

INITIAL STUDIES ON THE OXIDE SYSTEM $\text{Cr}_2\text{O}_3\text{--Sb}_2\text{O}_4$

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Abstract

Differential thermal analysis (DTA) and X-ray diffraction (XRD) were utilized to study the phase equilibrium established in the subsolidus area of the system $\text{Cr}_2\text{O}_3\text{--Sb}_2\text{O}_4$. It was found that the components of the title system interact in ambient air to produce CrSbO_4 . The compound is stable up to $\sim 1380^\circ\text{C}$, at which temperature it starts to decompose.

Keywords: antimony tetroxide, chromium(III) oxide, DTA, IR, XRD

Introduction

Antimony tetroxide and chromium(III) oxide, and especially their structures and physico-chemical properties, have long aroused the profound interest of many workers [1–13]. However, the available publications afford no information either on reactions that might take place between the oxides in the solid state in air, or on the phase equilibria established in the system $\text{Cr}_2\text{O}_3\text{--Sb}_2\text{O}_4$. Only a few works have dealt with the reaction of antimony(III) and chromium(III) oxides in air, to produce a compound to which the molecular formula CrSbO_4 has been attributed [14, 15]. This compound can be obtained by heating an equimolar $\text{Sb}_2\text{O}_3/\text{Cr}_2\text{O}_3$ mixture in air at 1473 K for 3 days. It can also be prepared by precipitation from solutions containing $\text{SbCl}_5/\text{CrCl}_3$ mixtures [16]. CrSbO_4 is reported to be isostructural with FeSbO_4 [16], to crystallize in a tetragonal system and to possess a rutile structure [15].

In order to identify the types and number of phases formed in air in the binary system $\text{Cr}_2\text{O}_3\text{--Sb}_2\text{O}_4$, a study was undertaken of the equilibrium phases established in the solid state of the system over its entire component concentration range.

Experimental

The following reagents were used: Sb_2O_3 (pure, Merck, Germany), Cr_2O_3 (pure, Aldrich Chemie, Germany), and $\alpha\text{-Sb}_2\text{O}_4$, prepared by heating Sb_2O_3 in air, in the following cycles:

400°C (1 h) \rightarrow 500°C (1 h) \rightarrow 600°C (1 h) \rightarrow 650°C (24 h).

In order to investigate the phase equilibria established in the solid state, 7 samples were prepared from α -Sb₂O₄ and Cr₂O₃, in proportions reflecting the entire component concentration range (Table 1). The oxide mixtures with the given contents were homogenized by mechanical grinding, shaped into pastilles and heated in cycles under conditions that led to samples in an equilibrium state, i.e.: 500°C (1 h)→600°C (48 h)→700°C (48 h)→800°C (48 h)→900°C (48 h)→1000°C (48 h)→1000°C (24 h).

Table 1 Contents of initial mixtures and X-ray analysis results on samples after the final heating cycle

No.	Contents of initial mixtures/mol%		Phases found
	Sb ₂ O ₄	Cr ₂ O ₃	
1	25.00	75.00	CrSbO ₄ , Cr ₂ O ₃
2	33.33	66.67	CrSbO ₄ , Cr ₂ O ₃
3	40.00	60.00	CrSbO ₄ , Cr ₂ O ₃
4	50.00	50.00	CrSbO ₄
5	60.00	40.00	CrSbO ₄ , α -Sb ₂ O ₄
6	66.67	33.33	CrSbO ₄ , α -Sb ₂ O ₄
7	75.00	25.00	CrSbO ₄ , α -Sb ₂ O ₄

In each heating cycle, the samples were slowly cooled to ambient temperature, weighed to verify their mass change, ground, subjected to X-ray phase analysis, and afterwards again shaped into pastilles and heated, the procedure being repeated until the samples achieved the equilibrium state.

Diffraction patterns of the samples were obtained with an HZG-4/A2 diffractometer, with a cobalt lamp as radiation source. The identification of the individual phases depended on the consistency of particular X-ray reflexions recorded with the data contained in PDF cards [17] and by referring to publications [15].

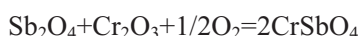
DTA/TG examinations of the samples were made at 20–1500°C in ambient air with a Q1500 derivatograph (MOM, Budapest). Samples weighing 300 mg each were placed in corundum crucibles.

A monophasic sample obtained in the final heating cycle was examined by IR spectroscopy. An equimolar mixture of Sb₂O₄ and Cr₂O₃ was examined similarly. The measurements were made within the wavenumber range 1500–200 cm⁻¹, with an IR SPECORD M-80 spectrophotometer (Carl Zeiss, Jena, Germany). The infrared spectra were made by pelleting a sample with KBr at 1:300 mass ratio.

Results and discussion

Table 1 lists the contents of the initial samples and data on the X-ray phase analysis of all the samples in the equilibrium state. The results indicate that Cr₂O₃ does not remain in equilibrium with α -Sb₂O₄ in the subsolidus area. Diffraction patterns of equilibrium samples containing up to 50.00 mol% of α -Sb₂O₄ in their initial mixtures ex-

hibit sets of diffraction lines, some of which were attributed to Cr₂O₃, whereas the positions of other lines and their intensity relations are characteristic of a diffraction line set for the phase CrSbO₄ [15]. In the final heating cycle, a sample containing an initial mixture of 50.00 mol% α-Sb₂O₄ was monophasic, containing only CrSbO₄. X-ray phase analysis of samples containing upwards of 50 mol% of α-Sb₂O₄ demonstrated the presence of antimony(IV) oxide together with CrSbO₄. The phase compositions of the samples in equilibrium are indicative of the reaction of α-Sb₂O₄ with Cr₂O₃ to yield CrSbO₄. The summary mass increment for samples after 6 heating cycles, between 0.11 and 1.68% mass, suggests that the reaction involves atmospheric oxygen, according to the equation



Such a reaction course may explain why this phase was not obtained when equimolar mixtures of Cr₂O₃/Sb₂O₃ and Cr₂O₃/Sb₂O₄ were heated in the absence of atmospheric oxygen in sealed quartz ampules.

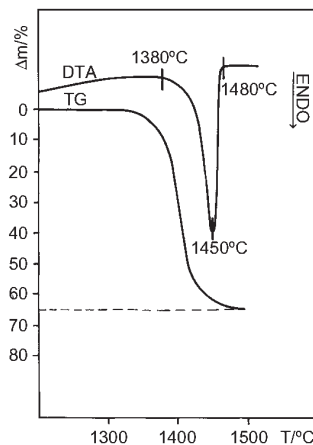
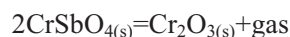


Fig. 1 DTA and TG curves of CrSbO₄

The DTA curve of a monophasic sample of CrSbO₄ demonstrated that the endothermic effect with an onset temperature of ~1380°C was associated with the 65% mass decrement recorded in the TG curve of the sample (Fig. 1). On close inspection of the sample analyzed by DTA, it appeared that, when heated to 1450°C, the sample had not melted and contained only Cr₂O₃. The experimental results suggest that CrSbO₄ suffers thermal decomposition at 1380°C, yielding Cr₂O₃ and a product which is gaseous at the decomposition temperature, according to the equation



The available information leads us to assume that the decomposition starts with the formation of Sb₂O₄ (among other products), which at 1273 K [6] decomposes to antimony(III) oxide and oxygen. The mass decrement recorded in the TG curve of the

phase CrSbO_4 may be indicative of this mechanism. CrSbO_4 and Cr_2O_3 remain in equilibrium in the solid state up to 1380°C , i.e. the temperature of CrSbO_4 decomposition, as evidenced by the temperature of onset of the endothermic effect recorded in the DTA curves of the samples from the relevant component concentration range for the system under consideration. The DTA curves of samples containing CrSbO_4 and $\alpha\text{-Sb}_2\text{O}_4$ in equilibrium show the onset of the first endothermic effect at $\sim 1160^\circ\text{C}$, which implies that the phases coexist in the solid state up to this temperature. The mass decrement related with this effect corresponds to thermal dissociation of the $\alpha\text{-Sb}_2\text{O}_4$ samples.

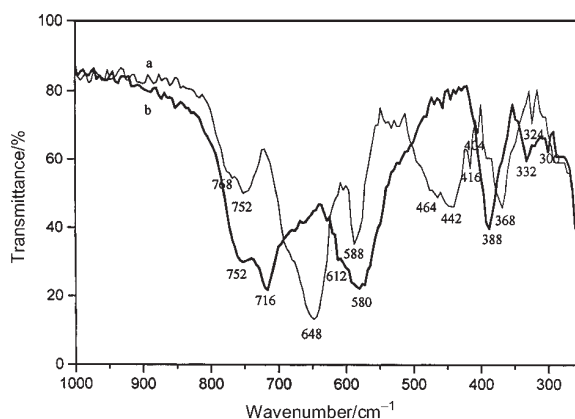


Fig. 2 IR spectra of: a – 50.00 mol% $\alpha\text{-Sb}_2\text{O}_4$ +50.00 mol% Cr_2O_3 ; b – CrSbO_4

As no reference to the IR spectrum of the phase CrSbO_4 has been found, the compound obtained in this work from the reaction of $\alpha\text{-Sb}_2\text{O}_4$ and Cr_2O_3 was examined by IR spectroscopy. Only the IR spectra of Cr_2O_3 and Sb_2O_4 are known. Figure 2 shows IR spectra of an equimolar $\alpha\text{-Sb}_2\text{O}_4/\text{Cr}_2\text{O}_3$ mixture and of CrSbO_4 . It can be seen that the IR spectrum of the phase CrSbO_4 is different from that of the oxide mixture both in the number of absorption bands and in their positions and intensities. Absorption bands characteristic of CrSbO_4 were observed within the wavelength range $250\text{--}900\text{ cm}^{-1}$. In contrast with the IR spectrum of the oxide mixture, that of the phase has two broad absorption bands with maxima at 716 and 580 cm^{-1} , and a sharp, very intense band with maximum at 388 cm^{-1} . The IR spectrum of CrSbO_4 contains two further absorption bands at lower wavelengths, 332 and 300 cm^{-1} . There is a broad band with maximum at 716 cm^{-1} , on the shoulder of which there is an inflexion at 752 cm^{-1} . The published data suggest that this can be attributed to the stretching vibrations of Sb-O bonds in SbO_6 octahedra [18]. Another broad absorption band, with maximum at 580 cm^{-1} , can be ascribed to the stretching vibrations of Sb-O and Cr-O bonds in MO_6 octahedra, and to stretching vibrations of the bridging linkage Cr-O-Cr . Still another absorption band in the CrSbO_4 oscillation spectrum, with maximum at 388 cm^{-1} , may be brought about by distortional vibrations of the Cr-O-Cr linkage [19, 20]. As it is impossible to associate other IR absorption bands

with the corresponding vibrations, the work has been deemed qualitative in character, and allows only the statement that CrSbO₄ is built up of SbO₆ and CrO₆ octahedra.

Conclusions

The investigations led to the following conclusions:

- The components of the system Cr₂O₃–Sb₂O₄ react in air atmosphere to form CrSbO₄.
- CrSbO₄ starts to decompose at 1380°C, yielding the solid product Cr₂O₃ and a gaseous product.
- The IR spectrum of CrSbO₄ has been recorded (Fig. 2).

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