JOURNAL OF SOLID STATE CHEMISTRY 38, 381–385 (1981)

Pattern-Fitting Structure Refinement of Tin(II) Oxide

F. IZUMI

National Institute for Research in Inorganic Materials, 1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

Received November 12, 1980; in final form January 23, 1981

The Rietveld profile-analysis refinement procedure has been applied to X-ray powder diffractometer data collected from tin(II) oxide with Cu$K\alpha$ radiation. Background corrections were calculated by Aitken–Lagrange interpolation to remove errors resulting from simple linear interpolation. Four symmetric profile functions were tested; the use of a modified or an intermediate Lorentz function led to a more satisfactory fit than use of the Gauss or Lorentz function. A preferred-orientation function proposed by Toraya and Marumo gave lower R values than Rietveld's function. The positional parameter of the tin atom was found to be 0.2369, which is almost identical with the corresponding value reported for isomorphous lead(II) oxide.

Introduction

Tin(II) oxide occurs in a metastable orthorhombic form (*1*) and a stable tetragonal one isomorphous with the low-temperature modification of lead(II) oxide. Moore and Pauling (*2*) determined the crystal structure of the tetragonal form, which is not available as single crystals, by using the photographic powder technique. The $P4/nmm$ unit cell contains two Sn atoms at 0.5, 0, z and 0, 0.5, $\bar{z}$, and two oxygen atoms at 0, 0, 0 and 0.5, 0.5, 0. It has a layer structure in which each oxygen layer is sandwiched between two tin layers.

Moore and Pauling were forced to use a very finely divided preparation of tin(II) oxide for the X-ray measurement, because coarser preparations gave anomalously high intensities for $00l$ reflections owing to the pronounced basal cleavage and platy habit of tin(II) oxide. Consequently, the sample gave diffuse lines, the intensities of which could not be estimated very accurately. They determined only six ratios of intensity for neighboring pairs of powder lines by visual comparisons and evaluated the positional parameter z as 0.2356 ± 0.0019. The above facts suggest that the structural parameters which they reported may be unreliable.

The present investigation was undertaken to refine the lattice and crystal-structural parameters for tin(II) oxide by applying the Rietveld profile-analysis procedure (*3, 4*) to the X-ray powder pattern of a well-crystallized sample. Structures have now been refined for a number of polycrystalline materials by the whole-pattern fitting of not only neutron diffraction data but also X-ray diffraction data (*4*). In this method, introduction of an appropriate factor makes it possible to correct intensities for preferred orientation (*3*). Furthermore, remarkably precise lattice parameters can be obtained as a result of the requirement that the calcu-

0022-4596/81/090381-05$02.00/0

lated and observed profiles match all along their steep sides as well as at their maxima (*5*). The Rietveld method is, therefore, expected to be most suitable for the present purpose.

Experimental

Tin(II) oxide was obtained from Wako Pure Chemical Industries, Ltd.; the lines of its X-ray powder pattern were sharp enough to measure intensities. Emission spectrography showed that the specimen contained as impurities Mg, Al, Si, Ca, Mn, Fe, Cu, In, and Pb and that the total content of these foreign metals was less than 400 ppm.

Preliminary experiments revealed that prolonged grinding did not aid in reducing the preferred orientation of crystals. On the other hand, the following procedure for preparing flat diffractometer specimens proved to be very effective in minimizing preferred-orientation errors. Tin(II) oxide powder was packed into a standard aluminum holder whose back side was covered with a glass slide bound firmly with Scotch tape and a clip. The specimen surface was flattened by moving another glass slide gently along it; the resulting surplus powder was wiped off. The holder was mounted on a Philips diffractometer equipped with an automatic step-scanning system for digital data collection, and the clip was taken off.

X-Ray intensity data were collected with nickel-filtered Cu$K\alpha$ radiation for 40 sec at 0.05° intervals over the 2θ range 17–107.6° (1796 observations and 34 unique Bragg reflections). Since a weak Cu$K\beta$ peak assigned to the 101 reflection of tin(II) oxide was observed, the intensities in the angular range of 26.6 to 27.4° were eliminated prior to structure refinement.

A computer program for pattern-fitting structure refinement, "XRPD", was written in FORTRAN IV by the author for the angle-dispersive X-ray case and run on a FACOM 230-35 computer. The XRPD program is of modular construction to facilitate user-desired changes. Least-squares analysis is carried out by utilizing four subprograms which were written by Bevington (*6*) and were modified so as to provide the possibility of keeping any parameter constant during refinement. The program incorporates a plotter output routine and can plot an X-ray diffraction pattern after profile and structure parameters have been either refined by regression analysis or input by a user. The atomic scattering factors used were those of Cromer and Mann (*7*) for neutral tin and oxygen and were corrected for anomalous dispersion.

Results and Discussion

In the profile-analysis refinement procedure, the background of a recorded diagram is usually evaluated in two ways: (a) linear interpolation between operator-selected points (*3*), (b) approximation by a function containing refinable parameters (*8*). The author employed Aitken–Lagrange interpolation (*9*) to remove errors resulting from the simple linear approximation in method (a). The advantage of this procedure over method (b) is that no equation to approximate background levels is needed explicitly. Thirty-nine points were selected at which gross intensities (Y_i) can be considered to have fallen to their background values (B_i). Background corrections at other positions were found by interpolating polynomials derived from the B_i values of the 39 points. To each net intensity, $y_i = Y_i - B_i$, a statistical weight, $W_i = 1/Y_i$ was assigned (*3*).

Four symmetric profile functions were

tested in the present work:

Gaussian

$$A \exp[-4 \ln 2(2\theta_i - 2\theta_k)^2/H_k^2], \quad (1)$$

Lorentzian

$$A[1 + 4(2\theta_i - 2\theta_k)^2/H_k^2]^{-1}, \quad (2)$$

modified Lorentzian (ML) (10)

$$A[1 + 4(2^{1/2} - 1)(2\theta_i - 2\theta_k)^2/H_k^2]^{-2}, \quad (3)$$

and intermediate Lorentzian (IL) (11)

$$A[1+4(2^{2/3} - 1)(2\theta_i - 2\theta_k)^2/H_k^2]^{-1.5}. \quad (4)$$

In the above functions, A is the normalization factor (11), $2\theta_i$ the angle at step i, $2\theta_k$ the calculated Bragg angle for a peak, and H_k the full width at half-maximum intensity. The procedures for calculating H_k and a correction factor for peak asymmetry were just the same as those of Rietveld (3). The Cu$K\alpha_2$ profile was assumed to be of one-half the intensity of the Cu$K\alpha_1$ profile and shifted from it toward larger angles by (12)

$$\Delta 2\theta = 0.285 \tan \theta. \quad (5)$$

The preferred-orientation function most commonly employed in line-profile analysis is that described by Rietveld (3):

$$P(\phi) = \exp(-C\phi^2). \quad (6)$$

Here, ϕ is the acute angle between the normal to plate-like cyrstallites and the scattering vector, which coincides with the normal of the flat specimen surface in the case of X-ray powder diffraction. C is the preferred-orientation parameter to be refined and is a measure for the half-width of the assumed Gaussian distribution of the normals about the preferred-orientation direction. On the basis of an X-ray investigation of taeniolite, $KLiMg_2Si_4O_{10}F_2$, Toraya and Marumo (8, 13) have recently proposed a new preferred-orientation function consisting of ϕ and two refinable parameters C_1 and C_2:

$$P(\phi) = C_1 + (1 - C_1)\exp(-C_2\phi^2). \quad (7)$$

Parameter C_1 was introduced to express the asymptotic convergence of the correction factor of taeniolite to a constant value at large ϕ. The suitability of the two different correction functions was tested in an effort to improve the overall fit.

Table I shows the reliability indices for the four profile functions and the two preferred-orientation functions. R_p (individual points) and R_{wp} (individual points-weighted) are defined in the usual manner as

$$R_p = 100 \sum_i |y_i(\text{obs}) - y_i(\text{calc})| / \sum_i y_i(\text{obs}), \quad (8)$$

$$R_{wp} = 100\left[\sum_i W_i\{y_i(\text{obs}) - y_i(\text{calc})\}^2 / \sum_i W_i\{y_i(\text{obs})\}^2\right]^{1/2}. \quad (9)$$

The results of profile refinements based upon Eq. (7) are listed in Table II, where standard deviations are given in parentheses and refer to the least significant digit.

Table I shows that the R_p and R_{wp} values were always lower with Eq. (7) than with Eq. (6) so long as the same

TABLE I

COMPARISON BETWEEN R FACTORS FOR TIN(II) OXIDE

	Gauss	ML	IL	Lorentz
(A) Refinement with Eq. (6) used				
R_p	23.4	19.5	20.1	24.6
R_{wp}	24.4	19.5	19.5	23.7
(B) Refinement with Eq. (7) used				
R_p	21.4	17.7	18.0	23.0
R_{wp}	23.1	17.7	17.6	22.0

TABLE II

COMPARISON OF LATTICE AND CRYSTAL-STRUCTURAL PARAMETERS FOR TIN(II) OXIDE

		Gauss	ML	IL	Lorentz
	a(Å)	3.7989(2)	3.7986(1)	3.7985(1)	3.7986(1)
	c(Å)	4.8412(3)	4.8408(2)	4.8411(2)	4.8408(2)
Sn	z	0.2368(4)	0.2369(3)	0.2369(3)	0.2368(4)
Sn[a]	B (Å^2)	0.60(6)	0.66(4)	0.66(4)	0.52(6)
O[a]	B (Å^2)	2.8(6)	2.6(4)	2.6(4)	2.4(6)

[a] Isotropic temperature factor.

profile functions were used. As the R factors indicate clearly, the profiles are described better by the ML and IL functions than by the Gauss and Lorentz functions. The Gaussian profiles fell off more rapidly and the Lorentzian more slowly than the tails of the observed peaks. Refinements with ML and IL profiles led to nearly the same parameters and R values. The conclusion to be drawn from these results is that selection of the ML or IL function coupled with that of Eq. (7) gives the best overall fit of calculated and observed profiles for tin(II) oxide (Fig. 1).

The R_p factors described in the literature for the pattern-fitting of angle-dispersive X-ray data range from 12 to 28% with an average around 20% (*4*). Taking into account the difficulty that tin(II) oxide is a very orientation-prone substance, the R_p values of ca. 18% obtained with either the ML or the IL function and Eq. (7) are considered fairly satisfactory. The positional parameter of the tin atom, z, was 0.2369 in these cases. This value is somewhat higher than that determined by Moore and Pauling (*2*) and almost identical with the value of z reported for isomorphous lead(II) oxide, 0.237 (*14*).

The bond angles and bond lengths in tin(II) oxide were calculated from the data for the ML function in Table II. Each oxygen atom is sp^3 hybridized, having four tetrahedrally disposed metal neighbors [Sn–O–Sn bond angles 117.8° (4) and 105.5° (2)]. Each tin atom is bonded to four oxygen atoms forming a square to one side of it [O–Sn–O bond

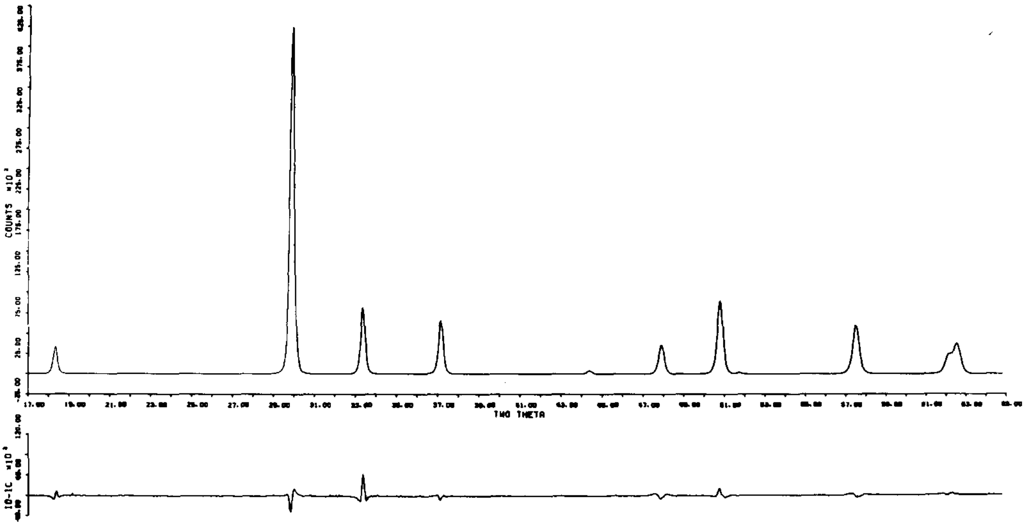

FIG. 1. X-Ray Rietveld refinement of tin(II) oxide. Modified Lorentzian profiles and Eq. (7) were used. The calculated pattern is shown by the upper solid curves, and the discrepancy in the fit [y_i(obs) − y_i(calc)] is shown by the lower solid curves.

angles 74.5° (4) and 117.8° (2)]; a fifth orbital is occupied by a stereochemically active unshared electron pair and directed toward the apex. The strong directional effect of the inert pair is achieved by hybridization with either d_z^2 or p_z, or an admixture of both (*15*). The bond distance Sn–O is 2.22 Å, corresponding to the radius 0.92 Å for tin(II). The Sn–Sn distances are 3.53 Å (separate layers with oxygen layer between), 3.70 Å (van der Waals contact), and 3.80 Å (between atoms in the same layer).

Acknowledgments

The author expresses his gratitude to Professor F. Marumo and Dr. H. Toraya of Tokyo Institute of Technology for sending him a draft of their paper prior to publication and to Drs. M. Umehara and T. Chiba for their assistance in the computer calculations. Thanks are also due to Dr. K. Uchida for his continuing interest and support.

References

1. J. D. Donaldson, W. Moser, and W. B. Simpson, *J. Chem. Soc.*, 839 (1961).
2. W. J. Moore and L. Pauling, *J. Amer. Chem. Soc.* **63**, 1392 (1941).
3. H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
4. R. A. Young, NBS Spec. Pub. (U.S.) 567, p. 143, Nat. Bur. Stand., Washington, D.C. (1980).
5. R. A. Young, P. E. Mackie, and R. B. Von Dreele, *J. Appl. Crystallogr.* **10**, 262 (1977).
6. P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences," p. 232, McGraw-Hill, New York (1969).
7. D. T. Cromer and J. B. Mann, *Acta Crystallogr. Sect. A* **24**, 321 (1968).
8. H. Toraya and F. Marumo, *Rep. Res. Lab. Eng. Mater. (Tokyo Inst. Technol.)*, No. 5, 55 (1980).
9. A. Ralston, "A First Course in Numerical Analysis," p. 57, McGraw-Hill, New York (1965).
10. G. Malmros and J. O. Thomas, *J. Appl. Crystallogr.* **10**, 7 (1977).
11. C. P. Khattak and D. E. Cox, *J. Appl. Crystallogr.* **10**, 405 (1977).
12. H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials," 2nd ed., p. 625, Wiley, New York (1974).
13. H. Toraya and F. Marumo, *Mineral. J.*, in press.
14. J. Leciejewicz, *Acta Crystallogr.* **14**, 1304 (1961).
15. D. M. Adams, "Inorganic Solids," p. 133, Wiley, London (1974).