

Pyrochlore-type tin niobate

Luisa Paula Cruz,^{a,c} Jean-Michel Savariault^{b*} and João Rocha^c^aDepartment of Environment, Polytechnic Institute of Viseu, 3510 Viseu, Portugal, ^bCentre d'Elaboration de Matériaux et d'Etudes Structurales—CNRS, 29 Rue Jeanne Marvig, BP 4347, 31055 Toulouse CEDEX 4, France, and ^cDepartment of Chemistry, University of Aveiro, 3810 Aveiro, Portugal
Correspondence e-mail: savariau@cemes.fr

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A single crystal of $\text{Sn}_{1.59}\text{Nb}_{1.84}\text{O}_{6.35}$ was grown at 1273 K from a mixture of sodium niobate and tin(II) chloride. The structure is of pyrochlore type $A_2B_2O_7$. The tin is partially oxidized to tin(IV) and competes with niobium for the occupation of site *B*. The stereoactivity of the Sn^{2+} lone pair induces displacement of tin towards the O atoms of the tunnel.

Comment

Ferroelectric compounds are of great interest in many applications (Kung *et al.*, 1977; Horowitz *et al.*, 1979; Bouhard & Rogers, 1975). Many of them crystallize in the perovskite structure. One of the cations presenting the greatest effect when incorporated in these compounds is lead, as in $\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$ (Auciello *et al.*, 1994), $(\text{Pb},\text{Ln})(\text{Zr},\text{Ti})\text{O}_3$ (Zhang *et al.*, 1999) or $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (Tavernor & Thomas, 1994). The important problem of environment pollution motivates research aimed at the substitution of less toxic metals. Since many physical properties and structural features of lead(II) compounds are due to the lone electron pair (LP), this metal must be replaced by divalent cations with a lone electron pair, for example, tin(II). The products of the synthesis of niobates are often contaminated with pyrochlore-type compounds. In the case of lead niobates, compounds $\text{Pb}_x\text{Nb}_2\text{O}_{6+x}$ with the pyrochlore structure are known (Sreedhar & Mitra, 1999), while for tin, only two niobates are known, *viz.* foordite, SnNb_2O_6 , which crystallizes in the monoclinic system, and $\text{Sn}_2\text{Nb}_2\text{O}_7$, which has the pyrochlore structure (Bodiot, 1968; Birchall & Sleight, 1975; Trunov *et al.*, 1963). This study reports the structure of a tin niobate with a lacunar pyrochlore-type structure. Two formulae are proposed for pyrochlore compounds, *i.e.* AB_2O_6 or $(A_2O')B_2O_6$. In both cases, the skeleton is composed of corner-sharing octahedra (B_2O_6) assembled in a tetrahedron. In such a structure, tunnels are developed in the [110], [101] and [011] directions. At their intersections, huge cavities are formed. The *A* atom occupies preferentially the center of the cavity (CC) in AB_2O_6 compounds and the center of the tunnel (CT) in $(A_2O')B_2O_6$ compounds, the CC being occupied by *O'*. The present struc-

ture determination confirms what was assumed from chemical analysis. Tin is partially located in the niobium (*B*) site and is assumed to be tin(IV). This site is of regular octahedral shape, with *B*—O distances of 1.981 (1) Å, a value which corresponds to a weighted average of pure Nb—O (1.97 Å; Shannon, 1976) and Sn—O (2.04 Å; given in Bergerhoff & Brown, 1987) distances: $d(B-O) = (1.6 \times 1.97) + (0.4 \times 2.04) = 1.984$ Å. Valence calculations (Brown & Altermatt, 1985) confirm the occupation of this site by a mixture of Nb and Sn [valence(Nb) = 4.96 and valence(Sn) = 4.88]. The remaining tin is found outside the classical CT site, which was already expected by Birchall & Sleight (1975). The two possible coordination polyhedra of tin in the tunnel are presented in Figs. 1 and 2. In both cases, an Sn shift of 0.39 (1) Å from CT is found. The average Sn—O distances [Sn21 polyhedron 2.6 (3) Å and Sn22 polyhedron 2.6 (3) Å] are shorter than that observed in foordite [2.7 (5) Å; Trunov *et al.*, 1963]; however, the shortest distance is observed in foordite (Sn—O1 = 2.177 Å), which allows an Sn valence of 1.98. The corresponding valences calculated using the whole set of Sn—O bonds are 1.86 and 1.87 for Sn21 and Sn22, respectively. The distortion of the tin(II) polyhedron has already been used to determine lone-pair stereoactivity (Galy *et al.*, 1975); these authors locate the electronic LP in the center of the coordination polyhedron. In the title compound, this center coincides with CT so that the Sn—LP distance is equal to the Sn offset [0.386 (13) and 0.395 (15) Å for Sn21 and Sn22, respectively]. Such a distance is shorter than the Sn—LP distance proposed by Galy *et al.* (1975) of 0.95 Å. So the tin environment cannot be 6O1 + 2O2. Moreover, since the O2 content in CC is less than expected, being half the tin(II) content, one of the O2 atoms is probably missing from the coordination sphere of Sn, *i.e.* some CC are empty. Galy *et al.* (1975) have proposed that the sphere of interaction of an LP has the same volume as an oxygen anion. So, competition between LP and O2 occurs in the occupation of a cavity and O2 cannot occupy a site at which a lone pair is pointing. Still,

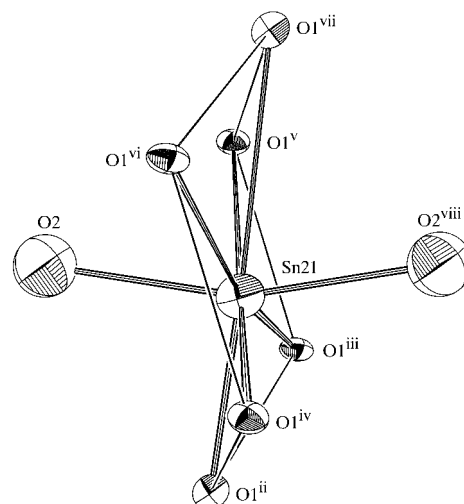


Figure 1

View of the observed surrounding of Sn21. Ellipsoids are shown at the 60% probability level. See Table 1 for symmetry codes.

they have shown that lone pairs can point at each other. In this compound, a maximum of four lone pairs can point at CC. The pyrochlore formula of a compound which includes this restraint is then $M_{1.6}^{II}Nb_2O_{6.6}$. Such a formula is close to the observed lead niobate formula of $Pb_{1.5}Nb_2O_{6.5}$. But cancelling one O2 around Sn gives bond valences that are unrealistic (1.45 and 1.46 for Sn21 and Sn22, respectively). A similar observation can be made for the lead pyrochlore compound. Although the agreement index (R) is good, vacancies in the CT and CC sites may induce changes of symmetry or commensurate or incommensurate arrangements and the use of a cubic cell with the $Fd\bar{3}m$ space group may result in finding only the average location of tin in the tunnels.

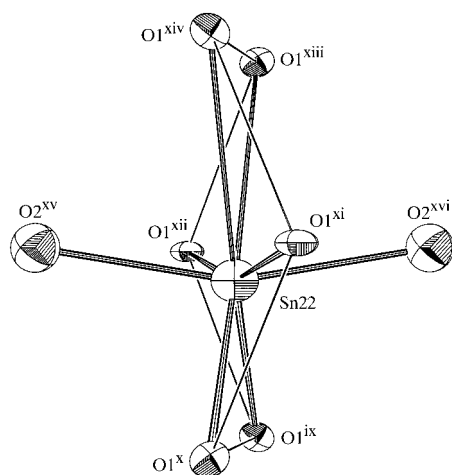


Figure 2
View of the observed surrounding of Sn22. Ellipsoids are shown at the 60% probability level. See Table 1 for symmetry codes.

The main result of this study is the chemical and structural behavior of tin(II); it is easily oxidized and exhibits strong lone-pair stereoactivity. Such behavior could be the reason for the difficulty in inserting tin(II) in the A site of ABO_3 perovskite-type compounds.

Experimental

The title compound was synthesized by the flux method using NaCl as the melting salt. A mixture of $NaNbO_3$ and an excess of $SnCl_2$ was heated with NaCl at 1273 K in a quartz tube under vacuum. Red crystals of regular octahedral shape were obtained. Elemental analysis for Sn and Nb suggested the formula $Sn_{1.6}Nb_{1.8}O_{6.3}$. Mossbauer spectroscopy indicated that tin(II) was partially oxidized to tin(IV). The ionic formula which complies with electroneutrality is $Sn_{1.4}^{II}Nb_{1.8}^{IV}Sn_{0.2}^{IV}O_{6.3}$.

Crystal data

$Sn_{1.59}Nb_{1.84}O_{6.35}$
 $M_r = 461.08$
Cubic, $Fd\bar{3}m$
 $a = 10.539$ (2) Å
 $V = 1170.5$ (4) Å³
 $Z = 8$
 $D_x = 5.233$ Mg m⁻³
Mo $K\alpha$ radiation

Cell parameters from 654 reflections
 $\theta = 1.0\text{--}39.4^\circ$
 $\mu = 10.19$ mm⁻¹
 $T = 293$ (2) K
Octahedral, clear intense red
 $0.06 \times 0.06 \times 0.06$ mm

Data collection

Nonius KappaCCD diffractometer
CCD scans
Absorption correction: numerical (Coppens *et al.*, 1965)
 $T_{\min} = 0.52$, $T_{\max} = 0.54$
640 measured reflections
198 independent reflections

172 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$
 $\theta_{\max} = 39.2^\circ$
 $h = 0 \rightarrow 18$
 $k = 0 \rightarrow 14$
 $l = 0 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.060$
 $S = 0.97$
198 reflections
24 parameters

$w = 1/[\sigma^2(F_o^2) + 13.1226P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.035$
 $\Delta\rho_{\max} = 0.94$ e Å⁻³
 $\Delta\rho_{\min} = -0.74$ e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0021 (2)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|---|-------------|--|------------|
| Nb1—O1 ⁱ | 1.9813 (10) | Sn22—O1 ^{ix} | 2.375 (17) |
| Sn21—O1 ⁱⁱ | 2.323 (17) | Sn22—O1 ^x | 2.375 (17) |
| Sn21—O1 ⁱⁱⁱ | 2.536 (14) | Sn22—O1 ^{xi} | 2.733 (10) |
| Sn21—O1 ^{iv} | 2.536 (14) | Sn22—O1 ^{xiii} | 2.733 (10) |
| Sn21—O1 ^v | 2.914 (14) | Sn22—O1 ^{xiv} | 3.049 (13) |
| Sn21—O1 ^{vi} | 2.914 (14) | Sn22—O2 ^{xv} | 2.316 (4) |
| Sn21—O1 ^{vii} | 3.087 (14) | Sn22—O2 ^{xvi} | 2.316 (4) |
| Sn21—O2 ^{viii} | 2.317 (14) | | |
| O1 ⁱ —Nb1—O1 ^{xviii} | 89.39 (10) | O1 ^v —Sn21—O1 ^{vi} | 105.4 (4) |
| O1 ^{xiii} —Nb1—O1 ⁱ | 90.61 (10) | O1 ^v —Sn21—O1 ^{vii} | 55.3 (2) |
| O1 ⁱ —Nb1—O1 ^{xviii} | 90.61 (10) | O2 ^{xv} —Sn22—O2 ^{xvi} | 160.4 (10) |
| O1 ⁱ —Nb1—O1 ^{xiv} | 180.00 (0) | O1 ^{ix} —Sn22—O1 ^x | 71.9 (4) |
| O2—Sn21—O2 ^{viii} | 160.8 (6) | O1 ^{ix} —Sn22—O1 ^{xi} | 65.7 (2) |
| O1 ⁱⁱ —Sn21—O1 ⁱⁱⁱ | 69.8 (4) | O1 ^{ix} —Sn22—O1 ^{xii} | 130.2 (6) |
| O1 ⁱⁱ —Sn21—O1 ^v | 124.1 (6) | O1 ^{ix} —Sn22—O1 ^{xiii} | 171.3 (4) |
| O1 ⁱⁱ —Sn21—O1 ^{vii} | 177.7 (6) | O1 ^{ix} —Sn22—O1 ^{xiv} | 116.9 (2) |
| O1 ⁱⁱⁱ —Sn21—O1 ^{iv} | 132.1 (5) | O1 ^{xi} —Sn22—O1 ^{xii} | 163.4 (6) |
| O1 ⁱⁱⁱ —Sn21—O1 ^v | 61.0 (3) | O1 ^{xi} —Sn22—O1 ^{xiii} | 106.4 (5) |
| O1 ⁱⁱⁱ —Sn21—O1 ^{vi} | 165.8 (6) | O1 ^{xi} —Sn22—O1 ^{xiv} | 57.3 (2) |
| O1 ⁱⁱⁱ —Sn21—O1 ^{vii} | 110.7 (5) | O1 ^{xiii} —Sn22—O1 ^{xiv} | 54.4 (3) |

Symmetry codes: (i) $y, \frac{1}{4} - x, \frac{1}{4} - z$; (ii) $\frac{1}{4} + y, \frac{1}{4} + z, 1 - x$; (iii) $x, \frac{1}{2} + y, \frac{1}{2} + z$; (iv) $\frac{3}{4} - z, x, \frac{3}{4} - y$; (v) $\frac{1}{4} + y, 1 - x, \frac{1}{4} + z$; (vi) $1 - x, \frac{1}{4} + z, \frac{1}{4} + y$; (vii) $\frac{3}{4} - y, \frac{3}{4} - z, x$; (viii) $\frac{1}{4} + y, 1 - z, \frac{1}{4} + x$; (ix) $-z, \frac{1}{4} + y, x - \frac{3}{4}$; (x) $y, \frac{3}{4} - x, -\frac{1}{4} - z$; (xi) $x - \frac{1}{2}, y, z - \frac{1}{2}$; (xii) $\frac{1}{2} - x, \frac{1}{4} + z, y - \frac{1}{4}$; (xiii) $y, \frac{1}{4} - z, \frac{1}{4} - x$; (xiv) $y - \frac{1}{2}, x - \frac{1}{4}, -z$; (xv) $\frac{1}{4} - z, x, \frac{1}{4} - y$; (xvi) $y - \frac{1}{4}, \frac{3}{4} - z, x - \frac{3}{4}$; (xvii) $-z, y - \frac{1}{4}, x - \frac{1}{4}$; (xviii) $\frac{1}{4} - x, \frac{1}{4} - y, z$.

The atomic positions were taken from the pyrochlore-type structure (Jona *et al.*, 1955; Sleight, 1968). The second setting, with the origin at $\bar{3}m$ of the $Fd\bar{3}m$ space group, was chosen. As expected, some of the niobium site (16c) is occupied by Sn atoms. The occupation factors of Sn and Nb were constrained in order to fill the site. Surprisingly, the atomic displacement parameter when tin is placed at CT, which is normally occupied by A atoms, indicates that no tin can occupy this site. Similarly, the CC site which contains either the A atom of the AB_2O_6 pyrochlore or the O atom of the $A_2B_2O_7$ pyrochlore cannot contain these remaining Sn atoms. A difference Fourier synthesis showed that Sn is delocalized around CT, and two sites, with coordinates $0, y, -y$ and x, x, z , were chosen in order to simulate the corresponding electron density. As in $Pb_{1.5}Nb_2O_{6.5}$ (Bernotat-Wulf & Hoffman, 1982), the residue which appeared at CC was attributed to oxygen. Because strong correlations appear between the Sn atomic parameters around CT, cycles of refinement with alternating optimization of coordinate parameters and atomic displacement parameters of both Sn21 and Sn22 were performed until convergence occurred. A general constraint of electroneutrality was applied to all occupation factors.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *maXus* (Mackay *et al.*, 1999) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1329). Services for accessing these data are described at the back of the journal.

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