

On the Structure of SrZrO₃

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Received November 26, 1990; in revised form April 15, 1992; accepted April 16, 1992

The structure of SrZrO₃ was studied from room temperature up to 1373 K. It was found that there are only minor structural changes. At room temperature SrZrO₃ was found to crystallize with either pseudocubic or orthorhombic symmetry, probably due to differences in preparation temperature and impurities. The sample studied could be indexed on the basis of a doubled cubic perovskite cell, with $a = 0.8206(1)$ nm; the space group is $P2_13$. Around 1023 K there is a transformation to space group $P2_1/n\bar{3}$, with $a = 0.8270(1)$ nm at 1063 K. Another, very smooth phase transformation, which probably results in space group $Pm\bar{3}m$, starts around 1273 K, with $a = 0.8287(2)$ nm at 1323 K. © 1992 Academic Press, Inc.

1. Introduction

The structural behavior of SrZrO₃ has been the subject of many investigations. Zachariassen (1), Hoffmann (2), and Megaw (3) indexed the room temperature structure of SrZrO₃ according to the ideal perovskite structure, although Megaw (3) suggested that probably all three cell edges had to be doubled. Later, Smith and Welch (4) showed that the room temperature structure of their sample could be indexed satisfactorily by assuming a cubic unit cell having approximately twice the normal a value. This structure will be referred to here as pseudo-cubic. Roth (5) made a classification of the $A^{2+}B^{4+}O_3$ perovskite-type oxide structures based on ionic radii of the constituent metal ions. In his diagrams SrZrO₃ falls in the pseudo-cubic region, at the border of the orthorhombic region. Nevertheless, Roth (5) determined an orthorhombic structure for several SrZrO₃ samples. An ortho-

rhombic structure for SrZrO₃ at room temperature was also observed by Carlsson (6), Swanson *et al.* (7), and Tilloca and Perez y Jorba (8), and by Ahtee *et al.* (9), who used neutron powder diffraction.

The high-temperature behavior of an orthorhombic sample of SrZrO₃ was studied by Carlsson (6) and by Ahtee *et al.* (10). Carlsson (6) found phase transformations at 1003, 1133, and 1443 K, corresponding with the formation of two different pseudo-tetragonal phases and a pseudo-cubic phase. Ahtee *et al.* (10), however, found an orthorhombic phase at 1033 K and a tetragonal phase at 1173 K. Carlsson (6) confirmed the 1003 and 1133 K phase transformations by DTA. However, the thermodynamic functions of SrZrO₃ do not show measurable enthalpies of transition (12). At 2273 K SrZrO₃ has the ideal perovskite-type structure, according to Traverse and Foex (11).

Since at room temperature SrZrO₃ seems to be at the border of the orthorhombic re-

gion and the pseudo-cubic region (5), impurities of any kind could influence the structural behavior enormously. Therefore, literature data have been used to evaluate the effect of impurities on the structural behavior. In addition, we studied the structure of SrZrO_3 from room temperature up to 1373 K.

2. Experimental

SrCO_3 (Baker) was dried at 673 K in air. ZrO_2 (Riedel de Haën A.G.) was heated to 1423 K in air to remove adsorbed water. Equimolar amounts of SrCO_3 and ZrO_2 were weighed and thoroughly mixed in an argon-filled glove box. The mixture was pressed and heated in air at 1423 K for 16 hr in an Al_2O_3 crucible. An underlying pellet of SrZrO_3 was used to prevent reaction with the crucible. No reflections from starting materials or impurities were observed in the X-ray pattern. The sample was thoroughly pulverized and heated at 1423 K for another 16 hr, to make sure that the reaction was complete. The color of the SrZrO_3 was palish white.

Impurities were determined by chemical analysis; the Hf percentage in the ZrO_2 starting material was determined by neutron activation. The results are listed in Table I. Room temperature lattice constants were determined using $\text{CuK}\alpha_1$ radiation (0.1540598 nm) and $\text{CuK}\alpha_2$ radiation (0.1544434 nm), using back-reflections and an internal standard of W ($a_0 = 0.316540$ nm). High-temperature measurements (Fig. 1) were performed from room temperature up to 1373 K with a Guinier-Lenné camera, using a Pt grid. Lattice constants at 1063 and 1323 K were obtained with $\text{CuK}\alpha_{1,2}$ radiation (0.15418 nm) in the 3° – 80° range, using α - SiO_2 (hexagonal, $a_0 = 0.49133$, $c_0 = 0.54053$ nm) as an external reference. Possible heat effects were measured using a Met-

TABLE I
IMPURITIES IN SrZrO_3 , IN mg/g,
AS DETERMINED BY CHEMICAL
ANALYSIS

Al	0.17
Si	2.0
Ca	0.10
Ba	0.047
Fe	0.084
Mg	0.022
Ti	0.18
Hf ^a	7.31

^a Hf was determined by neutron activation in the ZrO_2 starting material and calculated for SrZrO_3 .

tler TA-13 differential scanning calorimetry (DSC) apparatus.

3. Results

The room temperature Guinier-de-Wolff recording of SrZrO_3 , prepared as described above, did not show any line-splitting that could indicate an orthorhombic structure. Its back-reflection pattern showed only splitting due to $\text{CuK}\alpha_1$ and $\text{CuK}\alpha_2$ radiation. On these grounds its structure was determined to be cubic. The lattice parameter was determined from the back-reflection pattern to be 0.8206(1) nm. No systematic absences were observed in the Guinier-de-Wolff recording. Since space group $P23$ cannot be used satisfactorily, the correct space group is probably $P2_13$, in concordance with Smith and Welch (4). This means that the reflections $hkl = 300$ and 500 (Table II) do not occur. Figure 1 shows the Guinier-Lenné pattern from room temperature up to 1373 K. The reflections observed from this, and other, more sensitive recordings, are listed in Table II, in which the estimated intensities are also given.

The Guinier-Lenné pattern (Fig. 1) revealed a phase transformation at (1023 ± 30) K. Around (1273 ± 30) K the start of

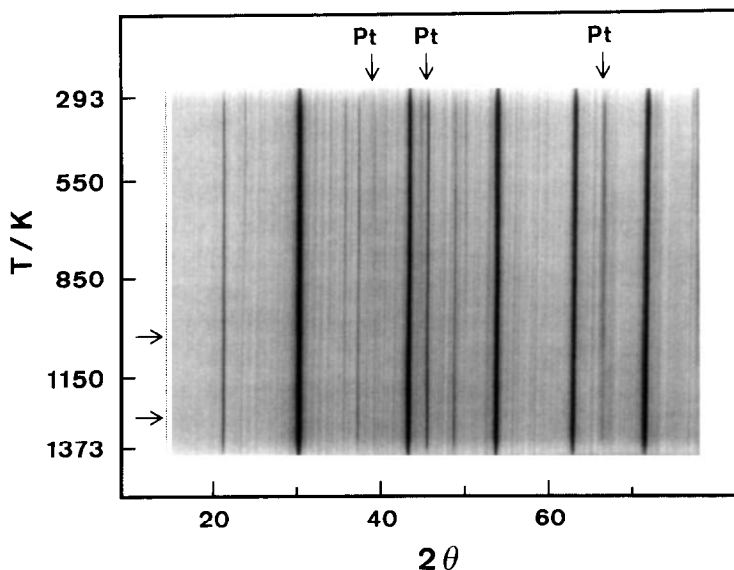


FIG. 1. Guinier-Lenné recording from room temperature up to 1373 K for pseudo-cubic SrZrO₃, showing a phase transformation at (1023 ± 30) K, and the start of a smooth phase transformation around (1273 ± 30) K. Some of the lines in the recording are due to the Pt grid.

another, smooth phase transformation was observed. The reflections that were still observable at 1063 and 1323 K are listed in Table II, with their estimated intensities. The systematic absences indicate space group $P2/n\bar{3}$ for the phase above (1023 ± 30) K. The smooth phase transformation that starts around (1273 ± 30) K will probably result in space group $Pm\bar{3}m$. Because of the large differences between strong and weak reflections two recordings were made for each temperature, one for 5 min and the other for 60 min. At 1063 K, $a = 0.8270(1)$ nm, the result of the weighed mean between 0.8270(1) and 0.8271(1), respectively. At 1323 K, $a = 0.8287(2)$ nm, the result of the weighed mean between 0.8289(1) and 0.8285(2) nm, respectively.

4. Characterization of the Structures

Even at high angles no splitting of the perovskite reflections could be observed other than the splitting due to $\text{CuK}\alpha_1$ and

$\text{CuK}\alpha_2$, indicating a cubic structure. However, weak reflections were observed in addition to the ideal perovskite reflections, indicating distortion from ideal symmetry. All reflections could be indexed on the basis of a doubled perovskite cell.

According to Glazer (13) and Ahtee *et al.* (9), a classification of reflections can be made to differentiate between the various possible distortions. The reflections with even indices (220, 222, etc.) are the main reflections; reflections with one even and two odd indices (211, 431, 110, etc.) suggest in-phase (+) tilts of O-octahedra, reflections with all indices odd (311, 331, 511, etc.) suggest antiphase (-) tilts, and reflections with one odd and two even indices (210, 322, 421) indicate cation displacement.

The room temperature pattern of SrZrO₃ shows all indices mentioned above (Table II); the space group is $P2_13$. An indication of the possible deviations (arbitrarily called α , β , γ) from the ideal perovskite structure

TABLE II

OBSERVED REFLECTIONS FOR SrZrO₃ AT ROOM TEMPERATURE, 1063 K, AND 1323 K, WITH ESTIMATED INTENSITIES AND MEASURED *d*-SPACINGS FOR SOME INTENSITIES

<i>hkl</i>	293 K <i>I</i> _{obs}	1063 K			1323 K		
		<i>d</i> (nm)		<i>I</i> _{obs}	<i>d</i> (nm)		<i>I</i> _{obs}
		5 min	60 min		5 min	60 min	
110	10			10			10
200	30	0.41443	0.41403	30	0.41399	0.41381	30
210	5			—			—
211	<5		0.33776	<5			<5
220	100	0.29263		100	0.29292		100
221/300	<5			—			—
310	<5			<5			—
311	20		0.24926	20		0.24965	<5
222	25		0.23874	25		0.23911	25
320	<5			—			—
321	5			—			—
400	70	0.20680		70	0.20711		70
322/410	5			—			—
331	<5			<5			—
420	25		0.18495	25		0.18530	25
421	15			—			—
422	80	0.16879		80	0.16919		80
430/500	<5			—			—
431/510	<5			<5			<5
511/333	<5			—			—
520/432	5			—			—
440	60	0.14617		60	0.14655		60
522/441	<5			—			—
530/433	<5			<5			<5

Note. Because of the large differences between strong and weak reflections two recordings were made to measure the *d*-spacings, one for 5 min and the other for 60 min.

is given in Table III for space group $P2_13$ and $P2/n\bar{3}$. The distortions from the ideal perovskite structure are probably mainly due to rotation of the octahedra around the fourfold axes, which makes γ the most important deviation. Distortions due to cation displacement and rotation around the twofold axes lead to smaller deviations (α , β). If α and β are supposed to be zero, the rotation of the octahedra around the fourfold axes (and γ) can be calculated using ionic radii (14, 15), and lattice parameters, in first approximation. In this way the rotation around the fourfold axes is estimated to be about 10°, γ being about 0.045, which is in good agreement with the results obtained by Ahtee *et al.* (9).

At (1023 ± 30) K all reflections with one odd and two even indices disappear (Table II), suggesting that there will be no cation displacement in the phase that exists above this temperature; this is in accordance with space group $P2/n\bar{3}$. Around (1273 ± 30) K the reflections with all indices odd (Table II) start to disappear, suggesting the anti-phase (−) tilts start to disappear at this temperature, leaving only in-phase (+) tilts. At higher temperatures there will probably be an additional phase transformation to the ideal perovskite structure (no tilts).

5. Discussion

Room Temperature Structure

The perovskite structure (AMO₃) is built up from MO₆ octahedra that form a network by sharing corners, in combination with the A-ion, which fills the hole in between the octahedra. The size of the hole for the A-ion is determined by the radius of the M-ion. If the M-ion is Zr⁴⁺, the radius of the hole is 0.160 nm (using the ionic radii by Shannon and Prewitt (14, 15)), which is exactly the radius of Ba²⁺ coordinated by 12 oxygen ions. BaZrO₃ is an example of a cubic perovskite with almost no distortions (5). However, a large number of perovskite-type

TABLE III

ATOMIC COORDINATES FOR SrZrO₃ WITH POSSIBLE DISPLACEMENTS (α , β , γ) FROM THE IDEAL CUBIC PEROVSKITE POSITIONS, ACCORDING TO SPACE GROUP $P2_13$, AND $P2/n\bar{3}$, Zr AT 0, 0, 0

	$P2_13$			$P2/n\bar{3}$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	
Zr 4(<i>a</i>)	0	0	0	Zr 4(<i>b</i>)	0	0	0
Zr 4(<i>a</i>)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	Zr 4(<i>c</i>)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Sr 4(<i>a</i>)	$\frac{1}{2} + \alpha_1$	$\frac{1}{2} + \alpha_1$	$\frac{1}{2} + \alpha_1$	Sr 2(<i>a</i>)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Sr 4(<i>a</i>)	$\frac{3}{4} + \alpha_2$	$\frac{3}{4} + \alpha_2$	$\frac{3}{4} + \alpha_2$	Sr 6(<i>d</i>)	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$
O 12(<i>b</i>)	$\frac{1}{2} + \beta_1$	γ_1	γ_1	O 24(<i>h</i>)	$\frac{1}{2} + \beta_3$	γ_3	γ_3
O 12(<i>b</i>)	$\frac{3}{4} + \beta_2$	γ_2	γ_2				

TABLE IV

PREPARATION TEMPERATURES AND UNIT CELL VOLUMES OF SrZrO₃ BASED ON A PEROVSKITE CELL WITH DOUBLED AXES

Structure	Volume (10 ⁻³⁰ m ³)	Preparation temperature (K)	Ref.
Pseudo-cubic	549.0	1273	1
Pseudo-cubic	546.5	1273	2
Pseudo-cubic	548.6	1523	3
Pseudo-cubic	555.0	1273	4
Pseudo-cubic	552.6	1423	This work
Orthorhombic	551.9	1773	5
Orthorhombic	551.7	1773	6
Orthorhombic	552.0	1773 ^a	7
Orthorhombic	551.9	≥3023	8
Orthorhombic	551.5	Unknown	9

^a Probably.

compounds is known with an A-ion smaller than the hole of the undistorted structure, for example, SrZrO₃ and CaZrO₃. The incorporation of a smaller A-ion in the perovskite-type structure is accompanied by rotations of the octahedra. This leads to a lowering of the symmetry with respect to the ideal perovskite structure.

The room temperature structure of SrZrO₃ is reported to be pseudo-cubic (1-4) and orthorhombic (5-9). The preparation temperatures and unit cell volumes, based on a perovskite cell with doubled axes, are listed in Table IV. The samples described as simple perovskite structures are regarded as pseudo-cubic here. It is not very likely that the orthorhombic structures determined by neutron powder diffraction by Ahtee *et al.* (9), and by X-ray powder diffraction by Swanson *et al.* (7), are wrong. The present sample cannot be described as orthorhombic as it was by Swanson *et al.* (7) and Ahtee *et al.* (9), since the reflection with $hkl = 110$ of the doubled perovskite cell, observed by us, is not allowed in that orthorhombic description and since no line splittings were observed. It is therefore suggested that

SrZrO₃ can be either pseudo-cubic or orthorhombic.

Since both cubic (doubled axes) and orthorhombic symmetry occur in SrZrO₃, the presence of impurities become important. Three types of impurities are discussed here: impurities due to foreign ions in solid solution, deviations from the metal-to-metal ratio, and defects introduced by the thermal treatment. A small amount of a larger ion, like Ba²⁺, in the Sr position makes the structure more cubic, while a smaller ion, like Ca²⁺, would make it more orthorhombic. In the same way larger and smaller ions in the Zr position can make the structure orthorhombic or cubic, respectively. There is no obvious relation between the unit-cell volumes and the symmetry (Table IV) and, unfortunately, chemical analyses are not available for most of the samples. The impurities of the sample in the present investigation are listed in Table I. The relatively large amount of Hf, present in most ZrO₂ starting materials, probably does not contribute severely to a difference in structure, since the radii of Zr⁴⁺ and Hf⁴⁺ differ only by 0.001 nm (2, 14, 15). A SrZrO₃ sample prepared by us using Hf-poor ZrO₂ (≤ 200 ppm Hf) also showed cubic symmetry. In addition to the SrZrO₃ reflections in the Guinier-the-Wolff recording this sample showed two very weak reflections that could not be indexed in either the orthorhombic or the cubic SrZrO₃ structure. These reflections are probably caused by an impurity in the ZrO₂ starting material. The unknown impurity is not in solid solution with SrZrO₃ and therefore has no influence on the cubic structure.

Not only is the purity of the sample of great influence on the structure, the metal-to-metal ratio can also change the symmetry. A possibility for a distortion due to the metal-to-metal ratio is an excess of Sr. In the Sr-Zr-O system there is a homologous range of compounds between SrZrO₃ and Sr₂ZrO₄ with the general formula

$\text{Sr}_{n+1}\text{Zr}_n\text{O}_{3n+1}$. Besides the end members, the compounds $\text{Sr}_3\text{Zr}_2\text{O}_7$ (11, 16) and $\text{Sr}_4\text{Zr}_3\text{O}_{10}$ (16) are known. These compounds consist of n layers of perovskite, followed by one layer of SrO. The diffraction patterns of these compounds have lines very near to the SrZrO_3 lines, as expected, since they contain SrZrO_3 units. Another possibility for a distortion due to the metal-to-metal ratio is an excess of Zr. From the pseudo-binary $\text{SrO}-\text{ZrO}_2$ phase diagram it is known that at relatively high temperatures there is a solid solution range between ZrO_2 and SrZrO_3 (16). An excess of Zr may be caused by the evaporation of SrO at high temperatures. It is thus very well possible that structural alterations do occur due to a deviating metal-to-metal ratio.

From Table IV it can be seen that the preparation temperature is of great influence on the structure. All pseudo-cubic samples have been prepared at relatively low temperatures while all orthorhombic samples have been prepared at much higher temperatures. Ahtee *et al.* (9) used a commercially available sample; no preparation temperature is specified. The high temperatures can introduce defects, for instance, oxygen deficiency or possibly a preferred evaporation of SrO, as mentioned before, that can have a severe influence on the structure. The sample used by Carlsson (6) did show some excess of ZrO_2 .

In the present investigation care was taken to have the proper metal-to-metal ratio. When the pseudo-cubic sample, prepared at 1423 K was heated to 1823 K, line splittings, indicating an orthorhombic structure, were observed after the heat treatment. The color changed from palish white to pink. It is concluded that the structure of pure SrZrO_3 at room temperature is probably cubic with a doubled axis (pseudo-cubic according to Roth's classification (5)) and that the structure is very sensitive to impuri-

ties and lattice defects governed by the preparation temperature.

High-Temperature Behavior

In general, if temperature is raised, bond lengths will increase. With the increase of the bond lengths the hole in between the ZrO_6 octahedra will become smaller with respect to the Sr radius, resulting in a smaller distortion from the ideal symmetry. The structure will become more symmetrical when the temperature is raised, until the ideal perovskite structure is reached.

The high-temperature behavior is thus straightforward. From Fig. 1 it is seen that the distortions from the ideal perovskite structure due to the rotations of the octahedra disappear gradually as a function of temperature. The extra intensities due to the cation displacement disappear more abruptly (at 1023 ± 30 K). The calculated patterns in the JCPDS file, which are based on the high-temperature phases reported by Ahtee *et al.* (10), suggest a different behavior, which is not in accordance with the observations of the high-temperature recording from room temperature up to 1373 K for the present sample (Fig. 1) and also seems not to be in accordance with the neutron powder profiles of Ahtee *et al.* (9, 10) and the observations by Carlsson (6).

DSC measurements up to 1373 K for the present sample did not show any heat effect. Carlsson (6) observed two transitions with DTA measurements, at 1003 and 1133 K. These heat effects are probably due to more abrupt transformations caused by cation displacement. Since the sample of Carlsson (6) at room temperature is orthorhombic, it will undergo still other phase transformations to become ideally cubic compared with the sample in the present study (pseudo-cubic at room temperature). Ahtee *et al.* (10) observed Sr displacement at 1033 K in a sample that was also orthorhombic at room temperature.

Acknowledgments

The authors thank Dr. D. J. W. IJdo of the Leiden University for helpful discussions, and Miss S. R. M. Meysen for preparing the samples.

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