Journal of Molecular Structure 1079 (2015) 167–172

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Sm^{3+}:Ag NPs assisted modification in absorption features of magnesium tellurite glass

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HIGHLIGHTS

- Fully amorphous tellurite glass system by controlling the ratio of Sm_2O_3 and AgCl contents is obtained.
- The formation of Ag NPs is stimulated via controlled melting and annealing process, thus confirmed by TEM image.
- Physical parameters of Sm^{3+}:Ag NPs tellurite glasses are examined.
- Optical absorption characteristic of Sm^{3+} in prepared glasses is investigated.
- Structural property of investigated glasses has been studied.

ARTICLE INFO

Article history:
Received 18 June 2014
Received in revised form 9 September 2014
Accepted 11 September 2014
Available online 19 September 2014

Keywords:
Tellurite glasses
Nanoparticles
Optical absorption
Vibrational modes

ABSTRACT

Metallic nanoparticles (NPs) assisted enhancements in absorption and emission cross-section of tellurite glass is the present challenge. The influences of samarium (Sm^{3+}) ions and silver (Ag) NPs ratio on physical and optical absorption properties of melt quench synthesized magnesium tellurite glasses are reported. XRD patterns verify the amorphous nature of glasses. Glass density, molar volume and ionic packing fraction are discerned to be in the range of 4.92–5.0 g cm^{-3}, 29.82–30.26 cm^3 mol^{-1} and 0.452–0.446, respectively. Moderate reduction potential of tellurite glass converted Ag^{1+} to Ag^0 via single step process and NPs are formed. TEM image manifest the existence of NPs of average diameter ~16.94 nm having Gaussian size distribution. The significant changes in structural properties in the presence of Ag NPs are discussed in terms of TeO_4 tetrahedra distortion and network depolymerization process. The Sm^{3+}:Ag NPs dependent variation in physical properties are ascribed to the alteration in the number of bridging oxygen to non bridging (NB) one. Enhancement in absorption intensity due to the local field effects of Ag NPs is attributed to the changes in Sm–O bond strength. Optical energy band gap (2.81–3.18 eV) and Urbach energy (0.18–0.24 eV) are found increase and decrease, respectively with the increase of Sm^{3+}:Ag NPs up to 1.33 then quenches and enhances, respectively thereafter which are related to the changes in cross-link and NBO numbers. The FTIR spectra reveal modification in network structures evidenced from vibrational wave-number shifts of TeO_4 and TeO_3 structural units. The observed notable increase in HOH vibration mode suggests its helpfulness in promoting the absorption of water and light. It is asserted that the physical, optical and structural properties of magnesium tellurite glass can be tuned by controlling Sm^{3+}:Ag NPs.

Introduction

Tellurite based-glass is the most promising host due to several special features such as wide transmission range from UV to infrared region (340 nm–15 μm), low dispersion [1–5], high transparency with refractive index from 2 to 2.5 [6–9] and high rare earth ion solubility. Consequently, they are attractive for lasers and optical amplifiers application [10–13]. These desirable features allowed intensive studies on their optical properties [14–16]. However, the modification in overall properties of noble metallic (Au and Ag) nanoparticles embedded tellurite glass containing Sm^{3+} ion is not much reported.

Recently, Sm^{3+} ion is verified as a dopant while Au or Ag NPs are demonstrated as stimulating agents for the enhancements of absorption and emission properties [17]. Nelson et al. [18] have proposed two important effects of dopant ions in terms of their local environment. Firstly, each of the dopant ions can occupy an

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http://dx.doi.org/10.1016/j.molstruc.2014.09.039
0022-2860/

individual site which is determined by the configuration of the structural unit in the melt. Lastly, they can modify the spatial geometry of the nearby glass network to outfit their own bonding requirement. Moreover, dopants can act as network modifiers and thus promote the formation of high number of non-bridging oxygen (NBO) [19]. Conversely, the metallic NPs assisted strong modifications in the rare earth transition probabilities caused by local field effect and energy transfer are easily detected from emission measurements [20]. The composition, shape and size of NPs play significant roles towards their interaction with external radiation [20].

TeO_2 glassy and crystalline states are built by co-ordination of Te^{4+} ions in TeO_4 groups as trigonal bipyramidal (tbp) form with bridging oxygen [21]. In TeO_4 tbp linkage, two oxygen atoms are located in the axial site, while the other two and the lone electron pair of tellurium are located in the three equatorial sites. Kim and Yoko [22] acknowledged that the equatorial Te–O bonds are slightly shorter than the axial bonds. Trigonal bipyramids are linked to each other by sharing their vertices which form a continuous three-dimensional structure [23]. The basic structure of TeO_2 glass network often changes from TeO_4 to TeO_{3+1} and/or TeO_3 in the presence of network modifier. The combined effects of Sm_2O_3 and AgCl on magnesium tellurite glass are far from being understood.

A series of Sm^{3+} ion doped magnesium tellurite glasses containing Ag NPs are synthesized using melt-quenching method by controlling the ratio of Sm_2O_3 and AgCl contents. Glasses are characterized using XRD, TEM, FTIR and UV–Vis spectroscopy. A correlation between optical and structural properties a function of Sm^{3+} ion to Ag NPs ratio is established. These glasses may be nominated as potential candidates for nanophotonic applications.

Experimental

Glasses with chemical composition $88.6TeO_2–10MgO–xSm_2O_3–(1.4-x)AgCl$ (x ranges between 0.2 and 1.0 mol%) are synthesized using melt quenching technique. Starting powdered materials of TeO_2, MgO, Sm_2O_3 and AgCl from Sigma Aldrich (analytical grade purity 99.9%) are mixed thoroughly. An aluminium crucible containing the glass constituents is placed in a furnace at 900 °C for 25 min and the melt is poured in a brass mould after the desired viscosity is attained. Subsequently, the sample is transferred to an annealing furnace and kept for 3 h at 295 °C to remove the thermal and mechanical strains completely. The samples are then cooled down to room temperature before polishing. Finally, they are cut and polished (thickness ~0.25 mm) for the structural and absorption measurements. Nominal compositions of prepared glasses (transparent and yellowish colour) with respective codes are listed in Table 1. The formation of Ag NPs is stimulated via controlled melting and annealing process in which Ag^+ cations are formulated and reduced to Ag neutral NPs ($Ag^+ + 1e^- \rightarrow Ag^0$) during the melting process.

Density (ρ) of each sample is measured using standard Archimedes principle (Analytical balance of specific density-PrecisaXT220A) with distilled water as an immersion liquid. The molar volume (V_m) is calculated following,

$$V_m = \frac{M}{\rho} \quad (1)$$

where M is the glass molecular weight.

The ionic packing density (V_t) is calculated using Makishima and Mackenzie approach [24–26],

$$V_t = \left(\frac{1}{V_m}\right) * \sum (V_i * x_i) \quad (2)$$

where x_i is the mole fraction (mol%) and V_i is packing density parameter (m^3/mol). For an oxide glass of the form M_XO_Y, the value of V_i yields [26],

$$V_i = \left(\frac{4\pi N_A}{3}\right)[Xr_M^3 + Yr_o^3] \quad (3)$$

where N_A is Avogadro's number (mol^{-1}), r_M and r_o are the Shannon's ionic radius of metal and oxygen, respectively.

The amorphous nature of glass is examined by Siemens X-ray Diffractometer D5000 using Cu Kα radiations (λ = 1.54 Å) at 40 kV and 100 mA, with scanning angle 2θ ranges between 10° and 80°. The room temperature absorption spectra in the range of 200–2000 nm are recorded using Shimadzu UV-3101PC scanning spectrophotometer (Kyoto, Japan). Transmission electron microscopic (TEM) imaging is carried out using a Philips CM12 operating at 200 kV with Docu version 3.2 image analyses. Fourier transform infrared (FTIR) transmission measurements over the range of 400–4000 cm^{-1} are performed using Perkin Elmer FTIR 1660 spectrometer followed by standard KBr pellet disc technique.

Results and discussion

The typical X-ray diffraction pattern for sample S4 as shown in Fig. 1 in the presence of a broad hump confirms its amorphous nature. Furthermore, the absence of any sharp crystalline peak verifies the short ranged order. TEM image for sample S4 as displayed in Fig. 2(a) reveals the growth of homogeneously dispersed Ag NPs in the glass matrix having varying shape and sizes. The average diameter Ag NPs discerned to be ~16.94 nm which is shown in Fig. 2(b).

The calculated physical parameters of all glass samples are listed in Table 1. Figs. 3–5 shows the Sm_2O_3 to Ag NPs ratio (here after

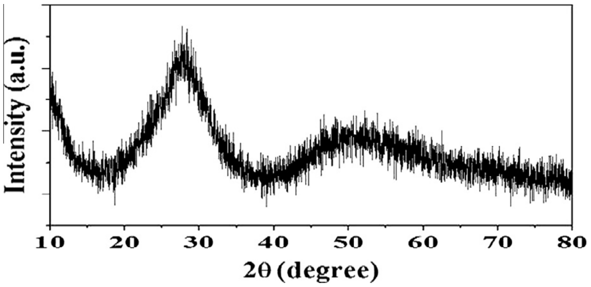

Fig. 1. XRD pattern of sample S4.

Table 1
The nominal composition of glasses with codes, density (ρ), molar volume (V_m) and ionic packing density (V_t).

Sample code	Nominal composition (mol%)				Sm^{3+}:Ag NPs	ρ (g cm^{-3})	V_m (cm^3 mol^{-1})	V_t
	TeO_2	MgO	Sm_2O_3	AgCl				
S1	88.6	10	0.2	1.2	0.17	4.92	30.05	0.447
S2	88.6	10	0.4	1.0	0.40	4.96	29.89	0.449
S3	88.6	10	0.8	0.6	1.33	5.00	29.82	0.452
S4	88.6	10	1.0	0.4	2.5	4.94	30.26	0.446