

The Structure of Orthorhombic SrZrO₃ by Neutron Powder Diffraction

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(Received 14 May 1976; accepted 18 June 1976)

The room-temperature structure of SrZrO₃ has been established by neutron powder-profile refinement. The space group is *Pbnm* and SrZrO₃ is isostructural with other perovskites, such as CaTiO₃.

Introduction

SrZrO₃ belongs to the perovskite family with general formula A²⁺B⁴⁺O₃. Roth (1957) has classified these perovskites on the basis of the ionic radii of A and B cations, and according to his diagram both SrZrO₃ and CaZrO₃ have orthorhombic structures. The orthorhombic nature of SrZrO₃ was verified by Swanson, Cook, Isaacs & Evans (1960), who found the values for the lattice parameters given in Table 1. Further work by Carlsson (1967, 1970) supported this view, but, in addition, he proposed that there were also two high-temperature tetragonal phases. However, no detailed work on the structure of SrZrO₃ at any temperature has been made. In this paper, we report the structure at room temperature.

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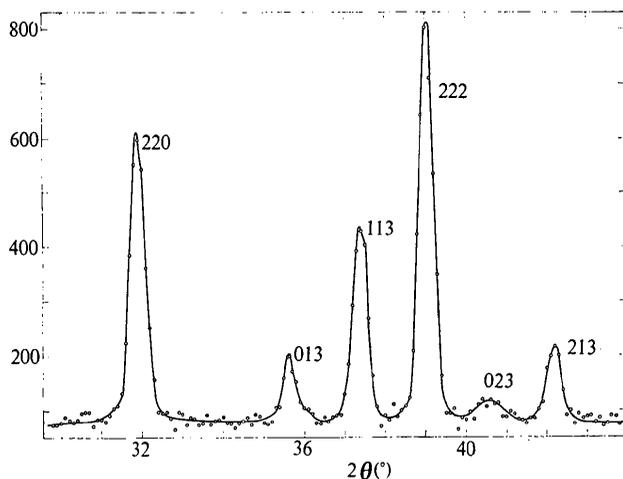


Fig. 1. Part of the neutron-diffraction powder pattern of SrZrO₃, showing the superlattice reflexions associated with tilted octahedra and displaced cations. Vertical axis shows counts.

Table 1. *The lattice parameters of SrZrO₃*

| X-ray diffraction | (Swanson <i>et al.</i> , 1960) | Neutron diffraction |
|---------------------------|-----------------------------------|--------------------------------|
| Orthorhombic | Pseudocubic* | Orthorhombic† |
| $a_o = 5.792 \text{ \AA}$ | $2a_p = 8.207 \text{ \AA}$ | $a_o = 5.7862 (5) \text{ \AA}$ |
| $b_o = 5.813$ | $2b_p = 8.207$ | $b_o = 5.8151 (6)$ |
| $c_o = 8.196$ | $2c_p = 8.196$ | $c_o = 8.1960 (8)$ |
| | $\gamma = 90.22^\circ$ | |

* a_p , b_p and c_p are the pseudocubic *subcell* parameters.

† Standard errors in parentheses do not include the error in the neutron wavelength.

Glazer (1972) has derived a simple way of describing and classifying octahedral tilts in perovskites and has shown how these tilts are related to the unit-cell parameters. From the doubling of the pseudocubic subcell parameters, a_p , b_p and c_p , and from the fact that in SrZrO₃ (Table 1) $a_p = b_p > c_p$ and $\gamma \neq 90^\circ$, Glazer has suggested two possibilities for the tilting: $a^-a^-c^+$ or $a^-a^-c^0$, the former giving *C* face-centring, the latter all-face-centring. The former was favoured because of the higher frequency with which it is found in practice.

The melting point of SrZrO₃ is high, 2799°C (Galasso, 1969), and it proved impossible to grow good untwinned crystals. Therefore, we decided to use the neutron powder-profile refinement technique (Rietveld, 1969; Hewat, 1973) to solve this structure.

Data collection

Neutron-diffraction measurements were made at room temperature on the PANDA diffractometer on the PLUTO reactor at AERE (Harwell). About 20g of SrZrO₃ powder (Cerac, 99.9% pure) were loosely packed in a thin-walled vanadium canister. The neutron wavelength was 1.532 Å, and the diffractometer was set to step through intervals of 0.1° in 2θ . The 2θ range (10–110.4°) was covered in about 24 h and the data were collected on a single BF₃ counter.

Refinement

In powder diffraction all reflexions for a given scattering angle are superimposed. When the symmetry of the structure is lowered, as in the perovskite structure, to one differing only slightly from the ideal cubic symmetry, these reflexions are split. In the pattern there may also be weak superlattice reflexions caused by the displacements of the cations or the tilting of the octahedra (Glazer, 1972, 1975; Ahtee & Glazer, 1976).

In Fig. 1 part of the neutron-diffraction powder pattern of SrZrO₃ is shown, the reflexions being indexed on the basis of the doubled pseudocubic subcell. Those reflexions having all indices even (220, 222) are the main reflexions; reflexions with one even and two odd indices (013, 213) suggest in-phase (+) tilts of O octahedra, whereas reflexions with all indices odd (311) suggest antiphase (-) tilts. Combining this with the knowledge that the pseudocubic lattice parameters have the relationship $a_p = b_p \neq c_p$, $\gamma \neq 90^\circ$, we find the tilt system $a^-a^-c^+$. This corresponds to space group $Pbnm$ with new axes chosen by the matrix

$$\begin{array}{c} a_o \\ b_o \\ c_o \end{array} \begin{pmatrix} a_p & b_p & c_p \\ 1 & 1 & 0 \\ \bar{1} & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

where a_o, b_o, c_o are the orthorhombic axes.

The fourth type of reflexion in Fig. 1, with one odd and two even indices (023), is consistent with having cations within any layer perpendicular to [001] displaced parallel to one another, but with the displacements in successive layers antiparallel. This arrangement is common in perovskites with this type of tilt system. As to the O environments around Sr ions caused by the tilting (Fig. 2), simple packing con-

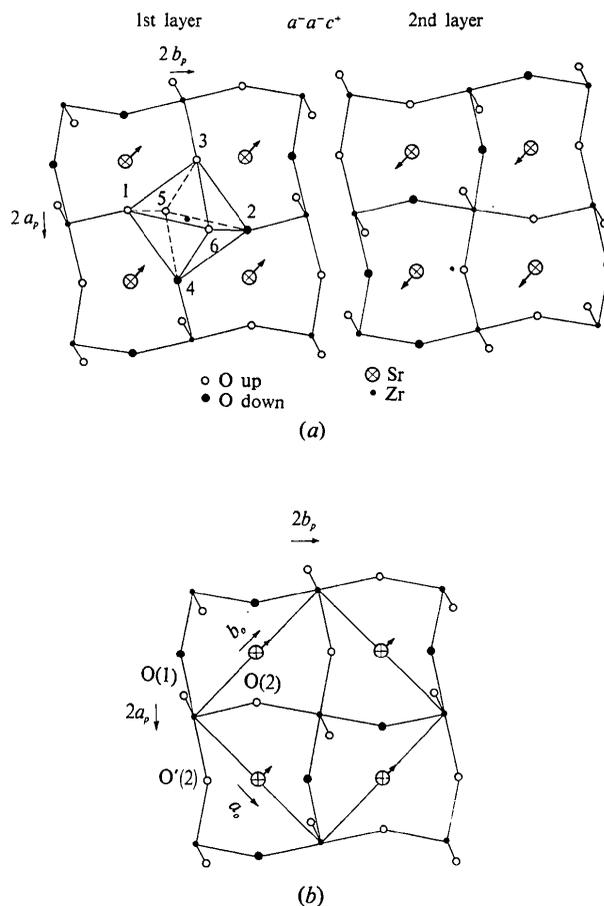


Fig. 2. Diagram of SrZrO₃ structure. (a) Two layers of octahedra perpendicular to c_p ; pseudocubic unit cell. (b) One layer of octahedra perpendicular to c_o ; orthorhombic unit cell.

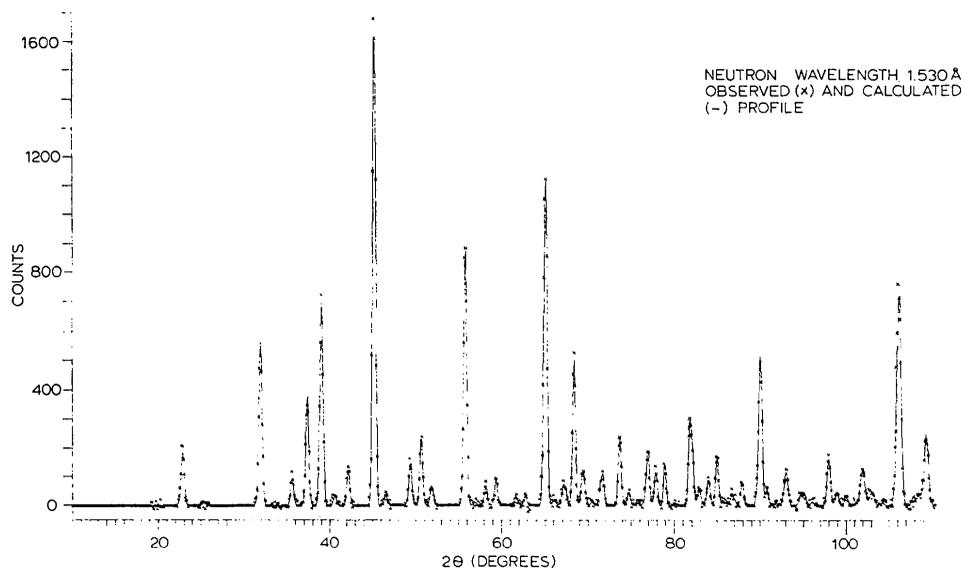


Fig. 3. Observed (x) and calculated (-) powder profile of SrZrO₃ at 25°C.

siderations suggest that the effect of the O atoms is to push the Sr ions slightly away from the centres. In Fig. 2(b) the true orthorhombic unit cell is indicated in relation to the pseudocubic unit cell. If we then choose the origin as marked in Fig. 2(b), the Zr ions lie on centres of symmetry and therefore cannot be displaced. There is an alternative position for the origin, but, as this would put the Sr atom on a centre of symmetry thus inhibiting the displacement suggested by the O environment, this is less likely. The atomic coordinates for the former model are given in Table 2 in terms of the displacements u , v and w from the special positions of the ideal cubic perovskite structure.

Table 2. Displacements u, v, w from the cubic perovskite positions according to space group $Pbnm$ with origin on the Zr atom

| | | u | v | w |
|------|------|--------------------------|--------------------------|---------------|
| Sr | 4(c) | u_{Sr} | $\frac{1}{2} + v_{Sr}$ | $\frac{1}{2}$ |
| Zr | 4(a) | 0 | 0 | 0 |
| O(1) | 4(c) | $u_{O(1)}$ | $v_{O(1)}$ | $\frac{1}{2}$ |
| O(2) | 8(d) | $\frac{1}{2} - u_{O(2)}$ | $\frac{1}{2} + v_{O(2)}$ | $w_{O(2)}$ |

The lattice parameters, fractional coordinates and both isotropic and anisotropic temperature factors were refined with the Rietveld program modified by Hewat (Harwell Report, RRL 73/897). This minimizes the sum over the squares of the differences between the calculated intensity data points, $y_i(\text{cal.})$, and observed counts, $y_i(\text{obs.})$, at each 2θ point in the pattern. The scattering lengths used were $b_{Sr} = 0.70$, $b_{Zr} = 0.71$, $b_O = 0.58 \times 10^{-12}$ cm (Bacon, 1972). The refinement converged quickly and the final nuclear R value on integrated intensities was 6.5% with refinement of iso-

tropic temperature factors and 5.3% with anisotropic B values. The atom positions are listed in Table 3 and the final observed and calculated profile is drawn in Fig. 3.

Discussion

Refinement with anisotropic temperature factors makes little difference to the coordinates of the atoms, so that either set of results will do. The Sr atoms are displaced along b_o parallel to one another within (001) layers, every successive layer being antiparallel. Within these layers the Sr atom is displaced by 0.15 Å. This can be compared with the displacement (0.16 Å) of Ca in the isostructural CaTiO_3 (Kay & Bailey, 1957). This seems a little surprising, considering the larger size of the Sr ion [if the Ca and Sr cations are assumed to be coordinated by eight oxygens because of the tilted octahedra, the ionic radii are 1.12 and 1.25 Å respectively, according to Shannon & Prewitt (1969)], as we might expect that the smaller the cation the larger the displacement. However, this becomes understandable when we consider the tilting of the octahedra. In Fig. 4, the bond lengths and angles pertaining to the O octahedra are given. It can be seen that the octahedra are very regular with mean $\text{Zr-O} = 2.091$ and mean $\text{O-O} = 2.957$ Å. Using these values and the coordinates specified with respect to the pseudocubic subcell we find that the octahedra are tilted through approximately 7.6° about c_p (c^+ tilt) and 8.0° about a_p and b_p (a^- tilts). With respect to the orthorhombic cell, the octahedra are tilted 7.6° about c_o and 11.2° about b_o , *i.e.* about the direction of Sr displacement. The tilt angles are considerably larger than in CaTiO_3 (4 and 6°

Table 3. Structural parameters in room-temperature SrZrO_3

$B_{11} = 4\beta_{11}/a^*$, $B_{12} = 4\beta_{12}/a^*b^*$ *etc.*, and the temperature factor is defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{31}lh)]$. $R_{\text{NUC}} = 100 \sum |I(\text{obs.}) - SI(\text{cal.})| / \sum I(\text{obs.})$, $R_{\text{PROF}} = 100 \sum |y_i(\text{obs.}) - Sy_i(\text{cal.})| / \sum y_i(\text{obs.})$, $R_{\text{EXP}} = 100 / [(N - P) / \sum W |y(\text{obs.})|^2]$, with $I(\text{obs.})$, $I(\text{cal.})$ integrated intensity of reflexion, $y_i(\text{obs.})$, $y_i(\text{cal.})$ observed intensity data point, W weighting factor, N number of observations y_i , P number of parameters, S scale factor.

Isotropic temperature factor refinement

| | x | y | z | B |
|------|------------|------------|---------------|-------------|
| Sr | 0.001 (2) | 0.525 (1) | $\frac{1}{2}$ | 0.928 (84) |
| Zr | 0 | 0 | 0 | 0.346 (66) |
| O(1) | -0.073 (2) | -0.015 (1) | $\frac{1}{2}$ | 0.809 (165) |
| O(2) | 0.216 (1) | 0.285 (1) | 0.035 (1) | 0.648 (106) |

$$R_{\text{NUC}} = 6.52\% \quad R_{\text{PROF}} = 13.57\% \quad R_{\text{EXP}} = 13.34\%$$

Anisotropic temperature factor refinement

| | x | y | z | B | | |
|------|------------|------------|---------------|----------|----------|----------|
| Sr | 0.003 (3) | 0.526 (1) | $\frac{1}{2}$ | B_{11} | B_{12} | B_{13} |
| Zr | 0 | 0 | 0 | B_{22} | B_{23} | B_{33} |
| O(1) | -0.073 (2) | -0.018 (2) | $\frac{1}{2}$ | B_{11} | B_{12} | B_{13} |
| O(2) | 0.217 (1) | 0.284 (1) | 0.035 (1) | B_{22} | B_{23} | B_{33} |

| | B_{11} | B_{22} | B_{33} | B_{12} | B_{13} | B_{23} |
|------|-----------|------------|-----------|------------|------------|-----------|
| Sr | 0.24 (34) | 1.48 (34) | 0.91 (48) | 0.23 (30) | 0 | 0 |
| Zr | 0.08 (35) | -0.01 (28) | 1.45 (54) | 0.02 (29) | -0.19 (67) | 0.30 (22) |
| O(1) | 1.44 (57) | 2.52 (56) | 0.34 (55) | -1.12 (40) | 0 | 0 |
| O(2) | 0.53 (22) | 0.77 (21) | 0.58 (27) | -0.40 (23) | 0.65 (24) | 0.52 (22) |

$$R_{\text{NUC}} = 5.29\% \quad R_{\text{PROF}} = 12.82\% \quad R_{\text{EXP}} = 13.18\%$$

respectively). It is this difference that probably accounts for the near equality of the Ca and Sr displacements. The larger tilt angle in SrZrO₃ means more distortion of the environment of the Sr atom and consequently some shorter Sr–O distances. For example, O(1) in Fig. 2(a) approaches the Sr atom as the angle of tilt about c_p increases, thus tending to push it in the $-a_p$ direction. The larger tilting forces the Sr atom to move further off-centre and so gives a displacement comparable to the smaller Ca atom in CaTiO₃. The off-centring, therefore, is the result of an interplay of two factors, the ionic radius of the cation and the angle of tilt of the octahedra.

While the isotropic temperature factors seem quite reasonable, the absolute magnitudes of the anisotropic temperature factors are certainly not (a common feature of the powder-profile refinement technique), although it is possible that their relative sizes and the orientations of the thermal ellipsoids may be realistic. Assuming this to be the case, diagonalization of the B_{ij} matrices indicates that all the ellipsoids are highly anisotropic, and that the Sr atom executes motion mainly in the plane perpendicular to a_o , the Zr atom along c_o and the O(1) atom along a_o .

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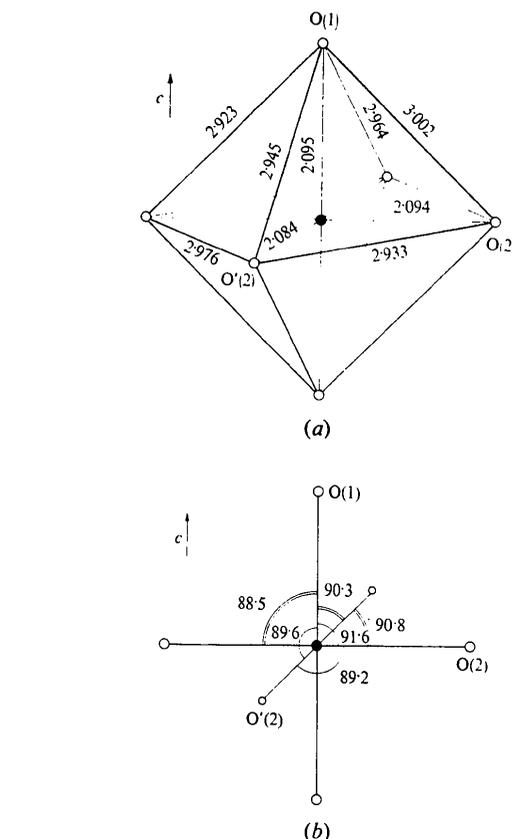


Fig. 4. (a) Bond lengths (Å) in O octahedron. (b) Bond angles (°) in O octahedron.

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Structure Cristalline du Trimétaphosphate de Plomb Trihydraté, Pb₃(P₃O₉)₂·3H₂O

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(Reçu le 17 mai 1976, accepté le 31 mai 1976)

The crystal structure of lead trimetaphosphate trihydrate, Pb₃(P₃O₉)₂·3H₂O, has been determined by single-crystal X-ray methods. The unit cell is tetragonal with $a=b=11.957$, $c=12.270$ Å. The space group is $P4_212$. The structure was solved from single-crystal diffractometer data, with Patterson and Fourier syntheses, and refined by the least-squares method. The final R value is 0.070 for 1157 reflexions.

Le trimétaphosphate de plomb trihydraté, Pb₃(P₃O₉)₂·3H₂O, a été signalé pour la première fois par Fleitman & Henneberg (1848). Son comportement

thermique a ensuite été étudié par Schülke (1968). Son étude cristallographique a été effectuée par Durif & Brunel-Laügt (1976).