Physica B 456 (2015) 191–196

Contents lists available at ScienceDirect

Physica B

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

# Effect of silver nanoparticles incorporated with samarium-doped magnesium tellurite glasses

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## ARTICLE INFO

*Article history:*
Received 4 June 2014
Received in revised form
22 August 2014
Accepted 26 August 2014
Available online 6 September 2014

*Keywords:*
Tellurite glasses
Samarium oxide
Nanoparticles
Transmission Electron Microscopy (TEM)
Optical energy band gap
Electronic polarizability

## ABSTRACT

Silver nanoparticles (Ag NPs) are incorporated in samarium doped tellurite glass of a composition $(89-x)TeO_2$–10MgO–$1Sm_2O_3$–$x$AgCl, where $0.0 \leq x \leq 0.6$ mol%, by a melt quenching technique. It is found that all the glasses are amorphous in nature, and the existence of Ag NPs with an average size of 16.94 nm is confirmed by Transmission Electron Microscopy. Meanwhile, their physical properties such as glass density, molar volume and ionic packing density are computed utilizing the normal method. The density and ionic packing density are observed to decrease with increasing Ag NPs, but increase when the Ag NPs are beyond 0.2 mol%. On the other hand, the molar volume behaves exactly opposite to the increase in Ag NPs content. It decreases when the Ag NPs content value is more than 0.2 mol%. The optical energy band gap and Urbach energy are evaluated from the absorption spectra in the range of 200–900 nm at room temperature. It is also observed that the direct and indirect optical energy band gaps reduce with Ag NPs content, but enhance when the Ag NPs are beyond 0.2 mol%. Meanwhile, the Urbach energy is found to increase as the Ag NPs content is increased but decreases when Ag NPs is 0.2 mol%. The refractive index is deduced from indirect optical energy band gap. Meanwhile, molar refraction and electronic polarizability have been calculated from the Lorentz–Lorentz relation. Refractive index and electronic polarizability are also observed to raise with Ag NPs content, but drop off when Ag NPs content is more than 0.2 mol%. In this paper, all properties are discussed with respect to the Ag NPs concentration.

## 1. Introduction

Among motivated studies of glassy materials, tellurite based glasses drew much interest because of their unique properties such as high dielectric constant and excellent transmission in the visible as well as IR wavelength regions, good mechanical strength and chemical durability [1–4]. These glasses also possess higher refractive index, which is approximately in the range of 2.0–2.5 [5–8], and their low melting temperature (about 800 °C) contributes to the high possibility of stable glass forming using a conventional melt quenching method [4]. Pure tellurium oxide cannot form glass by itself; it needs another element known as a glass modifier such as alkali metal, alkaline earth metal oxide and transition metal oxide (TMO) to improve the network connectivity to produce a stable tellurite glass [9,10] with increasing non-bridging oxygen [9]. In fact, it is believed that the properties of oxide glasses strongly depend on the nature and the concentration of the constituent oxides [11].

Tellurite glasses contain Te–O bonds, connecting each other, forming a normal glass network. However, Te–O bonds can be easily broken and therefore can accommodate heavy metal oxides or rare earth ions (RE) [12]. $TeO_2$ glass is good for hosting rare earth ions since it provides low phonon energy (~750 nm), which minimizes non-radiative losses [13,14]. Samarium oxide is one of the rare earth families that are used as a dopant to create a lasing character of $TeO_2$ glass. Ravi et al. [15] have proposed certain composition of $Sm_2O_3$ for use in laser and photonic devices. Further investigations towards glass containing RE ions incorporating metallic nanoparticles (NPs) such as gold (Au) or silver (Ag) NPs are extensively conducted. Metallic nanoparticles show great diverse fascinating properties compared to the usual glass system without NPs. The striking distinction of incorporated metallic NPs is addressed during the interaction of metallic NPs with electromagnetic light. Such interaction generates a collective oscillation of metallic NPs's conduction electrons at interface of NPs and surrounding of glassy medium, which is known as localized surface plasmons (LSP). It produces enhanced local field inside and near the NPs [16], hence raising the electromagnetic field that is very important in enhancing optical processes. It should be noted that the size and shape of metallic NPs as well as surrounding medium play important roles in enhancing optical properties.

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http://dx.doi.org/10.1016/j.physb.2014.08.039
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Yeshchenko et al. [17] have reported that the scattering rate of the conduction electrons increases with the smaller size of Ag NPs and results in a nonlinear redshifted SPR energy. This gains a paramount importance in surface-enhanced Raman spectroscopy [18]. Naranjo et al. [19] have reported the enhancement of down-conversion luminescence by embedding Ag NPs in $Pr^{3+}$ doped germinate glass system. Meanwhile, Kassab et al. [20] found a substantial increment of ionic optically stimulated second harmonic generation in tellurite glass containing Ag NPs. A recent research by Jimenez et al. [21] described the use of Ag NPs in the optical interaction of metal and rare earth in dielectric host.

Optical energy band gap and Urbach energy are important glass properties. The optical absorption is directly related to the size of particles in which the optical energy band gap is slightly blue-shifted towards higher energy, presumably due to the decreasing of the particle size, until it reaches the nanosize region [22–24]. However it is also important to note that the concentration of different nanoparticles plays a different role in tuning the optical energy band gap [25], which is due to the broadening or narrowing of the valence band or multivalence structures. It is also found that electronic polarizability is one of the important properties that reveal direct nonlinear response of materials when intense light beam is incident on the sample. Refractive index and molar refraction for isotropic materials are governed by electronic polarizability [26–28]. Refractive index is reduced when ions in the system are less polarized. Commonly, the polarization is directly proportional to field strength; smaller the field strength of ion lesser the ion polarization, thus decreasing the refractive index. However, it is observed that refractive index depends on glass composition [29].

According to the best of authors' knowledge based on literature survey, there is a lack of reports about the Ag NPs concentration effect on this glass. Therefore, the present study investigates many desirable features such as density, molar volume, ionic packing density, optical energy band gap, Urbach energy, polarizability and refractive index. The main objective of study is to observe the interesting changes in the said properties by incorporating Ag NPs.

## 2. Experimental procedure

Series of glasses based on $(89-x)TeO_2$–$10MgO$–$1Sm_2O_3$–$xAgCl$, where $0 \leq x \leq 0.6$ (mol%), composition have successfully been prepared by a melt quenching technique. A 15 g batch with a proportional amount of $TeO_2$ (purity 99%), MgO (purity 99.9%), $Sm_2O_3$ (purity 99.2%) and AgCl (purity 99.999%) in powder form was mixed in a platinum crucible. Then the mixture was melted at 900 °C in an electrical furnace for 1 h. During the melting process, chlorine was removed as gas molecules while $Ag^+$ cations were formulated and reduced to Ag neutral NPs ($Ag^+ + 1e^- \rightarrow Ag^0$), thus producing Ag NPs. The melt was quenched between two brass plates before annealing at 300 °C for 3 h and then allowed to cool down to room temperature. The glass was then cut, ground, and polished to a thickness of 2.5 mm to produce a shiny and scratch free surface for use in optical measurements. The amorphous nature of glass was confirmed using a Siemens X-ray Diffractometer D5000 with a scanning angle $2\theta$ ranging between 10° and 80°. A tube voltage of 30 kV and current of 20 mA were used. Meanwhile the Energy Dispersive of X-Ray (EDX) analysis was used to analyze the actual composition of the glass. The glass density was measured by the Archimedes method using distilled water as an immersion liquid. The density $\rho$ (g/cm$^3$) of each sample is determined by the relation [30],

$$\rho = \rho_L \frac{W_1}{W_1 - W_2} \tag{1}$$

where $\rho_L$ is the density of distilled water (0.9975 g/cm$^3$) $w_1$ and $w_2$ are the weight of the sample in the air and in water respectively. The molar volume $V_m$ is calculated using the relation [31],

$$V_m = \sum_i \frac{x_i M_i}{\rho} \tag{2}$$

where $x_i$ and $M_i$ denote the molar fraction and molecular weight of the $i$th component respectively. According to Makishima and Mackenzie [32–34], the ionic packing density $V_t$ can be expressed as

$$V_t = \left(\frac{1}{V_m}\right) \sum (V_i x_i) \tag{3}$$

where $V_m$ is the molar volume, $x_i$ is the molar fraction (mol%), and $V_i$ is packing density parameter (m$^3$/mol). For an oxide glass $M_xO_y$, the $V_i$ can be obtained from the following relation [34]:

$$V_i = \left(\frac{4\pi N_A}{3}\right)[X r_M^3 + Y r_O^3] \tag{4}$$

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 occurrence of Ag NPs in a glass matrix can be observed under a Phillips CM12 Transmission Electron Microscope (TEM). The absorption spectra were obtained with a Shimadzu 3101PC UV–vis–NIR spectrophotometer in the range of 200–900 nm at room temperature.

## 3. Results and discussion

### 3.1. X-ray diffraction

Table 1 shows a nominal chemical composition of the $(89-x)$ $TeO_2$–$10MgO$–$1Sm_2O_3$–$xAgCl$ prepared glass. Meanwhile, Fig. 1 shows a typical X-ray diffraction pattern for S1 and S4 glass samples. The glasses exhibit a wide halo, which shows the characteristic of an amorphous nature of the glass. Notably, the (1 1 1) largest diffraction peak of crystalline Ag expected at $2\theta = 38.784°$ [35–37] is missing from the two spectra. This might be due to the small amount of Ag NPs embedded in the glass system.

### 3.2. Glass morphology

Fig. 2(a) shows a TEM image for the glass containing Ag NPs. It can be seen that the spherical and non-spherical particles are dispersed homogeneously in the glass matrix. MEP_L_fig2 Fig. 2 (b) shows the distribution of particle size using a Gaussian plot. The calculated average diameter of Ag NPs is around 16.94 nm. Meanwhile, Fig. 2(c) shows the EDX spectrum for S3. Analyses for the other compositions have also been done and the results for the actual chemical composition are inserted in Table 2. From Table 2, it can be seen that S3 possesses an actual amount of 0.2 mol% of AgCl out of possible 0.4 mol%. From this analysis, the most possible

**Table 1**
A nominal chemical composition of $(89-x)TeO_2$–$10MgO$–$1Sm_2O_3$–$xAgCl$ glass system.

| Sample no. | Nominal chemical composition (mol%) | | | |
|---|---|---|---|---|
| | $TeO_2$ | MgO | $Sm_2O_3$ | AgCl |
| S1 | 89.0 | 10 | 1 | 0.0 |
| S2 | 88.8 | 10 | 1 | 0.2 |
| S3 | 88.6 | 10 | 1 | 0.4 |
| S4 | 88.4 | 10 | 1 | 0.6 |