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Crystallization of selenite glasses in reduction atmosphere

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Multicomponent selenite glass compositions for preparation of nanocomposite materials, containing chalcogenide compound were selected. The glasses are thermal stable below 300^{0}C. They were subjected to heat treatment in different reducing conditions at 200^{0}C: in a N_2+H_2 (20 %) gas flow and in a vacuum oven. There is a proof for the formation of small chalcogenide nanocrystals in an amorphous oxide matrix containing SeO_2.

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1. Introduction

Nanostructured solid materials with ultrafine metal and semiconductor particles are of great importance in materials science, covering broad applications from multifunctional ceramics to biosensors. The glasses are a suitable starting matrix for obtaining this kind of materials but special conditions are needed to control the microaggregation processes in them. Since Jain and Lind [1] first reported on the large third-order optical nonlinearity of semiconductor-doped glasses, many studies have been carried out to evaluate the usefulness of this type glass. Microcrystals, such as CdSe, CdTe, GaAs and Ge were successfully incorporated into silica glass thin films [2-5]. CuSe was also successfully introduced into silica glass [6]. Other compounds (PbTe, PbSe, PbS, CdTe and ZnTe) were incorporated into glass matrices either [7-10]. Mainly sol-gel processing was applied to incorporating chalcogenide micro and nano crystals [3-5]. The preferable glass matrices are titanium-silica [3], borosilicate [4], tellurite [7], silica [8] and phosphate [11]. Nanocomposite chalcogenide-polymer compositions were developed recently as an effective way to fabricate high refractive index composite materials [12-14]. These studies motivated us to investigate the new amorphous matrices subjected to different experimental conditions aimed at obtaining chalcogenide nanoparticles. Our team investigated in detail the glass formation and structure in binary and multicomponent systems containing SeO_2, but up to now they were not used as starting matrices for obtaining nano-heterogeneous structures. Our previous investigations in the TeO_2-Ag_2O-SeO_2 and Ag_2O-SeO_2-MoO_3 systems showed that low heat treatment led to separation of metallic silver particles only, without crystallization of the main oxide crystal phases [15-17]. There are no sufficient data on the early stages of crystallization and the thermal stability of glasses containing SeO_2. That is why more knowledge is needed to clarify the microaggregation processes in them.

The paper deals with the crystallization of selenite glasses in a reducing atmosphere and is aimed at obtaining more information about the microaggregation processes in different heating regimes.

2. Experimental

Glasses containing SeO_2, TeO_2, CuO and MoO_3 were selected. They were obtained by two different techniques. The first method consisted in melting oxide batch with the nominal composition $21CuO.29SeO_2.50MoO_3$ (wt %) in sealed silica ampoule evacuated at a pressure of P=0.1 Pa. In order to decrease the evaporation of SeO_2, this compound was introduced using previously synthesized copper selenite ($CuSeO_3$) [18]. The ampoule was situated in a metal container and heated at a temperature of 750 °C. The melt was cooled with a rate of 100 K/s. A black glass (A) was obtained in this case. The second method was specially developed for selenite glasses [19,20]. It consisted in melting the oxide batches at a high oxygen pressure. The composition $42SeO_2.42TeO_2.8Nb_2O_3.6MoO_3.2PbO$ (wt %), was melted in silica crucibles situated in an autoclave. The maximum oxygen pressure during the experiments was P = 35 MPa and the maximum temperature 650 °C, attained in 2h and maintained for 20 min. The melt was slowly cooled with a rate of 2 K/s. In this case, yellow transparent glass (B) was obtained. Both selected glasses were heat-treated at 200 °C in a N_2+H_2 (20 %) gas flow. On the further experiments, glass A covered with copper powder was situated in a crucible and heat-treated in a vacuum oven at 200 °C for 6h, while glass B was additionally heat-treated in the oven at 200^{0}C for 15 h. The phase transformations of the samples were verified by X-ray diffraction (Bruker D8 Advance, Cu Kα radiation). The differential thermal analyses (DTA) and thermogravimetry (DTA-TG) were carried out on a Stanton Redcroft STA 780 apparatus with a heating rate of 10 K/s in argon flow, using Al_2O_3 as a reference material. The microheterogeneity was determined by Scanning Electron Microscopy (JEOL Superprobe 733). For glass B the spectral behavior in the visible region was investigated by a UV-VIS Spectrophotometer (Cary 100 Scan, Varian).

3. Results

XRD patterns of the as quenched and heat treated glass sample A are shown in Fig. 1.

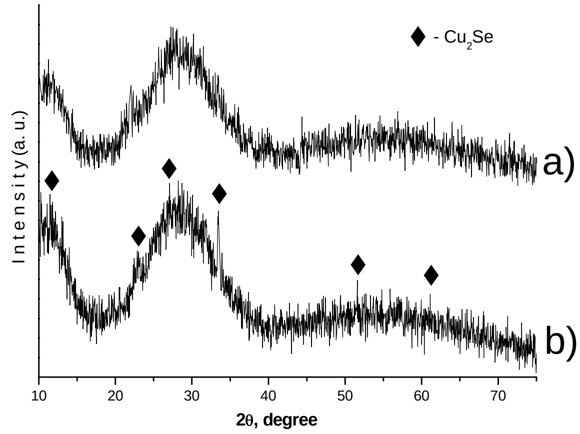

Fig. 1. X-ray diffraction of the 30CuO.30SeO$_2$.40MoO$_3$ sample (glass A) at different heat treatment: a) glass sample and b) heat treated sample at 200 ^{0}C for 6h.

Small diffraction peaks assigned to the Cu_2Se crystals are observed (JCPDS No 02-1426), but the sample has preserved its amorphous structure. DTA analysis of the black glass (A) heat treated at different temperatures showed it to be thermally stable below 200-230^{0}C (Fig. 2a). There is no well-shaped peak corresponding to crystallization. Fast mass loss occurs above 250^{0}C. An endothermic effect at 250 °C was established for the heat-treated glass (Fig. 2b). SEM observations (Fig. 3) showed that the microstructure of glass A had undergone some changes during the heat treatment. Pores appeared on the surface sample (Fig. 3a, b, c), while in the volume the amorphous state was preserved along with small bubbles (under 0,01 μm) (Fig. 3d, e). Higher magnification (x5400, Fig. 3c) showed formation of not well shaped microheterogeneities dispersed separately in the glass matrix.

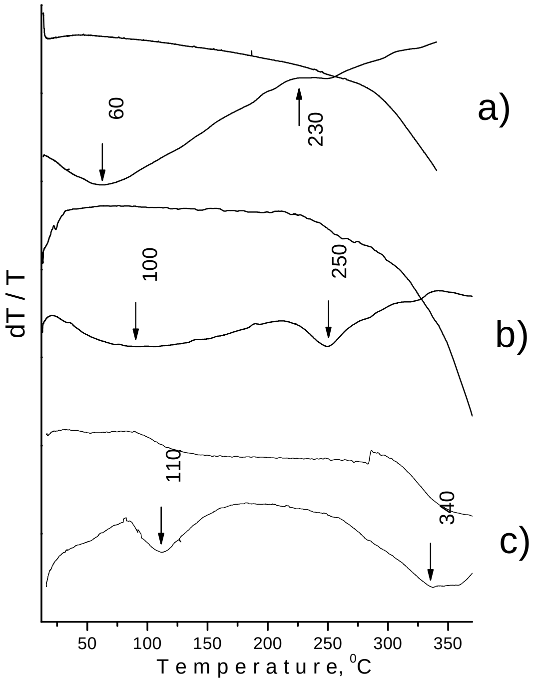

Fig. 2. DTA of the samples: a) glass sample, b) heat treatment 200^{0}C for 2h in N$_2$+H$_2$ (20 %) flow and c) sample 42SeO$_2$.42TeO$_2$.8Nb$_2$O$_3$.6MoO$_3$.2PbO heat treatment 300 ^{0}C for 2h.

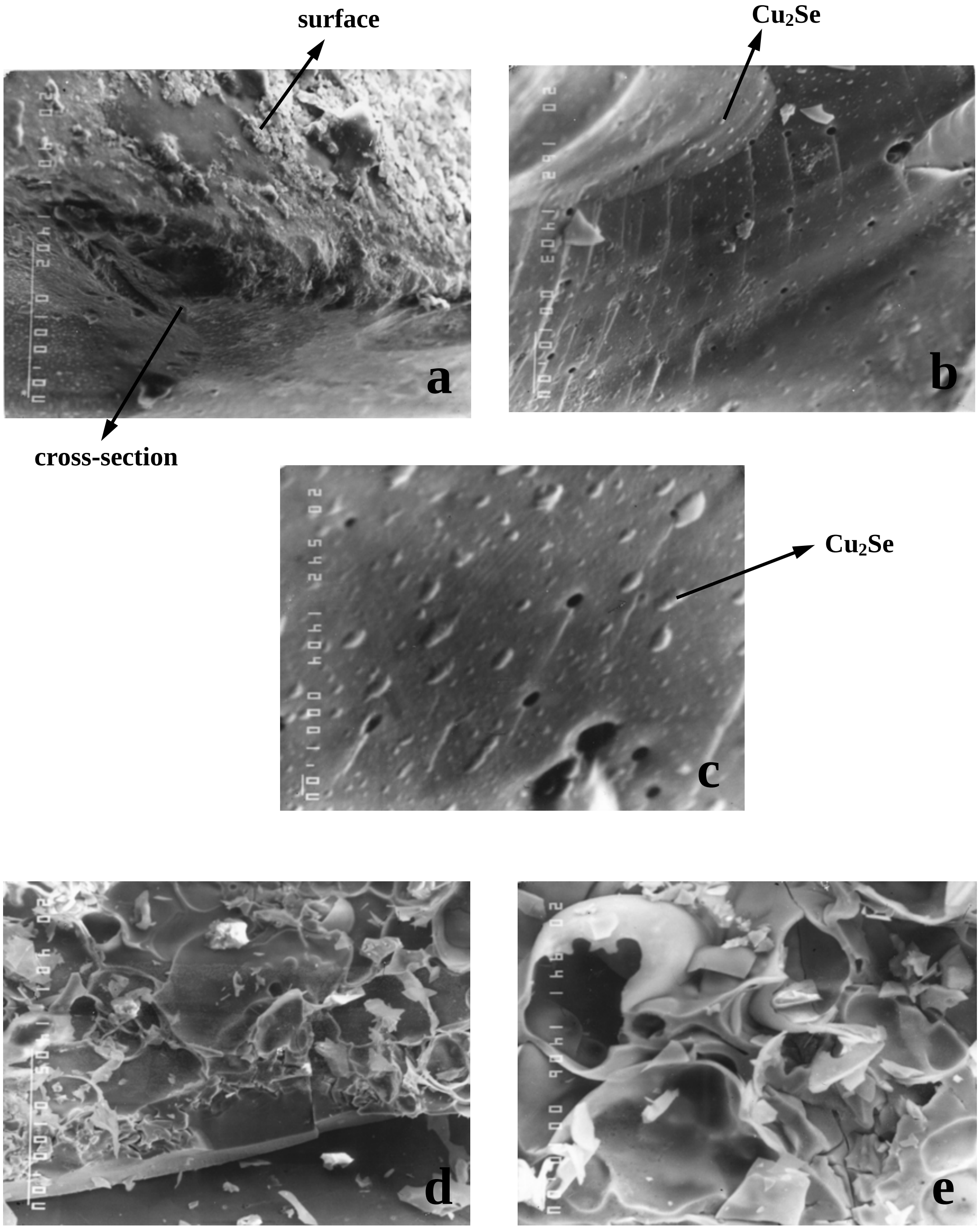

Fig. 3. SEM micrographs of the sample 30CuO.30SeO$_2$.40MoO$_3$ after heat treatment at 200 ^{0}C for 2 h in N$_2$+H$_2$ (20 %) flow: a) general view, b) and c) glass volume, d) and e) sample surface.

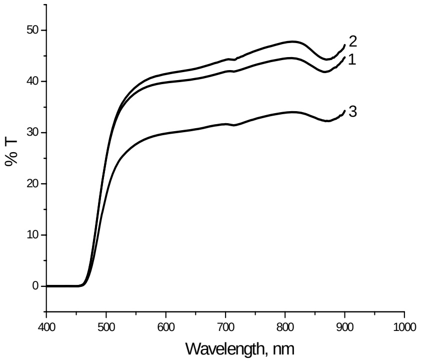

Fig. 4. Ultraviolet-vis absorption spectra of sample with nominal composition $42SeO_2*42V_2O_5*8Nb_2O_3*6MoO_3*2PbO$: 1-glass sample, 2-after heat treatment at 200^0C for 6 h and 3-after heat treatment in vacuum oven at 200^0C for 10 h.

The microprobe analysis at different points of the sample was made. The average Cu/Se ratio in the sample volume was 3:1 and on the surface, 1:2, respectively. DTA analysis of glass B showed it to be thermally stable up to 300^0C (Fig. 2c), after which fast mass loss was observed. An endothermic effect at 340^0C connected to this process was established. This yellow glass (B) was found transmittant in the visible range of the spectrum beginning with 480 nm (Fig. 4). A more intense yellow colour was observed after heat treatment along with decreasing transparency.

5. Discussion

The fast mass losses above 230^0C along with the increase in SeO_2 content on the surface as well as the appearance of pores are probably due to SeO_2 evaporation. This is typical of glass A. The results obtained indicated formation of small amount Cu_2Se crystals in the black glass (A) after 6h heating. Obviously it is necessary to prolong the heating time in order to continue the crystallization process of the chalcogenide component. Glass B demonstrated a higher thermal stability toward SeO_2 evaporation. The TeO_2 presence in the yellow glass composition increases its thermal stability and to initiate crystallization, a long-term heating is necessary. Probably the crystallization in this case starts at higher temperature (300^0C). Furthermore, the yellow glass transmittance decreases after heat treatment. Maybe this is due to the nano-aggregation processes in the amorphous matrix, connected to the changes of the sample colour. These interesting preliminary results need more experiments in order to elucidate the phenomenon.

6. Conclusion

It is proven that the selected compositions are suitable for the formation of small chalcogenide crystals in an amorphous oxide matrix containing SeO_2. To control this very slow process, a long-term heating at low oxygen pressure is necessary.

Acknowledgements

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