

Thermal stability of $\text{In}_2(\text{MoO}_4)_3$ and phase equilibria in the MoO_3 – In_2O_3 system

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Abstract Thermal stability of a compound forming in a binary system MoO_3 – In_2O_3 was investigated by DTA/TG, XRD and SEM methods in this study. For the first time, the diagram of phase equilibria established in the whole range of concentrations of this system's components has been constructed. The temperature and concentration ranges of the components of MoO_3 – In_2O_3 system in which the compound $\text{In}_2(\text{MoO}_4)_3$ co-exists in solid state with MoO_3 or In_2O_3 or with the liquid were determined. The composition and melting point of the eutectic mixture consisting of $\text{In}_2(\text{MoO}_4)_3$ and MoO_3 were found.

Keywords Indium(III) molybdate(VI) · MoO_3 – In_2O_3 system · DTA/TG · Thermal decomposition · XRD

Introduction

Binary and ternary metal oxide systems have been subjects of intense interest as their characterisation is essential for design of new materials of different types, like semiconductors, magnetic and optical materials or construction materials of specific thermal, mechanical or chemical properties. The above mentioned systems have also been studied in the aspect of testing the catalytic properties of the oxides, their mixtures and phases made by them [1]. An important source of information on the multicomponent oxide systems are the diagrams of phase equilibria reached

in them. Such diagrams provide information on the composition, type and thermal stability of compounds and phases formed in a given system as well as on the temperature and concentration ranges of their coexistence in the solid and liquid state [1].

Physicochemical properties, structure and applications of molybdenum(VI) oxide and indium(III) oxide are well known [2–7]. MoO_3 , In_2O_3 and $\text{In}_2(\text{MoO}_4)_3$ formed as a result of a reaction between the former two, are components of active and selective catalysts of different processes of oxidation of organic compounds, e.g. methanol to formaldehyde, propene to acrylaldehyde or acrylic acid, or benzene to maleic anhydride [8–10]. These oxides have been used in semiconducting sensors for detection of oxidating gases O_3 and NO_2 [11]. It has been established that the characteristics of the sensors based on MoO_3 and In_2O_3 significantly depend on the conditions of their synthesis, which affect the structure, phase composition and degree of oxidation of molybdenum and indium [11].

To the best of our knowledge, no diagram of phase equilibria has been published for MoO_3 – In_2O_3 , and the thermal properties of indium(III) molybdate(VI)—the only compound formed in this system—have been only partly recognised. It is known that at ~ 340 °C this compound ($\text{In}_2(\text{MoO}_4)_3$) undergoes a polymorphous transition from the variety of regular structure (C– $\text{In}_2(\text{MoO}_4)_3$, $a = 13.34 \pm 0.07$ Å) [9] to the variety of orthorhombic structure (R– $\text{In}_2(\text{MoO}_4)_3$, $a = 9.447$ Å, $b = 9.597$ Å, $c = 13.29$ Å) [10]. The authors of the study [10] gave the melting point of this compound as 1230 °C, however, with no information on the type of the melting process, i.e. whether it is congruent or incongruent.

As indium(III) molybdate(VI) belongs to the group of compounds showing negative thermal expansion and high electric conductivity [12], it can be used as electrolyte in

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fuel cells (galvanic cells), gas sensors [12] and laser materials [11]. It is also used as a catalyst in the process of production of olefins from paraffin by dehydrogenation with selective combustion of hydrogen [13].

In view of the available literature data, it seemed important to establish the conditions of formation of indium(III) molybdate(VI), determination of its thermal properties and the phase equilibrium diagram of the system $\text{MoO}_3\text{--In}_2\text{O}_3$ in the whole concentration range of its components.

Experimental

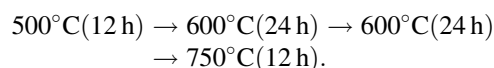
To study the phase equilibria in the $\text{MoO}_3\text{--In}_2\text{O}_3$ system, 11 samples of MoO_3 and In_2O_3 oxide mixtures were prepared. Contents of the initial mixture, heating conditions and X-ray phase analysis of the samples in the equilibrium state are given in Table 2. All the samples were prepared by solid–solid reactions according to the procedure described inter alia in [14–18].

The phase compositions of the samples, following the successive stages of their heating, were determined on the basis of XRD results (HZG-4, Jena, Germany, Cu-K α radiation) and the data included in PDF cards. After the last stage of heating, all the samples were subjected to DTA/TG examination. The DTA/TG measurements were performed on a F. Paulik–L. Paulik–L. Erdey derivatograph (the MOM Company, Budapest). The measurements were made in air atmosphere, within the temperature range of 20–1000 °C and at the heating rate of 10 °C/min. All the measurements were made in corundum crucibles. The mass of the samples examined was kept constant at 500 mg. The accuracy of the temperature readout determined on the basis of repetitive tests was established at ± 5 °C. The compound $\text{In}_2(\text{MoO}_4)_3$ and other selected samples were additionally examined by the DTA/TG method on an SDT 2960 apparatus, made by TA Instruments Company. The measurements were carried out in air atmosphere, within the temperature range of 20–1350 °C, at the heating rate of 10 °C/min. The test was made in corundum crucibles. The mass of the samples examined were ~ 15 mg.

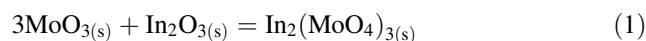
A sample of $\text{In}_2(\text{MoO}_4)_3$ and a sample of $\text{In}_2(\text{MoO}_4)_3$ heated at 935 °C were examined under a scanning electron microscope (JSM-1600, Joel, Japan).

Results and discussion

$\text{In}_2(\text{MoO}_4)_3$ was synthesised in the four-stage process of heating of a mixture containing of 75.00 mol% MoO_3 and 25.00 mol% In_2O_3 in the following temperature programme:



Phase analysis (XRD) proved that after the last stage of heating the sample is monophasic and contains only indium(III) molybdate(VI). The set of diffraction lines recorded, the interplanar distances (d_{hkl}) corresponding to them and their relative intensities (I/I_0) were in agreement with the PDF chart no 74-1791. The above observations led us to conclude that the following reaction took place in the mixture:



The white compound obtained in reaction (1) was then subjected to DTA/TG measurements in air atmosphere. The DTA curve of $\text{In}_2(\text{MoO}_4)_{3(s)}$ (Fig. 1) revealed two endothermic effects of which the first (a small one) started at 335 °C, while the second started at 1125 °C. On the basis of the literature data [9, 10], the first effect starting at 335 °C was assigned to the polymorphous transition of the regular indium(III) molybdate(VI) to the orthorhombic crystal form of this compound. The temperature of this transition is consistent with the values reported by other authors [9].

The second endothermic effect, starting at 1125 °C and of the hitherto unknown origin, was accompanied by a significant mass loss, indicated by TG results and its beginning already at 935 °C. The TG revealed that the mass loss percentage taking place in the range from 935 to 1300 °C was $\sim 54\%$. To enable establishing the origin of

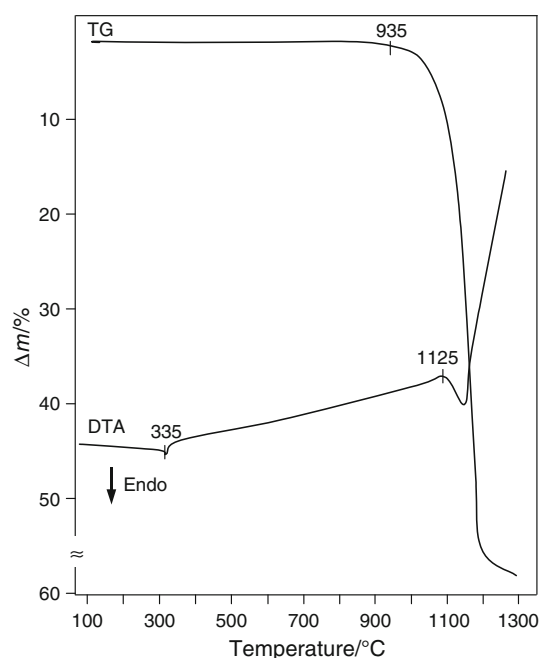


Fig. 1 DTA and TG curves of $\text{In}_2(\text{MoO}_4)_3$

the second thermal effect appearing on the DTA curve of $\text{In}_2(\text{MoO}_4)_3$, the samples of $\text{In}_2(\text{MoO}_4)_3$ of the known mass were subjected to additional 1-h heating in a muffle furnace at selected temperatures ranging from 935 to 1250 °C. After such an additional heating, the samples were rapidly cooled to room temperature, weighed, homogenised by grinding and subjected to XRD phase analysis. The temperature of heating, XRD results and the mass loss measured are presented in Table 1.

As seen from the results presented in Table 1, at about 935 °C, the thermal decomposition of indium(III) molybdate(VI) begins to yield the initial oxides, In_2O_3 and MoO_3 . The mass loss is related to the process of sublimation of MoO_3 formed upon decomposition [19, 20]. The occurrence of MoO_3 sublimation was confirmed by the inspection of the heating chamber of the furnace in which the process of additional heating was carried out. After cooling the furnace, its cooled elements were covered with crystals of resublimated MoO_3 . The obtained magnitude of the mass loss percentage of $\text{In}_2(\text{MoO}_4)_3$ heated at 1250 °C, equal to 59.85% is in a very good agreement with the one calculated from Eq. 2 to be 61%, and this agreement additionally confirms the decomposition of $\text{In}_2(\text{MoO}_4)_3$:

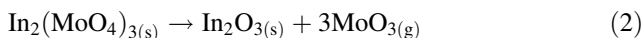


Figure 2 presents the SEM image of pure $\text{In}_2(\text{MoO}_4)_3$ (Fig. 2a) and $\text{In}_2(\text{MoO}_4)_3$ taken after its heating at 935 °C (Fig. 2b). On the surfaces of the well-developed crystallites of $\text{In}_2(\text{MoO}_4)_3$ of diameters ranging from ~2 to 11 μm , there are small crystallites of In_2O_3 appearing as a result of decomposition of $\text{In}_2(\text{MoO}_4)_3$ beginning at this temperature.

The above results have undoubtedly proven that the compound studied does not melt at 1230 °C as suggested by the authors of [10], but it undergoes a thermal decomposition in the solid phase to In_2O_3 with sublimation of MoO_3 . In the air atmosphere, this decomposition begins with a low rate even at 935 °C.

Taking into regard the thermal stability of $\text{In}_2(\text{MoO}_4)_3$, it seemed interesting to check in which temperature range this compound remains in solid state in equilibrium with the initial oxides MoO_3 and In_2O_3 . In order to establish the phase equilibria reached in the MoO_3 - In_2O_3 system in air atmosphere, 11 samples of the oxides were prepared of compositions representing the whole range of concentrations of the system studied (Table 2). The homogenised

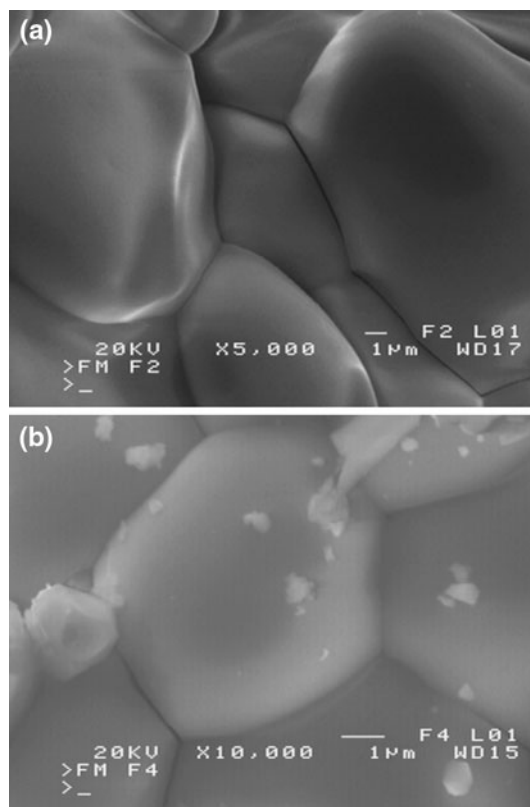


Fig. 2 a SEM image of $\text{In}_2(\text{MoO}_4)_3$, b SEM image of $\text{In}_2(\text{MoO}_4)_3$ heated at 935 °C for 1 h

mixtures of the oxides were formed into tablets and subjected to heating in the conditions specified in Table 2, ensuring that the equilibrium state is reached. The contents of initial mixtures, heating conditions and X-ray phase analysis of samples in equilibrium are presented in Table 2.

The XRD phase analysis of all the samples after the first stage of heating up to 550 °C revealed the presence of $\text{In}_2(\text{MoO}_4)_3$ besides the initial oxides. After further stages of heating, the samples reached equilibrium. The samples containing in the initial mixtures more than 75.00% mol MoO_3 were diphasic at equilibrium and contained MoO_3 and $\text{In}_2(\text{MoO}_4)_3$. Sample 6 of the initial mixture composition corresponding to the stoichiometry of $\text{In}_2(\text{MoO}_4)_3$, after the last stage of heating, contained only $\text{In}_2(\text{MoO}_4)_3$. In the samples representing the remaining range of concentrations of the system components, i.e. below 75% mol MoO_3 , the presence of $\text{In}_2(\text{MoO}_4)_3$ in equilibrium with In_2O_3 was found. The heating of the samples was

Table 1 The phase composition and mass loss after additional heating of $\text{In}_2(\text{MoO}_4)_3$

Heating conditions	935 °C (1 h)	1115 °C (1 h)	1175 °C (1 h)	1250 °C (1 h)
Phases after heating	$\text{In}_2(\text{MoO}_4)_3$, In_2O_3	In_2O_3 , $\text{In}_2(\text{MoO}_4)_3$	In_2O_3	In_2O_3
Mass loss (%)	2.33	36.50	53.00	59.85

Table 2 Contents of initial mixture, heating conditions and X-ray phase analysis of samples in an equilibrium state

No.	Contents of initial mixtures (mol%)		Heating conditions	Contents of equilibrium samples (mol%)
	MoO ₃	In ₂ O ₃		
1	97.50	2.50		97.30 MoO ₃ + 2.70 In ₂ (MoO ₄) ₃
2	95.00	5.00	Stage I:	94.12 MoO ₃ + 5.88 In ₂ (MoO ₄) ₃
3	90.00	10.00	400 °C (1 h) →	85.71 MoO ₃ + 14.29 In ₂ (MoO ₄) ₃
4	85.00	15.00	500 °C (12 h) →	72.73 MoO ₃ + 27.27 In ₂ (MoO ₄) ₃
5	80.00	20.00	550 °C (12 h)	50.00 MoO ₃ , + 50.00 In ₂ (MoO ₄) ₃
6	75.00	25.00	Stage II:	In ₂ (MoO ₄) ₃ ^a
7	60.00	40.00	550 °C (12 h) →	50.00 In ₂ O ₃ + 50.00 In ₂ (MoO ₄) ₃
8	50.00	50.00	600 °C (24 h)	66.66 In ₂ O ₃ + 33.34 In ₂ (MoO ₄) ₃
9	40.00	60.00	Stage III:	77.78 In ₂ O ₃ + 22.22 In ₂ (MoO ₄) ₃
10	25.00	75.00	600 °C (24 h)	88.89 In ₂ O ₃ + 11.11 In ₂ (MoO ₄) ₃
11	10.00	90.00		96.3 In ₂ O ₃ + 3.70 In ₂ (MoO ₄) ₃

^a The sample additionally heated at 750 °C (24 h)

accompanied by a small change in their mass. Total percentage of mass loss of the samples after all the stages of their heating varied from 0.16 to 1.07%. The greatest mass loss that was noted for the samples contained in the initial mixtures was ranging from 75.00 to 97.50% mol MoO₃.

This observation means that the mass loss is attributed mostly to MoO₃ which, to a small degree, underwent sublimation during heating. In consistence with the literature data, the sublimation of MoO₃ begins even at 550 °C [19, 20].

Although the sublimation of MoO₃ from the reaction mixtures of the oxides studied leads to a small change in their composition, the mixtures still represent the system MoO₃–In₂O₃. The small magnitude of the mass losses makes them irrelevant for the purpose of the study. All the samples in equilibrium were further subjected to the DTA/TG measurements.

The DTA curves recorded for the samples, which at equilibrium were mixtures of MoO₃ with In₂(MoO₄)₃ (Table 2, samples 1–5) in the range from ~20 to 1000 °C, showed one well-developed endothermic effect beginning at ~780 °C. The DTA curves of the other samples at the state of equilibrium, i.e. the samples containing In₂(MoO₄)₃ and In₂O₃ (Table 2, samples 6–11) did not show any large thermal effects in this temperature range. Only on the DTA curves recorded for samples 4–7 and 8, containing at equilibrium the greatest amounts of In₂(MoO₄)₃ in a mixture with MoO₃ or In₂O₃, a very small thermal effect was observed at ~335 °C, corresponding to a polymorphic transition of indium(III) molybdate(VI) [9].

The shape of the thermal effect starting at 780 ± 5 °C and the fact that it decreased with increasing content of In₂(MoO₄)₃ in the samples indicated that the effect corresponds to the melting of eutectic mixture forming of In₂(MoO₄)₃ and MoO₃. Moreover, this effect was the

greatest and most symmetric on the DTA curve of sample 1 (Table 2), which allowed concluding that the content of In₂(MoO₄)₃ in the eutectic mixture with MoO₃ was 2.70% mol or lower.

In order to establish the composition of eutectic mixture, four additional samples were prepared containing 2.5; 2.0; 1.5 and 1.0% mol In₂(MoO₄)₃ in mixtures with MoO₃ and studied by DTA. The most pronounced and most symmetric effect starting at 780 ± 5 °C was noted on the DTA curve of the sample with 2.5% mol In₂(MoO₄)₃. On the DTA curves of the other three samples, this thermal effect was much smaller and had a poorly developed maximum

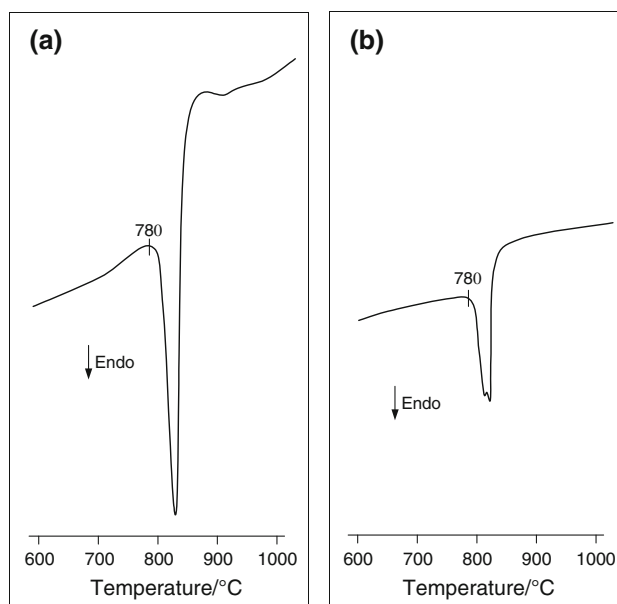
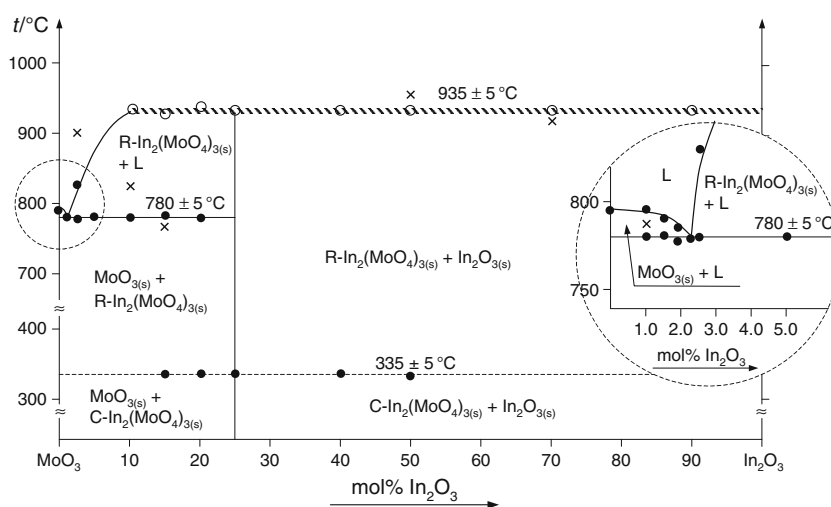


Fig. 3 DTA curve of **a** eutectic mixture composed of 2.5% mol In₂(MoO₄)₃ and 97.50% mol MoO₃, **b** the sample containing an excess of MoO₃ relative to the composition of the eutectic mixture

Fig. 4 Phase diagram of the MoO_3 – In_2O_3 system. *filled circle* points indicated DTA, *open circle* points indicated TG, *times* XRD analysis after quenched



(not a clearly pointed peak). For the sample containing 1.0% mol $\text{In}_2(\text{MoO}_4)_3$ this effect was recorded with a clearly marked inflection from the side of lower temperatures.

The above results imply that $\text{In}_2(\text{MoO}_4)_3$ and MoO_3 make the eutectic mixture composed of 2.5% mol $\text{In}_2(\text{MoO}_4)_3$ and 97.50% mol MoO_3 , which when expressed in the content of MoO_3 – In_2O_3 corresponds to $\sim 2.3\%$ mol In_2O_3 and melts at $780 \pm 5^\circ\text{C}$.

Figure 3 presents the DTA curve of the sample composition of which corresponds to that of the eutectic mixture (Fig. 3a) and that of the sample containing 1.0% mol of $\text{In}_2(\text{MoO}_4)_3$ (Fig. 3b) containing an excess of MoO_3 relative to the composition of the eutectic mixture.

The samples containing $\text{In}_2(\text{MoO}_4)_3$ and In_2O_3 at the equilibrium state (Table 2, samples 7–11) were further subjected to DTA/TG study in the range from ~ 20 to 1350°C . The effects on the DTA/TG curves started at the same temperatures as the effects recorded on the DTA/TG curves recorded for pure $\text{In}_2(\text{MoO}_4)_3$ (Fig. 1); however, the difference was in the size, and for the former samples, their sizes distinctly decreased with decreasing content of $\text{In}_2(\text{MoO}_4)_3$. This observation allowed us to conclude that $\text{In}_2(\text{MoO}_4)_3$ remains at equilibrium with In_2O_3 in solid state up to the temperature of $\text{In}_2(\text{MoO}_4)_3$ decomposition, i.e. 935°C .

The DTA/TG and XRD (phase analysis) results obtained for the samples at equilibrium were the basis for construction of the phase diagram of MoO_3 – In_2O_3 in the entire range of concentrations of the components, up to 935°C (Fig. 4). This diagram was constructed according to the procedure described, among other things in the studies [21–26].

The types of solid phases being at equilibrium with the liquid were identified on the basis of additional studies. In these additional studies, selected samples at equilibrium were heated for 1 or 3 h at temperatures chosen from that

corresponding to the solidus line to 1000°C . After this additional heating, the samples were rapidly quenched to room temperature, and after homogenisation by grinding, they were subjected to phase analysis by XRD. The compositions of these samples and the temperatures at which they were additionally heated are given in the diagram. The areas of the sample existence at equilibrium determined on the basis DTA and XRD methods are delineated by solid lines, while those established only on the basis of the XRD data for the additionally heated samples are marked with broken lines.

Conclusions

Analysis of the results obtained in the study permitted drawing the following conclusions:

1. $\text{In}_2(\text{MoO}_4)_3$ is the only compound forming in the binary system of MoO_3 – In_2O_3 oxides, and it is stable in the air atmosphere up to $\sim 935^\circ\text{C}$. Above this temperature, the compound starts thermal decomposition to In_2O_3 and MoO_3 accompanied by sublimation of the latter oxide.
2. Indium(III) molybdate(VI) in solid state remains in equilibrium with MoO_3 up to 780°C , i.e. to the melting point of the eutectic mixture formed between these compounds.
3. The eutectic mixture of the composition of 2.5% mol $\text{In}_2(\text{MoO}_4)_3$ and 97.5% mol MoO_3 when expressed in the contents of the mixture components, corresponds to the content of In_2O_3 of 2.3% mol.
4. Indium(III) molybdate(VI) co-exists in solid state with In_2O_3 up to $\sim 935^\circ\text{C}$.
5. The system MoO_3 – In_2O_3 in the range of components not exceeding 25% mol In_2O_3 , is a real binary system also above the solidus line.

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