Phase diagram on the system SnO₂–V₂O₅–MoO₃

Y. IVANOVA, E. GATTEF

University of Chemical Technology & Metallurgy, Sofia, 1756, Blvd. Kl. Ohridski 8, Bulgaria

The system $\text{SnO}_2-\text{V}_2\text{O}_5-\text{MoO}_3$ is of scientific and practical interest, since it has a low melting temperature and the glasses synthesized possess interesting properties such as high electric conductivity, low melting temperature, significant transparency in IR range, and high value of refractive index [1–3]. However, the phase diagram of the system has still not been studied.

In our former studies on the phase equilibrium in the two-component system $\text{SnO}_2-\text{V}_2\text{O}_5$ [4] it was established that it appears to be a simple eutectic system with the eutectic point at 50 mol% V₂O₅. The phase diagram of the system V₂O₅-MoO₃ is also known [5, 6]. It contains a chemical compound with composition V₂O₅·MoO₃ (V₂MoO₈), which melts congruent at 635 °C. The third binary system, SnO₂-MoO₃, has been the subject of investigation [7, 8] as the formation of a congruent composition 2MoO₃·SnO₂ (Mo₂SnO₈) (T = 903 °C) was established.

The purpose of the present study was to determine the phase diagram in the system $SnO_2-V_2O_5-MoO_3$ by X-ray diffraction and by thermal difference analysis.

The preliminary estimation for the probable quasibinary sections, made on the basis of the singular triangulation method [9], is shown in Fig. 1. At first the composition which corresponds to the crossing point X was studied. The batch was melted at 650 °C for 20 min, and the melt was quenched on copper plate. The X-ray pattern of the composition X shows characteristic interplanar spacing for SnO₂ (d = 3.34; 2.64; 1.75) and for V₂MoO₈ (d = 4.12; 3.56; 3.23; 2.70; 2.64), which was a proof for the absence of a ternary compound in the system. Moreover, the character of the phases precipitated shows that the section Mo₂SnO₈–V₂O₅ is not real. Most probable it should be the quasi-binary sections: SnO₂–V₂MoO₈ and Mo₂SnO₈–V₂MoO₈.

Section $SnO_2-V_2MoO_8$: The compositions from this section are shown in Table I. The synthesis was performed by two methods: (a) form oxides (SnO₂, V₂O₅, MoO₃), (b) from preliminary synthesized compounds (V₂MoO₈, Mo₂SnO₈). In both cases the batches were melted at 700–800 °C for 20 min in air and then super cooled. The samples were analyzed by DTA (Paulik-Paulik, Hungary, 10 °C/min, etalon substance Al₂O₃) and XRD (DRON-UM1, Cu K_{α} radiation).

All endothermic effects and the identified crystal phases are presented in Table I. The analysis of the results allows the construction of the polythermic section shown in Fig. 2. It appears to be a simple eutectic system with eutectic composition at 50 mol% V_2MoO_8 and eutectic temperature 500 ± 10 °C.

Section $Mo_2SnO_8-V_2MoO_8$: The compositions of this section are given in Table II. The methods and the analysis are the same as for the previous section. In Fig. 3 is shown the phase diagram, constructed from DTA and

TABLE I Section SnO₂-V₂MoO₈

N	SnO ₂ (mol%)	V ₂ MoO ₈ (mol%)	Endothermic effects	Identified crystal phases
1.	90	10	500 °C, 998 °C	Basic phase SnO ₂
2.	80	20	490 °C, 900 °C	SnO ₂ , weak lines
3.	70	30	495 °C, 795 °C	SnO ₂ , V ₂ MoO ₈
4.	60	40	500 °C, 710 °C	SnO ₂ , V ₂ MoO ₈
5.	50	50	520 °C	V ₂ MoO ₈ , SnO ₂
6.	40	60	490 °C, 560 °C	V ₂ MoO ₈ , SnO ₂
7.	30	70	500 °C, 570 °C	V_2MoO_8 , SnO_2
8.	20	80	500 °C, 610 °C	V ₂ MoO ₈ , SnO ₂
9.	10	90	500 °C, 630 °C	V2MoO8-basic phase

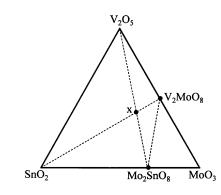


Figure 1 Possible quasi-binary sections in the system $SnO_2-V_2O_5-MoO_3$.

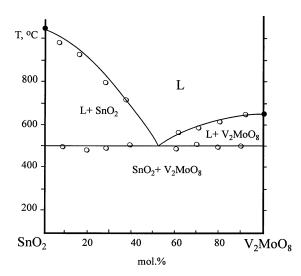


Figure 2 Phase diagram of the section $SnO_2\text{--}V_2MoO_8$ according to DTA and XRD data.

TABLE II Section V2MoO8-Mo2SnO8

N	V2MoO8 (mol%)	Mo ₂ SnO ₈ (mol%)	Endothermic effects	Identified crystal phases
1.	10	90	440 °C, 880 °C	Mo ₂ SnO ₈ -weak lines
2.	20	80	450 °C, 770 °C	Mo ₂ SnO ₈ -basic phase, V ₂ MoO ₈ -weak lines
3.	30	70	450 °C, 705 °C	Mo ₂ SnO ₈ , V ₂ MoO ₈
4.	40	60	455 °C, 635 °C	Mo ₂ SnO ₈ , V ₂ MoO ₈
5.	50	50	415 °C, 515 °C	Mo ₂ SnO ₈ , V ₂ MoO ₈
6.	60	40	500 °C	Mo ₂ SnO ₈ , V ₂ MoO ₈
7.	70	30	450 °C, 575 °C	V2MoO8, Mo2SnO8
8.	80	20	440 °C, 600 °C	V2MoO8, Mo2SnO8
9.	90	10	450 °C, 620 °C	V ₂ MoO ₈ -basic phase

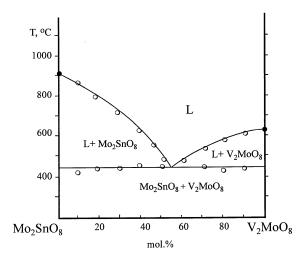


Figure 3 Phase diagram of the section $Mo_2SnO_8-V_2MoO_8$ according to DTA and XRD data.

XRD data. This section appears to be a eutectic system with an eutectic point at 55 mol% V_2MoO_8 and temperature 450 ± 10 °C.

Additionally, samples which belong to other polythermic sections were synthesized with an aim to precisely identify the position of the triple eutectics of the diagram. By summarizing the results the most probable phase diagram of the three-component system SnO_2 - V_2O_5 was constructed (Fig. 4).

The presence of two saddle-like points $(n_1 \text{ and } n_2)$; three triple eutectics $(E_1, E_2, \text{ and } E_3)$; and five fields

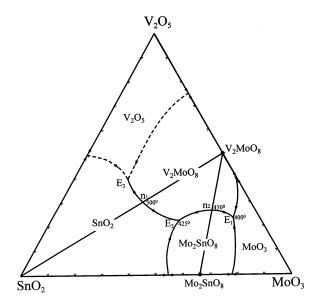


Figure 4 Phase diagram of the system SnO₂-V₂O₅-MoO₃.

of primary crystallization (SnO₂, Mo₂SnO₈, V₂MoO₈, MoO₃, and V₂O₅) was established. However, the formation of a triple chemical compound based on starting oxides was not found.

References

- C. CHUNG and L. MACKENZIE, J. Non-Cryst. Solids 42 (1980) 357.
- 2. H. OHTSUKA et al., Solid State Ionics 40/41 (1990) 964.
- N. BORRELI and D. HALL, in "Optical Properties of Glass," edited by D. Uhimmann and N. Kreidl (Amer. Ceram. Soc., 1997) p. 87.
- 4. Y. IVANOVA, V. VASILEV, S. STEFANOVA and M. STANEVA, *J. Mater. Sci. Lett.* **12** (1993) 455.
- 5. N. STRUPLER and A. MOCHETTE, *C.R. Acad. Sci.* **260** (1965) 1972.
- 6. V. VOLKOV and A. FOTIEV et al., Neorganichni Materiali 30 (1972) 2803.
- 7. V. MOLCHANOVA et al., ibid. 31 (1995)1225.
- 8. V. LASUNIK et al., Kataliz i katalizatori, Kiev (1966) 50.
- 9. V. V. SAFONOV et al., J. N. Chimii 28 (1983) 1029.
- 10. A. ZAHAROV, Diagrami Sostoyani Dvoinih, troinih sistem, Metalurg., Moskow, 1964.

Received 26 June and accepted 23 December 2003