

Formation and Structural Properties of SbTaO_4

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The solid-state reaction between Sb_2O_3 and Ta_2O_5 with the formation of SbTaO_4 has been studied by means of time-resolved powder neutron diffraction. High-temperature powder diffraction studies show that no discontinuous phase transitions occur for SbTaO_4 , or for the $\text{Sb}_{1.2}\text{Ta}_{0.8}\text{O}_4$ solid-solution phase at temperatures between 300 and 1300 K. Small changes in the temperature dependence of the unit cell dimensions around 800 K may be caused by a ferro- to paraelectric phase transition.

Time-resolved powder neutron diffraction has proved to be a powerful technique in studying reactions between, for example cement components (calcium aluminates and silicates), additives (like gypsum, calcium carbonate and calcium chloride) and water.^{1,2} The experimental method is hence adequate for studies of reactions involving liquid and solid phases. However, it should also be suitable for studying reactions between solids.

In this work, it was tested how well the solid-state reaction between Sb_2O_3 and Ta_2O_5 under the formation of SbTaO_4 could be studied. The product, SbTaO_4 , is in itself an interesting compound in that it shows ferroelectric properties, and it is reported to undergo a large number of structural phase transitions between room temperature and the ferro- to paraelectric transition temperature.^{3–10} These aspects were studied by means of high-temperature powder X-ray and neutron diffraction.

Experimental

As starting materials for the solid-state reactions, pressed samples (5 cm long, cylindrically shaped rods) of finely crushed mixtures of Sb_2O_3 (Merck, analytical grade) and Ta_2O_5 (Fluka, > 99.9%) were used. The Sb_2O_3 was of the cubic senarmonite type.

Time-resolved powder neutron diffraction (PND) patterns were collected on the D1B diffractometer at the Laue–Langevin Institute, Grenoble, using neutrons of wavelength 252 pm and a 400-cell multidetector covering 80° in 2θ . A vacuum furnace was used during the high-temperature experiments. The heating was accomplished by means of a vanadium resistance heating element surrounding the cylindrical Sb_2O_3 – Ta_2O_5 sample. Recorded intensities were extracted at 2.5–15 min intervals, depending on the reaction rate. The reflections were ascribed to

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different phases and their integrated intensities were evaluated by the INTEGREG program¹¹ and normalized to a standard monitor count. Three-dimensional representations of the diffraction patterns were obtained by the P3DD1B program.¹²

Room-temperature powder X-ray diffraction data were obtained using a Guinier camera ($\text{Cu } K\alpha_1$ radiation, $\lambda = 154.0598$ pm, Si as internal standard¹³). High-temperature powder X-ray diffraction data were collected between 300 and 1300 K using an Enraf–Nonius Guinier Simon camera ($\text{Cu } K\alpha_1$ radiation). Unit cell dimensions were obtained by least-squares refinements using data for some 20 reflections.

Ternary samples of $\text{Sb}_{1+t}\text{Ta}_{1-t}\text{O}_4$ with $0.00 < t < 1.00$ were synthesized by heating weighed amounts of Sb_2O_3 (senarmonite), Sb_2O_4 (cervantite) and Ta_2O_5 in sealed, evacuated silica-glass tubes at 1000 °C for 1 week. In duplicate experiments corundum boats were used in addition. After an intermediate crushing at room temperature, the samples were re-annealed at 1000 °C for 1 week and finally cooled to room temperature during 1 day.

Results and discussion

Time-resolved powder neutron diffraction data for the solid-state reaction between Sb_2O_3 and Ta_2O_5 were obtained at 500, 565, 590 and 600 °C. However, during the experiments it became evident that the rather long heating times required by the furnace system in order to reach the operating conditions made the study of the initial reaction between the two solids at the higher temperatures almost impossible.

The progress of the reaction was evaluated from the collected diffraction data by considering the time dependence of the integrated intensities of Bragg reflections ascribed to reactants and products. The PND diagram contained reflections that were only due to Sb_2O_3 , Ta_2O_5 and

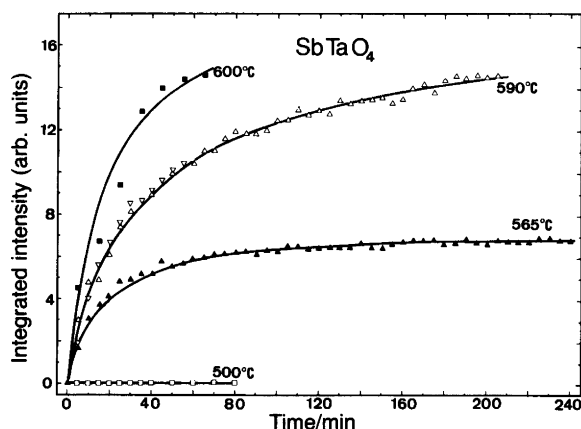


Fig. 1. Integrated intensity of reflections characteristic of the reaction product SbTaO_4 versus time for the reaction between Sb_2O_3 and Ta_2O_5 at temperatures between 500 and 600°C.

the SbTaO_4 product. Results concerning the time dependences are shown in Fig. 1. At low temperatures, e.g. 500°C, no reaction is observed within the first 80 min. However, by 565°C the reaction is fast. As seen in Fig. 1 for the formation of SbTaO_4 , the rather fast initial reaction slows down after 1–2 h and then almost stops, without ever approaching a level corresponding to a completely reacted sample (maximum observed conversion, some 60%, cf. Fig. 1). The intensity–time relation at 590°C can be fitted perfectly by a logarithmic function.

The variation of the integrated intensities with time shows that Sb_2O_3 is consumed faster than Ta_2O_5 . This observation probably reflects two effects: (i) that Sb_2O_3 is rather volatile under the actual conditions and can partly be transferred out of the beam region, and (ii) that the reaction product is a solid solution phase which can be enriched in antimony by some Sb replacing Ta in SbTaO_4 . These complicating features make a more detailed analysis of the kinetics (cf. the intensity–time relation above) impossible. However, the measurements clearly show that the present technique is in principle well suited for studies of the reaction kinetics of solid-state reactions, provided that great

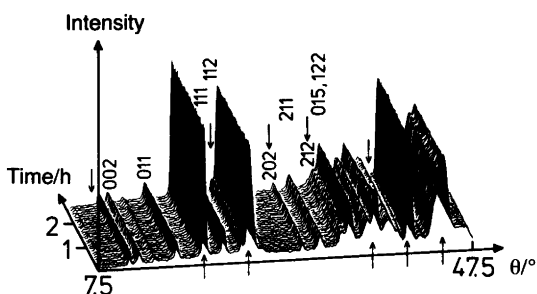


Fig. 2. Three-dimensional plot showing the variation of the neutron diffraction pattern of a Sb_2O_3 – Ta_2O_5 – SbTaO_4 mixture upon cooling from 500°C to room temperature. Indices are given for some reflections from SbTaO_4 . Reflections from Sb_2O_3 are indicated by \downarrow , reflections from Ta_2O_5 by \uparrow . The time scale for the experiment is 3 h.

care is taken in order to select systems where evaporation, the formation of solid solution phases etc. are reduced to an insignificant level.

The high-temperature structural features of SbTaO_4 are unclear.^{3–10} Several reports claim that SbTaO_4 undergoes numerous (up to eight) structural phase transitions connected with considerable volume jumps between room temperature and the ferro- to paraelectric transition temperature of some 400–600°C, whereas a few papers report a more normal, continuous thermal expansion of the unit cell. Upon a continuous slow cooling of the SbTaO_4 reaction product from, e.g., 590°C to room temperature, it should easily be possible to study such features as the additional information provided by the present time-resolved powder neutron diffraction study. A three-dimensional representation of such diffraction patterns (being an analogue to Guinier Simon photographs) is shown in Fig. 2. However, no indications for phase transitions are evident, either in the positions of the Bragg reflections or in their intensity variation. This negative observation was checked and confirmed by high-temperature powder X-ray diffraction studies. (The observed reflections are all somewhat broadened for the reaction product, probably owing to composition inhomogeneities.) Approximate, linear thermal expansion coefficients (space group setting $Pna2_1$) for the temperature interval 300–1100 K are $\alpha_a (= 1/a \times \Delta a / \Delta T) \approx 9 \times 10^{-6}$, $\alpha_b \approx 3.5 \times 10^{-6}$ and $\alpha_c \approx 5 \times 10^{-6} \text{ K}^{-1}$.

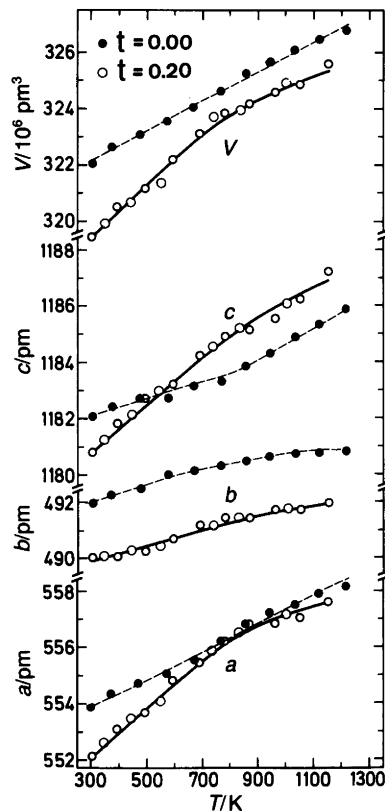


Fig. 3. Variation of unit cell dimensions of SbTaO_4 ($t = 0.00$; broken lines) and $\text{Sb}_{1.2}\text{Ta}_{0.8}\text{O}_4$ ($t = 0.20$; fully drawn lines) between 300 and 1200 K.

The numerous structural phase transitions claimed to occur for SbTaO_4 ^{8,10} were not detected (Figs. 2 and 3). (Note, in this respect, that such multi-transition features have also been reported by Russian research groups for several other ferro- and antiferroelectrics, such as BiTaO_4 ,⁸ LiTaO_3 ,¹⁴ LiNbO_3 ¹⁵ and CdTiO_3 .¹⁶) SbTaO_4 is, in accordance with its polar space group, ferroelectric under ambient conditions.^{4,5,8,10} There are considerable discrepancies in the literature concerning its ferro- to paraelectric transition temperature (values varying between 680 and 870 K).^{5,8,10} Furthermore, the reported unit cell dimensions of SbTaO_4 at ambient temperature vary considerably. In order to shed more light on its confusing nature, new, high-quality samples of SbTaO_4 and of the (possible) solid solution phase $\text{Sb}_{1+t}\text{Ta}_{1-t}\text{O}_4$ ($0.00 \leq t \leq 1.00$) were prepared and studied. Based on a careful visual inspection of the Guinier Simon films for well prepared samples of SbTaO_4 , giving very sharp Bragg reflections, the presence of any (larger) discontinuous phase transition can be ruled out (Fig. 3).

The variation of the unit cell dimensions of $\text{Sb}_{1+t}\text{Ta}_{1-t}\text{O}_4$ shown in Fig. 4 clearly demonstrates a complete solid solution between Sb_2O_4 and SbTaO_4 (present unit cell dimensions for SbTaO_4 , from 49 reflections: $a = 553.91 \pm 0.06$, $b = 491.98 \pm 0.06$, $c = 1182.14 \pm 0.15$ pm). The unit cell dimensions of the reaction product obtained during the on-line time-resolved powder neutron diffraction studies are $a = 552.6 \pm 0.2$, $b = 489.9 \pm 0.2$ and $c = 1180.6 \pm 0.3$

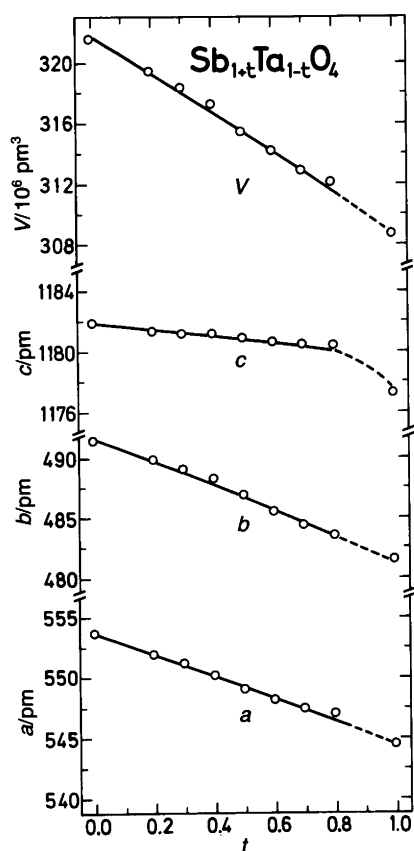


Fig. 4. Variation of unit cell dimensions of $\text{Sb}_{1+t}\text{Ta}_{1-t}\text{O}_4$ with t at room temperature.

pm. When comparing these values with the data in Fig. 4, one is led to infer that the reaction product is not pure SbTaO_4 but belongs to the solid solution phase with a composition parameter $t \approx 0.2$.

Sb_2O_4 crystallizes in the same polar space group as SbTaO_4 . This is also probably the case for the $\text{Sb}_{1+t}\text{Ta}_{1-t}\text{O}_4$ solid solution phase, and the latter should hence also be expected to exhibit cooperative electric properties at low temperature. Earlier studies⁵ (of the second harmonic signal) could not verify this unequivocally, possibly owing to the low crystallinity of the samples. The present high-temperature powder diffraction photographs do not show any indications of discontinuous phase transitions (see results for SbTaO_4 and $\text{Sb}_{1.2}\text{Ta}_{0.8}\text{O}_4$ in Fig. 3). However, the rather slight changes in the temperature dependence of the unit cell dimensions for these phases at some 800 K (Fig. 3) may be caused by the cooperative to paraelectric transition, although this should be substantiated by complementary measurements of physical properties.

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