

Neutron powder diffraction study of phase transitions in Sr_2SnO_4

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Received 4 March 2004; received in revised form 16 June 2004; accepted 17 August 2004

Available online 7 October 2004

Abstract

The phase transitions in Sr_2SnO_4 at high temperature have been studied using high resolution time-of-flight powder neutron diffraction. The room temperature structure of Sr_2SnO_4 is orthorhombic (*Pccn*), which can be derived from the tetragonal K_2NiF_4 structure by tilting the SnO_6 octahedra along the tetragonal $[100]_{\text{T}}$ - and $[010]_{\text{T}}$ -axes with non-equal tilts. At the temperature of about 423 K, it transforms to another orthorhombic structure (*Bmab*) characterized by the SnO_6 octahedral tilt around the $[110]_{\text{T}}$ -axis. At still higher temperatures (~ 573 K) the structure was found to be tetragonal K_2NiF_4 -type (*I4/mmm*).

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Keywords: High-resolution neutron powder diffraction; Crystal structure; Phase transition

1. Introduction

Phase transitions between the different structural variants of the ternary $A_2\text{BO}_4$ oxides with the K_2NiF_4 -type structure have received considerable attention in the past years since the discovery of high- T_c superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ [1]. This two-dimensional structure consist of perovskite-like corner linked BO_6 sheets interleaved by the rock salt-like AO layers, in which the large *A* cations are arranged in the plane formed by O atoms at the top (or bottoms) of the octahedra with nine nearest O neighbors.

One important factor that determines the structure of the $A_2\text{BO}_4$ compounds is the matching between the perovskite-like BO_6 layers and the rock salt-like AO layers. A measure of the bond-length matching is given by the Goldsmidt tolerance factor: $t = (r_A + r_O) / \sqrt{2}(r_B + r_O)$. Ideal matching occurs for $t \approx 1$, and the structure is tetragonal with the space group *I4/mmm*

(no. 139). Examples are the oxides with bigger *A* cations, e.g., Ba_2SnO_4 [2] and Ba_2PbO_4 [3]. On the other hand, the La_2MO_4 ($M = \text{Co}, \text{Ni}, \text{Cu}$) compounds have larger bond-length mismatch ($t < 1$) and show orthorhombic deformation of the tetragonal archetype due to the tilting of the octahedra [4–8]. The description of the space groups that may occur in $A_2\text{BO}_4$ due to the tilting of the rigid BO_6 octahedra has been reviewed by Hatch et al. [9].

Sr_2SnO_4 was also known to have the K_2NiF_4 -type structure. The structure of this compound has been described by Weiss et al. and Kennedy to be tetragonal with the space group *I4/mmm* [10,11]. Green et al. showed, from neutron powder diffraction study, the distortion from the tetragonal archetype [12]. At room temperature, the distortion of Sr_2SnO_4 was described as due to the tilting of the SnO_6 octahedra around the tetragonal $[110]_{\text{T}}$ -axis, resulting in the space group *Bmab* (no. 64) with an enlarged cell of $a \approx b \approx \sqrt{2}a_{\text{T}}$ and $c \approx c_{\text{T}}$, where a_{T} and c_{T} are the cell constants of the tetragonal structure. At 12 K, the space group was found to be *P4₂/ncm* (no. 138) with the SnO_6 octahedra tilted around the $[100]_{\text{T}}$ -axis. Since no group–subgroup relationship exists, a first-order phase transition was

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expected to occur below the room temperature [12]. However, the present authors have demonstrated [13], by using very high-resolution powder neutron diffraction technique, that the structure of Sr_2SnO_4 , at the temperature range between 4 and 300 K, belongs to the orthorhombic space group $Pccn$ (no. 56), which is the subgroup of both $Bmab$ and $P4_2/nm$ space groups. This space group can be derived from the tetragonal archetype by tilting the SnO_6 octahedra around the $[100]_T$ - and $[010]_T$ -axes (denoted as α and β), respectively, with non-equal tilts. Consequently, the earlier reported first-order phase transition from $Bmab$ to $P4_2/nm$ in Sr_2SnO_4 at low temperature has not been observed.

The present investigation is devoted to the study of the phase transitions that may occur in Sr_2SnO_4 . For many distorted $A_2\text{BO}_4$ oxides, increasing of temperature has, generally, the effect of decreasing the tilting angles, and, hence, the phase transition to the tetragonal archetype may occur at high temperature. La_2NiO_4 and La_2CuO_4 are, for example, both orthorhombic at room temperature with the space group $Bmab$, and become tetragonal ($I4/mmm$) at 770 K [5] and 533 K [8], respectively. In Sr_2SnO_4 , a continuous decrease of the tilting angle β with increasing temperature has previously been observed that may suggest possible phase transitions, such as $Pccn \rightarrow Bmab \rightarrow I4/mmm$ or $Pccn \rightarrow I4/mmm$, at elevated temperature [13]. We have, therefore, carried out the crystal structure study of Sr_2SnO_4 above the room temperature using high-resolution time-of-flight powder neutron diffraction technique, and report the results in this paper.

2. Experimental

The 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 one-week reaction accompanied with repeated regrinding, the furnace was left to cool to room temperature.

The sample's purity was checked by X-ray diffraction on a Philips PW 1050 diffractometer using $\text{CuK}\alpha$ radiation. High-resolution powder neutron diffraction data were collected on HRPD at the ISIS facility, Rutherford Appleton Laboratories. The sample was loaded into an 11 mm diameter vanadium can, which is then placed into the furnace. 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 spacings from 0.6 to 2.5 Å 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 vana-

dium rod. The patterns were recorded to a total incident proton beam of about 120 μAh , for approximately 4 h. The structure refinements were performed simultaneously on both back-scattering and 90° bank data by the Rietveld method using the GSAS computer program [14].

3. Results

Examination of the high-resolution backscattering data as the function of temperature has revealed the subtle structural changes (Fig. 1). From room temperature to about below 423 K, the (040) diffraction peak, although remains single within the instrument resolution, shows noticeable line broadening as compared to the (226) diffraction. The structure of Sr_2SnO_4 in this temperature range is, therefore, described in the orthorhombic space group $Pccn$, as was reported earlier [13]. At the temperature of about 423 K the (040) diffraction peak splits, indicative of a phase transition to another orthorhombic structure. As the temperature further increases, the peak splitting decreases progressively and merges to a single peak at about 573 K (Fig. 1). Since the remerged peak shows no more line broadening, it suggests that Sr_2SnO_4 becomes tetragonal.

The first structural change is not likely to occur within the space group $Pccn$, since the observed orthorhombic strain, first increasing and then decreasing, is not expected from the systematic change of tilting angles

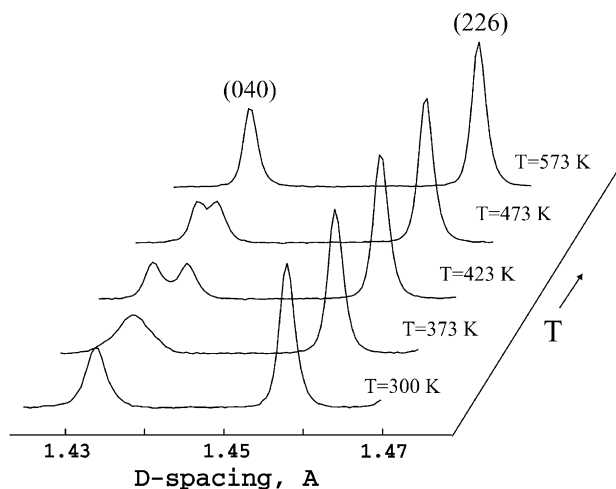


Fig. 1. A section of the high-resolution backscattering raw data of Sr_2SnO_4 , showing (040) and (226) reflections (indexed in $I4/mmm$), at different temperatures. Between room temperature and below about 423 K, the space group is $Pccn$, as was shown by a noticeable line broadening of the (040) reflection. At about 423 K, the splitting of (040) reflection is clearly resolved, indicating the transformation to orthorhombic $Bmab$. At above about 573 K, the structure of Sr_2SnO_4 is tetragonal (see discussion in the text).

[13]. Close examination showed also that some weak hkl reflections with $k+l=2n$ disappear across the structural change. Thus the neutron diffraction data can logically be explained with the space group $Bmab$, which is the supergroup of $Pccn$. This space group has been found in a number of orthorhombically distorted A_2BO_4 -type oxides, such as La_2CoO_4 [4], La_2NiO_4 [5], La_2CuO_4 [8] and $CaNdGaO_4$ [15], and is, thus, used to model the structure of Sr_2SnO_4 at the temperature between 423 K and below 573 K. Rietveld refinement of powder neutron diffraction data in $Bmab$ yielded satisfactory results.

The second phase transition at above about 573 K is also accompanied by the disappearance of the superlattice reflections, which are associated with the enlargement of the unit cell due to the octahedral tilts. Therefore, the structure of the observed tetragonal phase could easily be described in the space group $I4/mmm$.

Table 1 summarizes the refined atomic positions and the thermal parameters at various temperatures. Fig. 2 shows a few examples of the observed high-resolution backscattering and calculated profiles. Table 2 lists some interatomic distances and angles at some selected temperatures.

4. Discussion

As was mentioned above, the structural change at about 423 K was described as due to the space group change from the $Pccn$ to $Bmab$. This can also be seen by inspecting the refined atomic positions in the space group $Pccn$. For example, the Rietveld refinement of the powder neutron diffraction data at $T=423$ K showed that the shift of Sr atoms in x -direction is insignificant ($x_{Sr}=0.0001(9)$). Also the x -coordinate of the apical oxygen, which is a measure of the difference of two independent tilts around the tetragonal $[100]_T$ - and $[010]_T$ -axes, respectively, becomes distinctly small, $x_{O(3)}=-0.008(1)$. Considering further that the agreement factor in $Pccn$ ($wR_p=4.28\%$) is only marginally lower than that in $Bmab$ ($wR_p=4.46\%$), we concluded that the space group $Bmab$ describes correctly the structure of Sr_2SnO_4 at the temperature above about 423 K and below about 573 K.

The structures that occur in Sr_2SnO_4 at different temperature can logically be derived from the tetragonal K_2NiF_4 archetype by tilting the SnO_6 octahedra. The tilting pattern can be analyzed by considering two independent rotation angles around the tetragonal $[100]_T$ - (α) and $[010]_T$ -axes (β), respectively [13]. At high

Table 1
Refined atomic positions and thermal parameters of Sr_2SnO_4 at some selected temperatures

T (K)	300	373	423	473	573	673	773	873
Space group	$Pccn$		$Bmab$		$I4/mmm$			
a (Å)	5.72898 (5)	5.72635(4)	5.72395(3)	5.72735(4)	4.05493(1)	4.05919(1)	4.06375(1)	4.06817(1)
b (Å)	5.73524(5)	5.73787(4)	5.74073(4)	5.73724(4)				
c (Å)	12.58110(6)	12.60639(7)	12.62308(6)	12.64111(5)	12.66944(5)	12.68423(5)	12.69851(6)	12.71169(6)
Sn	4a (0,0,0)		Sn 4a (0, 0, 0)		Sn 2a (0, 0, 0)			
U_{iso}^*	0.89(4)	1.07(4)	U_{iso}^* 1.26(4)	1.32(4)	U_{iso}^* 1.34(4)	1.44(4)	1.49(4)	1.59(4)
Sr	8e (x, y, z)		Sr 8f (0, y, z)		Sr 4e (0, 0, z)			
x	0.0045(7)	0.0031(7)	y 0.0064(3)	0.0048(3)	z 0.35231(5)	0.35217(6)	0.35208(6)	0.35190(6)
y	0.0087(8)	0.0068(5)	z 0.35268(5)	0.35259(5)	U_{iso}^* 2.13(3)	2.42(3)	2.53(3)	2.90(4)
z	0.35276(5)	0.35257(6)	U_{iso}^* 1.63(3)	1.79(3)	O(1) 4c (0, 0.5, 0)			
U_{iso}^*	1.27(3)	1.52(3)	O(1) 8e (0.25, 0.25, z)		U_{iso}^* 2.85(3)	3.13(3)	3.23(3)	3.64(4)
O(1)	4c (0.25,0.25, z)		z 0.0089(1)	0.0072(2)	O(2) 4e (0, 0, z)			
z	0.0174(3)	0.0145(4)	U_{iso}^* 2.27(3)	2.39(3)	z 0.16303(9)	0.16291(9)	0.16288(9)	0.16270(10)
U_{iso}^*	1.8(1)	2.6(1)	O(2) 8f (0, y, z)		U_{iso}^* 3.26(3)	3.56(3)	3.76(4)	4.28(4)
O(2)	4d (0,75,0.25, z)		y -0.0244(4)	-0.0199(4)				
Z	0.0028(9)	0.0044(9)	z 0.16310(8)	0.16304(8)				
U_{iso}^*	1.5(1)	1.4(1)	U_{iso}^* 2.51(4)	2.71(4)				
O(3)	8e (x, y, z)							
x	-0.0234 (7)	-0.0176(7)						
y	-0.0251(8)	-0.0241(6)						
z	0.16271(9)	0.16288(9)						
U_{iso}^*	1.76(4)	2.17(4)						
wR_p (%)	4.19	4.61	4.46	4.45	4.81	4.91	5.03	5.14
R_p (%)	3.71	3.85	3.83	3.80	4.02	4.05	4.15	4.23

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

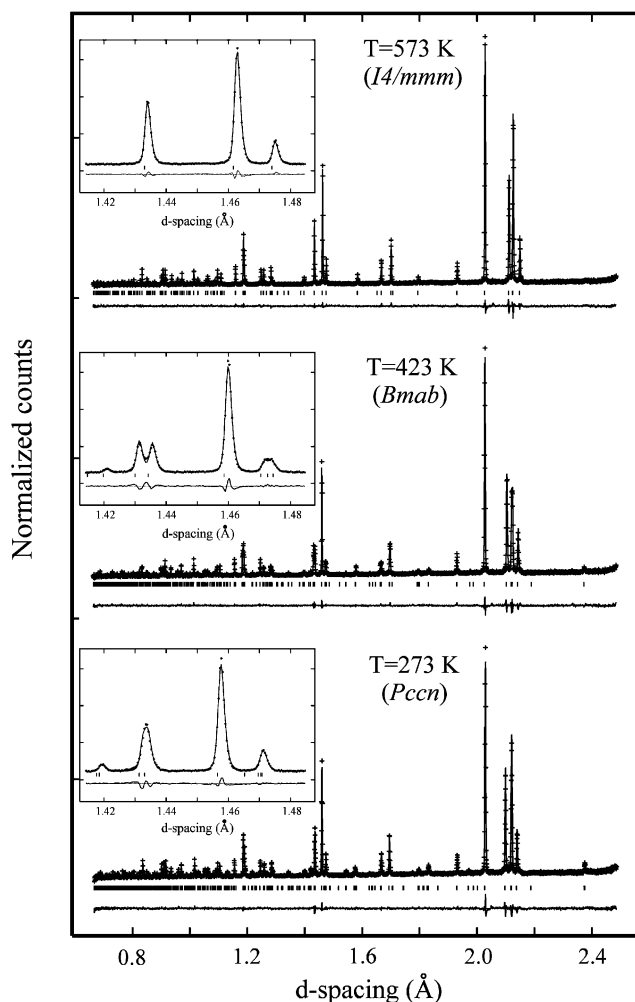


Fig. 2. Observed (+) and calculated (–) profiles of Sr_2SnO_4 at $T=373$ K, 423 K and 573 K in the space groups $Pccn$, $Bmab$ and $I4/mmm$, respectively. Insets illustrate an enlarged region that contains the critical reflections showing the structural changes. Tick marks indicate the positions of allowed reflections by each space group. A difference curve ($I_{\text{obs}} - I_{\text{cal}}$) is shown at the bottom.

temperature ($T \geq 573$ K), there are no tilts ($\alpha = \beta = 0$), and the corresponding space group is $I4/mmm$. As the temperature is lowered to below about 573 K, the SnO_6 octahedra tilt around both $[100]_T$ - and $[010]_T$ -axes with equal tilts ($\alpha = \beta \neq 0$), which is equivalent to the tilting of the SnO_6 octahedra around the tetragonal $[110]_T$ -axis. This results in the space group $Bmab$. At still lower temperature ($T \approx 423$ K), the tilting angles of α and β are no more equal ($\alpha \neq \beta \neq 0$), and the symmetry is lowered to $Pccn$. The space group $Pccn$ persists down to 4 K [13].

The temperature dependence of the tilting angles in Sr_2SnO_4 is shown in Fig. 3. In the $Bmab$ phase region the tilting angle around the tetragonal $[110]_T$ -axis increases steadily with decreasing temperature. In the $Pccn$ phase, however, the amplitude of the tilting angles is quite different. The tilting angle β is fairly larger and increases with decreasing temperature increases, but the

Table 2
Selected interatomic distances (Å) and angles (deg) in Sr_2SnO_4 at some selected temperatures

	373 K	423 K	573 K
Sr–O(1)	2.060 (1) × 2	2.064 (1) × 2	2.066 (1) × 2
Sr–O(2)	2.0348 (5) × 2	2.0298 (1) × 4	2.0275 (1) × 4
Sr–O(3)	2.0274 (4) × 2		
Sr–O(1)	2.401 (1)	2.400 (1)	2.398 (1)
	2.700 (3)	2.701 (2)	2.87385 (8) × 4
	2.753 (4)	2.8708 (2) × 2	
	2.990 (5) ^a	3.053 (4) ^a	
	3.054 (3) ^a		
Sr–O(2)	2.661 (4)	2.695 (2) × 2	2.7590 (5) × 4
	2.848 (4)	2.809 (2) × 2	
Sr–O(3)	2.724 (10)		
	2.777 (10)		
O(1)–Sn–O(2)	90.4 (2)	90.42 (7)	90
O(1)–Sn–O(3)	90.8 (4)		

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

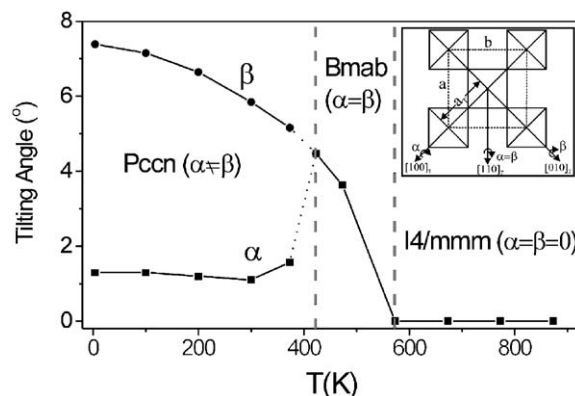


Fig. 3. Temperature dependence of the tilting angles in Sr_2SnO_4 . Inset shows two independent tilting angles, around the $[100]_T$ - (α) and $[010]_T$ -axes (β) of the tetragonal archetype.

tilting angle α is relatively small and remains virtually constant at low temperature.

In Sr_2SnO_4 , the SnO_6 octahedra are slightly elongated (Table 2). The Sr–O bond distances change insignificantly due to the tilting of the SnO_6 octahedra, and their mean value is in good agreement with that obtained from the sum of Shannon's ionic radii (2.09 Å) [16]. On the other hand, the octahedral tilt results in large changes in the Sr–O distances. In tetragonal $I4/mmm$ phase, the Sr atoms have nine coordinated oxygens with one relatively short Sr–O bond linked with the apical O atom of the above or below SnO_6 octahedral. In orthorhombic $Bmab$ and $Pccn$ phases, the tilting of the SnO_6 octahedra results in some Sr–O bond distances that are too large to be

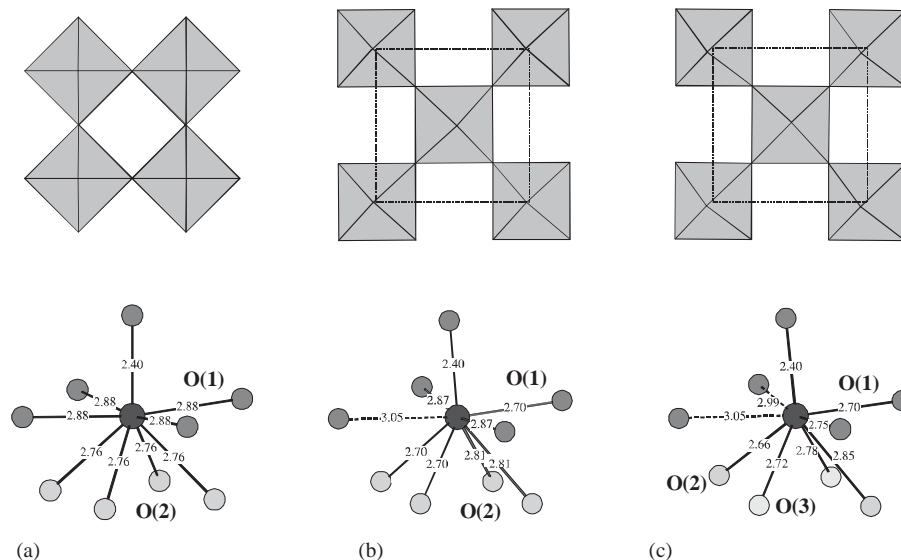


Fig. 4. A projected view of the SnO₆ octahedra (above) and the arrangement of oxygens about Sr (below) in Sr₂SnO₄ in the space groups *I4/mmm* (a), *Bmab* (b) and *Pccn* (c), respectively. Note that different tilting of the SnO₆ octahedra can clearly be seen. The Sr–O bonds that are too large to be counted into Sr coordination sphere are shown with dashed lines.

counted into the coordination sphere of Sr atom (Table 2); the Sr atoms are effectively coordinated with eight and seven oxygens, respectively (Fig. 4). Evidently, the reduction of coordination number of larger cations reflects the response of the compound to the bond-length mismatch between the SnO₆ and SrO layers. The tolerance factor of Sr₂SnO₄ is $t = 0.917$, showing that the Sr–O distances are somewhat smaller to match the perovskite layers. The tilting of the SnO₆ octahedra reduces the coordination number of Sr, so that the smaller Sr may accommodate in the structure.

The phase sequence of *I4/mmm* → *Bmab* → *Pccn* that occurs in Sr₂SnO₄ with decreasing temperature is what one would expect for a distorted *A₂BO₄*-type oxide, in which the distortion is caused by the octahedral tilt. It conforms also to with the group–subgroup relation. The nature of the phase transitions could not be, at present, explored in detail, since no sufficient data have been measured close to the phase transition temperatures. We notice, however, that the cell volume, as the function of temperature, changes quasi-linearly in the *I4/mmm* and *Bmab* phase regions (Fig. 5). This, together with the systematic changes in the lattice parameters, indicate that the *I4/mmm* → *Bmab* phase transition is likely to be continuous. On the other hand, the change of the cell volume, except at very low temperature, is also linear across the *Bmab* → *Pccn* phase transition, but characterized by a different slope. This may suggest that the later phase transition is first order in character.

It is interesting to note that the observed phase transitions in Sr₂SnO₄ appear to be a common feature

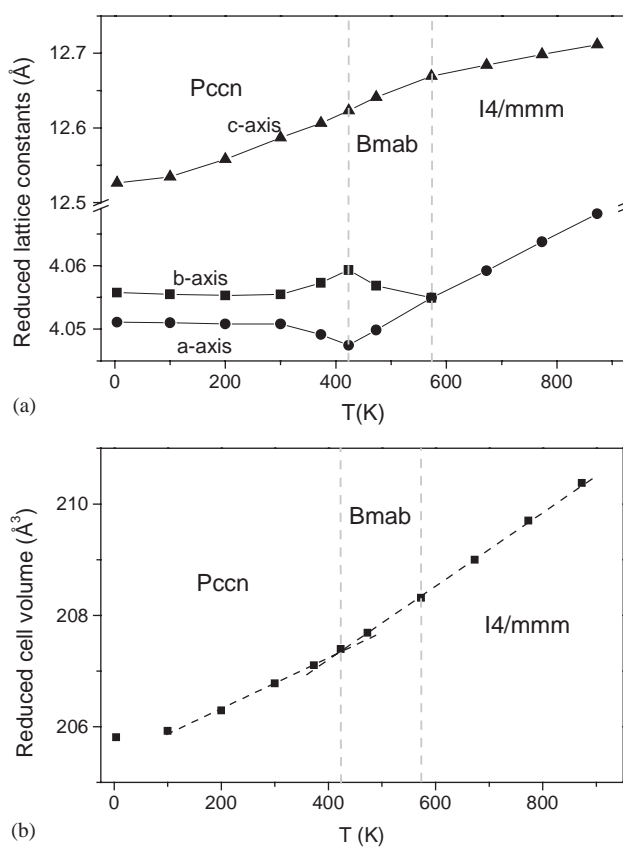


Fig. 5. Temperature dependence of: (a) reduced cell constants and (b) reduced cell volume in Sr₂SnO₄. The reduced cell constants and volume of the orthorhombic *Bmab* and *Pccn* structures are defined as $a_r = a/\sqrt{2}$, $b_r = b/\sqrt{2}$, $c_r = c$ and $V_r = V/2$. Note that the linear change of cell volume shows different slope across the *Pccn* → *Bmab* phase transition.

shared by other distorted A_2BO_4 -type oxides. In fact, the quite similar structural phase transitions have already been observed in, for example, La_2NiO_4 [5,6,17] and superconducting $\text{La}_{1-x}\text{Ba}_x\text{CuO}_4$ [18,19]. The high temperature form of these oxides is tetragonal $I4/mmm$. They transform into the orthorhombic $Bmab$ structure when the temperature is lowered. At still lower temperature of about 80 K and 30 K, respectively, they undergo another “anomalous” phase transition to a structure characterized by merging the orthorhombic splitting of diffraction peaks, but with significant line broadening of the remerged peaks. Although this low temperature structure was believed to be tetragonal $P4_2/nm$ and the observed line broadening was attributed either to the grain size effect [19] or to the microstrain [5], the possibility of the $Bmab \rightarrow Pccn$ phase transition was, as noticed by the authors, not discarded since it depicts equally well the observed diffraction patterns [6,19]. Rodríguez-Carvajal et al. have, in their neutron powder diffraction study on La_2NiO_4 [5], considered the micro-strain and derived a model that may account for the anisotropic line broadening of the (hkl) diffractions with $h \neq k$. This model was based, however, on the presence of micro-twins, characterized by the octahedral tilting axis being orthogonal from one domain to another, when the phase transition $I4/mmm \rightarrow Bmab$ takes place [5]. Inspection of the line profile of Sr_2SnO_4 across the same phase transition did not reveal any particular broadening associated with such micro twins. For example, the refined profile parameters of σ_1^2 (Gaussian) and γ_1 (Lorentzian) at 573 K ($I4/mmm$) ($\sigma_1^2 = 342$, $\gamma_1 = 22.4$) and 473 K ($Bmab$) ($\sigma_1^2 = 354$ and $\gamma_1 = 23.9$), respectively, differ only marginally. In addition, since the presence of the twins implies that the a - and b -axes of the $Bmab$ phase alternate across the twin domains [5], all (hkl) diffractions except for (00l)-type diffractions would show broadening across the $I4/mmm \rightarrow Bmab$ phase transition. We did not observe such anisotropic broadening neither (see Fig. 1 and insets in Fig. 2). Therefore, we concluded that the density of twin boundaries in Sr_2SnO_4 should be, if any, very low to produce significantly anisotropic broadening. It should be pointed out that the strain model [5], describing the anisotropic line broadening of the (hkl) diffractions with $h \neq k$, is basically identical to an orthorhombic structure. In a previous paper [13], we have shown that the space

group $Pccn$ is consistent with the observed structure of Sr_2SnO_4 at the temperature between 4 K and room temperature. The present investigation on the phase transitions in Sr_2SnO_4 at high temperature may, therefore, be helpful in understanding the structural properties of the A_2BO_4 -type oxides.

Acknowledgment

Financial support from the Netherlands Organisation for Scientific Research (NWO) for this work is gratefully acknowledged.

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