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LETTER

Phase equilibrium and glass formation in the SeO_2–Ag_2O–MoO_3 system

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Selective crystalline phases have been the subject of chemical and crystallographic investigations for many years. Detailed information and systematization of data on more than 300 selenite phases studied before 1999 has been published by Verma [1]. The taxonomy has been made according to their behavior in the respective groups in the Periodic Table of elements. It was adduce crystallographic data, data on their thermal stability and new spectral data. New literature data on the crystal selenite phases *containing mercury* [2–6]; *copper and zinc* [7]; *sodium and molybdenum* [8] were published recently. From the literature review it can be seen, that the subject of the investigations are mainly individual selenite phases, while the equilibrium phase diagrams with the participation of SeO_2 and selenites are poorly studied. Data on the following systems only have been published: SeO_2–TeO_2 [8–12]; SeO_2–V_2O_5 [13, 14]; $PbSeO_3$–PbO [15]; SeO_2–Bi_2O_3 [16–18]; SeO_2–MoO_3 [19]; $TeSeO_4$–TeO_2 [20] and SeO_2–$SeCl_4$ [21]. Another direction in the study of selenite systems is the obtaining of binary, three- and multi component glass phases, in which the main network former is SeO_2. According to Dimitriev et al. [22], the glass formation ability of SeO_2 can be compared with the influence of other non-traditional network formers: V_2O_5, TeO_2, MoO_3 and Bi_2O_3. Non-equilibrium glass systems with the participation of SeO_2 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 [23], colored glasses [24] and semiconductive glasses [25] are known. In our previous investigations on the glass formation in the systems Ag_2SeO_3–M_nO_m and $CuSeO_3$–M_nO_m ($M_nO_m = MoO_3$, B_2O_3) [26], some difficulties with the interpretation of the glass formation ability depending on the composition arose. One of the ways of solving these problems is comparison of the equilibrium phase diagrams with the glass formation regions and determination of the first crystal phases, which should be separated during the supercooling process of the melts. The classic rule that glass formation proceeds more easily around the eutectic compositions is well known [27].

The purpose of the present study was to investigate the phase formation in the SeO_2–Ag_2O–MoO_3 system. Comparison between the phase diagrams and the glass formation region will permit interpretation the glass formation tendency and assumption concerning the new glass compositions.

It is well known that the SeO_2–MoO_3 system is of a simple eutectic type where formation of three low-melting compounds *with ratios of* 1:1; 1:2 and 1:4 has been established. Only one compound, Ag_2SeO_3, is found in the SeO_2–Ag_2O system. According to Buketov et al. [28] this compound is incongruently melting.

The experiments in this study were performed using previously synthesized Ag_2SeO_3 (ICDD file No 34-0382) and Ag_2MoO_4 (ICDD file No. *08-0473*), prepared by the classical method [29] from saturated aqueous solutions of $AgNO_3$ with SeO_2. Molybdenum trioxide (MoO_3) was obtained by thermal treatment of

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ammonium *heptamolybdate tetrahydrate* (Aldrich) at 550 °C for 5 h. Selenium dioxide (Merck) was used additionally for the preparation of three-component compositions with a different ratio of the initial components. Five grams batches were prepared. The homogenized batches were heat treated in a vacuum drying-oven up to 250 °C and after that were transferred to *silica* ampoules, evacuated and sealed at a pressure $P = 0.1$ MPa. The samples were obtained by two methods: (a) melting and cooling (slow or fast) to room temperature; (b) heat-treatment of the batches below the melting temperature (solid state reactions), for 3 h. The DTA studies were performed using a nonstandard device with special silica holders for the samples. Alumina was the reference substance. The accuracy of temperature maintenance as determined on a standard *salts such as* $NaNO_3$, $AgNO_3$, $K_2Cr_2O_7$ *and pure Al*, was ±5 °C. The heating rate used was 10 °C/min. The phase formation was studied by X-ray phase analysis made with a TUR M65 apparatus using Cu-$K\alpha$ radiation.

The experiments started with investigations on the binary system SeO_2–Ag_2O, where formation of only one compound Ag_2SeO_3, [28] was established. Our DTA results show that this compound has one endothermic effect at 530 °C and after melting the sample corresponds to the same phase [ICDD file No. 34-0382]. That is why it can be affirmed that Ag_2SeO_3 is a congruently melting compound. In this sense the results obtained by [30], can be interpreted in contrast to the data of Buketov et al. [28] and Wenda et al. [31]. Table 1 shows DTA results on batches with a different ratio of Ag_2O and SeO_2, as well as the crystal phases identified after thermal treatment at 300 and 720 °C. They permitted plotting a phase diagram variant of the system Ag_2O–SeO_2 (Figs. 1, 2). Elemental silver (*ICDD 01-1167, the three strongest d values are* 2.36; 2.04; 1.23) was identified in the Ag_2O-rich region. This is due to the fact that in the region of compositions where the primary crystal phase should be Ag_2O, annealing of the compositions above 200 °C results in decomposition of the oxide, which is characterized by a low *decomposition* temperature [32]. The suggested phase regions, where there are insufficient experiments are shown by a dashed line. On the basis of the extrapolation made it may the assumed that the eutectic temperature between Ag_2SeO_3 and SeO_2 should be 240 ± 5 °C, and between Ag_2O and Ag_2SeO_3, about 100 ± 5 °C.

Table 1 DTA and X-ray diffraction data of the selected compositions from the system SeO_2–Ag_2O

No	Mol.%		T_L^a, T_S^b, T_E^c, °C According to DTA data	Identificated crystal phases by X-ray diffraction, using ICDD data
	Ag_2O	SeO_2		
1.	90	10	280 °C—T_L	Ag, Ag_2O, Ag_2SeO_3
2.	85	15	–	Ag, Ag_2O, Ag_2SeO_3
3.	75	25	–	Ag, Ag_2O, Ag_2SeO_3
4.	70	30	500 °C—T_L	Ag_2O, Ag_2SeO_3
5.	50	50	530 °C	Ag_2SeO_3
6.	60	40	–	Ag_2O, Ag_2SeO_3
7.	35	65	500 °C—T_L	Ag_2SeO_3
8.	30	70	–	Ag_2SeO_3, SeO_2
9.	25	75	240 °C—T_E	Ag_2SeO_3, SeO_2

T_L^a = T liquidus; T_S^b = T solidus; T_E^c = T eutectic

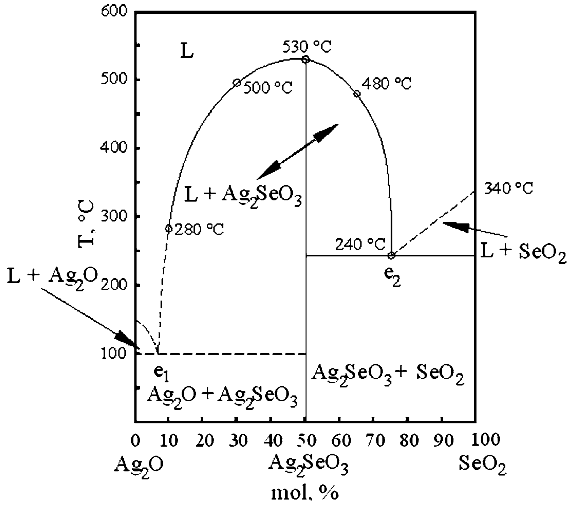

Fig. 1 Phase diagram of the SeO_2–Ag_2O system: ○:thermal effects according DTA

The preliminary estimation of the probable quasi-binary sections was made on the basis of the singular triangulation method [33]. Cross-sections built

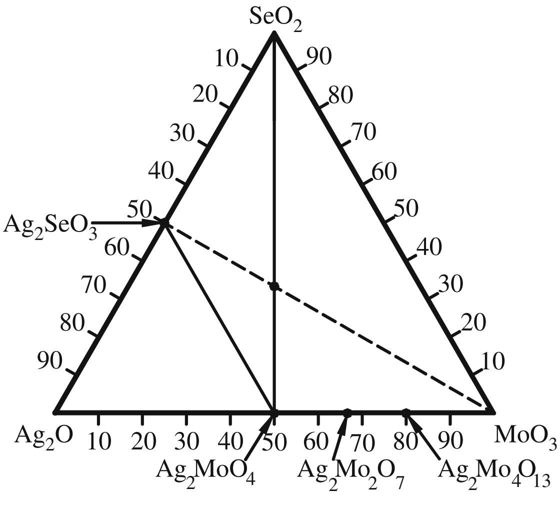

Fig. 2 Suggested quasi-binary sections in the SeO_2–Ag_2O–MoO_3 system

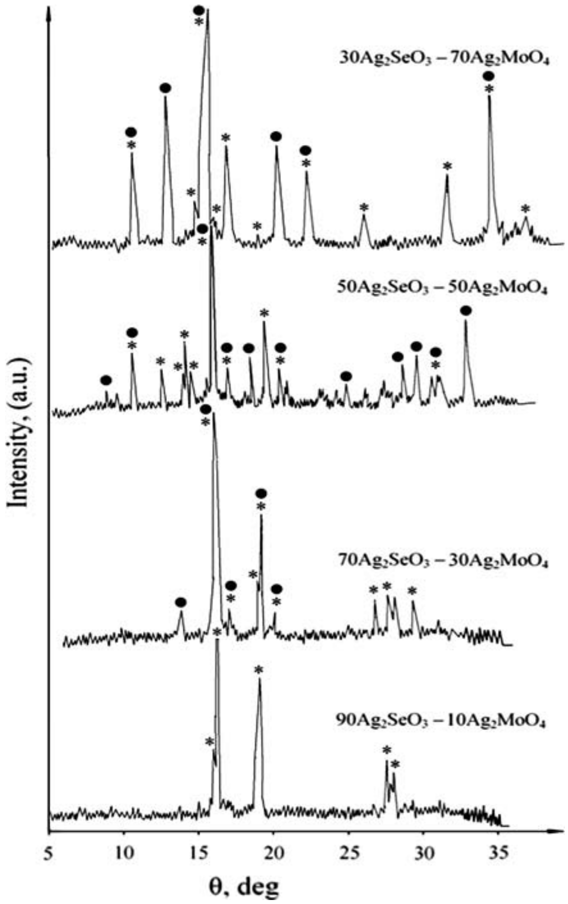

Fig. 3 X-ray diffraction *diagrams* of the selected compositions from the section Ag_2SeO_3–Ag_2MoO_4: ∗: Ag_2SeO_3; •: Ag_2MoO_4

between two congruently melting phases are assumed to be the real ones. This required testing the character of melting of Ag_2MoO_4 as there are contradictory data in this respect. According to Kohmuller et al. [34] Ag_2MoO_4 is a congruently melting compound, while according to Wenda et al. [31] Ag_2MoO_4 melts incongruently. In accordance with our results, the melting of Ag_2MoO_4 is determined by one well-defined endothermic effect (560 °C), one Ag_2MoO_4 phase only crystallizing from the melts. That is why we can assume that Ag_2MoO_4 is a congruently melting compound.

Two sections are possible: Ag_2SeO_3–MoO_3 and SeO_2–Ag_2MoO_4. Their crossing point corresponds to the composition $33.5SeO_2$:33.5 Ag_2O:$33MoO_3$, which lies on both sections simultaneously. To check the true phase diagram, two different batches were prepared using the initial phases ($Ag_2SeO_3 + MoO_3$ or $SeO_2 + Ag_2MoO_4$). They were thermally treated at 500 °C. Despite the initial phase combinations, phases Ag_2SeO_3 and Ag_2MoO_4 only were identified (Fig. 3). The three-component composition was made amorphous by overcooling of the melt. After crystallization (T = 300 °C, 2 h) as a result of the thermal treatment, the phases Ag_2SeO_3 and Ag_2MoO_4 only were identified again. That is why the quasi-binary sections Ag_2SeO_3–Ag_2MoO_4 (section A) and SeO_2–Ag_2MoO_4 (section B) should be the most probable ones.

On the basis of all DTA (Table 2) and X-ray data (Fig. 3), the most probable liquidus line of the system has been plotted (Fig. 4). The eutectic composition lies at about 40 mol.% Ag_2MoO_4, and the eutectic temperature is 450 ± 5 °C. The phase diagram of section B is also of a simple eutectic type (Figs. 5, 6; Table 2). The eutectic composition lies at about 80 mol.% SeO_2, and the eutectic temperature is 250 ± 5 °C. With non-equilibrium quenching of the samples from this section, glasses in the range 30–80 mol.% SeO_2 [35], situated around the eutectic point, were obtained.

In addition to the cross-sections, compositions with 10–90 mol.% SeO_2 were also subjected to heat-treatment using solid state reactions and overcooled melts. Three-component phases were not identified. On the basis of the investigations performed, the elementary triangles in the system should be Ag_2O–Ag_2MoO_4–Ag_2SeO_3, Ag_2MoO_4–SeO_2–MoO_3 and Ag_2O–Ag_2MoO_4

Table 2 DTA and X-ray diffraction data of the selected compositions from the systems Ag_2MoO_4–Ag_2SeO_3 and Ag_2MoO_4–SeO_2

No	Mol.%		T_L^a, T_S^b, T_E^c, °C According to DTA data	Identificated crystal phases by X-ray diffraction, using ICDD data
	Ag_2SeO_3	Ag_2MoO_4		
1.	30	70	450 °C—T_S	Ag_2SeO_3, Ag_2MoO_4
2.	50	50	450 °C—T_S 500 °C—T_L	Ag_2SeO_3, Ag_2MoO_4
3.	70	30	440 °C—T_S 500 °C—T_L	Ag_2SeO_3, Ag_2MoO_4
4.	90	10	450 °C—T_S 570 °C—T_L	Ag_2SeO_3
	SeO_2	Ag_2MoO_4	–	–
5.	10	90	400 °C -	Ag_2MoO_4
6.	20	80	260 °C—T_S 520 °C—T_L	SeO_2, Ag_2MoO_4
7.	33	67	430 °C—T_L	SeO_2, Ag_2MoO_4
8.	50	50	240 °C—T_S 410 °C—T_L	SeO_2, Ag_2MoO_4
9.	70	30	410 °C—T_L	SeO_2, Ag_2MoO_4

T_L^a = T liquidus; T_S^b = T solidus; T_E^c = T eutectic

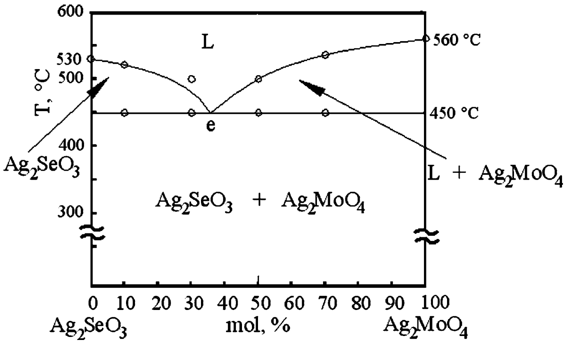

Fig. 4 Phase diagram of the Ag_2SeO_3–Ag_2MoO_4 system

–SeO_2 (Fig. 7). The results showed glass formation within the triangle Ag_2MoO_4–SeO_2–MoO_3. Irrespective of the fact that cross-section A is of a simple eutectic type, no glasses were obtained in it. This is due to the participation of two compounds whose crystal *structure* consists of isolated mobile SeO_3 and MoO_4 groups. The glass formation is concentrated in the elementary triangle Ag_2MoO_4–SeO_2–MoO_3 where the two network formers and the incongruent compounds ($Ag_2Mo_2O_7$ and $Ag_2Mo_4O_{13}$) participate in the region with a high MoO_3 content.

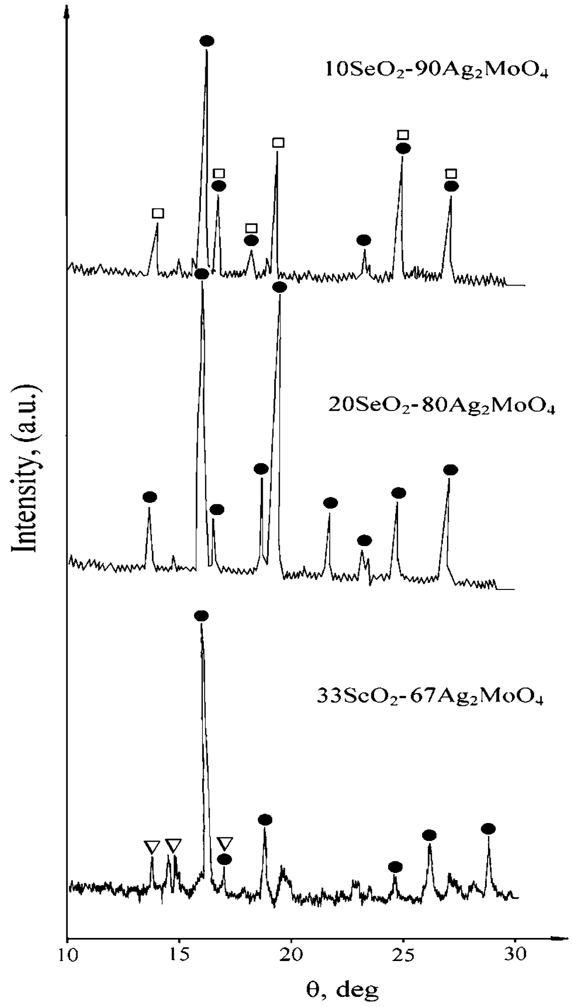

Fig. 5 X-ray diffraction *diagrams* of the selected compositions from the section SeO_2–Ag_2MoO_4: •: Ag_2MoO_4; □: $Ag_2O(Ag)$

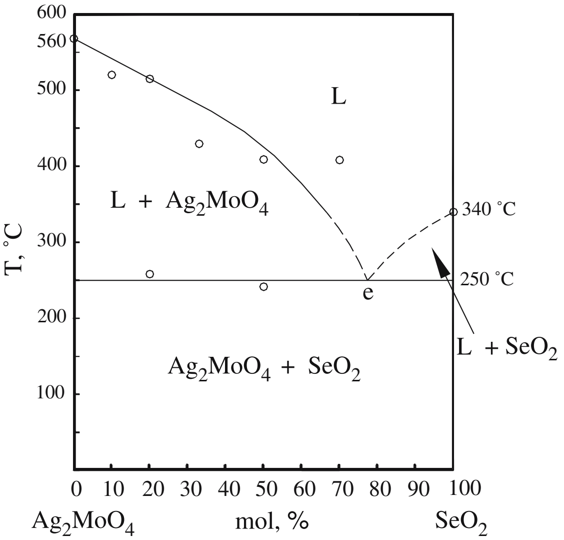

Fig. 6 Phase diagram of the SeO_2–Ag_2MoO_4 system

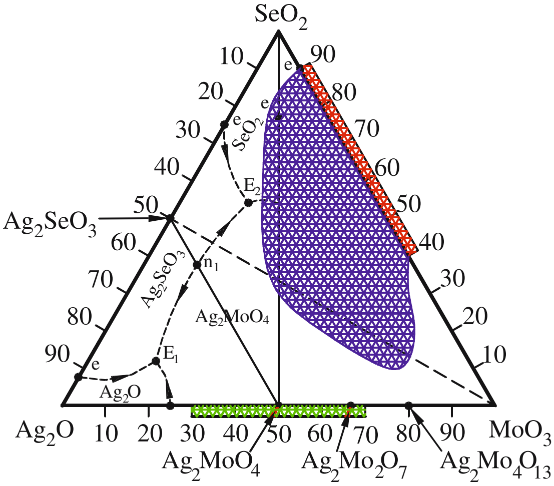

Fig. 7 Phase diagram of the SeO_2–Ag_2O–MoO_3 system and the glass formation region in the system

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