Journal of Molecular Structure 1108 (2016) 257–262

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Optical, elastic properties and DTA of TNZP host tellurite glasses doped with Er^{3+} ions

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ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form
23 November 2015
Accepted 24 November 2015
Available online 7 December 2015

Keywords:
Energy gap
Linear refractive index
Elastic properties
DTA
Tellurite glasses

ABSTRACT

Novel quaternary tellurite glasses within the composition $75TeO_2-10Nb_2O_5-10ZnO-5PbO$ (TNZP) doped with the following Er^{3+} concentrations: 2500, 3750, 5000, 6250, 7500 and 8750 ppm have been prepared by using conventional melt quenching method. The thermal parameters, such as the glass transition temperature (T_g), crystallization temperature (T_c) and thermal stability (ΔT) were determined. It is described that this system shows a stable glass formation, high thermal stability and low tendency crystallization. The linear refractive index, n, the optical energy gap, E_g, the nonlinear refractive index, n2, two photon absorption TPA, third order susceptibility, $\chi^{(3)}$, of prepared glasses have been determined. Moreover elastic properties like longitudinal (λ), shear (μ), Bulk (β) and Young's (Y) moduli, Poisson's ratio, Debye temperature, and the microhardness of the glasses were evaluated by measuring both longitudinal and shear velocities using the pulse-echo overlap technique at 5 MHz. The present glasses is a promising candidate for optical application.

1. Introduction

Tellurite glasses are of high scientific and technological importance. For example, tellurite-based Er^{3+} doped fiber amplifiers (EDFA) produced by the Nippon Telephone and Telegraph (NTT) showed a gain-flattened amplification of 20 dB across a wavelength range from 1530 to 1610 nm [1,2]. TeO_2-based glasses containing heavy metal oxides like Bi_2O_3, Nb_2O_5 or WO_3 possess high third-order nonlinear optical susceptibility as well as large nonlinear refractive indices and are favorable for applications in nonlinear optical devices such as optical switching or optical memory [2]. Due to their hyperpolarizability and weaker Te–O bonds, the atomic network in tellurite glasses appears more open than that in other glasses such as silicate, borate or phosphare glasses [3,4]. The Te–O bond is easily broken which is an advantage for hosting rare-earth or heavy metals ions with small multi-phonon decay rates [5]. The incorporation of Nb^{5+} ions contributes to better physical properties of tellurite glasses, because the hyperpolarizability of the Nb–O band induces high refractive indices to the glass [6]. Tellurite glasses doped with Er_2O_3 are potential materials for up-conversion lasers, optical fiber amplifiers, nonlinear optical devices and so on [5]. T. Hayakawa et al. [7,8] demonstrated the suitability for infrared femtosecond laser heating of $TeO_2-Nb_2O_5-ZnO_2$ glasses due to multiphonon absorption of two photons to achieve green up conversion luminescence of Er^{3+}. In lead glasses, the network is formed by O–Pb–O-linkages with [PbO_6] octahedra and [PbO_4] tetrahedra. The *s* and *p* orbitals of Pb^{2+} and *p* orbitals of oxygen interact with each other to form bonding and antibonding states which give rise to valence and conduction bands [9]. In this paper glasses obtained by adding PbO to $TeO_2-Nb_2O_5-ZnO$ are described which is excellent host of Er^{3+} ions.

Mohamed et al. [10] studied the effect of concurrent TeO_2 reduction and ZnO addition on the elastic properties of $TeO_2-Nb_2O_5-ZnO$ glasses. They concluded that the role of TeO_2 is very critical in the ternary glass system where ZnO addition leads to improved rigidity due to recovery of shear modulus and the weakening of longitudinal and bulk moduli. Recently both acoustic and optical studies of spectroscopic properties of rare earth ions in tellurite glasses have become a hot subject of current research. In this paper we studied elastic and optical properties which are required for fiber drawing.

2. Experimental

The Er^{3+} ions doped glass systems with the composition $75TeO_2-10Nb_2O_5-5PbO-10ZnO-xEr_2O_3$ (where x = 0.00, 2500,

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http://dx.doi.org/10.1016/j.molstruc.2015.11.066
0022-2860/

3750, 5000, 6250, 7500 and 8750 ppm) were prepared by using the conventional quench-melting method. The raw materials were powdered, and heated in a platinum crucible to a temperature of 920 °C kept for 45 min; the melt was stirred from time to time The highly viscous melt was cast in a graphite mould. The quenched samples were annealed at 340 °C for 2 h and then cooled inside the furnace down to room temperature. The densities of the glass samples were measured using a helium pycnometer (UltraPyc 1200e Pycnometer) with an accuracy of ±0·0003%. The glass samples were powdered in order to perform differential thermal (DTA) analysis using a Shimatzu DTA 50 instrument with a heating rate of 15 °C/min under air-atmosphere with an accuracy of ±3 °C. The refractive indices of the prepared samples were measured by Brewster's angle method using a spectrometer and sodium lamp of the wavelength 589.3 nm, He–Ne laser source of the wavelength 632.8 nm and high pressure mercury lamp with the two lines 546.1 nm and 435.8 nm.

Room temperature ultrasonic measurements were performed by the pulse-echo method using a flaw detector (USM3 Krautkramer). X-cut transducers were employed for longitudinal modes and Y-cut for transverse modes. The pulse transition time was measured using a Hewlett–Packard model 54502A oscilloscope. The velocity was therefore obtained by dividing the round trip distance by the elapsed time. Random errors in the measurements were about ±1%.

The microhardness measurements were carried out by using Vickers microhardness indentation tester (Shimadzu HMV-2, Japan). The Vickers indenter is a diamond pyramid having an angle of 136° between opposite pyramid faces. After loading by constant load of 0.49 N for 10 s, the lengths l_1, l_2 of both diagonals of the indentation were measured. The value of Vickers hardness was calculated by the following relation: $H_V = 0.1891 \cdot F/L^2$, where, $L = l_1 + l_2/2$ is the average of diagonal length (mm).

3. Results and discussion

3.1. Thermal stability

Results from DTA measurements (see Fig. 1), such as glass transition temperature, T_g, softening temperature, T_s, thermal relaxation resistance, $\Delta S = T_s - T_g$, onset of crystallization temperature, T_c, thermal stability, $\Delta T = T_c - T_g$ and melting temperature, T_m, as well as the composition of the prepared glasses are summarized in Table 1. The temperatures T_g, ΔS, ΔT, increase with increasing concentration of Er^{3+} ions in the glass matrix. The glasses transition temperature of glasses increases with increasing chemical bond strength. Herin the 75mol% of TeO_2 oxide based glasses permits incorporation of 10mol% of niobium oxide 10mol% of zinc and 5mol% of lead oxide leads to increasing order of solubility which means that the glass network is ability of forming more than one electric dipole environment for Er^{3+} ions. Hence incorporation of Er_2O_3 in the this composition of glasses enhances the T_g to increase glass network continuity through the formation of bridging oxygen sites and better packing of the overall 3d-structure due to the presence TeO_4 trigonal bipyramid (tbp), TeO_3 trigonal pyramid (tp), polyhedral of TeO_{3+1}. These indicate that the value of T_g increase from 650 to 667 in K when increasing of concentration of Er_2O_3 from 0 to 8750 ppm (see column 3 in Table 1). Besides, the Er^{3+} ions may occupy sites as modifying oxides and hence increase of ΔT from 127 to 147 °C and ΔS from 43 to 46 °C while increasing the Er^{3+} concentration from 0 to 8750 ppm. The temperatures ΔT and ΔS are important parameter for glasses fabrication. Fiber drawing from performs is a reheating process and any crystallization during the process leads to an increase of the scattering loss of the fiber. Hence to avoid this process, it is desire that ΔS and ΔT have value as large as possible. Herein the present glass has a high ΔS and a ΔT, in comparison with other tellurite glasses so the present glasses are a good candidates for optical devices [11,12]. Also the factor T_g/T_m is a good measure of the glass stability [13], many stable glasses have a value of approximately 2/3. For the studied glass compositions, the T_g/T_m values are all in the range from 0.659 to 0.682. This indicates that the prepared glasses should have an excellent stability.

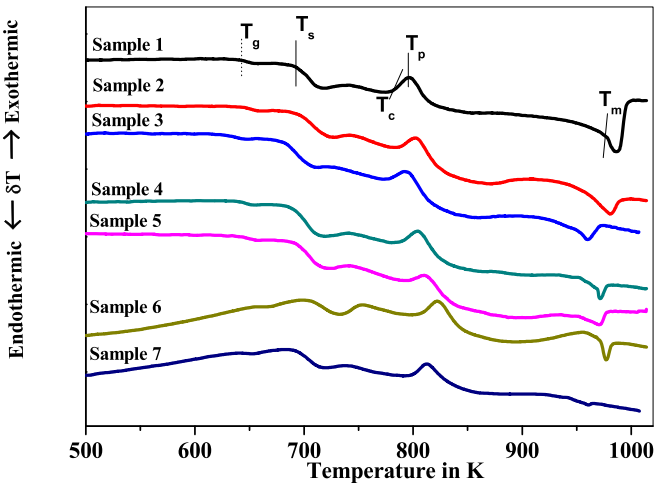

Fig. 1. DTA profile of prepared glasses at heating rate 15 K/min.

3.2. Optical properties

Fig. 2 presents measured UV–Vis–NIR absorption spectra of $75TeO_2$–$10Nb_2O_5$–5PbO–10ZnO glasses doped by Er^{3+} ions. They enable the calculation of the optical energy gap. For the absorption by indirect transition, the absorption coefficient, α(υ), is given by $(\alpha h\upsilon)^{1/2} = A(h\upsilon - E_g)$ [15]; where A is a constant, E_g is the optical band edge and $h\upsilon$ is the photon energy of the incident radiation. The optical band edge is obtained by extrapolation from the linear range in the plots of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ as shown in Fig. 3. The value of E_g decreases from 2.73 to 2.6 eV while increasing the Er^{3+} concentration from 0 to 8750 ppm. This means that energy levels of Er ions located between valance and conduction band of the TeO_2–Nb_2O_5–ZnO–PbO host glasses leads to a decrease of the optical energy required to transfer the electron from the ground state to the excited state. Furthermore, the density of the prepared glasses increases from 5.5696 to 5.6512 g cm^{-3} while increase the Er_2O_3 concentration from 0 to 8750 ppm. Er^{3+} ions incorporated in the TeO_2–ZnO–Nb_2O_5–PbO host glass network lead to higher mean molar weight and to an increase of the density. Consequently the molar volume, V_m, of the prepared glasses can be calculated by using the relation; $V_m = M/\rho$, where M is the molecular weight and ρ is the density of respective glass samples. The oxygen molar volume, V_o, is given as follows: $V_O = (\sum x_i M/\rho)(1/\sum x_i n_i)$, where x_i is the molar fraction of each component, i, and n_i is the number of oxygen atoms in each oxide [9,10]. Also the oxygen packing density, Opd, calculated by this relation $Opd = 100\rho O_i/M_i$, where O_i is number of oxygen atoms in the composition. The data of V_m, V_O, and Opd of the prepared glasses gives a good information on their structure. The value of V_m and V_O increasing from 29.73 to 73.2 and 13.83 to 32.46 cm^3 with increasing doping Er^{3+} concentrations. Otherwise the value of Opd decreases from 72.32 to 30.82 in g atom lit^{-3} with increasing Er^{3+} concentration. This indicates that the glass matrix gets more compact and cross-linking increases while increasing the Er_2O_3concentration. All these data were