

This type of K–K–□ ordering allows a relaxation of the strong electrostatic repulsion. The K atoms move towards the vacancies. They shift by 0.125*c* away from the 00½ position toward a neighboring empty site. Sequentially there exist two K–K distances: a short one of 3.589 Å and a longer one of 5.027 Å, both greater than the *c* parameter. This shift agrees well with the results of Beyeler & Schüler (1980) for Cs<sub>1.33</sub>(Ti, Mg)<sub>8</sub>O<sub>16</sub>. From the intensities of the diffuse-scattering streaks these authors concluded that the Cs atoms are shifted toward the vacancies by 0.12*c*. Relative intensities of the diffuse streaks for Cs<sub>1.33</sub>(Ti, Mg)<sub>8</sub>O<sub>16</sub> and K<sub>1.33</sub>Mn<sub>8</sub>O<sub>16</sub> are quite similar. The vacancy ordering is consistent with the poor ionic conductivity found for K<sub>1.33</sub>Mn<sub>8</sub>O<sub>16</sub> (Strobel *et al.*, 1984).

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#### References

- ABRIEL, W., RAU, F. & RANGE, K. J. (1979). *Mater. Res. Bull.* **14**, 1463–1468.
- BAYER, G. & HOFFMAN, W. (1966). *Am. Mineral.* **51**, 511–516.
- BEYELER, U. & SCHÜLER, C. (1980). *Solid State Ionics*, **1**, 77–86.
- BURSILL, L. A. & GRZINIC, G. (1980). *Acta Cryst.* **B36**, 2902–2913.
- BYSTRÖM, A. & BYSTRÖM, A. M. (1950). *Acta Cryst.* **3**, 146–154.
- CADÉE, M. C. & VERSCHOOR, G. C. (1978). *Acta Cryst.* **B34**, 3554–3558.
- ENDO, T., KUME, S., KINOMURA, N. & KOIZUMI, M. (1976). *Mater. Res. Bull.* **11**, 609–614.
- KUME, S., MATSUMOTO, T. & KOIZUMI, M. (1966). *J. Geophys. Res.* **71**, 4999.
- OKADA, H., KINOMURA, M., KUME, S. & KOIZUMI, M. (1978). *Mater. Res. Bull.* **13**, 1047–1053.
- PATRAI, G., DE BERGÉVIN, F., PERNET, M. & JOUBERT, J. C. (1983). *Acta Cryst.* **B39**, 165–170.
- POST, J. E., VON DREELE, R. B. & BUSECK, P. R. (1982). *Acta Cryst.* **B38**, 1056–1065.
- PRING, A., SMITH, D. J. & JEFFERSON, D. A. (1983). *J. Solid State Chem.* **46**, 373–381.
- REID, A. D. & RINGWOOD, A. D. (1969). *J. Solid State Chem.* **1**, 6–9.
- RINGWOOD, A. D., REID, A. F. & WADSLEY, A. D. (1967). *Acta Cryst.* **23**, 1093–1095.
- SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- SINCLAIR, W., MCLAUGHLIN, G. M. & RINGWOOD, A. E. (1980). *Acta Cryst.* **B36**, 2913–2918.
- STROBEL, P. & LE PAGE, Y. (1982). *Cryst. Growth*, **56**, 645–651.
- STROBEL, P., VICAT, J. & TRAN QUI, D. (1984). *J. Solid State Chem.* **55**, 67–73.
- WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., pp. 176 and 459. Oxford: Clarendon Press.
- YOSHIKADO, S., OHACHI, T., TANIGUCHI, I., ONODA, Y., WATANABE, M. & FUJIKI, Y. (1982). *Solid State Ionics*, **7**, 335.

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## The A<sub>2</sub>SnO<sub>6</sub> (A = Ca, Sr) Perovskites

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#### Abstract

The crystal structures of the perovskites A<sub>2</sub>SnO<sub>6</sub> (A = Ca, Sr) have been solved. Ca<sub>2</sub>SnO<sub>6</sub>:  $M_T = 206.77$ , orthorhombic, *Pbnm*,  $a = 5.532$  (2),  $b = 5.681$  (2),  $c = 7.906$  (2) Å,  $V = 248.46$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 5.52$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu(\text{Mo } K\alpha) = 11.3$  mm<sup>-1</sup>,  $F(000) = 376$ ,  $T = 295$  K. Its structure was refined from 381 (346 observed) X-ray single-crystal data to  $R = 0.026$ . Sr<sub>2</sub>SnO<sub>6</sub> single crystals, previously reported as cubic ( $a = 8.0682$  Å), were studied by electron microscopy and X-ray techniques, showing the presence of multitwinning which gives rise to the fictitious 'double' cubic cell. The real cell has  $a = 5.707$  (2),  $b = 5.707$  (2),  $c = 8.064$  (2) Å,  $V = 262.64$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 6.43$  Mg m<sup>-3</sup>,  $M_T = 254.31$ ,  $T = 295$  K, and probably the same space

group as Ca<sub>2</sub>SnO<sub>6</sub>. Because of the twin, the structure was solved topologically, by a novel use of the expressions given by O'Keeffe & Hyde [*Acta Cryst.* (1977), **B33**, 3802–3813] by assuming an Sn–O bond length of 2.062 Å, equal to that derived for Ca<sub>2</sub>SnO<sub>6</sub>.

#### Introduction

The perovskite structure is one of the most studied among the oxide structures (Goodenough & Longo, 1970; Galasso, 1969; Goodenough, 1971).

The aristotype, SrTiO<sub>3</sub>, is cubic with just the unit-cell dimension as unique parameter (Megaw, 1973) but many different versions showing lower symmetry are well known (Muller & Roy, 1974). Among them are rhombohedral, as the LaAlO<sub>3</sub> phases (Geller &

Bala, 1956), orthorhombic, like the rare-earth orthoferrites (Marezio, Remeika & Dernier, 1970) and the mineral perovskite  $\text{CaTiO}_3$  (Kay & Bailey, 1956) which gives the name to the whole family.

The reasons for a lowering of the symmetry are multiple and have already been widely discussed (Glazer, 1972; O'Keeffe & Hyde, 1977).

There are, however, several cases where a so-called 'double' cubic perovskite has been suggested to exist (Smith & Welch, 1960). For example, the JCPDS card No. 22-1442 corresponding to  $\text{SrSnO}_3$  indexes this compound on the basis of a double cubic cell with  $a = 8.0682 \text{ \AA}$ . Other examples given in Muller & Roy (1974) and Smith & Welch (1960) are  $\text{BaThO}_3$ ,  $\text{SrZrO}_3$ , etc.

In the case of solids with composition of the type  $A_2BB'O_6$  or, in general, in a multiple occupation of the  $A$  or  $B$  sublattices, one can understand the doubling of the perovskite cell through an ordering of the cations. However, there seems to be no *a priori* reason for an  $\text{ABO}_3$  perovskite to show a double cubic cell instead of the more usual ones: simple cubic as  $\text{SrTiO}_3$ , orthorhombic as  $\text{GdFeO}_3$  or even monoclinic as  $\text{PrAlO}_3$  (Burbank, 1970).

There are also marked differences between the Ca and Sr and, indeed, Ba perovskites of Sn, Fe, Ti, Mn, etc. For this reason and since, to our knowledge, the crystal structure of the orthorhombic  $\text{CaSnO}_3$  perovskite is not known, we have also determined it to compare it with  $\text{SrSnO}_3$ . We describe in the following some of the results that we have obtained by a combination of X-ray and electron diffraction and microscopy.

### Experimental

$\text{CaSnO}_3$  and  $\text{SrSnO}_3$  crystals have been grown by the flux method, *i.e.* slow cooling of a molten salt solution. A mixture of composition 2 mol %  $\text{ACl}_2$ :1 mol %  $\text{SnO}_2$  ( $A = \text{Ca}, \text{Sr}$ ) (Merck, AR) was heated, in an alumina crucible, to 1473 K and kept for 24 h at this temperature to ensure solution of all constituents. The furnace was then cooled slowly, with a programmed controller, at a rate of  $40 \text{ K h}^{-1}$ , to 1273 K, well below the solidus temperature. The crucible was then removed from the furnace and cooled in air to room temperature. Crystals were separated by leaching with distilled water until total absence of chlorides and then washed with acetone.

For  $\text{CaSnO}_3$ , the cell parameters were determined from the  $2\theta$  angles of 25 reflexions ( $12^\circ < \theta < 20^\circ$ ). Intensities of 1443 reflexions within a hemisphere up to  $\sin \theta/\lambda = 0.7035 \text{ \AA}^{-1}$  were measured on a computer-controlled Siemens-Stoe diffractometer with  $\omega/\theta$  scan and a prismatic crystal of dimensions  $0.10 \times 0.10 \times 0.08 \text{ mm}$ . The reflexions 004, 220 and  $\bar{2}20$  were used as standards; their maximum intensity variation was 5%. After correction for absorption (max. and

Table 1. Atomic parameters ( $\times 10^4$ ) for  $\text{CaSnO}_3$  (high angles) and  $\text{SrSnO}_3$

$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j (\cos a_i \cdot a_j)$ . E.s.d.'s are given in parentheses for  $\text{CaSnO}_3$ .

	x	y	z	$U_{\text{eq}} (\text{\AA}^2 \times 10^4)$
Ca	-131 (3)	509 (2)	$\frac{1}{4}$	75 (6)
Sn	0	$\frac{1}{2}$	0	35 (3)
O(1)	994 (10)	4615 (10)	$\frac{1}{4}$	70 (21)
O(2)	6992 (7)	2981 (7)	$\frac{1}{4}$	70 (15)
Sr	-9	124	$\frac{1}{4}$	
Sn	0	$\frac{1}{2}$	0	
O(1)	736	4896	$\frac{1}{4}$	
O(2)	7132	2853	$\frac{1}{4}$	

min. transmission factors 0.521 and 0.457), and Lorentz and polarization factors, the intensities were averaged ( $R_{\text{int}} = 0.046$ ). The  $F$  values of 381 independent reflexions were used in the refinement. Of these, 346 were significant and 35, with  $I < 3\sigma(I)$ , were considered as unobserved. Atomic scattering factors for neutral atoms and anomalous-dispersion coefficients for Sn, Ca and O were taken from *International Tables for X-ray Crystallography* (1974). Calculations were performed with the XRAY70 system (Stewart, Kundell & Baldwin, 1970).

The positional parameters of  $\text{CaMnO}_3$  (Poeppelmeier, Leonowicz, Scanlon, Longo & Yelon, 1982) were used as starting values in the least-squares refinement. Preliminary calculations, with isotropic temperature factors, led to a negative  $B$  for Sn, as a consequence of 14 reflexions affected by extinction. The refinement was thus continued using only 305 high-order reflexions ( $\sin \theta/\lambda > 0.4 \text{ \AA}^{-1}$ ). In this case, anisotropic least-squares calculations, using unit weights, led to an  $R$  value of 0.026,  $S = 1.3763$  and  $(\Delta/\sigma)_{\text{max}} = 0.18$ . The final atomic parameters are listed in Table 1. In addition, a secondary-extinction correction was applied (Stout & Jensen, 1968), giving a  $g$  coefficient of  $0.22 \times 10^{-5}$ , and a final refinement was carried out with all observed reflexions, but positional parameters did not vary significantly and the  $R$  value attained was 0.031,  $(\Delta\rho)_{\text{max}}$  being 1.5 and  $(\Delta\rho)_{\text{min}} - 1.3 \text{ e \AA}^{-3}$ .\* The more relevant bond lengths and angles are contained in Table 2 and Fig. 1(a) shows a projection of the structure in the  $ab$  plane.

For  $\text{SrSnO}_3$ , the X-ray powder data could be indexed on the basis of a cell of approximate dimensions  $a_c\sqrt{2} \times a_c\sqrt{2} \times 2a_c$ , where  $a_c$  is the simple cubic perovskite cell, making unnecessary the choosing of a bigger 'double' cell, as suggested by Smith & Welch (1960). To ascertain the real dimensions of the unit cell, an electron diffraction and microscopy study was undertaken.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42550 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Finely ground specimens were examined in a JEM-200 CX electron microscope fitted with a  $\pm 30^\circ$  double-tilt goniometer stage. The spherical-aberration coefficient is  $C = 1.2$  mm and the accelerating voltage 200 kV. Samples were ultrasonically dispersed in *n*-butanol and then transferred to carbon-coated copper grids. Images were normally recorded at close to Scherzer defocus, since, for thin specimens, the image intensity is then proportional to the projected potential of the sample. An objective aperture of  $0.47 \text{ \AA}^{-1}$  was used.

Fig. 2 shows an electron diffraction pattern along the  $[001]_c$  perovskite axis. Although the observed spots can be indexed on the basis of a double cubic cell, in at least two dimensions, the corresponding electron micrograph, shown in Fig. 3, suggests a very different situation. It can be seen that three different domains are present; the corresponding fringe spacings suggest that, in two of them, the perovskite cell is doubled but the doubling occurs in different directions in each domain, *i.e.* in domain  $\alpha$  it occurs along  $[100]_c$  while in domain  $\beta$  it occurs along  $[010]_c$ . Tilting around either of these axes showed that the third perovskite axis was also doubled but, in fact, this is simply due to the third domain having the double axis perpendicular to the other two domains. Consequently, domain  $\gamma$ , in Fig. 3, shows fringes of  $5.7 \times 5.7 \text{ \AA}$  corresponding to  $a_c\sqrt{2} \times a_c\sqrt{2}$ .

This agrees with the patterns obtained when diffraction occurs through each of the three domains  $\alpha$ ,  $\beta$  and  $\gamma$  (see Fig. 4*a, b, c*), but when the aperture is placed on the intersection of the three domains, one

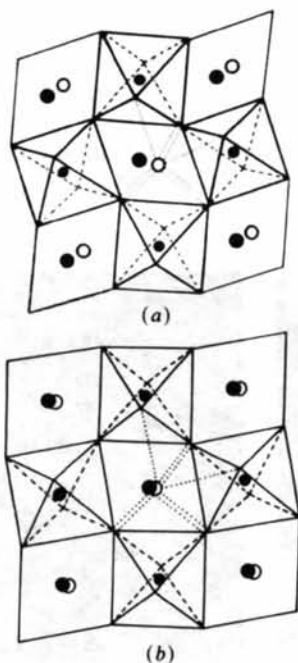


Fig. 1. (a) The  $\text{CaSnO}_3$  and (b) the  $\text{SrSnO}_3$  structures projected on the  $ab$  plane showing the tilting of the  $\text{SnO}_6$  octahedra. Those connected along the  $c$  axis have been omitted for clarity.

Table 2. *Interatomic bond lengths (Å) and angles (°) for  $\text{CaSnO}_3$  and  $\text{SrSnO}_3$*

E.s.d.'s are given in parentheses for  $\text{CaSnO}_3$ .

AO <sub>8</sub> bicapped trigonal prisms (A = Ca, Sr)					
	Ca	Sr		Ca	Sr
A-O(1)	2.414 (6)	2.75	A-O(2 <sup>s</sup> )	2.792 (4)	2.86
O(2 <sup>ii</sup> )	2.640 (4)	2.83	O(2 <sup>siv</sup> )	2.640 (4)	2.83
O(1 <sup>vi</sup> )	2.344 (6)	2.44	O(2 <sup>xvi</sup> )	2.792 (4)	2.86
O(2 <sup>vi</sup> )	2.364 (4)	2.47	O(2 <sup>xs</sup> )	2.364 (4)	2.47
SnO <sub>6</sub> octahedron					
	Ca	Sr		Ca	Sr
Sn-O(1)	2.063 (2)	2.06			
O(1 <sup>iv</sup> )	2.063 (2)	2.06			
O(2 <sup>ii</sup> )	2.061 (4)	2.06			
O(2 <sup>iii</sup> )	2.061 (4)	2.06			
O(2 <sup>xvi</sup> )	2.061 (4)	2.05			
O(2 <sup>xix</sup> )	2.061 (4)	2.05			
O(1)-Sn-O(1 <sup>iv</sup> )	180.0 (4)	180.0			
O(1)-Sn-O(2 <sup>iii</sup> )	91.9 (2)	90.2			
O(1)-Sn-O(2 <sup>ii</sup> )	88.1 (2)	89.8			
O(1)-Sn-O(2 <sup>xvi</sup> )	87.6 (2)	89.9			
O(1)-Sn-O(2 <sup>xix</sup> )	92.4 (2)	90.1			
O(2 <sup>ii</sup> )-Sn-O(2 <sup>iii</sup> )	180.0 (7)	180.0			
O(2 <sup>ii</sup> )-Sn-O(2 <sup>xvi</sup> )	90.8 (2)	91.1			
O(2 <sup>ii</sup> )-Sn-O(2 <sup>xix</sup> )	89.2 (2)	88.9			
Sn-O(1)-Sn	146.6 (4)	156.2			
Sn-O(2)-Sn	148.2 (2)	156.7			

Symmetry code: (ii)  $x-1, y, z$ ; (iii)  $1-x, 1-y, -z$ ; (iv)  $-x, -y, -z$ ; (vi)  $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$ ; (x)  $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$ ; (xiv)  $x-1, y, \frac{1}{2}-z$ ; (xvi)  $x-\frac{1}{2}, \frac{1}{2}-y, -z$ ; (xix)  $\frac{1}{2}-x, \frac{1}{2}+y, z$ ; (xx)  $\frac{1}{2}-x, y-\frac{1}{2}, z$ .

obtains the pattern represented in Fig. 2. The reciprocal unit cell corresponding to this crystal - and in fact to all crystals of  $\text{SrSnO}_3$  that we observed on the microscope - is formed by the juxtaposition of three identical reciprocal cells, each one corresponding to a different domain. For this reason, with just an electron diffraction pattern or, indeed, an X-ray precession photograph (Smith & Welch, 1960), one gets the impression of a double cubic perovskite cell.

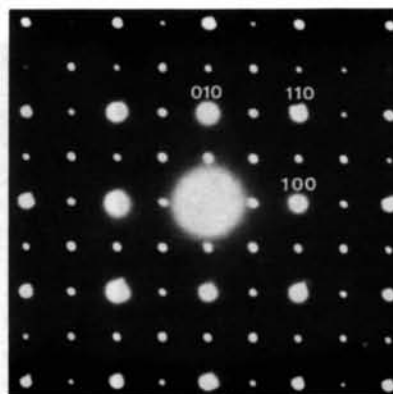


Fig. 2. Electron diffraction pattern through a multitwinned crystal of  $\text{SrSnO}_3$ , showing the apparent cubic supercell ( $a = 2a_c$ ). Miller indices correspond to spots of the 'ideal' cubic ( $a = a_c$ ) perovskite cell.

In view of the multitwinning, invariably present in all  $\text{SrSnO}_3$  crystals, to sort out the structures we used an alternative procedure, based on a topological approach to the perovskite structure introduced by O'Keeffe & Hyde (1977).

The following expressions relate the O(1) and O(2) coordinates with the octahedra rotation angle  $\varphi$  around  $[111]_c$  (O'Keeffe & Hyde, 1977):

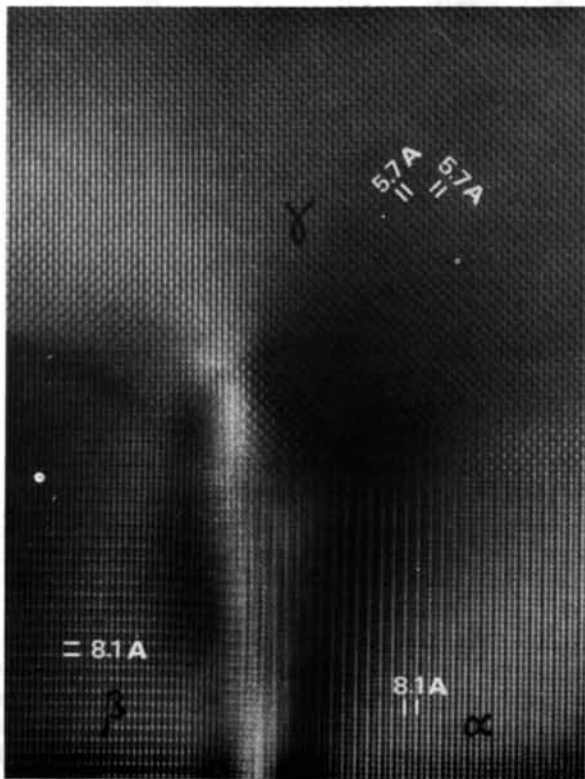


Fig. 3. Electron micrograph of a multitwinned crystal of  $\text{SrSnO}_3$ , showing the three domains  $\alpha$ ,  $\beta$ , and  $\gamma$  which give rise to patterns such as in Fig. 2.

for O(1):

$$\begin{aligned} x &= (\sqrt{3} + \text{tg } \varphi) / \sqrt{12} \\ y &= (\cos^2 \varphi - 1) / (2 \cos^2 \varphi + 4) \end{aligned} \quad (1)$$

and for O(2):

$$\begin{aligned} x &= (3\sqrt{3} + \text{tg } \varphi) / \sqrt{48} \\ y &= (2 - \sqrt{3} \sin \varphi \cos \varphi + \cos^2 \varphi) / (8 + 4 \cos^2 \varphi) \\ z &= -(\text{tg } \varphi / \sqrt{48}). \end{aligned} \quad (2)$$

If we assume that the Sn–O distance is the same, in  $\text{SrSnO}_3$ , as in  $\text{CaSnO}_3$  and apply this principle to the Sn–O(1) bond length, it follows that:

$$d = [(1/2) - x]^2 a^2 + y^2 b^2 + (c^2/16), \quad (3)$$

$a$  and  $c$  being the unit-cell constants of  $\text{SrSnO}_3$ . In this case, Sn is located at  $(\frac{1}{2}, 0, 0)$  and O(1) at  $(x, y, \frac{1}{4})$ . If  $x$  and  $y$ , in (3), are substituted by the expressions (1), one obtains:

$$128 m^6 + 471 m^4 + 262.58 m^2 - 19.063 = 0, \quad (4)$$

where  $m = \text{tg } \varphi$ .

Because  $\varphi$  must be small, the term  $m^6$  can be neglected and the quadratic equation solved. This gives as real solutions  $\varphi = \pm 14.30^\circ$ . Substitution of the negative value in equations (1) and (2) allows one to locate O(1) and O(2) at the positions  $(0.4264, -0.0103, \frac{1}{4})$  and  $(0.7132, 0.2853, 0.0368)$ , respectively. In Table 1, these coordinates are referred to the same asymmetric unit as in  $\text{CaSnO}_3$ .

At this point, the skeleton of  $\text{SnO}_6$  octahedra is established and only the Sr position at  $(x, y, \frac{1}{4})$  remains unknown. To determine it, we took into account the following facts observed in the whole series of  $(\text{RE})\text{FeO}_3$  (Marezio, Remeika & Dernier, 1970; Marezio & Dernier, 1971), as well as in  $\text{CaMnO}_3$  (Poepelmeier, Leonowicz, Scanlon, Longo & Yelon, 1982) and  $\text{CaSnO}_3$  (this work):

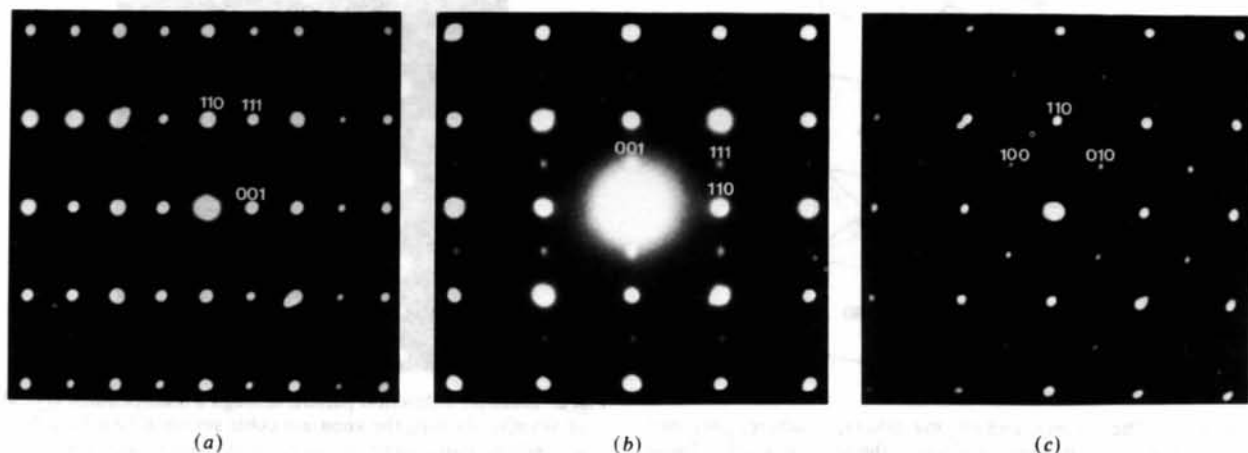


Fig. 4. Electron diffraction patterns through the domains  $\alpha$ ,  $\beta$  and  $\gamma$  ( $a$ ,  $b$  and  $c$  respectively).

(1) The distances  $M-O(1^{vi})$  and  $M-O(2^{vi})$  differ by only 0.02–0.03 Å.

(2) The  $M-O(1^{vi})$  distance is approximately 0.15–0.17 Å shorter than the sum of the ionic radii.

So, if O(1) and O(2) are located at (0.0736, 0.4896,  $\frac{1}{4}$ ) and (0.7132, 0.2853, 0.0368), respectively, and Sr is at  $(x, y, \frac{1}{4})$ , the equations

$$\begin{aligned} [X_{O(1)} - X_{Sr}]^2 a^2 + [Y_{O(1)} - Y_{Sr}]^2 b^2 &= r^2 = 2.44^2 \\ [X_{O(2)} - X_{Sr}]^2 a^2 + [Y_{O(2)} - Y_{Sr}]^2 b^2 & \\ + [Z_{O(2)} - \frac{1}{4}]^2 c^2 &= r'^2 = 2.47^2 \end{aligned} \quad (5)$$

allow us to locate Sr at the position (0.5009, 0.5124,  $\frac{1}{4}$ ), which is equivalent to that in Table 1. The derived bond lengths and angles are in Table 2 and the structure is represented in Fig. 1(b).

Finally, this model was tested by means of a structure factor calculation, carried out with the program LAZYPULVERIX (Yvon, Jeitschko & Parthé, 1977), which showed a good agreement between observed and calculated intensities ( $R = \sum |I_o - I_c| / \sum I_o = 0.18$ ).

### Discussion

The above results show conclusively that  $SrSnO_3$  is not a double cubic perovskite and that the appearance of such a double cell is a consequence of the profound three-dimensional multitwinning invariably present in these crystals. In the case of these complex solids, electron microscopy is then an essential tool to ascertain the presence of multitwinning and the geometry of the unit cell, in combination with the usual X-ray techniques.

The really double cubic perovskite-type structures are so because of: (1) multiple occupation of the A position as in  $A'A''_2B_4O_{12}$  [where, moreover,  $A''$  is a Jahn–Teller cation, as, for example, in  $ThCu_3Mn_4O_{12}$  (Deschizeaux, Joubert, Vegas, Collomb, Chenavas & Marezio, 1976)]; (2) multiple occupation of the B position as in  $A_2BB'O_6$ , for example  $Ba_3Fe_2UO_9$ , or  $Ba_3FeU_2O_9$  (Kemmler-Sack, 1969); or (3) a hydrogen-bonding network as in  $Sc(OH)_3$  (Schubert & Seitz, 1948).

We have also observed that the presence of twinning at this scale is strongly correlated with the magnitude of the  $\varphi$  angle. According to Marezio, Remeika & Dernier (1970), the importance of twinning in the rare-earth orthoferrites as determined from X-ray intensities decreases in the order  $LaFeO_3$  (27%),  $PrFeO_3$  (8%),  $NdFeO_3$  (3%), was barely observable in  $EuFeO_3$  and absent in  $LuFeO_3$ , the  $\varphi$  angle being 13.7, 17.0, 17.6, 20.0 and 22.7°, respectively. Interestingly enough, in  $CaMnO_3$   $\varphi$  is 13.1° and gives diffraction patterns that are analogous to those in Fig. 2. Moreover, Poepelmeier, Leonowicz, Scanlon, Longo & Yelon (1982) have shown it to be unequivocally orthorhombic.

It is also interesting to consider the solid solution  $Ca_xSr_{1-x}SnO_3$  studied by Smith & Welch (1960). According to those authors, this solid solution is orthorhombic up to 45% Sr after which it becomes 'double' cubic. This seems now to be a reflexion of the decreasing value of  $\varphi$  with the increase in the Sr concentration. If we assume, in this case, a linear correlation to exist between  $\varphi$  and the amount of Sr present in the solid solution, the threshold angle for multitwinning to appear will be 17.2°.

On the other hand, it is worth indicating that the  $AO_3$  layers, in Sr-containing perovskites, are more regular if compared with those containing Ca, because of the analogy between the sizes of Sr and O, while the smaller Ca originates greater distortion of the O packing (*cf.*  $CaTiO_3$  is orthorhombic and  $SrTiO_3$  is cubic). Or, in other words, in our case, the greater size of Sr with respect to Ca atoms makes the Sr–Sn and Sn–Sn distances greater and, consequently, the Sn–O bond length can be satisfied with smaller distortion of the O arrangement.

A comment should also be made about the validity of the novel application of the expressions deduced by O'Keeffe & Hyde (1977) to the solution of such perovskite structures. The results expressed above (see Table 2) indicate that, in the absence of a single crystal, the structure can be solved if the unit-cell constants are known and the cation (B)–O distance is taken as the sum of their ionic radii (Shannon & Prewitt, 1969). In this particular case, some doubts remain about the true unit-cell dimensions of  $SrSnO_3$ , because of the lack of splitting in some peaks of the powder diagram and very small differences between  $a$  and  $b$  could be possible. Also, the supposed  $Pbnm$  space group could not be confirmed. This led us to consider the possibility of  $SrSnO_3$  being tetragonal but, if so, the structure should be that of  $A'A''A'''_2B_4O_{12}$  compounds, such as  $NaSb(OH)_6$  (O'Keeffe & Hyde, 1977), with a different tilt of the octahedra. Another possibility, *i.e.* maintaining the proposed structure with a tetragonal, higher symmetry, was also excluded because  $Pbnm$  has no tetragonal supergroup.

In the light of the present report, it is clear that other supposedly 'double' cubic perovskites such as  $BaThO_3$  (Smith & Welch, 1960) and  $SrZrO_3$  (Carlsson, 1967) are worthy of further study.

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### References

- BURBANK, R. D. (1970). *J. Appl. Cryst.* **3**, 112–120.
- CARLSSON, L. (1967). *Acta Cryst.* **23**, 901–905.
- DESCHIZEAUX, M. N., JOUBERT, J. C., VEGAS, A., COLLOMB, A., CHENAVAS, J. & MAREZIO, M. (1976). *J. Solid State Chem.* **19**, 45–51.

- GALASSO, F. S. (1969). *Structure Properties and Preparations of Perovskite-Type Compounds*. London: Pergamon Press.
- GELLER, S. & BALA, V. B. (1956). *Acta Cryst.* **9**, 1019–1025.
- GLAZER, A. M. (1972). *Acta Cryst.* **B28**, 3384–3392.
- GOODENOUGH, J. B. (1971). *Prog. Solid State Chem.* **5**, 313–344.
- GOODENOUGH, J. B. & LONGO, J. M. (1970). *Landolt–Börnstein. Numerical Tables*. New Ser., Vol. 4, ch. 3. Berlin: Springer-Verlag.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- KAY, H. F. & BAILEY, P. C. (1956). *Acta Cryst.* **10**, 219–226.
- KEMMLER-SACK, S. (1969). *Z. Anorg. Allg. Chem.* **369**, 217–237.
- MAREZIO, M. & DERNIER, P. D. (1971). *Mater. Res. Bull.* **6**, 23–30.
- MAREZIO, M., REMEIKKA, J. P. & DERNEIR, P. D. (1970). *Acta Cryst.* **B26**, 2008–2022.
- MEGAW, H. D. (1973). *Crystal Structures: A Working Approach*. London: Sanders.
- MULLER, O. & ROY, R. (1974). *The Major Ternary Structural Families*. Berlin: Springer-Verlag.
- O'KEEFE, M. & HYDE, B. G. (1977). *Acta Cryst.* **B33**, 3802–3813.
- POEPELMEIER, K. R., LEONOWICZ, M. E., SCANLON, J. C., LONGO, J. M. & YELON, W. B. (1982). *J. Solid State Chem.* **45**, 71–79.
- SCHUBERT, K. & SEITZ, A. (1948). *Z. Anorg. Allg. Chem.* **256**, 226–238.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
- SMITH, A. J. & WELCH, A. J. E. (1960). *Acta Cryst.* **13**, 653–656.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY70 system of crystallographic programs. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*. New York: Macmillan.
- YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977). *J. Appl. Cryst.* **10**, 73–74.

*Acta Cryst.* (1986). **B42**, 172–180

## The Relation between Crystal Structure and Solubility for the Diastereoisomeric Salts formed when Enantiomers of Bis(ethylenediamine)glycinatocobalt(III) are Resolved with Di- $\mu$ -[(*R,R*)-tartrato(4-)]-diantimonate(III)

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### Abstract

The structures of the two diastereoisomeric salts which are obtained when bis(ethylenediamine)glycinatocobalt(III) is resolved with di- $\mu$ -[(*R,R*)-tartrato(4-)]-diantimonate(III) have been determined by X-ray diffraction methods. Both compounds crystallize in space group  $P2_1$  with  $Z=2$  and four water molecules of hydration per formula unit. The less soluble salt,  $\Delta$ -bis(ethylenediamine)glycinatocobalt(III) di- $\mu$ -[(*R,R*)-tartrato(4-)]-diantimonate(III) tetrahydrate,  $\Delta$ -[Co(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>NO<sub>2</sub>)][Sb<sub>2</sub>(C<sub>4</sub>H<sub>2</sub>O<sub>6</sub>)<sub>2</sub>].4H<sub>2</sub>O,  $M_r = 860.76$ , has, at 105 K,  $a = 12.696$  (2),  $b = 7.837$  (2),  $c = 13.271$  (2) Å,  $\beta = 95.18$  (1)°,  $V = 1315.1$  (7) Å<sup>3</sup>,  $D_x(105)$  K = 2.174(1),  $D_m(296$  K) = 2.152 (1) g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 27.5$  cm<sup>-1</sup>,  $F(000) = 848$ ,  $R(F) = 0.022$  for 5423 reflections with  $I \geq 2\sigma(I)$ . The more soluble salt,  $\Lambda$ -bis(ethylenediamine)glycinatocobalt(III) di- $\mu$ -[(*R,R*)-tartrato(4-)]-diantimonate(III) tetrahydrate,  $\Lambda$ -[Co(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>NO<sub>2</sub>)][Sb<sub>2</sub>(C<sub>4</sub>H<sub>2</sub>O<sub>6</sub>)<sub>2</sub>].4H<sub>2</sub>O,  $M_r = 860.6$ , has, at 100 K,  $a = 7.968$  (2),  $b = 17.232$  (2),  $c = 9.983$  (2) Å,  $\beta = 105.38$  (1)°,  $V = 1321.6$  (6) Å<sup>3</sup>,  $D_x(100)$  K =

2.163 (1),  $D_m(296$  K) = 2.137 (1) g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 27.5$  cm<sup>-1</sup>,  $F(000) = 848$ ,  $R(F) = 0.026$  for 5646 reflections with  $I \geq 2\sigma(I)$ . The number and strength of the hydrogen bonds appear similar in the two structures, but the structure of the optically active cation is significantly different in the two compounds. In the less soluble salt the stereochemistry and absolute configuration of the cation can be described as  $\Delta(\lambda\delta\lambda)$ , compared with the stereochemistry in the more soluble salt which is  $\Lambda(\lambda\lambda\lambda)$ . This difference in stereochemistry is accompanied by significant structural differences involving the glycinato ligand. The chiral discrimination as expressed in the different solubilities of the two salts appears partly to be caused by the difference in conformational energy of the cation in the two salts.

### Introduction

A widely used method to isolate one of the enantiomers from a racemic mixture is to add a suitable chiral reagent. When resolution is desired for a cationic racemate precipitation with an optically active anion is often attempted. Two different diastereoisomeric salts may result and sometimes their difference in solubility allows both of them to

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