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NANO CRYSTALLIZATION IN NON-TRADITIONAL OXIDE GLASSES

A. Bachvarova-Nedelcheva[1], R. Iordanova[1], Y. Dimitriev[2], S. Yordanov[3]

[1] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, G. Bonchev str., bld. 11, 1113 Sofia, Bulgaria, E-mail: albenadb@svr.igic.bas.bg*

[2] *University of Chemical Technology and Metallurgy 8 Kl. Ohridski, 1756 Sofia, Bulgaria*

[3] *Institute of Metal Science "Acad. A. Balevski", 67"Shipchenski prohod" str., 1574 Sofia, Bulgaria*

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ABSTRACT

The aim of the present investigation is to establish the appropriate route of nano particles formation during the heat treatment of selected selenite glasses. Different preparation methods of the initial glass samples have been combined with heat treatment to influence the glass microstructure and formation of different types of microheterogeneites. The glasses were subjected to heat treatment in different reducing conditions at 200°C: in a N_2+H_2 (20 %) gas flow and in a vacuum oven. TEM and SEM have been used to prove the formation of nanosized particles. Various types of microheterogeneous structures have been observed as a consequence of the crystallization: small chalcogenide crystals in an amorphous oxide matrix and oxide particles.

Keywords: glasses, nanoparticles, microheterogeneities.

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 suitable starting matrix for obtaining nanostructured solid materials but the special conditions are needed to control the microaggregation processes in them. Depending on the methods of preparation and glass compositions it is possible to obtain different microheterogeneous structures as a consequence of the crystallization, phase separation and reduction processes. Such glasses and glass-ceramics are a new class of materials, which are not yet fully investigated.

The preparation of selenite glasses was first described by Rawson and Stanworth, who successfully synthesized glasses in the systems SeO_2-K_2O and SeO_2-TeO_2-PbO [1, 2]. As they pointed out, the main difficulty in the synthesis of this type of glasses is the rapid volatilization of selenite melts and the sublimation of SeO_2 at atmospheric pressure and temperatures above 315°C. Dimitriev, Lakov and their co-workers investigated the glass formation and structure in binary and multicomponent systems containing SeO_2 [3, 4] and the results obtained during the last 20 years were reviewed [5].

At present the selenite glasses are still exotic objects. They are interesting mainly from a fundamental point of view because of insufficient data on their practical application. Only a few articles on the synthesis of amorphous hard electrolytes [6], colored glasses [7] and semiconductive glasses [8] are known. There is no detailed information about the selenite glasses behavior at high temperatures and the preparation of new functional materials by crystallization of these glasses. Our study in this direction was motivated by this fact.

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 [9-11]. 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 different reducing conditions (in a N_2+H_2 (20 %) gas flow and in a vacuum oven) and is aimed to establish the formation of nanoparticles in selected compositions during heat treatment.

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 the oxide batch with the nominal composition $21CuO.29SeO_2.50MoO_3$ ($\%_{mass}$) 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 ($CuSeO_3$) [12]. 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 [13, 14]. It consisted in melting the oxide batches at a high oxygen pressure. The composition $42SeO_2.42TeO_2.8Nb_2O_3.6MoO_3.2PbO$ ($\%_{mass}$), 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°C for 15 h. The phase transformations of the samples were verified by X-ray diffraction (Bruker D8 Advance, CuK_α radiation). The microheterogeneity, the degree of crystallinity and the size of the crystals were determined by Scanning Electron Microscopy (JEOL Superprobe 733) and Transmission Electron Microscopy (EM-400, Philips). TEM experiment was made by C+Pt replicas from surfaces of the bulk samples. For glass B the spectral behavior in the visible region was investigated by a UV-VIS Spectrophotometer (Cary 100 Scan, Varian).

RESULTS AND DISCUSSION

XRD patterns of the glass sample A are shown in Fig. 1. Small diffraction peaks assigned to the Cu_2Se crystals are observed (JCPDS No 02-1426), but the sample has preserved its amorphous structure. SEM observations of that sample showed that the microstructure had undergone some changes during the heat treatment (Fig. 2). Pores appeared on the surface sample (Fig. 2b), while in the volume the amorphous state was preserved along with small bubbles (under 0,01 μm) (Fig. 2c). The appearances of pores are probably due to SeO_2 evaporation. Higher magnification (x4000, Fig. 2d) showed formation of not well shaped microheterogeneities dispersed separately in the glass matrix. The results obtained indicated formation of small amount Cu_2Se crystals in the black glass (A) after 6h heating. Electron microprobe analysis established the following relative amounts: 27 % of elementary selenium, 66 $\%_{mass}$ of elementary copper. Obviously it is necessary to prolong the heating time in order to continue the crystallization process of the chalcogenide component. The microprobe analysis at different points of that sample was made. The average Cu/Se ratio in the sample volume was 3:1 and on the surface, 1:2, respectively.

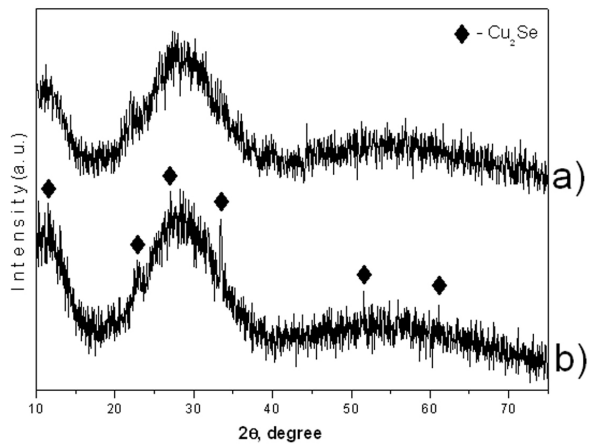

Fig. 1. X-ray diffraction of the $21CuO.29SeO_2.50MoO_3$ sample (glass A) at different heat treatment: a) glass sample and b) heat treated sample at 250°C for 6h.

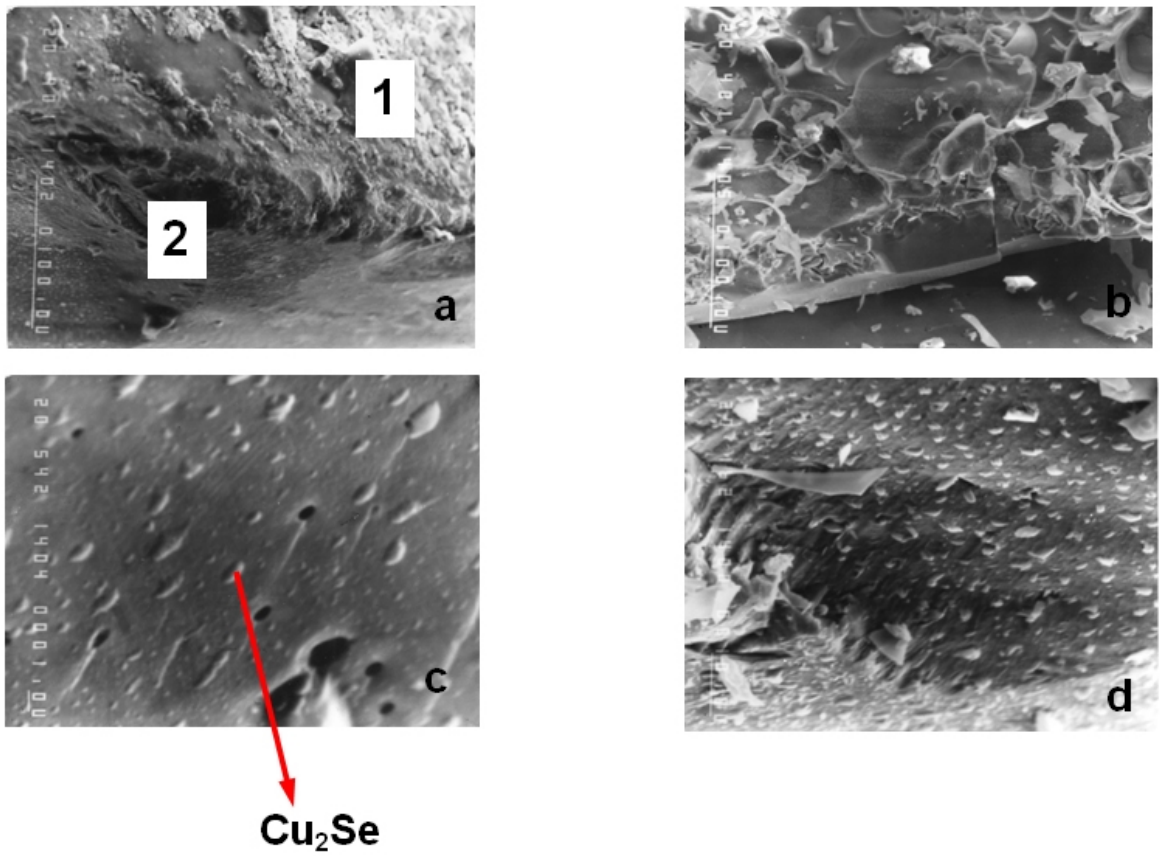

Fig. 2. SEM micrographs of the glass sample $30CuO.30SeO_2.40MoO_3$ after heat treatment at 200^0C for 2 h in N_2+H_2 (20 %) flow: a) general view (1- surface and 2 – cross section) (magnification x1600); b) – sample surface; c) – glass volume (magnification x1600) and d) – glass volume (magnification x4000).

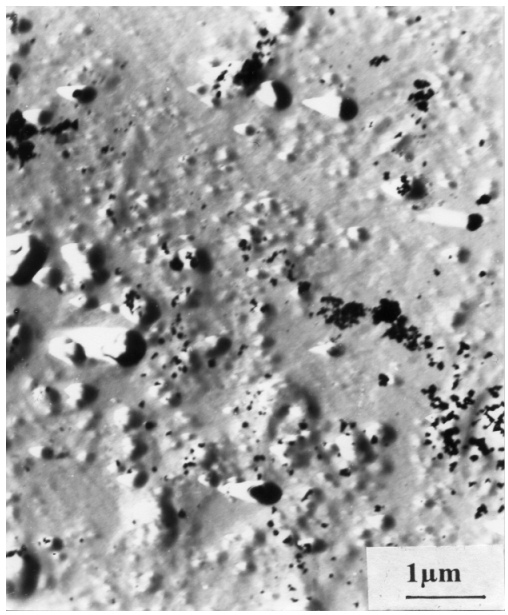

Fig. 3. TEM micrograph of the glass sample $42SeO_2.42TeO_2.8Nb_2O_3.6MoO_3.2PbO$: after heat treatment at 200^0C for 2 h in N_2+H_2 (20 %) flow.

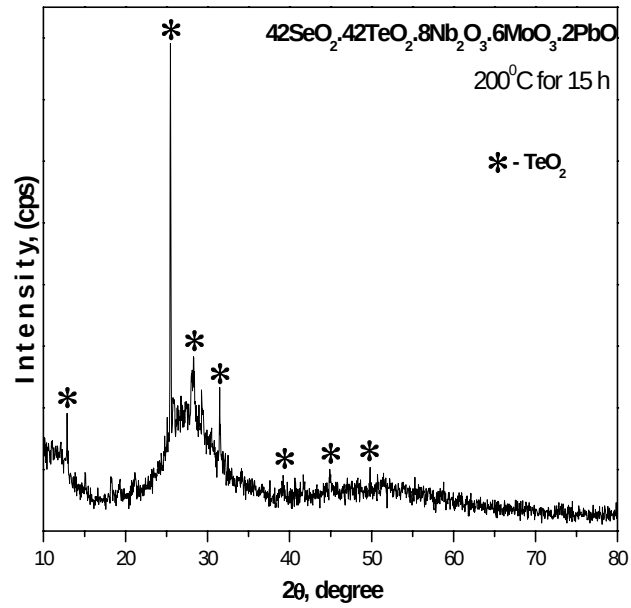

Fig. 4. X-ray diffraction of the $42SeO_2.42TeO_2.8Nb_2O_3.6MoO_3.2PbO$ (wt %) sample (glass B) heat treated at 200^0C for 15 h.

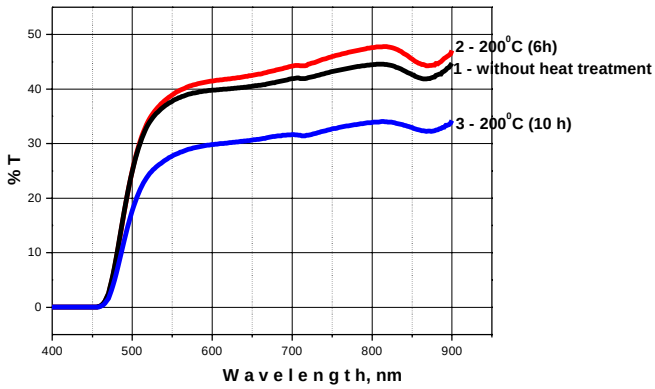

Fig. 5. UV-VIS absorption spectra of sample with nominal composition $42SeO_2.42V_2O_5.8Nb_2O_3.6MoO_3.2PbO$: 1-glass sample, 2-after heat treatment at 200°C for 6 h and 3-after heat treatment in vacuum oven at 200°C for 10h.

TEM micrograph of the other glass sample with nominal composition $42SeO_2.42TeO_2.8Nb_2O_3.6MoO_3.2PbO$ (glass B) after heat treatment in a reduction atmosphere (at 200°C for 2 h – Fig. 3) is presented in Fig. 3. A transparent yellow nanocrystalline glass-ceramic product was observed due to the volume crystallization [15]. The well defined volume crystallization corresponds to a particle size about 0,47 μm (Fig. 3). This glass B was additionally heat-treated in the vacuum oven at 200°C for 15 h and after that the glass became dark yellow colored. By X- ray diffraction analysis it was established that the observed diffraction peaks were assigned to the TeO_2 crystals (JCPDS No 41-0945) (Fig. 4). The average crystalline size of as obtained TeO_2 calculated from the broadening of the diffraction line using Sherrer's equation is at about 48 nm (Fig. 4). The yellow glass (B) was found transmittant in the visible range of the spectrum beginning with 480 nm (Fig. 5). A more intense yellow colour was observed after heat treatment along with decreasing transparency. Furthermore, the yellow glass transmittance decreases after heat treatment. May be 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.

CONCLUSIONS

Various types of microheterogeneous structures have been prepared by heat treatment of the selected amorphous samples at different reducing conditions: small chalcogenide crystals in an amorphous oxide matrix and oxide particles. To control the crystallization process, a long-term heating at low oxygen pressure is necessary. These preliminary results will contribute to develop methods for obtaining composite materials containing chalcogenide or oxide particles for modification of their optical and electrical properties.

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