dans ces liaisons sur un seul site cristallin, d'où l'absence de phase ferroélectrique pour les hydrogéno-orthophosphates de thallium(I).

Références

Frazer, B. C. & Pepinsky, R. (1953). *Acta Cryst.* **6**, 273–285.

Le Montagner, E. & Le Donche, L. (1966). *Proceedings of the International Meeting on Ferroelectricity*, Tome 1, pp. 244–249.

Magyar, H. (1948). *Anz. Oesterr. Akad. Wiss. Math. Naturwiss. Kl.* **85**, 166. [*Struct. Rep.* **11**, 383–384.]

Matthias, B., Merz, W. & Scherrer, P. (1947). *Helv. Phys. Acta*, **20**, 273.

Oddon, Y. & Tranquard, A. (1980) *C.R. Acad. Sci. Sér. C*, **235**. Sous presse.

Oddon, Y., Tranquard, A. & Pèpe, G. (1979). *Acta Cryst.* B**35**, 542–545.

Oddon, Y., Vignalou, J. R., Tranquard, A. & Pèpe, G. (1978). *Acta Cryst.* B**34**, 3510–3514.

Oddon, Y., Vignalou, J. R., Tranquard, A. & Pèpe, G. (1979). *Acta Cryst.* B**35**, 2525–2528.

Prewitt, C. T. (1966). *SFLS*-5. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Rammelsberg, C. (1882). *Sitzungsber. Dtsch. Akad. Wiss. Berlin Kl. Math. Phys. Tech.* p. 287.

Tenzer, L., Frazer, B. C. & Pepinsky, R. (1958). *Acta Cryst.* **11**, 505–509.

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Tin(II) Oxide: Structure Refinement and Thermal Expansion

By J. Pannetier

Institut Laue–Langevin, 156 X, avenue des Martyrs, 38042 Grenoble CEDEX, France

and G. Denes

Laboratoire de Chimie Minérale D (LA N° 254), Université de Rennes, 35042 Rennes CEDEX, France

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Abstract. SnO, tetragonal, $P4/nmm$, $a = 3{\cdot}8029\,(5)$, $c = 4{\cdot}8382\,(8)$ Å (neutrons, 293 K), $Z = 2$. Profile and integrated-intensity refinements at room temperature confirm the regular square-pyramidal coordination of $\mathrm{Sn^{II}}$, with Sn—O 2·224 (8) Å. Final R for the integrated-intensity refinement was 4·3% for 28 measured intensities. The thermal expansion is less anisotropic than expected for a layer structure.

Introduction. Various forms of tin monoxide, SnO, have been reported (Moore & Pauling, 1941; Donaldson, Moser & Simpson, 1963; Kwestroo & Vromans, 1967). The blue-black modification of SnO is isostructural with the tetragonal form of PbO but it is the only example of a regular square-pyramidal tin(II) coordination. The present neutron study, which was undertaken to check this tin(II) configuration, confirms the previous X-ray powder structure determination (Moore & Pauling, 1941).

The sample material was powdered SnO obtained from OSI. High-temperature X-ray powder data were recorded on a CGR diffractometer with a high-temperature device (Barret, Gerard & Watelle-Marion, 1968) using pelleted samples and working under dry nitrogen. The unit-cell parameters were obtained by least-squares refinement from 20 lines (Cu $K\alpha$; $5° < \theta < 65°$) and were subsequently fitted by least squares by a polynomial of the form $a(T) = a_0 + a_1T + a_2T^2$ where a denotes the cell constant a or c in Å and T the temperature in °C. Neutron diffraction patterns at 293 K were collected on the D1B diffractometer of the Institut Laue–Langevin with $\lambda = 1{\cdot}282$ Å. The sample was inserted in a 10 mm diameter vanadium tube. Data were collected in two steps ($2° < 2\theta < 82°$ and $65° < 2\theta < 145°$) of two and a half hours and reduced using conventional ILL programs (Wolfers, 1970). Integrated intensities were determined by fitting the shape of the Bragg peaks to Gaussians.

The method of profile-fitting structure refinement (Rietveld, 1969; Hewat, 1973) was applied in the space group $P4/nmm$ [tin in 2(c) and oxygen in 2(a)]. The refinement included the scale factor, three half-width parameters, the zero-point correction, the lattice constants, one positional parameter, two isotropic thermal parameters, the preferred-orientation parameter and the peak-asymmetry parameter for peaks below $2\theta = 30°$. The conventional integrated-intensity refinement used a local program (L'Helgoualch, Fonteneau & Pan-

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netier, 1975) allowing for the refinement of a preferred-orientation parameter G (Rietveld, 1969); the refinement included the scale factor, one positional parameter, two isotropic thermal parameters and the preferred-orientation parameter and was based on 28 measured intensities (42 *hkl*). The scattering amplitudes $b(\mathrm{Sn}) = 6{\cdot}2$ and $b(\mathrm{O}) = 5{\cdot}8$ fm were used.

The final parameters are given in Table 1;* there is fair agreement between the results of the two methods, both for the refined parameters and their standard deviations.

The cell parameters in the range 273 K to 593 K are as follows (T in °C):

$$a\,(\text{Å}) = 3{\cdot}7984\,(6) + 3{\cdot}31\,(36) \times 10^{-5}\,T + 7{\cdot}9\,(16) \times 10^{-8}\,T^2$$

$$c\,(\text{Å}) = 4{\cdot}8368\,(7) + 1{\cdot}25\,(4) \times 10^{-4}\,T + 6{\cdot}2\,(19) \times 10^{-8}\,T^2.$$

Discussion. The regular square-pyramidal coordination of $\mathrm{Sn^{II}}$ in tetragonal SnO is confirmed; as expected (Shannon, 1976), the Sn—O distance (Table 1) is shorter for this regular coordination than the average Sn—O distances observed in distorted square pyramids: 2·302 Å in $\mathrm{Na_2Sn(C_2O_4)_3}$ (Donaldson, Donoghue & Smith, 1976), 2·312 Å in $\mathrm{SnC_2O_4}$ (Gleizes & Galy, 1979), 2·288 Å in α-$\mathrm{SnWO_4}$ (Jeitschko & Sleight, 1972). However, the most important feature of the SnO structure does not lie in the Sn—O distance but rather in the O—Sn—O angles: the coordination of $\mathrm{Sn^{II}}$ is usually described as being derived from an octahedron distorted by the lone pair (Brown, 1974) which leads, for the fourfold coordination, to two sets of O—Sn—O angles of about 80 and 140° ($\mathscr{A}$ configuration according to Brown, 1974). The two angles of 117·3° observed in tetragonal SnO indicate a strong departure from the usual bond directions from which the low thermal stability* and high reactivity† of solid SnO could result.

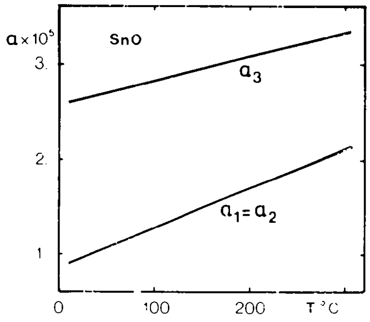

Fig. 1. Thermal-expansion coefficients *vs* temperature.

Table 1. *Final refined parameters*

	Neutrons[a]	Neutrons[b]	X-ray
a (Å)	3·8036 (12)	3·8029 (5)	3·804 (6)[d]
c (Å)	4·8385 (15)	4·8382 (8)	4·826 (8)[d]
c/a	1·2721 (5)	1·2722 (2)	1·269
z(Sn)	0·2384 (11)	0·2383 (8)	0·2356 (19)[e]
B(Sn) (Å^2)	1·02 (14)	0·57 (7)	
B(O) (Å^2)	1·06 (13)	0·99 (9)	
G[c]	0·063 (16)	0·023 (11)	
R_N, R_{wN} (%)	4·3, 4·3	4·4	
R_p, R_{wp} (%)	–	10·9, 11·6	
d(Sn—O) (Å)	2·224 (8)	2·224 (6)	2·22 (2)[e]

(*a*) Integrated-intensity refinement. (*b*) Profile-fitting structure refinement. (*c*) Preferred-orientation parameter (see Rietveld, 1969). (*d*) Swanson, Fuyat & Ugrinic (1955). (*e*) Moore & Pauling (1941); cell constants given in this reference (a = 3·796, c = 4·816 Å) differ from those quoted in more recent works.

The thermal-expansion coefficients in layer components are usually quite anisotropic, a feature which is generally attributed to weak binding between layers; in this respect, the anisotropy of the thermal expansion of SnO (Fig. 1) is somewhat smaller than would be expected from the structure (no electrostatic binding but lone-pair–oxygen repulsion between the sheets). However, this can be understood on a simple geometric basis; the Sn—O bond is rather strong which means that its thermal expansion must be quite small; then the thermal dilatation in the *ab* plane ($\alpha_a = \alpha_b$) comes from the O—O repulsive interaction‡ and, from purely geometric arguments, one can see that this thermal expansion α_1 together with a negligible Sn—O bond expansion will lead to a decrease of z(Sn) with increasing temperature, *i.e.* to a 'negative contribution' to α_c; this effect partly cancels the 'true' thermal expansion along c.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35531 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Dissociation to Sn + $\mathrm{SnO_2}$ occurs above 643 K.

† For instance, solid SnO quickly reacts with aqueous $\mathrm{SnF_2}$ solutions to give $\mathrm{Sn_2OF_2}$.

‡ This O—O distance is short (2·69 Å), which explains the small values of the compressibility coefficients in the *ab* plane (Serebryanaya, Kabalkina & Vereshchagin, 1970).

References

Barret, P., Gerard, N. & Watelle-Marion, G. (1968). *Bull. Soc. Chim. Fr.* **8**, 3172–3176.

Brown, I. D. (1974). *J. Solid State Chem.* **11**, 214–233.

Donaldson, J. D., Donoghue, M. T. & Smith, C. H. (1976). *Acta Cryst.* B**32**, 2098–2101.

Donaldson, J. D., Moser, W. & Simpson, W. B. (1963). *Acta Cryst.* **16**, A22.

Gleizes, A. & Galy, J. (1979). *J. Solid State Chem.* **30**, 23–33.

Hewat, A. W. (1973). UKAERE, Harwell, report RRL 73/897.

JEITSCHKO, W. & SLEIGHT, A. W. (1972). *Acta Cryst.* B**28**, 3174–3178.
KWESTROO, W. & VROMANS, P. H. G. M. (1967). *J. Inorg. Nucl. Chem.* **29**, 2187–2190.
L'HELGOUALCH, H., FONTENEAU, G. & PANNETIER, J. (1975). Unpublished computer program.
MOORE, W. & PAULING, L. (1941). *J. Am. Chem. Soc.* **63**, 1392–1394.
RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
SEREBRYANAYA, N. R., KABALKINA, S. S. & VERESHCHAGIN, L. F. (1970). *Sov. Phys. Dokl.* **14**, 672–674.
SHANNON, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
SWANSON, H. E., FUYAT, R. K. & UGRINIC, G. M. (1955). *Natl Bur. Stand. US Circ.* 539, Vol. IV.
WOLFERS, P. (1970). Unpublished computer programs.

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Fluorure d'Ammonium et d'Uranium(IV): $NH_4U_3F_{13}$

PAR HICHAM ABAZLI, ALAIN COUSSON, ALAIN TABUTEAU ET MONIQUE PAGÈS

Laboratoire Curie, associé au CNRS, 11 *rue P. et M. Curie,* 75231 *Paris CEDEX* 05, *France*

ET MADELEINE GASPERIN

Laboratoire de Minéralogie–Cristallographie, associé au CNRS, Université Pierre et Marie Curie,
4 *place Jussieu,* 75230 *Paris CEDEX* 05, *France*

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Abstract. $NH_4U_3F_{13}$, orthorhombic, $Pm2_1b$, $a = 8\cdot045$ (2), $b = 8\cdot468$ (2), $c = 7\cdot375$ (2) Å, $Z = 2$, $d_x = 6\cdot47$ Mg m^{-3}. Intensities were measured diffractometrically with Mo $K\bar{\alpha}$ radiation [μ(Mo $K\bar{\alpha}$) = 48·0 mm^{-1}]. The structure was refined to $R = 0\cdot044$, $R_w = 0\cdot058$ for 2272 independent reflexions. This compound is isostructural with $RbTh_3F_{13}$.

Introduction. L'étude récente du système NH_4F–NpF_4 (Abazli, Jové & Pagès, 1979) a permis de mettre en évidence quatre phases nouvelles, dont deux sont encore de structure inconnue. Or, la connaissance des données structurales est nécessaire pour interpréter les mesures de résonance Mössbauer de ^{237}Np de ces composés (H. Abazli, thèse d'Etat en cours). Une méthode de cristallogenèse, la méthode des flux de chlorures, nous a permis d'obtenir sous forme monocristalline les fluorures doubles d'ammonium et d'uranium et en particulier la phase la plus stable: $NH_4U_3F_{13}$, isotype de $NH_4Np_3F_{13}$. A une composition voisine de l'eutectique, le mélange NH_4Cl–$ZnCl_2$ présente un point de fusion relativement bas ($\theta_F \simeq 453$ K). Les fluorures d'ammonium et d'uranium ont donc été mélangés aux chlorures d'ammonium et de zinc dans les proportions suivantes: $NH_4F + UF_4 + 2(NH_4Cl + ZnCl_2)$. Les divers constituants, placés dans un creuset de platine, ont été soumis à un dégazage prolongé sous vide secondaire, puis chauffés à 873 K sous atmosphère d'argon. Après refroidissement lent (5 K h^{-1}), on obtient de nombreux monocristaux de couleur vert clair ayant la forme de plaquettes rectangulaires. Les différents essais de cristallogenèse ont été effectués sur des quantités relativement faibles de tétrafluorure d'uranium (80 mg); les résultats positifs obtenus permettent d'envisager la préparation de monocristaux des fluorures de neptunium correspondant.

L'étude d'un monocristal de dimensions 0,072 × 0,092 × 0,024 mm a été conduite à partir des données recueillies sur un diffractomètre Enraf-Nonius CAD-4 muni d'un monochromateur en graphite. La maille et le groupe d'espace, déterminés précédemment à l'aide d'une caméra de précession et d'une chambre de Weissenberg, ont été confirmés. Les paramètres ont été affinés par moindres carrés dans le système orthorhombique. (Groupe de Laue *mmm*; règles d'extinction: $hk0$, $k = 2n$; groupes d'espaces possibles $Pmmb$, $Pm2_1b$ ou $P2mb$.) Les mesures d'intensité ont été faites avec la radiation Mo $K\bar{\alpha}$ [balayage ω–2θ, angle de balayage $(1,2 + 0,35\,\mathrm{tg}\,\theta)^\circ$, vitesse variable]. Les indices maximaux sont 14 pour h, 15 pour k et 13 pour l. Trois raies de référence étaient remesurées toutes les heures. 3281 réflexions furent enregistrées dans ces conditions et corrigées des facteurs de Lorentz–polarisation. Des corrections d'absorption ont été effectuées en utilisant la méthode analytique de de Meulenaer & Tompa (1965), à l'aide du programme *AGNOST* (Ahmed, 1974).

L'étude de la fonction de Patterson tridimensionnelle a permis de localiser les atomes

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