SELENITE GLASSES CONTAINING Ag⁺ AND Cu²⁺ IONS AS MODIFIERS

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ABSTRACT

This work is a review of the new results obtained in several selenite systems. Selenite glasses are interesting mainly from a fundamental point of view in order to verify the glass formation ability depending on compositions and to connect to the glass structural transformations. This kind of study is important to make a generalization for the design of new glass compositions. It is well known that the main difficulty in the preparation of such kind of glasses is their volatilization and the sublimation of SeO₂ at atmospheric pressure and temperatures above 315 °C. New data about the glass formation and crystalline phases in the three component systems SeO₂-Ag₂O-MO₃ and SeO₂-CuO-MO₃(MO₃=MoO₃, B₂O₃) were obtained. In order to decrease the volatility, selenite compounds CuSeO₃ and Ag₂SeO₄ synthesized in advance were used for preparation of the batches. Using the information about the main structural units building the amorphous network (SeO₃, MoO₃ and BO₃), several models explaining the role of modifiers (Ag⁺ and Cu²⁺ ions) on the amorphous structure were suggested. These models can be useful as a base for synthesis of more complex glasses and glass-crystalline materials.

Keywords: selenite glasses, network, structure.

INTRODUCTION

The idea of synthesizing selenite glasses belongs to Rawson [1] and Stanworth [2] who obtained glasses in the K₂O-SeO₂ and SeO₂-TeO₂-PbO systems. At present the selenite glasses are still exotic objects due to their difficult preparation, due mainly to the sublimation of SeO₂ (at atmospheric pressure) and the hygroscopicity of the samples. Up to now selenite glasses have been interesting from a scientific point of view in order to verify the glass formation ability and to obtain information on their structure with varying composition. Some of them possess specific properties due to which they are potential candidates for technological applications as low melting compositions, amorphous semiconductors, solid electrolytes, infrared transmission components, in non linear optical devices, sensors, filters, colored glasses, reflecting windows and soluble microfertilizers [3 - 9]. From 1981 to date, the glass formation and the structure of different binary and multicomponent selenite systems without participation of typical network modifiers have been investigated [10-14].

The results on the glass formation in the systems SeO₂-TeO₂-MO₃, SeO₂-V₂O₅-MO₃, SeO₂-MoO₃-MO₃ and SeO₂-Bi₂O₃-MO₃ (MO₃=MoO₃, CuO, MgO, CoO, SeO₂, Sb₂O₃, B₂O₃, Nd₂O₃, Pr₂O₃, WO₃) obtained during the last 20 years were reviewed [15].
This work is a summary of the results achieved by a research group in the Institute of General and Inorganic Chemistry at Bulgarian Academy of Sciences and the Department Technology of Silicates, UCTM-Sofia, for the selenite glasses containing Ag⁺ and Cu²⁺ ions as modifiers.

The aim of the present work is to generalize the obtained results concerning the glass formation, formation of the amorphous network and prognosis of new selenite glass compositions. The investigations have been made in the following directions:

- Determination of the glass formation regions in the three component systems using combination of the glass formers: SeO₂, MoO₃ or B₂O₃ and modifiers CuO and Ag₂O;
- Determination of the main structural units building the amorphous network, based on diffraction studies and IR spectral data and suggestions for the topological models;
- Correlation between the glass forming ability, compositions and structural peculiarities.

**Glass formation**

The method for preparation of selenite glasses consisted in melting oxide batches with different nominal compositions in a sealed silica ampoule evacuated to a pressure of 0.1 Pa. In order to decrease the evaporation of SeO₂, these compounds were introduced using previously synthesized silver (Ag₂SeO₃) and copper selenites (CuSeO₃) [16]. The ampoules were situated in a metal container and heated at different temperatures depending on compositions. The melts were cooled with a rate of 100 K/s.

For most selenite systems, the vitrification regions were situated near the SeO₂ corner. A peculiarity of all binary systems is the existence of two (upper and lower) boundaries of glass formation. As it is well known pure SeO₂ is not vitrified. From a structural point of view, the first boundary is related to the possibility to depolimerize the selenite chains and to increase the structure disorder during the cooling of the melts. The lower glass formation boundary is determined by the compositions containing mainly isolated units with high mobility. The widest glass formation regions are obtained in the systems SeO₂·TeO₂·MoO₃, SeO₂·TeO₂·V₂O₅ and SeO₂·V₂O₅·MoO₃ [13, 14] containing network formers. The situation was different when in the compositions Ag⁺ and Cu²⁺ ions as modifiers were introduced. In order to elucidate the effect of the ionic modifiers on the amorphous network formation, four three-component selenite systems, SeO₂·Ag₂O·MoO₃, and SeO₂·CuO·M₂O₃ (M = B₂O₃ and MoO₃), have been investigated. As shown in Fig. 1, the glass formation regions are located in different parts of the triangles. In general, the glass formation regions are situated near the SeO₂ corner in both systems. A peculiarity is that in the system with Ag₂O this region is extended towards MoO₃.

According to the IR spectra, the independent SeO₃ pyramids with νₐ = 860 - 810 cm⁻¹ and ν₁ = 730 - 710 cm⁻¹ participate in the boundary compositions when the SeO₂ concentration is low. As the SeO₂ content increases, SeO₃ groups become associated into chains which contain isolated Se=O bonds with a vibration frequency at 900 - 880 cm⁻¹ [13]. Obviously, from the analysis of the IR spectra it can be concluded that Ag₂O and CuO as modifiers stimulate the formation of more flexible isolated SeO₃, BO₃ and MoO₃ units. This process prevents MoO₃ and B₂O₃ being a network formers [17].

**Phase diagrams**

It is well known that glass formation proceeds more easily around the eutectic compositions. The pre-

![Fig. 1. Glass formation regions in the systems: (a) Ag₂O-SeO₂-MoO₃; (b) CuO-SeO₂-MoO₃; (c) Ag₂O-SeO₂-B₂O₃; (d) Ag₂O-SeO₂-B₂O₃.](image-url)
liminary estimation of the probable quasi-binary sections was made on the basis of the singular triangulation method [18]. Cross-sections built between two congruently melting phases are assumed to be the real ones. The obtained results are presented on Fig. 2. It is interesting to note that all investigated sections are out of the glass formation regions [19]. They consist of compounds (Ag₅SeO₅, Ag₅MoO₄) containing small building units (SeO₂ and MoO₃) with high mobility. There is no data for obtaining of new phases in the system investigated. That is why we interpret the glass formation ability on the basis of existing binary compounds confirmed by this study. The experiments show that the simultaneous presence of modifiers and isolated groups with high mobility (SeO₂, BO₂ and MoO₃) deteriorate the glass formation ability due to the diffusion processes and as a result the more easy separation of crystalline phases.

**Hypothesis on the glass formation ability**

On the basis of the results obtained for the glass formation ability in SeO₂-Ag₂O-MoO₃ and SeO₂-CuO-MoO₃ systems, an attempt is made to distinguish the specific effect of the modifiers (Ag⁺ and Cu²⁺) on the depolimerization of the glass network. The IR spectra give some preliminary proofs about the transformation of the structural polyhedra. Our hypothesis is based on comparison of spectral data obtained in systems containing Ag⁺ and Cu²⁺ ions [20-25] with data on systems without modifiers [13,14,17]. An analogy with the crystal structure of the phases in the corresponding binary equilibrium systems and quasi-binary sections has been made too. It is well known that Ag₂O and SeO₂ form one compound (Ag₅SeO₅) only (Fig. 2a) [26], built by isolated SeO₃ pyramids [27]. As the eutectic point is at about 80 mol % SeO₂, this is an indirect proof that isolated SeO₃ groups will be separated immediately in the
Fig. 3. Hypothesis for the depolymerization process in the systems: a) SeO₂-Ag₂O-MoO₃ and b) SeO₂-CuO-MoO₃.

melts irrespective of the SeO₂ amount. For comparison, the situation is different in selenite systems containing K₂O and Na₂O oxides [28]. As it was established by Sekiya et al. [28] the addition of alkali ions resulted in cleavage of Se-O-Se linkages, but in the glass network, short (SeO₂)ₖ chains, Se⁴⁺ and SeO₃²⁻ ions, simultaneously existed. Thus, it is possible to explain the wider glass formation regions in the systems SeO₂-KO₁₂₂ and SeO₂·NaO₁₂₂ [28]. Taking in mind the IR spectral results obtained in our three-component systems we concluded that there is no stepwise transformation of the amorphous network. This fact allows us to propose a new hypothesis. We assume that silver ions attack predominantly the selenite units in the melts. In this manner, isolated SeO₃ groups are formed in the glasses, as indicated by absorption bands at 850 - 830 and 730 cm⁻¹ [22]. The polymerization will not take place and the mobility of these small building units should be higher. This structural transformation is shown on Fig. 3a. As the silver ions are located mainly near SeO₃ units, polymerized molybdate octahedra remain in the glass structure because there is not enough silver ions which could interact in the molybdate network. As is seen from the phase diagram MoO₃-Ag₂O, three compounds, Ag₂MoO₄, Ag₂Mo₂O₇, and Ag₂MoO₉, are formed under equilibrium conditions [29]. The crystal Ag₂MoO₄ only consists of isolated MoO₄ polyhedra [30]. The other Ag₂Mo₂O₇ compound consists of definite chains formed by blocks of four edge-shared MoO₄ octahedra [31]. This means that the Ag₂O influence is different on the MoO₃ as compared to that on SeO₂. That is why the glass formation region in the SeO₂-Ag₂O-MoO₃ system is extended towards MoO₃ (Fig. 1a). In the other SeO₂-CuO-MoO₃ system the mechanism of network formation is different (Fig. 3b). In the phase diagram SeO₂-CuO several compounds are found: Cu₂SeO₄, Cu₂Se₂O₇, CuSeO₃ and CuSe₂O₄ [31, 32]. The crystal structure of the CuSe₂O₄ phase consists of pyro groups (Se₂O₅) containing bridging Se-O-Se bonds and terminal SeO₂ units [33]. That is why it is possible to suppose that in the system with CuO the depolymerization process in the melts starts at lower SeO₂ content. We assume that the copper ions attack the molybdate compound and isolated MoO₃ units are formed predominantly. Their main absorption bands were detected at 830, 730-720 cm⁻¹ [21, 34]. This fact is also proven in the binary system CuO-MoO₃ [35], where MoO₄ groups are found to be dominant in the amorphous network below 80 mol % MoO₃. In other glass systems containing copper molybdates, different molybdate polyhedra were formed, but MoO₄ tetrahedra were prevailing [36]. That is why in our case in the presence of high MoO₃ content there is no possibility for formation of a continuous network with bridging bonds and, as a result, the glass formation boundary is situated near the SeO₂ corner only (Fig. 3b).

The replacement of MoO₃ with B₂O₃, which is a typical network former leads to deterioration of the glass formation ability. Two models for the glass structure transformation were suggested in both systems SeO₂-B₂O₃-Ag₂O and SeO₂-B₂O₃-CuO [37] (Fig. 4a
and 4b). In the quenched melts from the SeO$_2$-B$_2$O$_3$-Ag$_2$O system, uniform distribution of borate, selenite groups and silver ions should be present (Fig. 4a). As it was mention above, silver selenite crystallizes only in super cooled melts in wide concentration region. That is why we accept that in the melt Ag$^+$ ions attack predominantly the isolated selenite units and this prevents the possibility of polymerization. As it was discussed above Ag$_2$O does not form other compounds with SeO$_x$, besides Ag$_2$SeO$_4$. In this way, the formation of isolated SeO$_x$ units hinders the polymerization processes. Thus, there will be not sufficient free Ag$^+$ ions, which could interact with the borate groups and help the formation of super-structural units, which is typical for the modifiers in borate glasses. Hence, formation of sufficient mixed bridging bonds in a polymer network is not being possible. The result is that B$_2$O$_3$ can not perform the role of a typical network former. In the other system SeO$_2$-B$_2$O$_3$-CuO, CuB$_2$O$_4$ crystallizes only from super cooled melts over a wide concentration range (Figure 4b). In the binary system SeO$_2$-CuO, compounds CuSeO$_2$ and CuSe$_2$O$_5$, which can dissociate easier at higher temperatures, are formed. They contain isolated SeO$_4$ pyramids and pyrogroups, respectively [32, 38]. That is why the glass formation was extended towards the SeO$_2$-B$_2$O$_3$ boundary in compositions where the depolymerization processes were developed gradually.

From the discussed above structural hypothesis we can generalize that the modifiers (Ag$^+$ and Cu$^{2+}$) deteriorate the glass formation ability because of the formation of isolated SeO$_x$ groups. Instead, according to Lakov et al. [14], in the selenite glasses without participation of modifiers, the isolated SeO$_x$ groups are surrounded by polyhedra of other network formers. Thus, mixed and strong bridging bonds are formed and that improves the glass formation ability.

CONCLUSIONS

The obtained results show that the silver (Ag$^+$) and copper (Cu$^{2+}$) ions in selenite compositions do not stimulate the formation of strong mixed bridging bonds and lead to formation of isolated SeO$_x$ units. Moreover, it was proved that modifiers attack predominantly the selenite units in the melts and slightly the other components (MoO$_3$ and B$_2$O$_3$). In this manner the increasing of the amount of isolated SeO$_x$ groups deteriorates the glass formation processes. The introducing of silver ions in low concentration improved the chemical resistances of the glasses, while glasses containing Cu$^{2+}$ ions were highly hygroscopic.

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