Rutile-Type Mn$_{1-x}$Sb$_{1+x}$O$_4$ Phases, 0 ≤ x ≤ 1/3, Synthesized by the Sol–Gel Technique

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Antimonates with the composition $M$SbO$_4$, where $M$ is a trivalent atom with about the same size as Sb$^{5+}$, often exhibit disordered rutile-type structures [space group P4$_2$/mnm : $M$ and Sb randomly distributed on 2(a), O on 4(f)]. Several meta-antimonates, $M$Sb$_2$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$_6$ in 4(f) and O$_{11}$ in 8(j)] and a trebled c-axis.

MnSb$_2$O$_6$ is reported to exhibit several structures. Byström et al. found that heating MnSb$_2$O$_6$, 7H$_2$O 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 MnSb$_2$O$_6$ rutile or an MnSb$_2$O$_6$ tri-rutile. Brandt reported that heat treatment of a mixture of Mn and Sb$_2$O$_3$ at 1000°C for 24 h yielded a diphasic material. One phase was identified as an orthorhombic Mn$_2$Sb$_2$O$_6$ modification with the columbite (FeNb$_2$O$_6$) type structure, and the other phase was of the rutile type. Evidence for a tri-rutile modification of MnSb$_2$O$_6$ has also been given by Sala et al. They heat-treated intimate mixtures of Sb$_2$O$_3$ and Mn(NO$_3$)$_2$·4H$_2$O 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$_2$O$_4$ and a tri-rutile MnSb$_2$O$_6$ phase.

A trigonal modification of MnSb$_2$O$_6$ was obtained more recently by Scott by reacting MnO and Sb$_2$O$_3$ at 1100°C; it was designated γ-MnSb$_2$O$_6$ in order to distinguish it from the previously reported columbite- and trigonolite-type phases. The γ-MnSb$_2$O$_6$ structure was determined by 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. from neutron powder diffraction data. Vincent et al. reported the structure of a trigonal modification of MnSb$_2$O$_6$ 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$_2$O$_6$. The modification is, however, very likely identical with γ-MnSb$_2$O$_6$, considering the nearly identical synthesis conditions, cell parameters and atomic positions.

A rutile phase of the MnSb$_2$O$_6$ composition has not been reported, despite the fact that FeSb$_2$O$_4$ and CrSb$_2$O$_4$ adopt rutile structures, and the radius for Mn$^{2+}$ (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 ≤ x ≤ 1/3, using the sol–gel method. The phases have been characterized by their X-ray powder patterns, and the crystal structure of Mn$_{29}$Sb$_{45}$O$_{94}$ has been refined from X-ray powder diffraction 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_{x}O_{4} 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_{2}O 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 sois. 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.9

The preparations were characterised by their X-ray powder patterns, recorded with Guinier–Hägg cameras, CuKα 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 CuKα 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_{2}O_{3}, and for x = −0.33, −0.20 several weak peaks attributable to Mn_{1−x}O and Mn_{x}O.

The variation of the cell parameters with composition is shown in Fig. 1, as a function of x in Mn_{1−x}Sb_{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 ≈ 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 homogeneity range for the rutile Mn_{1−x}Sb_{x}O_{4} phase is found to be roughly 0 ≤ x ≤ 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_{x}O_{4}.
The cell parameter variation indicates, however, that the homogeneity 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 ≥ 0.27 the rutile phase and trigonal γ-MnSb₂O₆. The amount of γ-MnSb₂O₆ formed increased with increasing Mn content. In addition, the sample with x = 0.43 contained β-Sb₂O₄.

The X-ray powder patterns of compositions with x = 0.27, 0.33 and 0.43 contained, besides reflections associated with γ-MnSb₂O₆, 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 Mn₂/₃Sb₂/₃O₄ (MnSb₂O₆) was refined, from its X-ray powder diffraction pattern, using a Rietveld package. In addition to the rutile peaks, the diffractometer data showed a few very weak Bragg peaks attributable to γ-MnSb₂O₆, 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 2θ ≈ 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 (Durbin–Watson d-index = 0.65). The negative displacement parameters clearly include a sample absorption component and are thus not measures of atomic vibrations.

The Mn:Sb atomic ratio in the rutile Mn₂/₃Sb₂/₃O₄ phase was checked with a Jeol 2000FXII transmission electron microscope equipped with a Link AN10000 energy-dispersive spectrometer and with γ-MnSb₂O₆ 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.

**Table 1.** Atomic coordinates for Mn₂/₃Sb₂/₃O₄: tetragonal, a = 4.709(1), c = 3.126(1) Å, z = 1, P4₁/mmm.

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R_p = 3.9; R_w = 5.1; R_i = 8.0; R_f = 4.9%. Goodness-of-fit index S = 0.96.

**Discussion**

The M–O distances, M = Mn, Sb, in the Mn₂/₃Sb₂/₃O₄ rutile phase are 2.02(2) (2x) and 2.04(1) Å (4x), with the average 2.03(1) Å. This average M–O distance agrees.
well with that in γ-MnSb₂O₆, 2.05 Å, as well as with an expected value of 2.04 Å, calculated from Shannon–Prewitt ionic radii for octahedrally coordinated Mn²⁺ in a high-spin (HS) state. The observed cell volume, 69.32 Å³, is somewhat smaller than the corresponding volume for γ-MnSb₂O₆, 70.42 Å³.

M₅Sb₂O₈ compounds with tri-rutile unit cells are generally found for M²⁺ ions (M = Zn, Mg, Fe, Co and Ni) with ionic radius \( r(M^{2+}) \leq 0.78 \) Å, similar to the ionic radius of Sb⁵⁺, 0.60 Å. For larger M²⁺ ions (M = Ca, Sr, Ba, Cd, Hg and Pb)], with \( r(M^{2+}) \geq 0.95 \) Å, the PbSb₂O₆ structure is adopted. The radius of Mn²⁺ (HS), 0.89 Å, occupies an intermediate position between the M²⁺ ion radii in the two types of structures. The rutile unit cell of Mn₅Sb₂O₈ is thus larger than the cells of other reported M³⁺Sb⁵⁺O₄ rutiles or M²⁺Sb²⁺O₈ trirutiles, all with cell volumes <67.5 Å³.

The unit-cell volume observed for MnSb₂O₄, 66.75 Å³, is similar to those of the rutiles FeSb₂O₄ and CrSb₂O₄, 66.01 and 64.03 Å³, respectively. This is in accordance with the similar radius of Mn³⁺ (HS), 0.65 Å, to the radii of Fe³⁺ (HS), 0.65 Å, and Cr³⁺, 0.62 Å.

The magnetic susceptibility data given in Ref. 1 for the related compounds M₅Sb₂O₈, M = Cr and Fe, and M₅Sb₂O₂, M = Co, Ni and Cu, are in agreement with the ionic models M³⁺Sb⁵⁺O₄ and M²⁺Sb²⁺O₄, respectively. Furthermore, no indications of order/disorder transitions for the M₅Sb₂O₄ compounds were found in that study. Assuming that all Sb ions have the oxidation number +5, the Mn ions in the Mn₅₋ₓSbₓ⁺ₓO₄ rutile phases have a mixed Mn²⁺–Mn³⁺ state, according to the formula Mn₂⁺Mn₁₋ₓSbₓ⁺ₓO₄. There is, however, the possibility that Sb is partly present as Sb⁵⁺ for high x-values in the structures, as well as the possibility that Mn may be partly present as Mn⁴⁺ 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 specify accurate phase boundaries for the rutile phase.

We conclude that rutile phases with compositions Mn₅₋ₓSbₓ⁺ₓO₄, 0 ≤ x ≤ 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-MnSb₂O₆. Upon decomposition, a partially ordered tri-rutile phase is observed for x ≥ 0.27. Our findings are thus in agreement with previous studies, which indicated that Mn₅₋ₓSbₓ⁺ₓO₄ (MnSb₂O₄) can adopt a rutile or tri-rutile structure.

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References

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