

SOLID SOLUTIONS IN THE Cr_2O_3 – α - Sb_2O_4 – MoO_3 SYSTEM

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Abstract

DTA and XRD methods used to examine the Cr_2O_3 – α - Sb_2O_4 – MoO_3 system have shown that a substitution solid solution of MoO_3 in CrSbO_4 is formed. A study of all the theoretically possible solid solution models has pointed to the fact that Mo^{6+} ions are incorporated into the CrSbO_4 crystal lattice, in the place of Sb^{5+} ions and the compensation of redundant charges takes place through cation vacancies arising in an Sb^{5+} sub-lattice. The solubility limit for MoO_3 in CrSbO_4 does not exceed 25.00 mol%. $\text{CrSbO}_{4(\text{s.s.})}$ is stable to $\sim 1320^\circ\text{C}$.

Keywords: Cr_2O_3 – α - Sb_2O_4 – MoO_3 system, DTA, solid solution models, XRD

Introduction

The oxides MoO_3 , Sb_2O_4 and Cr_2O_3 and compounds formed in some systems built by the oxides find many applications, first of all, as catalysts [1–3]. Therefore, studies on reactions between oxides, leading to phases not known before, are of crucial importance.

It follows from our earlier works that components of the Cr_2O_3 – MoO_3 system interact in the solid state to form one compound, that is, $\text{Cr}_2(\text{MoO}_4)_3$ [4, 5]. The compound is stable in air to 810°C – an onset temperature of its breaking down to Cr_2O_3 , accompanied by the sublimation of MoO_3 [4]. On the other hand, the reaction in air between the oxides, α - Sb_2O_4 and Cr_2O_3 , brings about CrSbO_4 [6, 7]. The compound decomposes at 1380°C upwards to yield Cr_2O_3 and a gaseous product [6]. In contrast, the oxides, α - Sb_2O_4 and MoO_3 , fail to interact in the solid state. It is only known that the presence of MoO_3 decreases the temperature of α - Sb_2O_4 → β - Sb_2O_4 polymorphic conversion from 935 to 850°C ; with concurrent originating a low-concentrated solid solution of MoO_3 in β - Sb_2O_4 [8].

Contrary to the oxide systems: MoO_3 – Sb_2O_4 , Sb_2O_4 – Cr_2O_3 and Cr_2O_3 – MoO_3 that are known fairly well, the three-component Cr_2O_3 – α - Sb_2O_4 – MoO_3 system had not been an objective of research before ours [6, 9]. The results of our introductory investigation of Cr_2O_3 , α - Sb_2O_4 reactivity with MoO_3 suggested that solid solutions of MoO_3 in CrSbO_4 were formed in the system under study [9].

The aim of this work was to verify the recent results achieved and to define the practical models of MoO₃ solid solutions in CrSbO₄.

Experimental

The following substances were used in the experiments: Sb₂O₃ – pure (Merck, Germany), Cr₂O₃ – pure (Aldrich, Germany), MoO₃ – pure (POCh, Gliwice, Poland), α -Sb₂O₄ (prepared by heating in air a commercial Sb₂O₃), Cr₂(MoO₄)₃ and CrSbO₄ (prepared by methods described in works [4, 6]).

For the experiments 31 samples were prepared from the oxides, α -Sb₂O₄, MoO₃ and Cr₂O₃ (Nos 1–5; 7; 8; 10; 11; 15; 16; 17–35) and 4 samples from the compounds Cr₂(MoO₄)₃, CrSbO₄ and suitable oxides (Nos 6; 9; 12; 14). The compositions of the samples have been tabulated in Tables 1 and 2.

Table 1 Compositions of initial mixtures and X-ray phase analysis of samples representing the CrSbO₄-MoO₃ system after the final heating cycle

No.	Composition of initial mixtures/mol%					Phases found
	MoO ₃	α -Sb ₂ O ₄	Cr ₂ O ₃	CrSbO ₄	Cr ₂ (MoO ₄) ₃	
1	2.50	48.75	48.75	–	–	CrSbO _{4(s.s.)} + α -Sb ₂ O ₄
2	5.00	47.50	47.50	–	–	CrSbO _{4(s.s.)} + α -Sb ₂ O ₄
3	7.50	46.25	46.25	–	–	CrSbO _{4(s.s.)} + α -Sb ₂ O ₄
4	10.00	45.00	45.00	–	–	CrSbO _{4(s.s.)} + α -Sb ₂ O ₄
5	15.00	42.50	42.50	–	–	CrSbO _{4(s.s.)} + α -Sb ₂ O ₄
6	20.00	–	–	80.00	–	CrSbO _{4(s.s.)} + α -Sb ₂ O ₄
7	25.00	37.50	37.50	–	–	CrSbO _{4(s.s.)} + α -Sb ₂ O ₄ +MoO ₃
8	30.00	35.00	35.00	–	–	CrSbO _{4(s.s.)} + α -Sb ₂ O ₄ +MoO ₃
9	33.33	–	–	66.67	–	CrSbO _{4(s.s.)} +MoO ₃ + α -Sb ₂ O ₄
10	33.34	33.33	33.33	–	–	CrSbO _{4(s.s.)} +MoO ₃ + α -Sb ₂ O ₄
11	35.00	32.50	32.50	–	–	CrSbO _{4(s.s.)} +MoO ₃ + α -Sb ₂ O ₄ *
12	50.00	–	–	50.00	–	MoO ₃ +CrSbO _{4(s.s.)} + α -Sb ₂ O ₄ *
13	50.00	25.00	25.00	–	–	MoO ₃ +CrSbO _{4(s.s.)} + α -Sb ₂ O ₄ *
14	–	50.00	–	–	50.00	MoO ₃ +CrSbO _{4(s.s.)} + α -Sb ₂ O ₄ *
15	66.67	16.66	16.67	–	–	MoO ₃ +CrSbO _{4(s.s.)} + α -Sb ₂ O ₄ *
16	75.00	12.50	12.50	–	–	MoO ₃ +CrSbO _{4(s.s.)} + α -Sb ₂ O ₄ *

*traces

The reagents were weighed in appropriate proportions, homogenised by milling, shaped into pellets and heated under conditions that would secure establishing equilibrium; i.e.:

400°C (1 h)→500°C (24 h)→550°C (48 h)→600°C (48 h)
→650°C (48 h)→700°C (48 h)→750°C (48 h).

After each heating cycle the samples, still kept in the furnace, were slowly cooled down to ambient temperature, weighed in order to determine their mass change, milled and examined by DTA and XRD to establish their compositions.

Phases of the thermally treated samples were identified by XRD method (a diffractometer DRON-3, CoK α radiation, Fe filter) and with the help of PDF cards [10] and works [11].

DTA/TG measurements were made using an instrument of a SDT 2960 type (TA Instruments, USA). The measurements were made by DTA method in air, samples of ~7 mg each, the samples were placed in platinum crucibles, at a temperature range of 20–1500°C and heated at a rate of 10 K min⁻¹.

Results and discussion

Table 1 shows the compositions of initial mixtures and X-ray phase analysis of samples representing the CrSbO₄-MoO₃ system after the final heating cycle, that is, in a state of equilibrium.

After each cycle of heating the samples, the change in their mass was monitored. It was found that the sum of the mass losses recorded after consecutive heating cycles was fluctuating between 0.96 and 2.69% by mass. Hence it can be assumed that the mass losses follow from the presence of MoO₃ in the samples, the sublimation of the oxide starts to negligible extent at 550°C.

The mass re-counted from percentage by mass into percentage by mole of MoO₃ made up 1.5–3.7 mol%. Hence it can be acknowledged that the magnitude of the mass found in the samples is of inconsiderable importance to the results of our work.

XRD analysis showed that samples comprising up to 25.00 mol% of MoO₃ in their initial mixtures contained CrSbO₄ and α -Sb₂O₄ after the last heating cycle but they were lacking MoO₃. X-ray diffraction patterns of the samples showed reflections, characteristic of CrSbO₄, slightly shifted towards smaller angles (2 θ), so they were corresponding to greater interplanar distances (d_{hkl}).

Samples representing the other component concentration range of the CrSbO₄-MoO₃ system, say, over 25.00 mol% of MoO₃, comprised three phases: MoO₃, CrSbO₄ and α -Sb₂O₄.

These facts have led to the conclusion that MoO₃ forms a solid solution with CrSbO₄, and Mo⁶⁺ ions are built into the CrSbO₄ crystal lattice, in the place of Sb⁵⁺ ions; the substitution could be evidenced by the presence of α -Sb₂O₄. The results of our previous works were somewhat different from the present ones and implied that it was the Cr³⁺ ions that were substituted by Mo⁶⁺ ions [9]. In face of the fact that Sb⁵⁺ radius (61 pm) and that of Cr³⁺ (60 pm) [12] are very similar, there is much probability of substituting either of them by Mo⁶⁺ ions (59 pm) [12]. That possibility was taken into consideration in further studies depending on devising all theoretically acceptable models of the MoO₃ solid solutions in CrSbO₄. As for the incorporation of

Mo⁶⁺ ions into the CrSbO₄ lattice, in the place of Cr³⁺, the compensation of redundant positive charge is feasible by:

- originating cationic vacancies (□) in a Cr³⁺ sub-lattice bound with a concurrent removal of an equivalent number of Cr³⁺ ions from the CrSbO₄ lattice. A solid solution corresponding to the model is described by a formula: Cr_{1-2x}□_xMo_xSbO₄ (model I)
- originating cationic vacancies in the Sb⁵⁺ sub-lattice – the formula of the solid solution can be written as Cr_{1-5x}Mo_{5x}Sb_{1-3x}□_{3x}O₄ (model II)
- reduction of Cr³⁺ to Cr²⁺ ions: Cr_{1-4x}Cr_{3x}²⁺Mo_xSbO₄ (model IIIA)
- reduction of Sb⁵⁺ to Sb³⁺ ions: Cr_{1-2x}Mo_{2x}Sb_{1-x}⁵⁺Sb_x³⁺O₄ (model IIIB)

As for the models IIIA and IIIB, the contents of the initial mixture result from the common expression: Cr_{1-x}Mo_xSbO_{4-3x}.

With substitution by Mo⁶⁺ of Sb⁵⁺ ions in the CrSbO₄ lattice, the compensation of redundant positive charges is feasible by:

- originating cationic redundancies in a Cr³⁺ sub-lattice: Cr_{1-x}□_xSb_{1-3x}Mo_{3x}O₄ (model IV)
- originating cationic redundancies in a Sb⁵⁺ sub-lattice: CrSb_{1-6x}□_xMo_{5x}O₄ (model V)
- reduction of Sb⁵⁺ to Sb³⁺ ions: CrSb_{1-3x}⁵⁺Sb_x³⁺Mo_{2x}O₄ (model VIA)
- reduction of Cr³⁺ to Cr²⁺ ions: Cr_{1-x}Cr_x²⁺Sb_{1-x}Mo_xO₄ (model VIB)

Compositions of samples in terms of the oxides: MoO₃, Cr₂O₃, α-Sb₂O₄, corresponding to models VIA and VIB are the same and result from the expression: CrSb_{1-x}Mo_xO_{4-x}.

Studies that aimed at finding which of the theoretical solid solution models is carried into effect consisted in synthesising samples possessing a composition matching each of the models presented. Table 2 shows contents of the oxide initial mixtures. Pellets made from the oxides were calcinated under conditions identical with those applied to the samples of the CrSbO₄-MoO₃ system.

X-ray phase analysis of the samples after the final heating cycle (Table 2) have shown that their initial mixtures comprising up to 15 mol% of MoO₃, with contents corresponding to models I, II, III, IV and VI, contained, apart from a solid solution of MoO₃ in CrSbO₄, α-Sb₂O₄ whereas samples with the composition described by model V (samples 32 and 33) were mono-phases and contained the MoO₃ solid solution in CrSbO₄ only. The results indicate that the formation of the solid solution takes place following model V, that is, Mo⁶⁺ ions are incorporated into the CrSbO₄ lattice, in the place of Sb⁵⁺, and the compensation of redundant positive charges is realised by formation of cationic vacancies in a Sb⁵⁺ sub-lattice. In order to verify the solubility limit for MoO₃ in CrSbO₄, a sample containing 25.00 mol% of MoO₃ was prepared and its composition corresponding to model V. XRD analysis of the sample after the final heating cycle has proved it to be a three-phase and contain, beside CrSbO_{4(s.s.)} and Cr₂(MoO₄)₃, inconsiderable amounts of Cr₂O₃. This result provides a proof that the solubility limit for MoO₃ in the CrSbO₄ crystal lattice does not exceed 25 mol%; the proof can be tested through the phase composition of other samples obtained in this work.

Table 2 Compositions of initial mixtures and X-ray phase analysis of samples representing theoretical models of the MoO₃ solid solutions in CrSbO₄ after the final heating cycle

No.	Composition of initial mixtures/mol%			Formula of the solid solutions	Phases found
	MoO ₃	α-Sb ₂ O ₄	Cr ₂ O ₃		
17	2.50	50.00	47.50		CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
18	5.00	50.00	45.00		CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
19	10.00	50.00	40.00		CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
20	15.00	50.00	35.00	Cr _{1-2x} □ _x Mo _x SbO ₄	CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
21	20.00	50.00	30.00	(model I)	CrSbO _{4(s.s.)} +α-Sb ₂ O ₄ +MoO ₃
22	25.00	50.00	25.00		CrSbO _{4(s.s.)} +α-Sb ₂ O ₄ +MoO ₃
23	35.00	50.00	15.00		CrSbO _{4(s.s.)} +α-Sb ₂ O ₄ +MoO ₃
24	45.00	50.00	5.00		CrSbO _{4(s.s.)} +α-Sb ₂ O ₄ +MoO ₃
25	10.00	46.00	44.00	Cr _{1-5x} Mo _{5x} Sb _{1-3x} □ _{3x} O ₄	CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
26	15.00	44.00	41.00	(model II)	CrSbO _{4(s.s.)} +α-Sb ₂ O ₄ +β-Sb ₂ O ₄
27	10.00	47.50	42.50	Cr _{1-4x} ³⁺ Cr _{3x} ²⁺ Mo _x SbO ₄	CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
28	15.00	46.25	38.75	(model IIIA)	
29	10.00	43.33	46.67	Cr _{1-2x} Mo _{2x} Sb _{1-x} ⁵⁺ Sb _x ³⁺ O ₄	CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
30	15.00	40.00	45.00	(model IIIB)	
31	50.00	16.67	33.33	Cr _{1-x} □ _x Sb _{1-3x} Mo ₃ O ₄	CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
32	10.00	42.00	48.00	(model IV)	CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
33	15.00	38.00	47.00	CrSb _{1-6x} □ _x Mo _{5x} O ₄	CrSbO _{4(s.s.)} +Cr ₂ (MoO ₄) ₃ +MoO ₃
34	10.00	42.50	47.50	(model V)	CrSbO _{4(s.s.)}
35	15.00	38.75	46.25	CrSb _{1-3x} ⁵⁺ Sb _x ³⁺ Mo _{2x} O ₄	CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
				(model VIA)	
				Cr _{1-x} ³⁺ Cr _x ²⁺ Sb _{1-x} Mo _x O ₄	CrSbO _{4(s.s.)} +α-Sb ₂ O ₄
				(model VIB)	

DTA curves of samples with compositions presenting models I-IV and VI, viz. comprising the solid solutions of MoO₃ in CrSbO₄ and α-Sb₂O₄ after the final heating cycle, showed that the first endothermic effect started at ~1020°C, accompanied by the mass loss fluctuating between 15 and 25% by mass – recorded on TG curves. In accordance with the data published [13], at this temperature range starts decomposition of α-Sb₂O₄ to gaseous products, probably to Sb₄O₆ (dimer) and O₂. Loss in mass of the samples under study, starting at this temperature, corresponded to the contents of α-Sb₂O₄ in mixtures with the MoO₃ solution in CrSbO₄. The fact justifies the reason that α-Sb₂O₄ remains in equilibrium with the MoO₃ solid solution in CrSbO₄ to ~960°C, say, to the temperature of the α-Sb₂O₄ decomposition.

Another small endothermic effect recorded at ~1320°C on DTA curves of the samples was deemed to relate with mass of the samples, making up 47–53% by mass. The results of studying the after-DTA remains by XRD have shown that this effect

can pertain to the decomposition of the MoO₃ solid solution in CrSbO₄ to deposit Cr₂O₃ and release gaseous products.

A small endothermic effect with an onset temperature fluctuating between 1320 and 1380°C was noticed on DTA curves comprising only the MoO₃ solid solution in CrSbO₄. Mass decrement of ~60.00% by mass producing this effect is believed to be bound with decomposition of the MoO₃ solid solution in CrSbO₄.

Conclusions

1. Components of the Cr₂O₃-α-Sb₂O₄-MoO₃ system interact to produce a substitution solid solution of MoO₃ in CrSbO₄ with a formula: CrSb_{1-6x}□_xMo_{5x}O₄.
2. Substitution of Sb⁵⁺ by Mo⁶⁺ in the CrSbO₄ crystal lattice gives rise to originating of redundant charges, the compensation of which is realised by arising vacancies in a Sb⁵⁺ sub-lattice.
3. The solid product of the CrSb_{1-6x}□_xMo_{5x}O₄ decomposition starting at ~1320°C is Cr₂O₃.
4. Solid solutions of MoO₃ in CrSbO₄ remain in equilibrium with α-Sb₂O₄ up to ~1020°C, that is, at a temperature of thermal dissociation of α-Sb₂O₄.
5. The results obtained have allowed to divide the Cr₂O₃-α-Sb₂O₄-MoO₃ system into five subsidiary systems as it has been shown in Fig. 1.

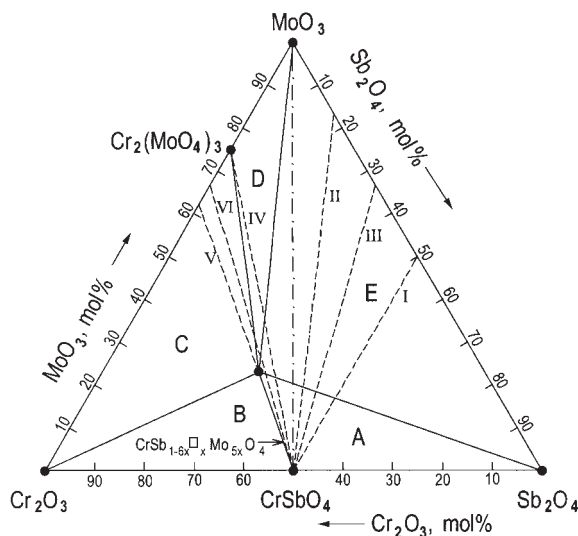


Fig. 1 The component concentration triangle of the Cr₂O₃-α-Sb₂O₄-MoO₃; ----- position of theoretical models of the MoO₃ solid solution in CrSbO₄; - - - - - CrSbO₄-MoO₃ intersection; — division of the system studied into subsidiary system: A – CrSbO_{4(s.s.)}-α-Sb₂O₄; B – CrSbO_{4(s.s.)}-Cr₂O₃; C – CrSbO_{4(s.s.)}-Cr₂O₃-Cr₂(MoO₄)₃; D – CrSbO_{4(s.s.)}-Cr₂(MoO₄)₃-MoO₃; E – CrSbO_{4(s.s.)}-MoO₃-α-Sb₂O₄

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