at around 680, 1000 and 1400 cm^{-1} , along with a weak band at around 550 cm^{-1}. As the Gd_2O_3 content increases, the IR spectra shows a shift to higher wavenumbers of the center of the band around 1000 cm^{-1}, and a shift to lower wavenumbers of the center of the band around 1400 cm^{-1}. In addition to the above features, there is a small absorption band appears in the spectra of all glasses around 3465 cm^{-1} (not shown in the figures). Such a band is attributed to the water molecules incorporated into the glasses during the room temperature ion exchange process [25].

The observed broadening of the bands in the IR spectra may be arising from the overlapping of some individual bands with each other. Each individual band has two characteristic parameters; the center (C), which is related to some type of vibrations of a specific structural group and the relative area (A), which is proportional to the concentration of this structural group [5]. A curve fitting process should be performed to extract such parameters. Table 1 summarizes the characteristic parameters of IR absorption bands along with their assignment. Fig. 2 depicts the curve fitting of the IR spectra of the sample having 7 mol% Gd_2O_3 as an example. There is a good agreement between the glass have 0 mol% Gd_2O_3 and those from the literature [6].

Table 2 summarizes the determined and derived data for the studied glasses. The data reveals a linear decrease in the density ρ, the refractive index (n), and the optical polarizability with