

MICROSTRUCTURE OF GLASSES AND GLASS-CRYSTALLINE MATERIALS IN THE SYSTEM $\text{TeO}_2\text{-V}_2\text{O}_5\text{-Ag}_2\text{O-AgI}$

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The aim of this paper was to investigate the formation of nano- and microheterogeneities in glasses and glass-ceramics in the system $\text{Ag}_2\text{O-TeO}_2\text{-V}_2\text{O}_5\text{-AgI}$. The phase formation is studied by XRD analysis and the microstructure by TEM and SAED analysis. The particle size distribution of silver was obtained by computer analysis of TEM micrographs. Various types nano- and micro-scale heterogeneities were found: background nanostructure, nano- and microcrystals, droplet-like immiscibility formations as heterogeneous targets for crystal development and separated metal silver particles.

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1. Introduction

The ionic conducting silver containing glasses hold an important place between the amorphous solid electrolytes [1-5]. They are respective materials with promising properties especially when their compositions are based on combination of several glass formers, glass modifiers, Ag-oxide and Ag-chalcogenide.

The clustering tendency in silver containing materials involves makes necessary a detailed microstructure investigation because the phases with high ionic conductivity could be concentrated in the microaggregate structures. The appearance and development of nano- and micro-scale heterogeneities, their interaction with the homogeneous glassy matrix and further evolution towards metastable immiscibility formations determines the conducting behaviour of the materials.

The present work is dedicated to glasses and glass-ceramics in the four component system $\text{Ag}_2\text{O-TeO}_2\text{-V}_2\text{O}_5\text{-AgI}$. Our interest towards this system is stimulated by the combination of both non-conventional glass-forming oxides TeO_2 and V_2O_5 , coupled with Ag_2O and AgI . Recently, in several publications there was discussed the synthesis of ionic conductive glasses containing the above noted glass-formers [6-14]. The aim of the work is to study the formation of nano- and microheterogeneities in glasses and glass-ceramics in the system $\text{Ag}_2\text{O-TeO}_2\text{-V}_2\text{O}_5\text{-AgI}$. This work is a continuation of some previous investigations concerning the phase formation and crystallisation in this system [15-18].

2. Experimental

As precursors for synthesis of glasses and glass-crystalline materials in the system $\text{TeO}_2\text{-V}_2\text{O}_5\text{-Ag}_2\text{O-AgI}$ grade reagents TeO_2 , V_2O_5 , Ag_2O and AgI are used. The batches are melted in porcelain crucibles at 600 - 800°C temperature range. In order to trace the evolution of various types microaggregation processes in the glassy and crystalline materials convenient compositions with different thermal history are chosen. Two kinds of cooling were applied: slowly cooling of the melts in the crucibles and fast cooling between copper plates. Cross sections containing 50 mol. % and 60 mol. % AgI are studied for the Ag_2O content from 10 to 30 mol. %. For comparison, compositions without Ag_2O or TeO_2 were investigated.

The phase formation was studied by X-ray diffraction (XRD) analysis using DRON UM 1 with Cu K_α radiation. The microstructure of the samples was studied by transmission electron microscopy (TEM) by means of EM-400, Philips electron microscope. TEM was applied on C+Pt replicas from fresh fractured surfaces of the bulk materials. TEM and SAED analysis of silver particles were made on replicas

with single or double stage extraction. The particle size distribution was determined by computer analysis of TEM micrographs.

3. Results and discussion

In some samples of the three component system $\text{TeO}_2\text{-V}_2\text{O}_5\text{-AgI}$ the process of stable liquid phase separation leads to formation of two visually separated layers with different macro- and microstructure. A composition 50% $2\text{TeO}_2\text{-V}_2\text{O}_5$, 50% AgI is shown as an example. At micro-scale level the glassy layer is homogeneous. Very rarely in some regions nano- and microheterogeneities with technological origin we are observed (Fig. 1a). Clearly developed crystalline formations situated in the range 10 - 15 μm are typical for the second layer (Fig. 1b). The XRD analysis (Fig. 2) shows that the main crystalline phase is β -AgI which is stable at low temperatures in relation to the cooling rates applied. For both layers these data are in good agreement with the microstructure of the sample.

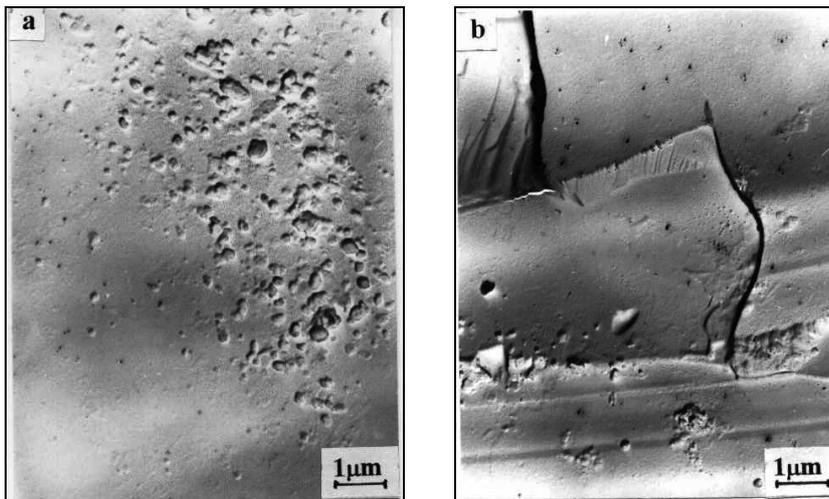


Fig. 1. TEM micrographs of the sample with composition 50% $2\text{TeO}_2\text{-V}_2\text{O}_5$, 50% AgI: a) glassy layer; b) crystalline layer.

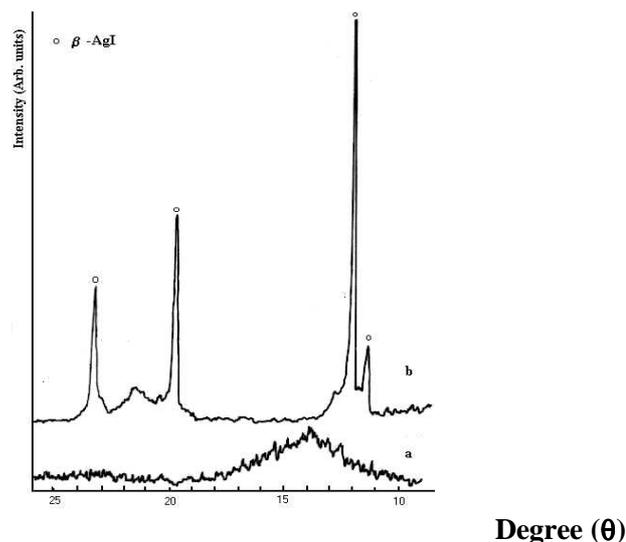


Fig. 2. XRD spectra of sample with composition 50% $2\text{TeO}_2\text{-V}_2\text{O}_5$, 50% AgI: a) glassy layer; b) crystalline layer.

In the samples from the four component system, containing a constant amount of 50 mol. % AgI, for Ag_2O content from 10 to 15 mol. %, visually homogeneous glasses were obtained. According to the XRD analysis these samples are amorphous. By TEM observation it is found that different kinds of

microaggregation processes take place (Fig.3a): i) background nanostructure ranged in size between 20 and 50 nm; ii) crystals with sizes about 200-300 nm; iii) droplet-like immiscibility formations as heterogeneous targets for crystal development; iiiii) silver particles between 10 nm and 200 nm, that are extracted on the replica surface. These particles are presented in Fig. 3b for sample with composition $20\text{TeO}_2, 15\text{V}_2\text{O}_5, 15\text{Ag}_2\text{O}, 50\text{AgI}$. According to the histogram (Fig. 4) the size of metal silver particles is situated mainly at two intervals between 5-10 nm and 20-25 nm. They are observed in all samples studied, only in some separated regions and their appearance could be result of reduction processes.

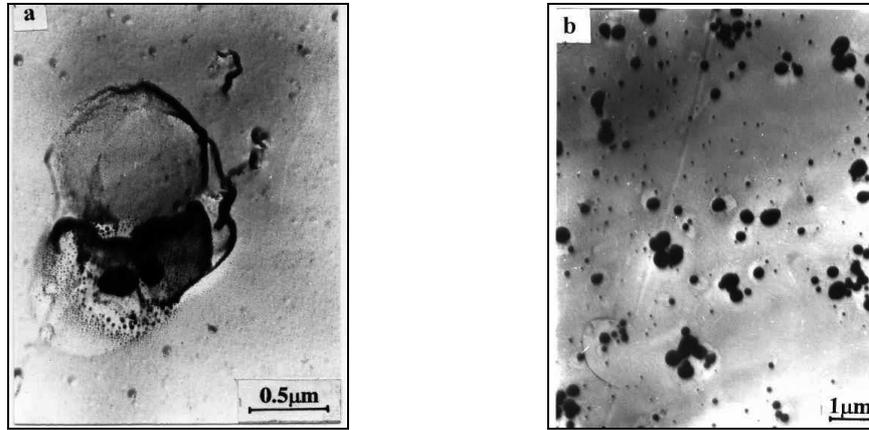


Fig. 3. Microstructure of samples with composition:
 a) $10\text{TeO}_2, 30\text{V}_2\text{O}_5, 10\text{Ag}_2\text{O}, 50\text{AgI}$; b) $20\text{TeO}_2, 15\text{V}_2\text{O}_5, 15\text{Ag}_2\text{O}, 50\text{AgI}$.

Their concentration is higher when Ag_2O content increases as it can be seen in (Fig. 5) for one composition of the three component system $\text{V}_2\text{O}_5\text{-Ag}_2\text{O-AgI}$ containing 30 mol. % Ag_2O . The obtained SAED patterns correspond to pure metal silver (Fig. 5).

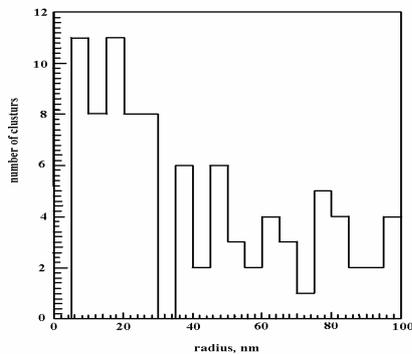


Fig. 4. Histogram showing the distribution of silver particles in sample with composition $20\text{TeO}_2, 15\text{V}_2\text{O}_5, 15\text{Ag}_2\text{O}, 50\text{AgI}$.

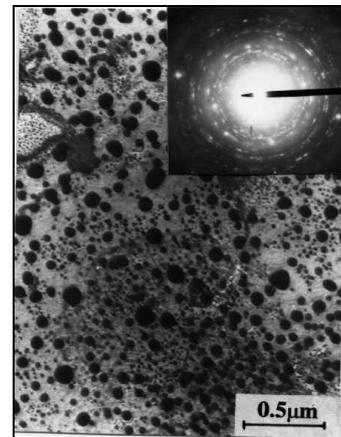


Fig. 5. TEM micrograph and SAED of the sample with composition.

Its presence simultaneously with the main crystalline phase $\beta\text{-AgI}$, is confirmed by XRD analysis of glass-crystalline sample of the four component system containing 60 mol. % AgI (Fig. 6). The microstructure of these visually glass-crystalline samples depends on the cooling rate applied. By fast cooling in the samples remains an amorphous matrix in which are dispersed droplet-like immiscibility formations and crystals (Fig. 7a). At slow cooling the aggregation trend is better pronounced and allows the crystallisation development in all bulk samples (Fig. 7b).

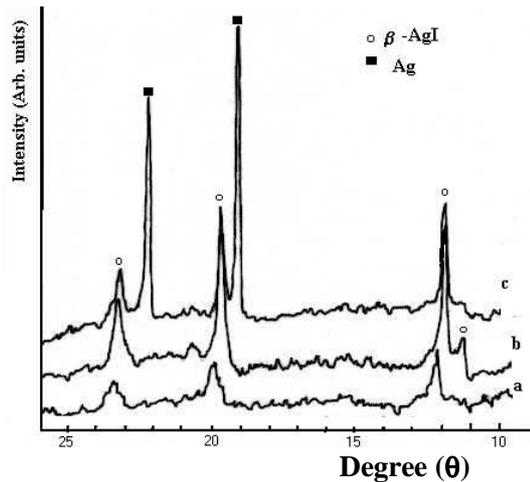


Fig. 6. XRD spectra of:

- a) glass-crystalline sample with composition: $5\text{TeO}_2, 17.5\text{V}_2\text{O}_5, 17.5\text{Ag}_2\text{O}, 60\text{AgI}$;
 b) glass-crystalline sample with composition: $10\text{TeO}_2, 15\text{V}_2\text{O}_5, 15\text{Ag}_2\text{O}, 60\text{AgI}$;
 c) crystalline sample with composition: $10\text{TeO}_2, 15\text{V}_2\text{O}_5, 15\text{Ag}_2\text{O}, 60\text{AgI}$.

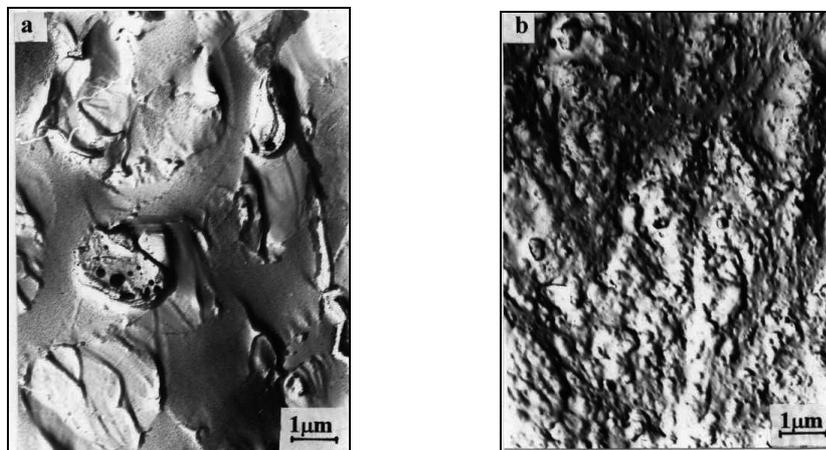


Fig. 7. Microstructure of the samples with the compositions:
 a) $10\text{TeO}_2, 15\text{V}_2\text{O}_5, 15\text{Ag}_2\text{O}, 60\text{AgI}$; b) $5\text{TeO}_2, 17.5\text{V}_2\text{O}_5, 17.5\text{Ag}_2\text{O}, 60\text{AgI}$.

4. Conclusions

Depending on the composition and thermal history of the samples various types of nano- and micro-scale heterogeneities were found in the glasses and glass-crystalline materials obtained in the system $\text{TeO}_2\text{-V}_2\text{O}_5\text{-Ag}_2\text{O-AgI}$: background nanostructure, nano- and microcrystals, droplet-like immiscibility formations as heterogeneous targets for crystal development and dispersed metal silver particles. The possibility for the appearance of these structures should be taken into account at the synthesis of ionic conductive silver containing solid electrolytes.

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