Effect of thermal treatment on morphological properties of borosilicates glass doped with silver

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Abstract

Glasses containing metallic nanoparticles are promising materials that should also possess the best spectroscopic, chemical, mechanical and thermal characteristics for technological applications in optics and photonics. For this reason it was chosen to synthesize and characterize the pure silver doped borosilicate glasses and silver nitrate. The present work investigates the generation of silver nanoparticles on the surface and the mass of a borosilicate glass in which it was directed to the synthesis process in which it was consisted: in the stoichiometric calculations, in the determination of the melting temperature, in the choice of reagents with high degree of purity, in the manufacture of the samples, in the appropriate polishes and in the determination of heat treatments close to Tg of the glass in question. From this phase, the research followed the application of techniques of differential thermal analysis (ATD) and transmission electron microscopy (MET). Thus, from the results and analyzes obtained, it was possible to observe that the borosilicate glass samples of this work will obtain satisfactory experimental results, in which it was possible to prove its optical and structural properties similar to those recognized in literature, thus making it a promising material in area of vitreous materials applied to nanotechnology borosilicate glasses are obtained from the combination of silicon dioxide (SiO_2) with boron oxide (B_2O_3) and the resulting samples were annealed at various temperatures. Due to the structural shape, these glasses have a high resistance to thermal shock, good chemical durability and excellent electrical resistivity compared to other glasses on the market today. Therefore, based on these important structural, physical and chemical characteristics and also in the variety of applications, this study was chosen for the synthesis and characterization of pure borosilicate glass and doped with silver nitrate. We verified the formation of silver nanoparticles, after the heat treatment, by transmission electron microscopy.

Keywords: *borosilicate glasses, silver nanoparticles, transmission electron microscopy (TEM).*

1. Introduction

One of the main interests in metallic nanoparticles arises from the local field enhancement effect that has been used for a great number of applications, from sensors to nonlinear optics [1, 2, 3, 4]. The light absorption by nanoparticles produces a coherent and collective oscillation of the electrons, contributing to the enhancement of linear and nonlinear optical properties [1].These properties are influenced not only by the size and the shape of the nanoparticles but also by the dielectric environment of the host material [5]. Glasses containing metallic nanoparticles are promising materials for photonic applications because they exhibit ultrafast response times and high third order nonlinearities [6, 7, 8, 9].

Glasses containing boron oxide (B_2O_3) are obtained by the dehydration of the boric acid (H3BO3) above a temperature of between 260 ^{0}C and 270 ^{0}C at a reduced pressure in the range of 130 to 260 Pa. In a glass made of pure boron oxide, the basic structures are formed exclusively by BO3 triangles so the oxygens of the structure form bridges between the two boron atoms.These units are constituted of planar triangles of B_2O_3 where each B_2O_3 triangle is connected to the other by bridging oxygens forming a plan hexagonal ring, like the boroxol ring. The oxygen bridge between two cations of either B or Si is a strong bond that helps hold the amorphous network togheter [10, 11]. The schematic representation of the structure of network formers and network modifier in borosilicate glass is shown in Figure 1.

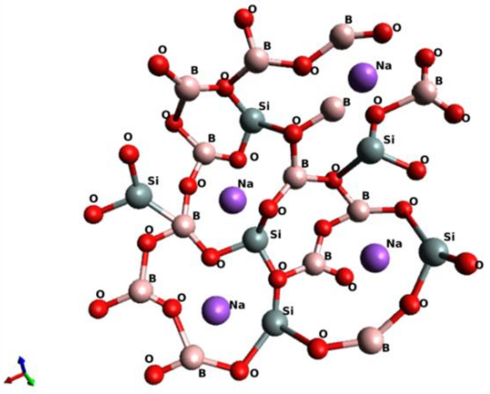

Figure 1: Schematic representation of the structure of network formers and network modifier in borosilicate glass, using the Avogadro 3d molecular editor.

This paper presents a study on the generation and the interactions of silver nanoparticles in the host matrix$(40-x)B_2O_3(30-x)SiO_2(2-x)Al_2O_3(23-x)Na_2O(5-x)ZnO_2$ where x=0.25mol% $AgNO3$ prepared from high purity raw materials. The effect of annealing temperature on optical and structural properties of synthesized Ag-glass nanocomposite has been investigated in detail. The presence of the nanoparticles was confirmed by transmission electron microscopy.

2. Methodology

The samples were prepared by using conventional melting- quenching technique with a mixture of the constituent oxides heated in an electrical furnace at a temperature around 1450^{0}C for four hours under normal atmospheric conditions and then quenched onto a stainless-steel plate. Better homogeneity of the melt was achieved by removing the crucible from the de furnace and swirling several times. SiO_2, Al_2O3, B_2O_3 oxides (Aldrich Chemical Company having 99,99% percent purity level) were used as starting materials, as it can be seen in Table 1.

Table 1: Molar composition (mol%) of samples prepared in this study: BSP (glass no dopped) BSDAg (glass doped with silver).

Sample	B_2O_3 (Mol%)	SiO_2 (Mol%)	Al_2O_3 (Mol%)	Na_2O (Mol%)	ZnO (Mol%)	$AgNO_3$ (Mol%)
BSP	40,00	30,00	2,00	23,00	5,00	-
BSDAg	39,90	29,93	1,99	22,94	4,99	0,25

Glass transition temperature (Tg) was determined by Differential Scanning Calorimetry (DSC), using a Shimadzu DTA-50 instrument, in platinum pans, within a range of 20 ^{0}C to 900 ^{0}C with a heating rate of 10 ^{0}C/min, and in a synthetic air atmosphere. From DSC curve was obtained Tg value of the 496 ^{0}C ± 2 ^{0}C and no exothermic peak was found, indicating that there is no formation of crystalline phases during the heating up to 700 ^{0}C.The Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDX) analysis were accomplished using a Philips CM 200 Microscope operating at a 200kV. For this study, samples were prepared in the following way: a diamond scriber was utilized to scratch the surface (a few microns below) of the glass containing silver nanoparticles. The samples selected for TEM were scraped surface and diluted in water, where only the particles that remained on the surface of the solution were placed in a micro-screen with previously deposited carbon. Consequently, the larger glass particles settled down and the finer ones floated on the surface of the liquid. The finest layer on the surface was collected on the carbon coated copper grid for observation [12, 13]. To obtain the size and size distributiondata was used a free program for particle counting named image J [14, 15].

3. Discussion and Results

Temperatures are identified by T_g (glass transition temperature), T_x (crystallization onset temperature), Tm (melting temperature) and K_H (Hruby parameter). These temperatures were determined graphically by the intersection of tangents to the baseline and the slope of the curve. The dates are shown in Figure 2 shows the thermogram where the BSP powder samples. where Tg: glass transition temperature (496 ^{0}C); Tx: crystallization temperature (559 ^{0}C); Tf: melting temperature (684 ^{0}C) and K_H: Hrubry parameter (0.39).

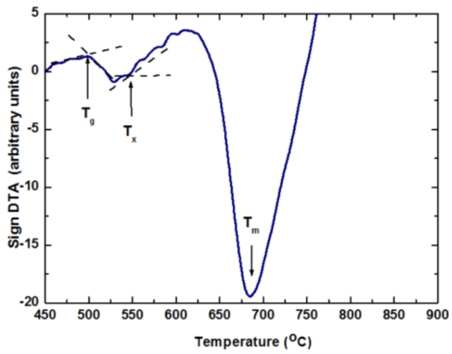

Figure 2: Thermogram for the pure borosilicate glass sample without heat treatment BSP sample. Tg: glass transition temperature; Tx: crystallization temperature; Tm: melting temperature.

It is known from the literature that the thermal stability can be evaluated by the entity difference of temperatures Tx-Tg, where values above 100 ^{0}C indicates a good thermal stability of the glass. The glass used in this study was pure borosilicate, the value found for this difference was 53 ^{0}C. It is possible to conclude that thermal stability of the glass is not very good. But on the other hand, the Hruby parameter shows that the behavior of the vitreous network of the BSP has a parameter which is between $0.1 < K_H < 0.5$

do not exhibit crystallization, and which may be easily manufactured. It was decided to analyze by TEM technique only samples having obtained the best optical absorption spectrum, so it was chosen by B3 samples (treated at 300 ^{0}C for one hour) and B5 (treated by 400 ^{0}C for one hour) with the aim of studying the types of changes that the heat treatment causes the vitreous samples and the formation of nanoparticles that are part of this internal structure. The Tables 6 lists the parameter used for obtaining the EDX spectra of the samples B3 and B5 respectively [16].

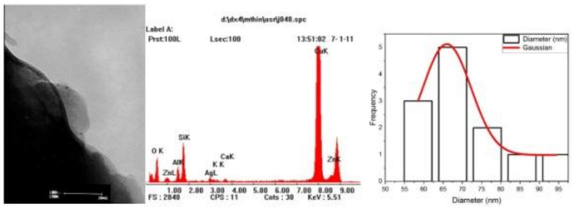

Figure 3: (a) Results of TEM micrographs and (b) EDX of borosilicate glass sample doped with silvernitrate and heat treated at 300 ^{0}C for one hour (B3). Showing distinct regions: (A) B3. (c) Correspondingsize distribution with Gaussian curve fit.

Table 2: Parameters used for obtaining the EDX spectra of the sample B3 and B5.

EDX	FS	CPS	Cnts	KeV
B3	2840	11	30	5.51
	2851	6	32	5.51
	6866	5	30	5.51
B5	3409	8	32	5.51
	4370	7	49	5.51
	3479	7	46	5.51

The Figures 3, 4, 5 and 6 show the effect of annealing on the Ag dispersion in the glass matrix. As can be seen in these figures nanoparticles are condensed into small agglomerates. In Figures 4, 5 and 6 can observe the three micrographs with their respective spectra EDX (sample B3), where it is possible to see the silver nanoparticles with diameters ranging from 10 to 100 nm, which in the picture correspond to black spherical dots indicated by arrows. Observing these figures was observed the presence of few silver nanoparticles dispersed among themselves and the presence of silver nanoparticles, which are closer to each other. This increase in the number of nanoparticles due to the heat treatment of the samples. Figure 6 shows an abundant presence of silver nanoparticles, even when compared with the other samples, where it was possible to obtain the isolated nanoparticles, since some are dispersed and correspond to the black spherical dots, while in the other samples there are four small clusters distributed on the surface. Observing the EDX spectra is remarkable the presence of CuK peak that belongs to the copper-sample holder used for performing the measurement. For all EDX spectrum is always observed the presence of Ag, Al, Zn, Si, Ca, O and Cu, but it is not possible to observe the presence of boron crystals and the sample B5 shows the presence of the Cl and S. This shows that the Boron did not crystallize and therefore not formed crystallites and then one can say that in the sample was analyzed nanoparticles are completely insulated in the glass matrix. In these spectra of the B5 sample as the sample B3 was also possible to observe two peaks related to silver nanoparticles. Analysis of the TEM micrographs showed that the thermally treated borosilicate glass samples contain nanoparticles due to the result of diffusion processes, reduction, aggregation and crystal growth, where the size of the nanoparticles increases with the heat treatment (time and temperature).

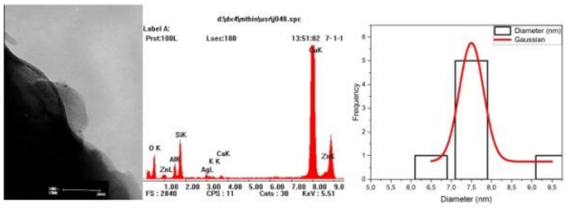

Figure 4: (a) Results of TEM micrographs and (b) EDX of borosilicate glass sample doped with silver nitrate and heat treated at 300 ^{0}C for one hour (B3). Showing distinct regions: Sample (B) B3. (c) Corresponding size distribution with Gaussian curve fit.

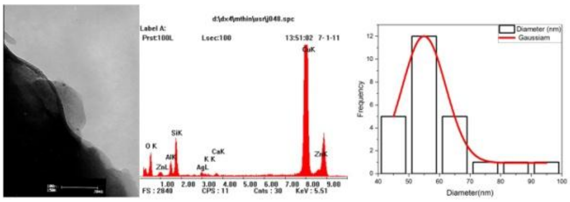

Figure 5: (a) Results of TEM micrographs and (b) EDX of borosilicate glass sample doped with silver nitrate and heat treated at 300 ^{0}C for one hour. Showing the region (C) Sample B3. (c) Corresponding size distribution with Gaussian curve fit.

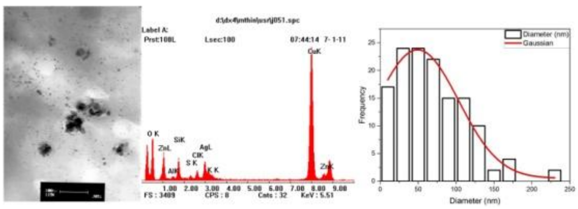

Figure 6: a) Results of TEM micrographs and (b) EDX of borosilicate glass sample doped with silver nitrate and thermally treated at 400 ^{0}C for one hour (B5). Showing the region (A) Sample B5. (c) Corresponding size distribution with Gaussian curve fit..

4. Conclusion

From the differential thermal analysis (DTA) it was not possible to obtain good thermal stability, but in return the Hruby parameter was found to be satisfactory, indicating that the glass produced did not show any crystallization, which is a very important factor due to the applicability of pure glass materials for technological applications. For borosilicate glass samples doped with silver nitrate undergone different heat treatments in the range of 200 0C to 500 0C for one hour, it is possible to see that micrographs confirms the presence of silver particles or their aggregates, that had the same spherical shape with average diameters ranging from 10nm to 100nm, since their absorption bands were included in the range between 400nm and 600nm. And can also verify that results from the diffusion processes, reduction, aggregation and crystal growth. The size of the nanoparticles increased linearly with the increase of annealing temperature. Through the EDX spectra obtained by the technique of transmission electron microscopy was not observed the presence of the boron crystal in any of them, then it can be said that in the sample analyzed the nanoparticles were fully isolated in the glass matrix. One can verify the presence of the following chemical elements: Ag, Al, Zn, Si, Ca, O, S, Cl, and Cu. No Na peaks found in the EDX spectrum.

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