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FORMATION AND DECOMPOSITION OF THE RUTILE-TYPE COMPOUND $FeSbO_4$

TG-DTA study

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Abstract

The reaction between Fe_2O_3 (hematite) and Sb_2O_3 leading to the formation of the rutile-type compound $FeSbO_4$ was analysed by means of DTA and TG, performed under various O_2 partial pressures up to 1673 K. The reaction products were identified by means of XRD analysis. Three transformations occur in the analysed temperature range: 1. oxidation of Sb_2O_3 to Sb_2O_4 between 745 and 768 K; 2. formation of $FeSbO_4$ between 1226 and 1246 K; 3. decomposition of $FeSbO_4$ without melting above 1543–1591 K. The TG-DTA and XRD analysis results indicate that deviations from perfect stoichiometry are likely to exist inside $FeSbO_4$.

Keywords: $FeSbO_4$, rutile-type compound, TG-DTA, XRD analysis

Introduction

The stability of the rutile-type compound $FeSbO_4$ (space group $P4_2/mnm$) as a function of temperature and oxygen partial pressure was not yet fully investigated. The reaction between Fe_2O_3 and Sb_2O_3 in air was studied by Walczak *et al.* [1] and by Tianshu and Hing [2] by means of TG-DTA. They concluded that the reaction between Fe_2O_3 and Sb_2O_3 involves two steps: 1. oxidation of Sb_2O_3 into α-Sb_2O_4 between 573 and 773 K; 2. reaction among Fe_2O_3, α-Sb_2O_4 and O_2 that leads to the formation of $FeSbO_4$ at ~1213 K. Complete conversion of equimolar mixtures of Fe_2O_3 and Sb_2O_3 into $FeSbO_4$ was obtained at 1173 K [2]. The endothermic effect observed at 1543 K was attributed to incongruent melting of $FeSbO_4$ [2].

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Experimental

Stoichiometric amounts (molar ratio 1:1) of Fe_2O_3 (Pfizer; 99.9%) and Sb_2O_3 (99%) were mixed for 24 h in pure water, then dried and sieved. The oxide mixture was investigated by means of thermogravimetric and differential thermal analysis (TG-DTA; Netzsch STA 409 C) with a heating rate of 5 K min^{-1}, up to 1673 K in dynamic atmosphere under various O_2 partial pressures (100, 40 and 20% of O_2 in N_2). Phase identification was performed by means of XRD analysis (Philips PW1830; Bragg–Brentano geometry; CuK_α; secondary monochromator; range 20–80°2θ; step 0.025°2θ; sampling time 10 s). Crystallographic data for $FeSbO_4$ were taken from the work of Amador and Rasines [3].

Results and discussion

The starting powder mixture is characterised by the typical hematite red colour; at the end of the thermal analysis a loose dark brownish powder is obtained in every case, indicating that melting does not occur up to 1673 K.

Thermal analysis

Two exothermic peaks in the DTA curve associated to two mass gain in the TG curve were observed (Fig. 1). The temperature at which they occur changes as partial pressure of O_2 varies (Table 1). The first exothermic reaction occurs between 745 and 768 K (Fig. 2a); the mass gain is due to the oxidation of Sb_2O_3 into α-Sb_2O_4 and increases as the partial pressure of O_2 increases; moreover the peak in the DTA curve enlarges as the O_2 activity decreases. This result accords quite well with that obtained by Tianshu and Hing [2] who report an oxidation temperature for Sb_2O_3 in air equal to 738 K, while for the same reaction in air Walczak *et al.* [1] report a very wide temper-

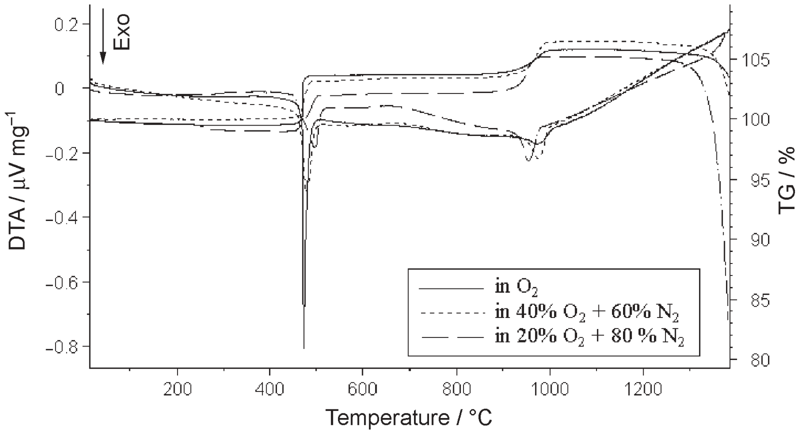

Fig. 1 DTA-TG analysis performed on Fe_2O_3+Sb_2O_3 powder mixture in pure O_2 and O_2+N_2 mixtures

ature range (573–773 K). In this latter case the lower limit was determined on samples isothermally heated for 24 h. The second exothermic peak observed in the DTA curve between 1226 and 1246 K (Fig. 2b) is originated by the reaction between α-Sb_2O_4 and Fe_2O_3, involving O_2, that leads to the formation of $FeSbO_4$. The corresponding mass gain decreases as the partial pressure of O_2 increases. It is interesting to observe that the reaction in air occurs at a lower temperature than at higher O_2 partial pressure (Table 1), as predicted by thermodynamics. The observed temperature range inside which $FeSbO_4$ grows is comparable to the value reported by Tianshu and Hing [2] (~1213 K in air). At temperature higher than 1543–1591 K a continuous mass loss is observed in all the TG curves (Fig. 1), but a clear thermal effect can only be noticed for the treatment carried out in 20% O_2, where the mass loss is much higher. In the same temperature range Walczak *et al.* [1] observed an endothermic effect which was attributed to the incongruent melting of $FeSbO_4$.

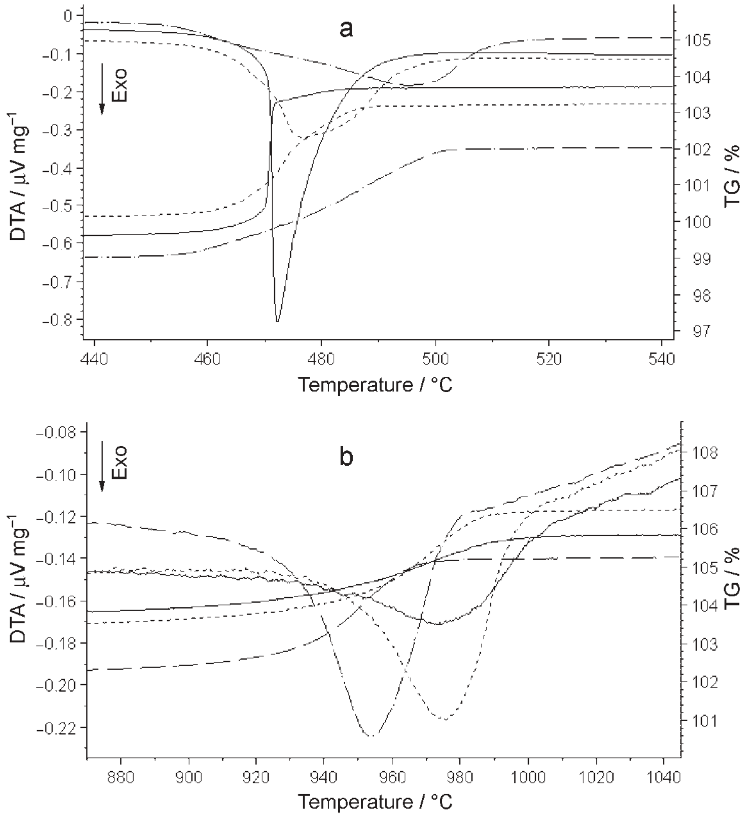

Fig. 2 Particular of the TG-DTA curves of Fig. 1 (— in O_2; ··· in 40% O_2+60% N_2; — in 20% O_2+80% N_2) in the temperature ranges corresponding to formation of α-Sb_2O_4 (a) and $FeSbO_4$ (b)

Table 1 Chemical reactions occurring in the temperature range of the thermal analysis (298–1673 K) and their temperatures as a function of the O_2 partial pressure

Atmosphere	Reaction temperature/K		
	Formation of α-Sb_2O_4	Formation of $FeSbO_4$	Decomposition of $FeSbO_4$
O_2	745	1246	1591
40% O_2	749	1248	1578
20% O_2	768	1226	1543

XRD analysis

X-ray patterns analysis reveals that $FeSbO_4$ decomposes above ~1543–1591 K with formation of Fe_2O_3 (haematite). The intensity of the peaks generated by Fe_2O_3 increases as the partial pressure of O_2 decreases (Fig. 3). Prolonged annealing in air at 1573 K leaves a residue entirely composed of Fe_2O_3. These results, combined with the strong dependence of the rate of the mass loss on the O_2 partial pressure, indicates that $FeSbO_4$ decomposes with formation of solid Fe_2O_3 and release of O_2 and a volatile antimony oxide, probably Sb_4O_6.

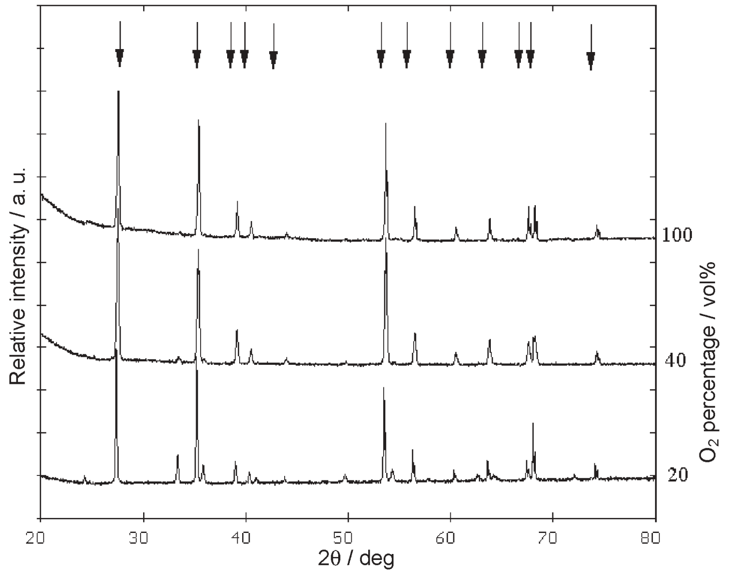

Fig. 3 XRD analysis performed on the reacted Fe_2O_3+Sb_2O_3 powder mixture in pure O_2, and O_2+N_2 mixtures; the arrows indicate the characteristic peaks of the rutile-type compound $FeSbO_4$. The increase of the background level at low 2θ angle is due to the polymeric sample holder

The lattice parameters of $FeSbO_4$ calculated from the X-ray powder data significantly decrease as the O_2 partial pressure in the reaction ambient decreases. This behaviour may be originated by a cation excess/oxygen deficiency stabilised by cationic mixed-valency or crystallographic shear planes such that occurring with reduced d^0 oxides of transition metals [4], or by a cation deficiency such that observed in the rutile-type compound $SbVO_4$ [5]. Anyway the dependence of the lattice parameters on the oxygen partial pressure and temperature indicates that deviation from stoichiometry is likely to occur inside $FeSbO_4$.

Conclusions

The formation of $FeSbO_4$ from a $(Fe_2O_3+Sb_2O_3)$ powder mixture in the presence of oxygen involves two steps: 1. the oxidation of Sb_2O_3 to α-Sb_2O_4 at 745–768 K; 2. the reaction among Fe_2O_3, α-Sb_2O_4 and O_2 that leads to the formation of $FeSbO_4$ at 1226–1246 K. Melting of $FeSbO_4$ was not observed, whilst decomposition of the phase occurs above ~1543–1591 K with formation of Fe_2O_3 (hematite) and the release of a volatile antimony oxide (probably Sb_4O_6) and oxygen. Thermal gravimetric-differential thermal analysis (TG-DTA) performed at different partial pressure of O_2 and X-ray diffraction (XRD) analysis indicate that non-stoichiometry is likely to occur in the rutile-type compound $FeSbO_4$.

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