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Rutile-Type $Mn_{1-x}Sb_{1+x}O_4$ Phases, $0 \leqslant x \leqslant 1/3$, Synthesized by the Sol–Gel Technique

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The sol–gel method has been used to synthesise $Mn_{1-x}Sb_{1+x}O_4$ compounds, $0 \leqslant x \leqslant 1/3$, with the rutile-type structure. Xero-gels containing Mn and Sb were prepared with $Mn(OAc)_2 \cdot 4H_2O$ and $Sb(OnBu)_3$ as precursors. The gels were heated to 370°C for 10 min, and these X-ray-amorphous Mn–Sb oxide mixtures were then heat treated at 740°C for 14 h in air. The cell dimensions of the rutile phases are $a = 4.671(4)$, $c = 3.060(4)$ Å, $V = 66.75$ Å^3 for $MnSbO_4$ ($x = 0$) and $a = 4.709(1)$, $c = 3.126(1)$ Å, $V = 69.32$ Å^3 for $Mn_{2/3}Sb_{4/3}O_4$ ($x = 1/3$). The structure of $Mn_{2/3}Sb_{4/3}O_4$ was refined by the Rietveld method, using X-ray diffractometer data, to $R_F = 4.9$ %. The $Mn_{1-x}Sb_{1+x}O_4$ rutile phases decompose on prolonged heating at 800°C, with the formation of trigonal γ-$MnSb_2O_6$. A partially ordered tri-rutile phase is observed in decomposed samples for $x \geqslant 0.27$.

Antimonates with the composition MSbO$_4$, where M is a trivalent atom with about the same size as Sb^{5+}, often exhibit disordered rutile-type structures[1] [space group $P4_2/mnm$: M and Sb randomly distributed on 2(a), O on 4(f)]. Several meta-antimonates, MSb$_2$O$_6$, M = e.g. Mg, Zn, Co or Ni, are furthermore found to adopt the tri-rutile structure, with ordered M and Sb atomic arrangements [space group $P4_2/mnm$: M in 2(a), Sb in 4(e), O_I in 4(f) and O_{II} in 8(j)] and a trebled c-axis.

$MnSb_2O_6$ is reported to exhibit several structures. Byström *et al.*[2] found that heating $MnSb_2O_6 \cdot 7H_2O$ at 800°C for 4 h yielded a compound which exhibited a weak X-ray powder pattern of the rutile type. No tri-rutile reflections could be observed. However, taking into account the possibility that the tri-rutile superstructure reflections might go unobserved, the authors concluded that the compound formed was probably an $MnSbO_4$ rutile or an $MnSb_2O_6$ tri-rutile. Brandt[3] reported that heat treatment of a mixture of Mn and Sb_2O_3 at 1000°C for 24 h yielded a diphasic material. One phase was identified as an orthorombic $MnSb_2O_6$ modification with the columbite ($FeNb_2O_6$) type structure, and the other phase was of the rutile type. Evidence for a tri-rutile modification of $MnSb_2O_6$ has also been given by Sala *et al.*[4] They heat-treated intimate mixtures of Sb_2O_5 and $Mn(NO_3)_2 \cdot 4H_2O$ in the proportion 2 : 1 at a final temperature of 900°C for 1 h. The X-ray powder pattern of the reaction product was interpreted as originating from a mixture of α- and β-Sb_2O_4 and a tri-rutile $MnSb_2O_6$ phase.

A trigonal modification of $MnSb_2O_6$ was obtained more recently by Scott,[5] by reacting MnO and Sb_2O_3 at 1100°C; it was designated γ-$MnSb_2O_6$ in order to distinguish it from the previously reported columbite- and trirutile-type phases. The γ-$MnSb_2O_6$ structure was determined from Guinier–Hägg X-ray powder diffraction data [space group $P321$, $Z = 3$, $a = 8.8054(4)$ Å and $c = 4.7229(4)$ Å]. The structure has subsequently been confirmed and more accurately determined by Reimers *et al.*[6] from neutron powder diffraction data. Vincent *et al.*[7] reported the structure of a trigonal modification of $MnSb_2O_6$ with space group $P3$, at approximately the same time as Scott. The structure was determined by single-crystal X-ray diffraction, and the modification was designated β-$MnSb_2O_6$. The modification is, however, very likely identical with γ-$MnSb_2O_6$, considering the nearly identical synthesis conditions, cell parameters and atomic positions.

A rutile phase of the $MnSbO_4$ composition has not been reported, despite the fact that $FeSbO_4$ and $CrSbO_4$ adopt rutile structures, and the radius for Mn^{3+} (HS), 0.65 Å, is very similar to the radii of Fe^{3+} (HS), 0.65 Å, and Cr^{3+}, 0.62 Å.

The present paper describes the preparation of rutile-type $Mn_{1-x}Sb_{1+x}O_4$ phases, with $0 \leqslant x \leqslant 1/3$, using the sol–gel method. The phases have been characterized by their X-ray powder patterns, and the crystal structure of $Mn_{2/3}Sb_{4/3}O_4$ has been refined from X-ray powder diffractometer data by the Rietveld technique.

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Experimental

Gels with Mn : Sb ratios of 2 : 1, 1.5 : 1, 1 : 1, 1 : 1.25, 1 : 1.5, 1 : 1.75, 1 : 2 and 1 : 2.5 were prepared. The Mn : Sb atomic ratios correspond to x-values in $Mn_{1-x}Sb_{1+x}$ of −0.33, −0.20, 0.00, 0.20, 0.27, 0.33 and 0.43, respectively. The preparation route, which is described in detail in Ref. 8, comprised dissolution of $Mn(OAc)_2 4H_2O$ in methanol to form 0.33 M solutions. One equivalent of diethylamine per Mn was then added under stirring. The addition caused oxidation of Mn, as seen by the formation of dark brown solutions. After 15 min $Sb(OnBu)_3$ was added and the stirring was continued for 15 min, generally yielding cloudy sols. Xero-gels were prepared by evaporating the solvent at 50–65°C from open beakers. X-Ray-amorphous oxide mixtures were obtained by heating the xero-gels to 370°C for 10 min, thus decomposing the organic part, which consisted mainly of acetato groups and loosely bound ligands. The oxide mixtures were then tempered at 740°C for 14 h in air. These temperatures were chosen with the aid of previous TG-DTA recordings.[8]

The preparations were characterised by their X-ray powder patterns, recorded with Guinier–Hägg cameras, $CuK\alpha_1$ radiation and Si as internal standard. The patterns were evaluated with a film-scanning system constructed at this department.[9]

Powder X-ray diffraction data of $Mn_{2/3}Sb_{4/3}O_4$ were collected on a STOE STADI/P diffractometer, using $CuK\alpha_1$ radiation, a rotating sample in symmetric transmission mode and a linear position-sensitive detector covering 4.6° in 2θ. The detector was moved in steps of 0.2° in 2θ, yielding an average intensity from 23 measurements at each 2θ position. To reduce the background from Mn fluorescence a thin Al foil was placed in front of the detector. The data were collected in steps of 0.02°, and the 2θ-range 15–100° was covered over a period of 80 h, yielding an intensity of ca. 3600 counts for the strongest $Mn_{2/3}Sb_{4/3}O_4$ peak.

Results

The powder patterns of samples heat-treated at 740°C/14 h all exhibited Bragg peaks from a rutile-type phase. No superstructure reflections indicating a tri-rutile cell were observed for these samples. The rutile peaks were in general broad, with half-widths increasing with Mn content, from 0.23° in 2θ at 2θ = 30° for x = 0.33, 0.43 to 0.87° for x = −0.33. In addition to the rutile reflections the powder patterns for x = 0.43 contained one weak peak associated with Sb_6O_{13}, and for x = −0.33, −0.20 several weak peaks attributable to Mn_2O_3 and Mn_3O_4.

The variation of the cell parameters with composition is shown in Fig. 1, as a function of x in $Mn_{1-x}Sb_{1+x}O_4$. The a-axis shows an increase from 4.671(4) Å for $MnSbO_4$ (x = 0) to 4.709(1) Å for $Mn_{2/3}Sb_{4/3}O_4$ (x = 1/3), and is, within error, constant outside this compositional range. The c-axis exhibits a somewhat larger, non-linear, dependence on x. It increases with x, from c = 3.060(4) Å for $MnSbO_4$ (x = 0), and reaches a maximum at $x \approx$ 0.25–0.33, with c = 3.126(7) Å for $Mn_{2/3}Sb_{4/3}O_4$ (x = 1/3). The unit cell volume, V, shows a similar compositional dependence as the c-axis. The homogenity range for the rutile $Mn_{1-x}Sb_{1+x}O_4$ phase is found to be roughly $0 \leqslant x \leqslant 1/3$, since the preparations with both $x < 0$ and $x > 1/3$ contained additional phases.

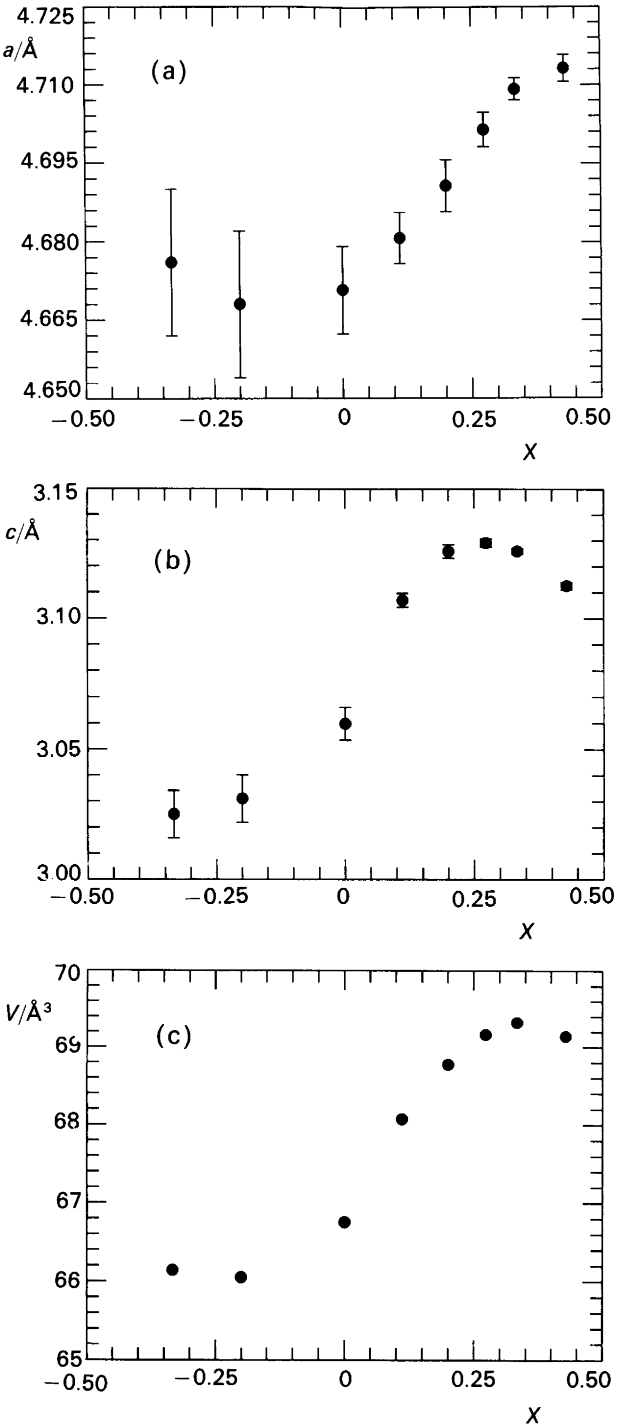

Fig. 1. Cell parameters versus x in $Mn_{1-x}Sb_{1+x}O_4$.

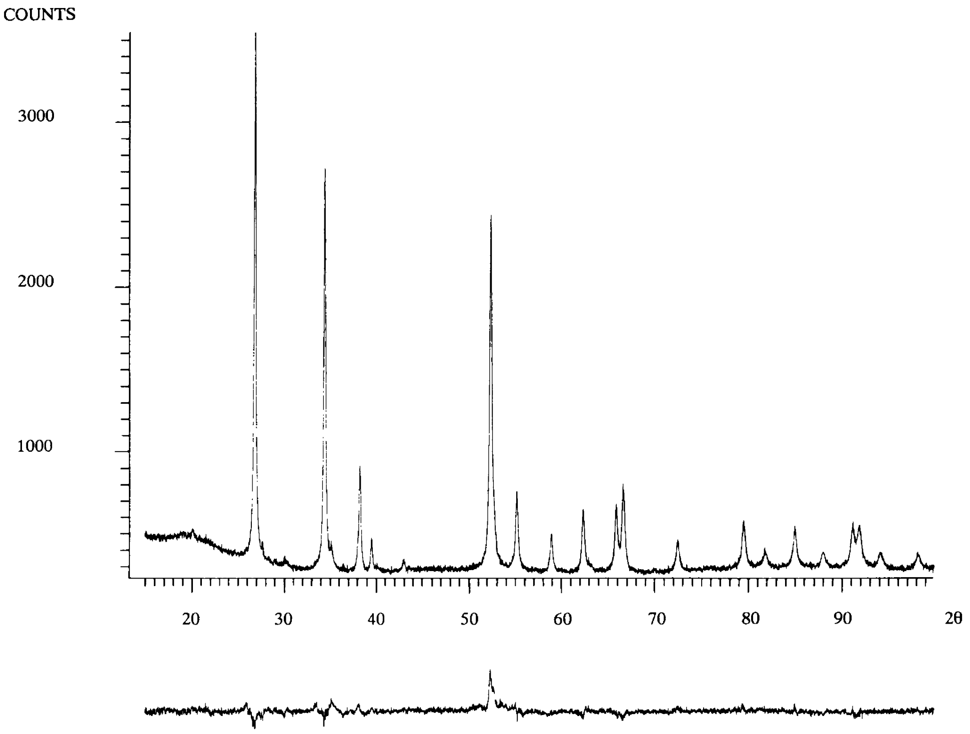

Fig. 2. Observed and difference intensity X-ray powder diffraction patterns of $Mn_{2/3}Sb_{4/3}O_4$.

The cell parameter variation indicates, however, that the homogenity range may be slightly larger (*cf.* discussion).

Additional heat treatment of the samples at 800°C/50 h yielded materials containing two or more phases: for x-values $\geqslant 0.27$ the rutile phase and trigonal γ-$MnSb_2O_6$. The amount of γ-$MnSb_2O_6$ formed increased with increasing Mn content. In addition, the sample with $x = 0.43$ contained β-Sb_2O_4.

The X-ray powder patterns of compositions with $x = 0.27$, 0.33 and 0.43 contained, besides reflections associated with γ-$MnSb_2O_6$, reflections which could be ascribed to a tri-rutile unit cell. The strongest tri-rutile reflection, (101), exhibited a relative intensity of ca. 1, 6 and 7 %, respectively, for the three compositions. These intensities are weaker than the calculated intensity, 15–20 %, for a fully ordered tri-rutile, and the ordering of Mn and Sb atoms is thus found to be only partial.

The structure of $Mn_{2/3}Sb_{4/3}O_4$ ($MnSb_2O_6$) was refined, from its X-ray powder diffraction pattern, using a Rietveld package.[10] In addition to the rutile peaks, the diffractometer data showed a few very weak Bragg peaks attributable to γ-$MnSb_2O_6$, which was included as a second phase in the refinements. The final refinement was carried out with a total of 16 parameters and the pseudo-Voigt profile function to model the peak shape (refined Lorentzian fraction = 0.93). The background was modelled by linear interpolation between 20 specified background points. Fig. 2 shows the fit between the calculated and observed patterns. A small misfit of unknown origin is observed at $2\theta \approx 52°$. A list of atomic coordinates is given in Table 1. The e.s.d.'s are multiplied by 4.5 in order to account for serial correlation[11] (Durbin–Watson d-index = 0.65). The negative displacement parameters clearly include a sample absorption component and are thus not measures of atomic vibrations.

Table 1. Atomic coordinates for $Mn_{2/3}Sb_{4/3}O_4$; tetragonal, $a = 4.709(1)$, $c = 3.126(1)$ Å, $z = 1$, $P4_2/mnm$.

Atom	Position	x	y	z	B/Å
(Mn, Sb)	2(a)	0	0	0	−1.1(1)
O	4(f)	0.3030(7)	0.3030(7)	0	−1.4(5)

$R_P = 3.9$; $R_{wp} = 5.1$; $R_I = 8.0$; $R_F = 4.9\%$. Goodness-of-fit index $S = 0.96$.

The Mn : Sb atomic ratio in the rutile $Mn_{2/3}Sb_{4/3}O_4$ phase was checked with a Jeol 2000FXII transmission electron microscope equipped with a Link AN10000 energy-dispersive spectrometer and with γ-$MnSb_2O_6$ as standard for Mn and Sb. Twenty analyses of micro-crystallites yielded an Mn : Sb ratio of 0.99(5) : 2, in good agreement with the nominal one. The micro-crystallites were of the size 300–1000 Å. No amorphous phases could be observed to be present in the sample.

Discussion

The M–O distances, M = Mn, Sb, in the $Mn_{2/3}Sb_{4/3}O_4$ rutile phase are 2.02(2) (2×) and 2.04(1) Å (4×), with the average 2.03(1) Å. This average M–O distance agrees well with that in γ-$MnSb_2O_6$, 2.05 Å, as well as with an expected value of 2.04 Å, calculated from Shannon–Prewitt ionic radii[12] for octahedrally coordinated Mn^{2+} in a high-spin (HS) state. The observed cell volume, 69.32 Å^3, is somewhat smaller than the corresponding volume for γ-$MnSb_2O_6$, 70.42 Å^3.

MSb_2O_6 compounds with tri-rutile unit cells are generally found for M^{2+} ions (M = Zn, Mg, Fe, Co and Ni) with ionic radii $r(M^{2+}) \leqslant 0.78$ Å, similar to the ionic radius of Sb^{5+}, 0.60 Å. For larger M^{2+} ions (M = Ca, Sr, Ba, Cd, Hg and Pb), with $r(M^{2+}) \geqslant 0.95$ Å, the $PbSb_2O_6$ structure is adopted.[13] The radius of Mn^{2+} (HS), 0.89 Å, occupies an intermediate position between the M^{2+} ion radii in the two types of structures. The rutile unit cell of $Mn_{2/3}Sb_{4/3}O_4$ is thus larger than the cells of other reported $M^{3+}Sb^{5+}O_4$ rutiles or $M^{2+}Sb_2^{5+}O_6$ trirutiles,[1] all with cell volumes < 67.5 Å^3.

The unit-cell volume observed for $MnSbO_4$, 66.75 Å^3, is similar to those of the rutiles $FeSbO_4$ and $CrSbO_4$,[1] 66.01 and 64.03 Å^3, respectively. This is in accordance with the similar radius of Mn^{3+} (HS), 0.65 Å, to the radii of Fe^{3+} (HS), 0.65 Å, and Cr^{3+}, 0.62 Å.

The magnetic susceptibility data given in Ref. 1 for the related compounds $MSbO_4$, M = Cr and Fe, and MSb_2O_6, M = Co, Ni and Cu, are in agreement with the ionic models $M^{3+}Sb^{5+}O_4$ and $M^{2+}Sb_2^{5+}O_6$, respectively. Furthermore, no indications of order/disorder transitions for the MSb_2O_6 compounds were found in that study. Assuming that all Sb ions have the oxidation number +5, the Mn ions in the $Mn_{1-x}Sb_{1+x}O_4$ rutile phases have a mixed Mn^{2+}–Mn^{3+} state, according to the formula $Mn_{2x}{}^{2+}Mn_{1-3x}{}^{3+}Sb_{1+x}{}^{5+}O_4$. There is, however, the possibility that Sb is partly present as Sb^{3+} for high x-values in the structures, as well as the possibility that Mn may be partly present as Mn^{4+} for low x-values. In view of these possibilities, it is difficult to evaluate in more detail the unit-cell variation with x, as well as to specifify accurate phase boundaries for the rutile phase.

We conclude that rutile phases with compositions $Mn_{1-x}Sb_{1+x}O_4$, $0 \leqslant x \leqslant 1/3$, are formed when corresponding Mn–Sb gels are heat-treated at 740°C for 1 h. The phases decompose at 800°C, accompanied by the formation of γ-$MnSb_2O_6$. Upon decomposition, a partially ordered tri-rutile phase is observed for $x \geqslant 0.27$. Our findings are thus in agreement with previous studies,[2–4] which indicated that $Mn_{2/3}Sb_{4/3}O_4$ ($MnSb_2O_6$) can adopt a rutile or tri-rutile structure.

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