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Nanoparticles in low melting amorphous selenite materials

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Abstract The aim of the present investigation is to establish the appropriate route of nanoparticles formation during heat treatment of selected selenite glasses. Multicomponent compositions containing SeO_2, V_2O_5, TeO_2, MoO_3, ZnO and Ag_2O have been selected. 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. TEM and SEM have been used to prove the formation of nanosized particles, randomly distributed in the amorphous matrix volume. Samples containing above 50 wt% Ag_2O show the formation of elementary silver with an average particle size of 50–100 nm. Glass-ceramic materials have been obtained after a long thermal treatment. The main crystal phases detected are Ag_2SeO_3, Ag_2TeO_3 and TeO_2.

Introduction

Selenite glasses and glass-ceramics on their basis are a new class of materials, which are not yet fully investigated. The modification of optical and electrical properties of these low melting materials can be achieved by nanoparticles formation. Depending on the methods of preparation, it is possible to obtain different microheterogeneous structures as a consequence of the crystallization or liquid phase separation and reduction processes.

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.

The aim of the present investigation is to establish the appropriate route of nano-particles formation in the selected selenite glasses during heat treatment. Multicomponent compositions containing different oxides have been selected: (i) Ag_2O for easier reduction and obtaining of nanosized particles; (ii) oxides (such as V_2O_5 and MoO_3), of transition metals, which

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can change their oxidation state during heat treatment and (iii) oxides, such as TeO_2, PbO and ZnO, which favor the glass formation.

Experimental

Various melt quenching preparation methods of the initial glass samples were applied, including different atmosphere conditions, which were selected depending on the type of the compounds:

(a) Melting of the oxide batches containing SeO_2, Ag_2O and MoO_3 in sealed silica ampoules evacuated at a pressure $P = 0.1$ Pa. The melts were cooled with a rate of 100 °C/min. This method is suitable for the compositions with high volatility components.

(b) Mixing of low-melting oxide glasses containing Ag_2O, ZnO, BaO, Nb_2O_5 and TeO_2 with Ag_2SeO_3 and melting in air. The melts were cooled with a rate of 100 °C/min. This method is suitable for stable low melting glasses, which will easily incorporate the silver particles.

(c) Melting of the oxide batches containing SeO_2, V_2O_5, MoO_3 and TeO_2, at a high oxygen pressure. The samples (5 g) were melted in quartz crucibles situated in an autoclave. The maximum oxygen pressure during the experiments was $P = 35$ MPa and the maximum temperature 550 °C, attained in 2 h and maintained for 20 min. The melts were slowly cooled with a rate of 2 °C/min. This method was specially developed for the selenite glasses and is suitable for the systems containing transition metal oxides, in order to achieve their high oxidation state.

The batches containing 10–50 wt% SeO_2 were melted up to 650–700 °C. The type of the vitrificated samples was observed visually and microscopically (magnification 120×). The quenched samples were additionally heat-treated at 200–250 °C for different exposure times.

The structural and phase transformations of the samples were verified by X-ray diffraction (TUR M62, Cu Kα radiation). The morphology, crystallinity and size of selenite crystals were determined by Scanning Electron Microscopy (JEOL SUPERPROBE 733) and Transmission Electron Microscopy (EM-400, Philips). Electron microprobe analysis EMRA (JEOL SUPERPROBE 733) was performed on polish samples. TEM experiments were made by C + Pt replicas from surfaces of the bulk samples. Extraction pseudo replicas for several compositions, containing silver nanoparticles were applied.

Results and discussion

Stable homogeneous glasses of the system SeO_2–Ag_2O–MoO_3 were obtained in a wide concentration range up to 70 mol% SeO_2 [9] using evacuated and sealed quartz ampoules. Figure 1 shows the SEM micrograph of a glass with the composition $25SeO_2*25Ag_2O*50MoO_3$ and a homogeneous structure. Electron microprobe analysis has established a relative SeO_2 amount of 24 wt%, MoO_3 of 21 wt% and Ag_2O of 57 wt%, which is close to the initial batch composition. The TEM micrograph of the same sample has shown it to be amorphous before crystallization, containing a low amount of isolated particles of a technological origin and a size of 50–100 nm (Fig. 2a). After additional heat treatment at 200 °C for 6 h (Fig. 2b), a microheterogeneous structure was observed due to the volume crystallization. In this case the particle size varied between 100 and 400–500 nm. Part of the sample showed crystal orientation. The reason for this phenomenon is not yet clear. XRD proved the main crystal phase formed after crystallization to be Ag_2SeO_3 (ICDD No 34-0382, three strongest *d* values 2.80; 2.44 and 2.42), which corresponds to our previous investigations [9].

A SEM micrograph of the $70(20ZnO*80TeO_2)*30Ag_2SeO_3$ sample melted in air, shows again a homogeneous structure similar to that in the previous case. Electron microprobe analysis established the following relative amounts: 12 wt% of SeO_2, 46 wt%

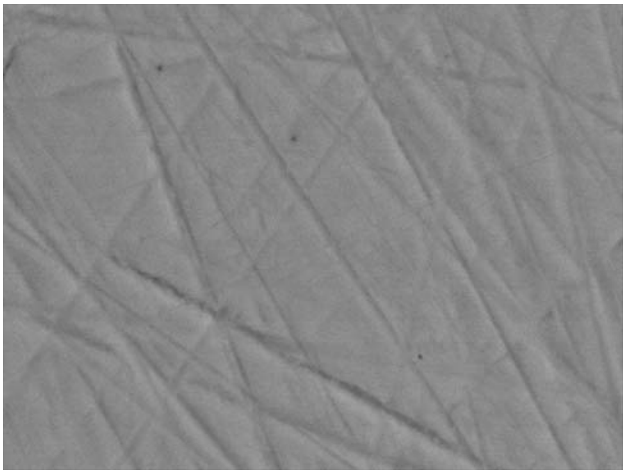

Fig. 1 SEM micrographs of the amorphous sample: $25SeO_3*25Ag_2O*50MoO_3$ before crystallization

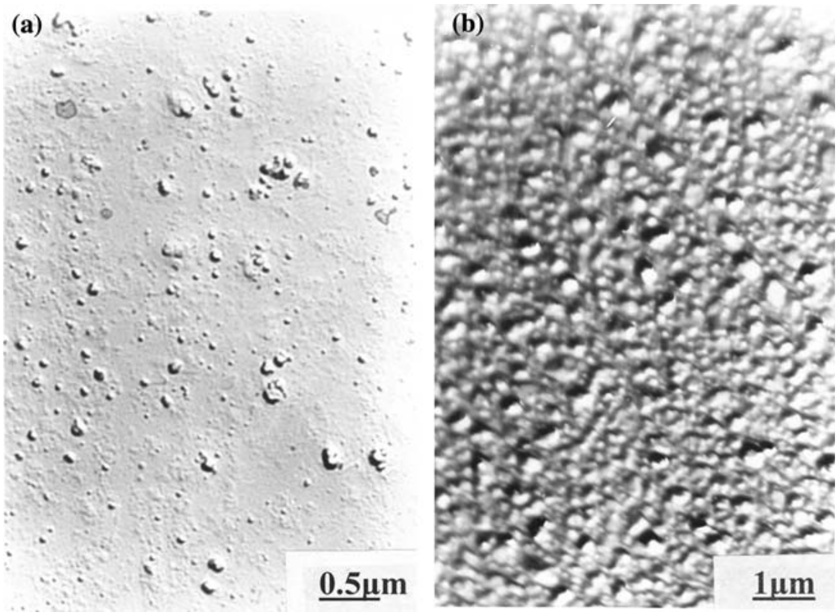

Fig. 2 TEM micrographs of the $25SeO_2*25Ag_2O*50MoO_3$ sample: (**a**) the glass before crystallization and (**b**) after crystallization at 200 °C-6 h

TeO_2, 30 wt% Ag_2O and 12 wt% ZnO. TEM data on the same sample are presented in Fig. 3a. The well-defined volume crystallization corresponds to a particle size of 100–300 nm. The other sample, nominal composition $50(20ZnO*80TeO_2)*50Ag_2SeO_3$ with a higher content of Ag_2SeO_3, melted under the same conditions, demonstrated formation of silver nanoparticles (black spots) with a size of 30–100 nm (Fig. 3b). In this case, a more complicated nanocrystallization was observed. With the other example—nominal composition $70(70TeO_2*25Ag_2O*2,5BaO*2,5Nb_2O_5)*30Ag_2SeO_3$ (Fig. 4), the situation was similar: after crystallization, silver nanoparticles were observed on the sample surface and proved by X-ray diffraction again (Fig. 5). The initial amorphous sample crystallized, forming: Ag_2TeO_3 (ICDD No 46-0036, three strongest *d* values 2.85; 2.41; 2.59), TeO_2-tetragonal (ICDD No 74-0269, three strongest *d* values 2.98; 3.39; 1.87) and elementary silver (ICDD No 01-1167, three strongest *d* values 2.36; 2.04; 1.23).

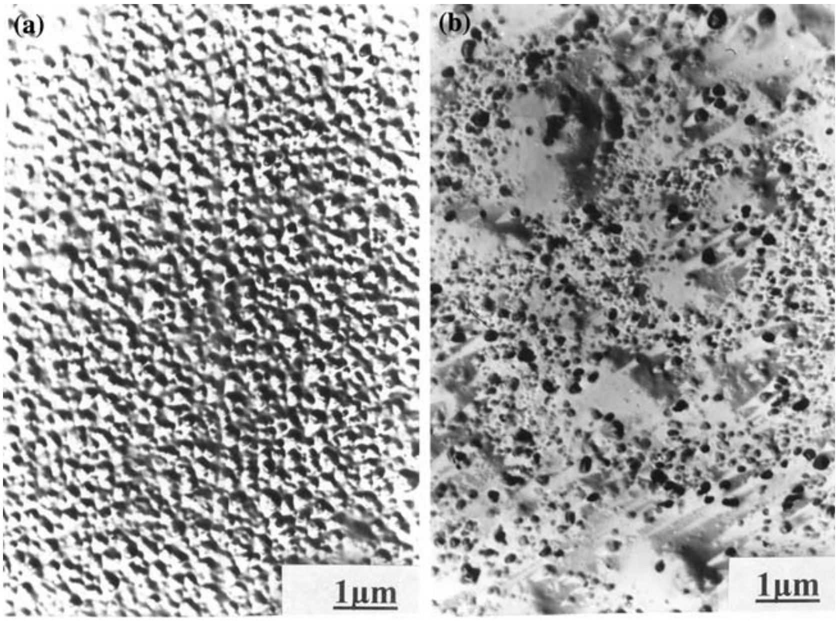

Fig. 3 TEM micrographs of the samples: $70(20ZnO*80TeO_2)*30Ag_2SeO_3$ (**a**) and $50(20ZnO*80TeO_2)*50Ag_2SeO_3$ (**b**), after crystallization at 200 °C-6 h

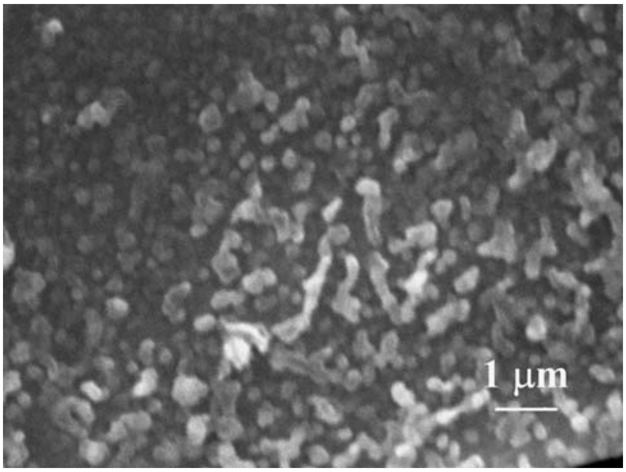

Fig. 4 SEM micrograph (magnification 10 000×) of the $70(70TeO_2*25Ag_2O*2.5BaO*2.5Nb_2O_5)*30Ag_2SeO_3$ sample—after crystallization

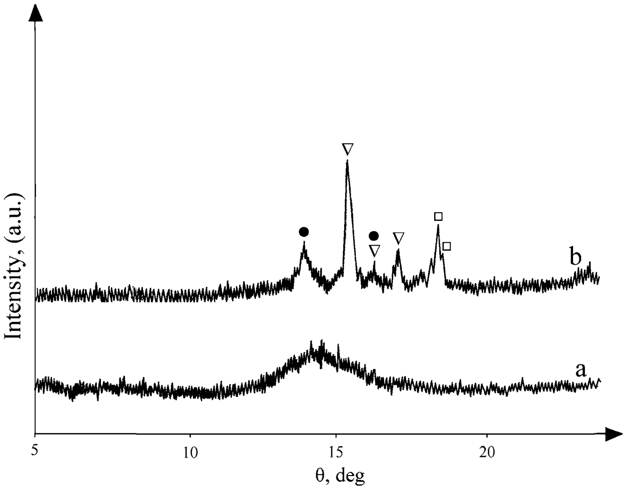

Fig. 5 XRD of the $70(70TeO_2*25Ag_2O*2.5BaO*2.5Nb_2O_5)*30Ag_2SeO_3$ sample **(a)** before crystallization and **(b)** after crystallization (300 °C-6 h): •-TeO_2, ∇-Ag_2TeO_3 and □-elementary silver

The $20TeO_2*35SeO_2*25V_2O_5*20MoO_3$ sample obtained by autoclave equipment at a high oxygen pressure and subjected to very slow cooling, showed a different type of crystallization, which started from the surface and proceeded to the glass volume (Fig. 6a). According to X-ray diffraction the crystal corresponded to MoO_3-orthorhombic (ICDD No 75-0912, strongest *d* values 3.24, 3.77, 6.97) and V_2O_5 (ICDD No 76-1803, strongest *d* values 4.36, 3.39, 4.07) were observed (Fig. 7). SEM data on the sample showed well-shaped MoO_3 crystals together with small not well shaped V_2O_5 crystals (Fig. 6b).

The experiments performed under various experimental conditions permit elucidating some peculiarities of the methods used and their applicability for the preparation of nanoglasscrystalline materials. Melting of selenite glasses in evacuated quartz ampoules is easy to perform but is not applicable to the preparation of both large volumes and easily reducible compositions. As was mentioned above, the preparation of selenite glasses in air is a difficult and complicated task due to the high volatility and the sublimation of SeO_2. That is why another scheme, which is well known in glass technology, is more suitable. It consists in preliminary melting part of the components and obtaining glasses without the participation of SeO_2. The second step includes mixing of these glasses with a crystal selenite phase and a new melting of the mixture. The last experimental step is heat treatment aimed at achieving crystallization. It is easier to control visually and microscopically. This method was applied to nanocrystallization of different compositions (Figs. 3a, b and 4).

The autoclave experimental technique is only suitable, for compositions with a good glass forming ability because the melting technology is achieved by a slow cooling process of the samples. Using this method it is impossible to control the microaggregation processes during the cooling. In our case the selected composition had a very good glass formation ability. Surface crystallization was detected during the autoclave experiments (Fig. 6). The advantage of this method is that the high oxygen pressure in the autoclave (P = 35 MPa) guarantees a high oxidation state of the components, which is essential for glasses containing transition metal oxides.

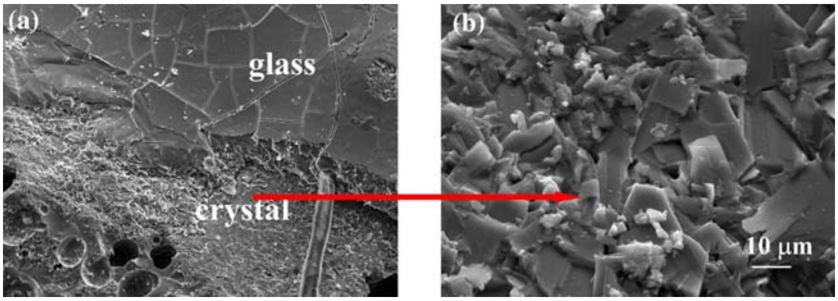

Fig. 6 SEM micrographs of the partially crystallized $20TeO_2*35SeO_2*25V_2O_5*20MoO_3$ sample: **(a)** magnification 160× and **(b)** magnification 1,600×

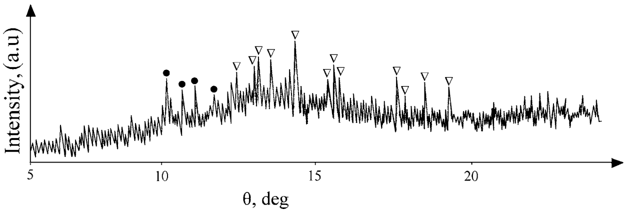

Fig. 7 X-ray diffraction of the samples 20TeO_2*35SeO_2*25-V_2O_5*20MoO_3: •-V_2O_5 and ∇-MoO_3

Conclusions

Different types of microheterogeneous structures have been prepared by heat treatment of an amorphous sample. Formation of elemental silver particles (30–100 nm) in multicomponent selenite glasses containing above 30 wt% silver ions was achieved at low temperature heat treatment (about 200 °C).

Concerning the applicability of the methods of preparation, some conclusions can be drawn: (i) melting in evacuated quartz ampoules is suitable for a large number of compositions, because by varying the cooling rate of the melts or the heat treatment of the glasses can control the aggregation processes; (ii) concerning melting in air, a similar conclusion can be drawn. However, with selenite glasses this technique is a many-step process, thus decreasing the SeO_2 sublimation.

This study represents the beginning of investigations on the crystallization processes and structural micro-aggregation in amorphous selenite systems aimed at the developing a technology for obtaining new functional materials.

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