



High-resolution neutron powder diffraction study on the structure of Sr_2SnO_4

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Abstract

From the high-resolution time-of-flight neutron powder diffraction data, the crystal structure of Sr_2SnO_4 at the temperature range between 4 and 300 K has been investigated. The Rietveld refinement has shown that Sr_2SnO_4 belongs to the space group $Pccn$, which can be derived from the tetragonal K_2NiF_4 structure by tilting the SnO_6 octahedra along the $[100]_{\text{T}}$ - and $[010]_{\text{T}}$ -axis, respectively, with non-equal tilts. The earlier reported first-order phase transition in Sr_2SnO_4 , from $Bmab$ to $P4_2/nm$, has not been observed. © 2002 Elsevier Science (USA). All rights reserved.

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1. Introduction

The ternary oxides of general formula A_2BO_4 crystallize in a variety of ways. In a structure-field map, plotting the radius of A versus the radius of B , the K_2NiF_4 -type structure occurs when $r_A > 1.1 \text{ \AA}$ and $0.6 < r_B < 0.9 \text{ \AA}$ [1]. This includes several deformed K_2NiF_4 structures. For instance, the oxides Ba_2SnO_4 and Ba_2PbO_4 crystallize in the tetragonal space group $I4/mmm$ [1]. On the other hand, Sr_2SnO_4 [2], La_2CuO_4 [3], La_2NiO_4 [4–6] and $\beta\text{-Na}_2\text{UO}_4$ [7] show deformation of the tetragonal archetype, due to the tilting of the BO_6 octahedra.

The K_2NiF_4 -type structure of A_2BO_4 oxides consists of perovskite-like BO_6 octahedral layers separated by a rock salt-like AO layers. This two-dimensional layered structure has received considerable attention in the past years since the discovery of high-temperature superconductivity in the copper oxide-based $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ system [8]. Equal interest is the layered variants of the superconducting perovskites $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ [9] with the general formula $\text{Ba}_{n+1}(\text{Pb}, \text{Bi})_n\text{O}_{3n+1}$ ($n = 1, 2$ and 3) [10–12]. These so-called Ruddlesden–Popper phases show quite different electronic properties. For instance,

Ba_2PbO_4 ($n = 1$) is a large-gap semiconductor [11]. The electric conductivity increases with increasing the number of perovskite-like layers, and becomes essentially metallic for $\text{Ba}_4\text{Pb}_3\text{O}_{10}$ ($n = 3$) [10,12]. Unlike the three-dimensional $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($n = \infty$), however, no superconductivity has been observed in these layered materials.

In a study of the possible deformations of K_2NiF_4 structure, we noticed a recent neutron powder diffraction study on the structure determination of Sr_2SnO_4 [2]. At room temperature, the distortion from the tetragonal aristotype (axes a_0 , a_0 and c_0) was described as due to the tilting of the SnO_6 octahedra around the $[110]_{\text{T}}$ -axis, resulting in the space group $Bmab$ (no. 64) with the new axes $a \approx b \approx \sqrt{2}a_0$ and $c \approx c_0$. At 12 K, the space group was found to be $P4_2/nm$ (no. 138) with the SnO_6 octahedra tilted around the $[100]_{\text{T}}$ -axis, indicating a first-order phase transition below the room temperature. The structure refinements in the space group $Pccn$ (no. 56) were reported to be always inferior to the one carried out in either $Bmab$ or $P4_2/nm$ space group. This model was, therefore, judged to be inappropriate for both the room temperature and the low-temperature structures of Sr_2SnO_4 [2]. However, the space group $Pccn$ is a subgroup of the both above-mentioned space groups. It is rather unexpected that refining in a subgroup gives worse agreement factor than that of the corresponding

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super group. Moreover, although the nature of the phase transition has been described as due to the different soft phonon tilts of the oxygen octahedra, the details of the phase transition have not been characterized and the transition temperature was not determined.

The purpose of the present investigation was to reexamine the crystal structure of Sr_2SnO_4 and to look for details of the phase transition using very high-resolution time-of-flight neutron powder diffraction technique in the temperature range between 4 and 300 K. In this paper we report the new results of the structure of Sr_2SnO_4 .

2. Experimental

A sample of Sr_2SnO_4 for neutron powder diffraction was prepared from SrCO_3 and SnO_2 in an alumina crucible. The mixture was intimately ground and heated in air at 1450 K. After 1-week reaction accompanied with repeated regrinding, the furnace was left to cool to room temperature.

X-ray diffraction patterns were collected with a Philips PW1050 diffractometer using the monochromatic $\text{CuK}\alpha$ in steps of 0.02 degrees (2θ) and 12 s counting time at each step in the 2θ -range $10^\circ < 2\theta < 117^\circ$. High-resolution powder neutron diffraction data were recorded at the ISIS facility, Rutherford Appleton Laboratories. The sample was loaded into a 11 mm diameter vanadium can. The diffraction patterns were recorded in both the backscattering bank and the 90° detector bank, over the time-of-flight range 32–120 and 35–114 ms, corresponding to the d -spacings from 0.6 to 2.5 and 1.0 to 3.3 Å, respectively. The patterns were normalized to the incident beam spectrum as recorded in the upstream monitor, and corrected for detector efficiency according to prior calibration with a vanadium scan. Preliminary scan of the lattice parameters as the function of temperature did not reveal an abrupt change of the a - and b -axis that might indicate a tetragonal to orthorhombic phase transition (see Discussion). Consequently, four patterns were recorded to a total incident proton beam of about $300 \mu\text{A h}$, for approximately 8 h, at $T = 4, 100, 200$ and 300 K, respectively. The structure refinements were performed simultaneously on both backscattering and 90° bank data by the Rietveld method using the GSAS computer program [13].

3. Results

The X-ray diffraction pattern of Sr_2SnO_4 at room temperature showed a single phase. The diffraction peaks could be indexed in a supercell with cell

dimensions: $a \approx b \approx \sqrt{2}a_0$ and $c \approx c_0$, where a_0 and c_0 are the cell parameters of the tetragonal K_2NiF_4 structure.

The structure analysis of the neutron powder diffraction data was first carried out in the space groups $Bmab$ and $P4_2/nm$, respectively, as was previously reported [2]. The Rietveld refinements have indeed confirmed the earlier findings: i.e., the space group $Bmab$ fits better to the data at $T = 300$ K ($R_{\text{wp}} = 3.95\%$ in $Bmab$ vs $R_{\text{wp}} = 4.20\%$ in $P4_2/nm$), whereas the space group $P4_2/nm$ results in a lower R -values for the data at $T = 4$ K ($R_{\text{wp}} = 4.55\%$ in $P4_2/nm$ vs $R_{\text{wp}} = 4.76\%$ in $Bmab$). However, close inspection of high-resolution backscattering bank data has shown that neither $Bmab$ nor $P4_2/nm$ describes correctly the structure of Sr_2SnO_4 . For example, a weak superreflection at the d -value of about 1.37 Å is present at all measured temperatures (Fig. 1). This reflection, which is indexed as (136) in the space group $P4_2/nm$, is not allowed in the space group $Bmab$. On the other hand, the (040) diffraction peak shows noticeable line broadening as compared to that of the (226) diffraction (Fig. 1). This indicates the presence of the orthorhombic distortion. Taking these discrepancies into account, the structure of Sr_2SnO_4 was then modelled with the space group $Pccn$, which is the subgroup of both $Bmab$ and $P4_2/nm$ space groups. The refinements carried out in $Pccn$ resulted in a superior fit of the neutron powder diffraction data at all measured temperatures; the agreement factors are always lower than those obtained in either $Bmab$ or $P4_2/nm$ model (Table 1). Some other models have also been tested. For example, the space group $Pbca$, which is adopted by $\beta\text{-Na}_2\text{UO}_4$ [7], corresponds to a tilt scheme along the $[110]_{\text{T}}$ - and $[001]_{\text{T}}$ -axis, respectively. These refinements did not yield improvement and result in higher values of R_{wp} . We concluded, therefore, that the orthorhombic space group $Pccn$ structure is consistent with the present data, and describes correctly the crystal structure of Sr_2SnO_4 .

Table 1 lists the refined atomic positions and cell parameters. Table 2 gives some selected interatomic distances and angles. The plots of the observed and calculated profiles at some selected temperatures are shown in Fig. 2.

4. Discussion

The space group of Sr_2SnO_4 has once been described to be $Bmab$ ($T = 300$ K) and $P4_2/nm$ ($T = 12$ K), respectively, and the corresponding phase transition is, thus, the first-order in nature [2]. Contrary to these results, our refinements have clearly demonstrated that the space group $Pccn$ resulted always in better fit and describes adequately the high-resolution neutron powder diffraction data in the temperature range between

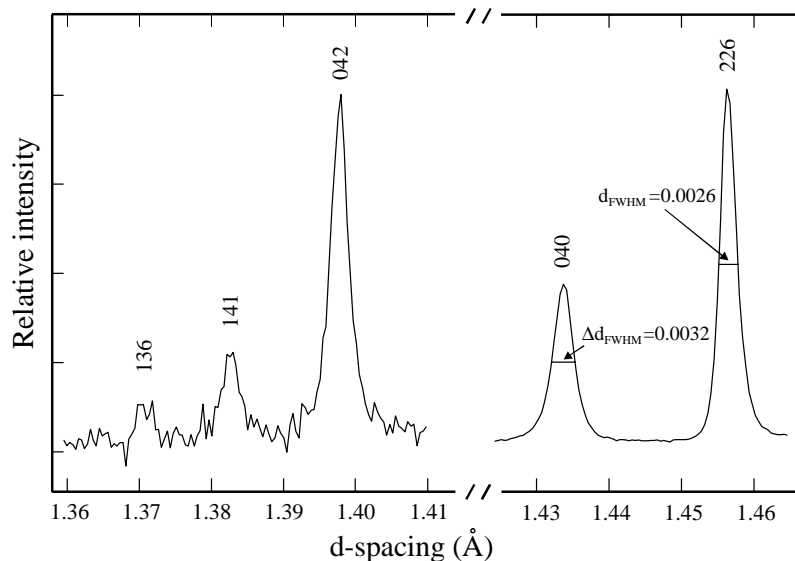


Fig. 1. A section of the high-resolution backscattering raw data of Sr_2SnO_4 at $T = 200$ K, showing the presence of a weak (136) superreflection as well as the line broadening of the (040) reflection. All peaks are indexed in the space group $P4_2/nm$. The significance of them are discussed in the text.

Table 1
Refined atomic positions and cell parameters of Sr_2SnO_4 in $Pccn$ at different temperatures

	300 K	200 K	100 K	4 K
a (Å)	5.73529(4)	5.73505(6)	5.73534(7)	5.73569(8)
b (Å)	5.72873(4)	5.72869(6)	5.72896(7)	5.72910(7)
c (Å)	12.58701(5)	12.55809(6)	12.53442(7)	12.52639(7)
<i>Sr</i> ($8e$) (x, y, z)				
x	0.0082(5)	0.0087(5)	0.0099(5)	0.0104(5)
y	0.0043(5)	0.0066(5)	0.0073(6)	0.0075(6)
z	0.35291(4)	0.35312(4)	0.35333(4)	0.35341(4)
U_{iso}^*	1.42(2)	1.16(2)	0.96(2)	0.84(2)
<i>Sn</i> ($4a$) ($0, 0, 0$)				
U_{iso}^*	1.08(3)	0.97(3)	0.87(3)	0.82(3)
<i>O</i> (1) ($8e$) (x, y, z)				
x	-0.0252(5)	-0.0282(5)	-0.0315(6)	-0.0319(6)
y	-0.0233(5)	-0.0271(5)	-0.0284(6)	-0.0296(6)
z	0.16295(2)	0.16293(7)	0.16295(7)	0.16302(7)
U_{iso}^*	1.91(3)	1.51(3)	1.21(3)	1.12(3)
<i>O</i> (2) ($4c$) ($0.25, 0.25, z$)				
Z	0.0165(2)	0.0188(2)	0.0202(2)	0.0210(1)
U_{iso}^*	1.84(8)	1.42(7)	1.18(7)	1.08(7)
<i>O</i> (3) ($4d$) ($0.25, 0.75, z$)				
Z	0.0029(9)	0.0033(8)	0.0038(8)	0.0036(8)
U_{iso}^*	1.61(8)	1.38(7)	1.14(7)	0.95(3)
R_{wp}	3.73%	3.82%	4.23%	4.36%
R_{p}	3.39%	3.53%	3.95%	4.10%

$$U_{\text{iso}}^* = U_{\text{iso}} \times 100.$$

4 and 300 K. Consequently, a first-order phase transition has not been observed in the present investigation. The fact that such an orthorhombic to tetragonal phase transition is unlikely to occur can also be seen from the

refined lattice parameters as the function of the temperature (Table 1). Upon cooling, the a - and b -axis remain nearly constant, and the c -axis contracts smoothly and continuously. There is no discontinuity

Table 2
Selected atomic distances (Å) and angles (deg) in Sr₂SnO₄ at 4 and 300 K

	4 K	300 K
Sr–O(1)	2.057(1) × 2	2.0605(8) × 2
Sr–O(2)	2.0438(3) × 2	2.0372(3) × 2
Sr–O(3)	2.0272(2) × 2	2.0269(2) × 2
Sr–O(1)	2.407(1)	2.404(1)
	2.636(4)	2.685(3)
	2.663(4)	2.715(4)
	3.087(4) ^a	3.031(4) ^a
	3.121(4) ^a	3.068(3) ^a
Sr–O(2)	2.623(2)	2.649(2)
	2.828(2)	2.854(2)
Sr–O(3)	2.714(8)	2.732(9)
	2.758(8)	2.759(9)
O(1)–Sn–O(2)	90.44(7)	90.37(9)
O(1)–Sn–O(3)	91.0(3)	90.8(4)

^a These Sr–O bonds are too large to be counted into the coordination sphere of Sr atom.

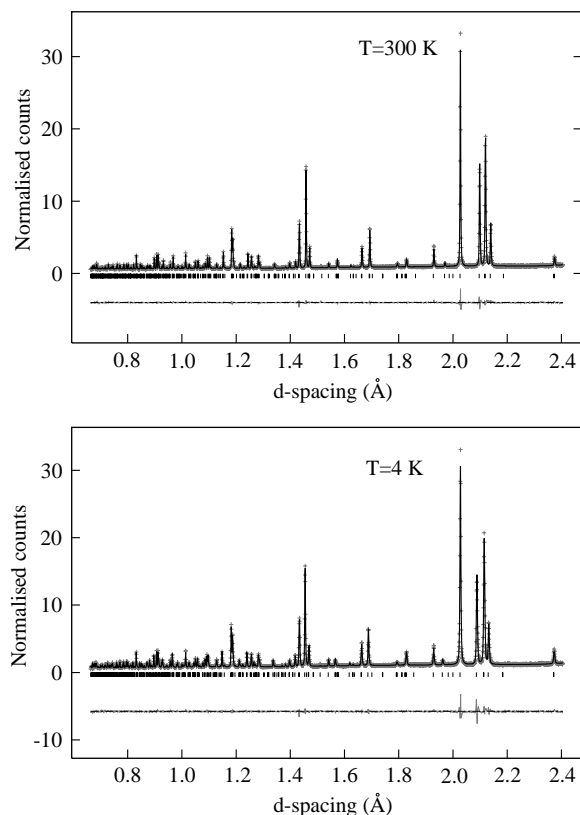


Fig. 2. Observed (crosses) and calculated (continuous line) profiles of Sr₂SnO₄ at $T = 300$ and 4 K. The plots shown are the backscattering bank data. Tick marks indicate the positions of allowed reflections. A difference curve ($I_{\text{obs.}} - I_{\text{cal.}}$) is shown at the bottom.

of the lattice parameters that might suggest a first-order phase transition in Sr₂SnO₄.

The structure of Sr₂SnO₄ can be derived from the K₂NiF₄ aristotype by tilting the normally rigid SnO₆ octahedra. In Sr₂SnO₄ the octahedra share corners to

form a two-dimensional perovskite-like layer. Between these layers the Sr and the apical O atoms form rock salt-like layers (Fig. 3). In the ideal A_2BO_4 (K₂NiF₄) structure, the void for A has about the same size as an O atom. If the radius of A is too small, as is the case in Sr₂SnO₄, the size of void is reduced by tilting of the octahedra. The tilt pattern can be analyzed by using two independent rotation angles, α and β , around the tetragonal [100]_T- and [010]_T-axis, respectively of the undistorted K₂NiF₄ structure (Fig. 3(c)). For $\alpha = \beta$, which is equivalent to a rotation of the octahedra about the [110]_T-axis of the tetragonal structure, the symmetry is lowered to $Bmab$ or to $Amaa$ (no. 66), depending on the rotations of the adjacent layers. For $\alpha = 0$, the space group becomes $P4_2/nm$. For $\alpha \neq \beta$, the space group $Pccn$ should be used. The magnitude of the tilting angles in $Pccn$ can be calculated from the z -coordinate of O(2) and O(3) atoms

$$\alpha = \arctan \frac{z_{\text{O}(3)} \cdot c}{\sqrt{\left(\frac{1}{4}a\right)^2 + \left(\frac{1}{4}b\right)^2}}$$

$$\beta = \arctan \frac{z_{\text{O}(2)} \cdot c}{\sqrt{\left(\frac{1}{4}a\right)^2 + \left(\frac{1}{4}b\right)^2}}$$

The values of α and β at different temperatures are plotted in Fig. 4. As can clearly be seen, the tilting angle α is relatively small and remains virtually constant (1.1° and 1.3° at 300 and 4 K, respectively), but β is fairly larger and increases with decreasing temperature (5.8° and 7.4° at 300 and 4 K, respectively). Since the tilting angle β is about a basal plane diagonal of the enlarged unit cell, the orthorhombic strain persists upon cooling, whereas the c -axis steadily shrinks.

It is interesting to review that the refinements of neutron diffraction data using only the space groups $Bmab$ and $P4_2/nm$ do support one structure model over the other at different temperatures. This may arise from the systematic change of the tilting angle as was determined in the space group $Pccn$. As was mentioned above, the orthorhombic space group $Bmab$ is characterized by equal tilts of α and β . When the difference between α and β is relatively small, e.g., at room temperature, the $Bmab$ model leads to a superior fit. At low temperature, however, the difference between α and β becomes larger. The space group $P4_2/nm$ resulted in a better fit despite the presence of orthorhombic strain. Thus, the observed apparent phase transition may well be accidental.

In Sr₂SnO₄, the SnO₆ octahedra are slightly elongated, with the averaged Sn–O bond distance of 2.0415 Å (Table 2). This value is in excellent agreement with that obtained from the sum of the Shannon's ionic radii (2.09 Å) [14]. In the undistorted K₂NiF₄ structure,

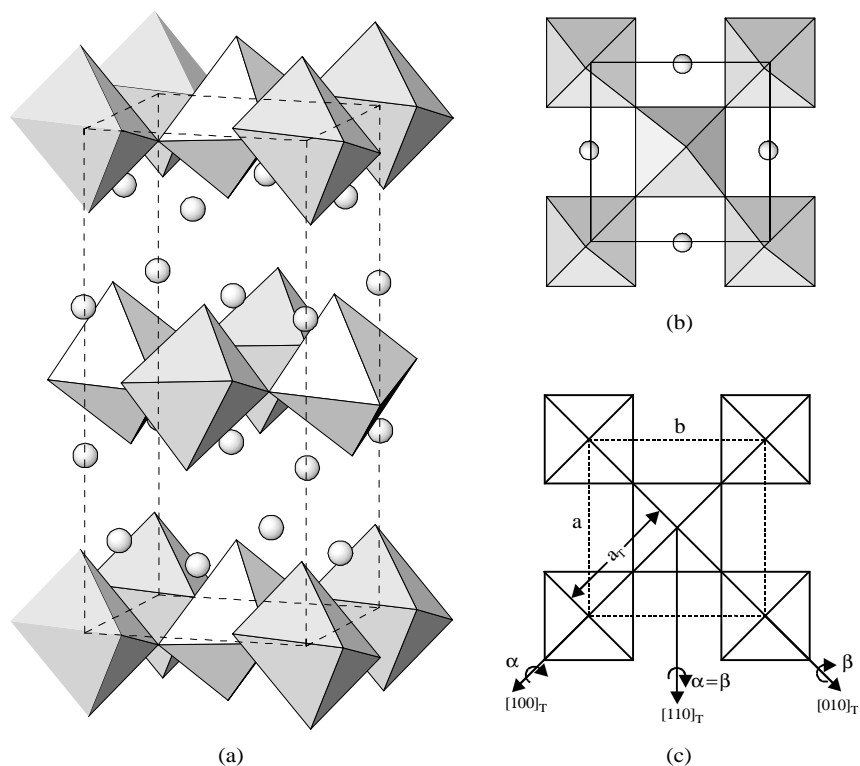


Fig. 3. (a) Structure of Sr_2SnO_4 . Only SnO_6 octahedra and Sr atoms are shown. (b) A projected view of SnO_6 layers in Sr_2SnO_4 along the c -axis. The octahedral tilting can clearly be seen. (c) Schematic drawing of the tilt pattern using two independent rotation angles around the tetragonal $[100]_{\text{T}}$ and $[010]_{\text{T}}$ -axis of the undistorted K_2NiF_4 structure. The space groups derived from the tilts are discussed in the text.

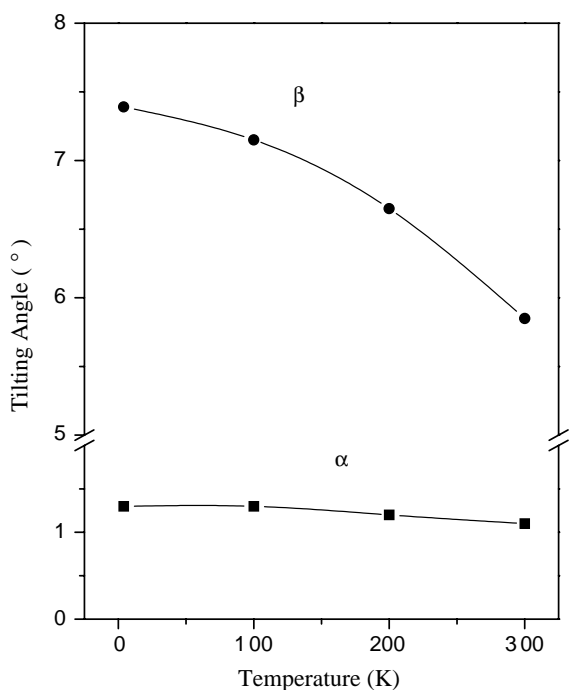


Fig. 4. Tilting angles of α and β in Sr_2SnO_4 at different temperatures.

the larger cation is surrounded by nine anions. This coordination number is, however, reduced to seven in Sr_2SnO_4 due to the tilting of the SnO_6 octahedra. As can

be seen from the Table 2, two of the Sr–O(1) bonds are relatively too large to be counted into the coordination sphere of Sr atom.

A related structural problem is found in La_2NiO_4 . Above about 770 K, it has the tetragonal K_2NiF_4 structure. Below this temperature, it transforms to the orthorhombic $Bmab$ structure [4], and at 80 K to the tetragonal $P4_2/nm$ structure [5,6]. The later phase transition is associated with a strong micro strain, producing significantly anisotropic broadening of the Bragg reflections. However, no discontinuity in the cell volume as well as in the c -axis is observed at the phase transition in La_2NiO_4 [5]. Sr_2SnO_4 did not show such a sort of broadening at low temperature. On the other hand, a continuous decrease of the tilting angle β with increasing of the temperature may suggest possible phase transitions, such as $Pccn \rightarrow Bmab \rightarrow I4/mmm$ or $Pccn \rightarrow I4/mmm$, at elevated temperature. High-resolution powder neutron diffraction experiments above the room temperature are in progress.

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