

Short Communications

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J. Appl. Cryst. (1978), **11**, 284–286

A spinel form of cadmium stannate. BY L. A. SIEGEL, *Chemical Research Division, American Cyanamid Company, 1937 West Main Street, Stanford, Connecticut 06904, USA*

(Received 1 August 1977; accepted 14 March 1978)

Bulk cadmium stannate, Cd_2SnO_4 , normally crystallizes in the orthorhombic system. Cadmium stannate obtained from sputtered thin films and from a high-temperature, high-pressure procedure has now been shown, on the basis of an X-ray diffraction investigation, to crystallize in the cubic system. The lattice parameter of the face-centered cell is 9.143 ± 0.001 Å. The data are consistent with a spinel structure, analogous to cadmium indate.

The preparation and properties of thin films of cadmium stannate, Cd_2SnO_4 , deposited on fused quartz and other substrates has been described by Nozik (1972) and by Haacke (1976). These films have been found to be promising candidates for transparent electrodes and for coatings in solar-heat collectors by Haacke (1976, 1977). In the course of this work, X-ray diffraction patterns of the films, *in situ*, were obtained by mounting the substrate in the sample post of a powder diffractometer. The patterns usually showed several strong lines, although the relative intensities of the lines varied among the different film samples. There was no agreement between the interplanar spacings of the thin-film patterns and those reported by Trömel (1969) for the orthorhombic form of bulk cadmium stannate. It was not possible to find agreement with any of the tin or cadmium oxide diffraction patterns.

In one case, a small portion of film deposited on single-crystal sodium chloride was freed from its substrate. This material was ground and powder patterns were obtained both with a Guinier–Nonius focusing camera and with a standard 114.6 mm diameter Debye–Scherrer camera. $\text{Cu } K\alpha$ radiation was employed, nickel-filtered when used with the Debye–Scherrer camera. These patterns, which showed some line broadening, were also clearly different from that of orthorhombic cadmium stannate. Further investigation showed, however, that the patterns of the film material, with the exception of one weak line, showed substantial agreement both in interplanar spacings and intensities with the powder pattern of cadmium indate, CdIn_2O_4 . The latter had been reported by Skribljak, Dasgupta & Biswas (1959) who indexed the pattern on the face-centered cubic lattice and who proposed that CdIn_2O_4 had the inverse spinel structure. This was supported by intensity calculations.

The agreement between the diffraction patterns of Cd_2SnO_4 and CdIn_2O_4 , together with the similarity of the scattering powers of Cd^{2+} , In^{3+} and Sn^{4+} and their ionic radii, suggests that Cd_2SnO_4 also crystallizes in a spinel structure.

Subsequently, examples of the spinel form of Cd_2SnO_4 were found in bulk samples. One of these was a preparation made from a sample of precipitated mixed hydroxides of cadmium and tin that was fired at 900°C . The diffraction pattern of this material was also slightly broadened.

A second bulk sample was prepared by fusion at high-temperature and high-pressure conditions. Bulk orthorhombic Cd_2SnO_4 was densely packed in an aluminum oxide crucible which was placed in a quartz ampoule. The ampoule

was evacuated, sealed off, and placed in a graphite holder which was closed with a threaded graphite cap. This assembly was placed in an RF heater and held at 1430°C for 10 min. (Orthorhombic Cd_2SnO_4 heated to this temperature at atmospheric pressure will decompose. The pressure in the ampoule at 1430°C cannot be calculated since data on the equilibrium vapor pressure of CdO over Cd_2SnO_4 are not available.) A maximum of approximately 2 g of material could be made in this way. This preparation yielded a photographic diffraction pattern which showed the cubic phase as the major constituent, plus a small amount of cadmium oxide and other material. In this case, the pattern of the cubic phase was quite sharp. While there is no independent chemical analysis of this material, the pattern matches that of the thin-film samples, and the Cd:Sn ratio of the latter had been verified by X-ray fluorescence analysis. Analysis of preparations of bulk Cd_2SnO_4 indicate that only small deviation from an oxygen:metal ratio of 4:3 is possible.

The measured interplanar spacings and visually estimated intensities, uncorrected for absorption, of the cubic phase found in the fused material are given in Table 1, together with the cubic indexing. These data are from a Debye–Scherrer pattern. The indexing shows the extinctions expected for the face-centered lattice and the spinel structure space group, $Fd3m$. The lattice parameter of the cell, obtained by extrapolation of high-angle reflections, is 9.143 ± 0.001 Å, and calculated spacings for this value are given. The spacing data for CdIn_2O_4 , based on a parameter of 9.115 Å are also shown.

Skribljak, Dasgupta & Biswas (1959) gave intensity calculations based on an inverse spinel structure. In this structure eight of the trivalent In ions are located on the eight tetrahedral sites, while the remaining eight trivalent In ions and the eight divalent Cd ions are randomly distributed over the sixteen octahedral sites. If the unit cell whose origin is at $43m$ is used, the tetrahedral sites are the $8(a)$ positions, the octahedral sites are the $16(d)$ positions, and the oxygen ions are on the $32(e)$ positions. Skribljak, Dasgupta & Biswas (1959) gave 0.385 for the oxygen parameter. They also pointed out that the similarity of the Cd^{2+} and In^{3+} scattering factors makes it impossible to distinguish between the normal and the inverse distribution of cations.

The inverse spinel structure of Cd_2SnO_4 , following the discussion of Blasse (1964), would have eight Cd^{2+} ions on the tetrahedral sites and eight Cd^{2+} and eight Sn^{4+} ions on the octahedral sites. Here too, however, the similarity of the Cd^{2+} and Sn^{4+} scattering factors precludes distinction of the normal *versus* the inverse distribution. The relative intensi-

Table 1. X-ray powder diffraction data for Cd_2SnO_4 and CdIn_2O_4

Cd_2SnO_4						$\text{CdIn}_2\text{O}_4^*$				
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> ₀ (Å)	<i>d</i> _c (Å)	<i>I</i> ₀	<i>I</i> _c	<i>d</i> ₀ (Å)	<i>d</i> _c (Å)	<i>I</i> ₀	<i>I</i> _c
1	1	1	5.25	5.279	10	8	5.309	5.263	13	13
2	2	0	3.22	3.233	40	28	3.232	3.222	38	38
3	1	1	2.74	2.757	100	100	2.757	2.749	100	132
2	2	2	2.63	2.639	30	23	2.620	2.631	30	28
4	0	0	2.28	2.286	25	13	2.287	2.279	27	17
3	3	1	—	2.098	—	<1	1.973	2.091	3	<1
4	2	2	1.858	1.866	30	12	1.863	1.861	25	15
5	1	1	1.754	1.760	70	38	1.755	1.754	50	56
3	3	3	—	—	—	8	—	—	—	—
4	4	0	1.612	1.616	80	49	1.609	1.611	50	61
5	3	1	1.542	1.545	<10	2	1.536	1.541	3	3
4	4	2	—	1.524	—	<1	—	1.519	<1	<1
6	2	0	1.442	1.446	10	6	1.438	1.441	5	7
5	3	3	1.391	1.394	30	16	1.381	1.390	45	51
6	2	2	1.375	1.378	30	15	—	1.374	—	—
4	4	4	1.316	1.320	<10	3	1.318	1.316	9	3
7	1	1	1.277	1.280	<10	<1	1.275	1.276	5	1
5	5	1	—	—	—	1	—	—	—	—
6	4	2	1.220	1.222	20	9	1.216	1.218	12	9
7	3	1	1.188	1.190	60	18	1.186	1.187	44	29
5	5	3	—	—	—	12	—	—	—	—
8	0	0	1.141	1.143	20	9	1.136	1.139	15	9
7	3	3	—	1.117	—	<1	—	1.113	<1	<1
6	4	4	—	1.109	—	<1	—	1.106	<1	<1
8	2	2	1.076	1.078	10	3	1.071	1.074	5	4
7	5	1	1.054	1.056	40	18	1.050	1.052	35	24
5	5	5	—	—	—	4	—	—	—	—
6	6	2	1.048	1.049	20	9	—	1.046	—	—
8	4	0	1.020	1.022	10	5	1.024	1.019	6	4
6	6	4	0.9727	0.9746	10	3	—	0.972	<1	<1
9	3	1	0.9577	0.9584	40	21	0.953	0.955	17	11
8	4	4	0.9325	0.9332	60	35	0.931	0.930	22	16
10	2	0	0.8964	0.8965	10	4	—	—	—	—
8	6	2	—	—	—	7	—	—	—	—
9	5	1	0.8834	0.8839	50	29	—	—	—	—
7	7	3	—	—	—	9	—	—	—	—
10	2	2	0.8793	0.8798	20	14	—	—	—	—
6	6	6	—	—	—	5	—	—	—	—
10	4	2	0.8343	0.8346	20	10	—	—	—	—
11	1	1	0.8242	0.8244	50	15	—	—	—	—
7	7	5	—	—	—	17	—	—	—	—
8	8	0	0.8080	0.8081	50	38	—	—	—	—
10	6	0	0.7840	0.7840	30	9	—	—	—	—
8	6	6	—	—	—	16	—	—	—	—
11	3	3	0.7755	0.7755	70	54	—	—	—	—
9	7	3	—	—	—	143	—	—	—	—

* Data of Skribljak, Dasgupta & Biswas (1959).

ties calculated for the Cd_2SnO_4 inverse spinel structure, using an oxygen parameter of 0.392, are given in Table 1. These calculations do not include a temperature factor. The intensities calculated by Skribljak, Dasgupta & Biswas (1959) for CdIn_2O_4 are also reproduced.

The 331 line is not observed for Cd_2SnO_4 in agreement with the structure factor calculation. A weak 331 line is reported for CdIn_2O_4 . In the table of spacings given for CdIn_2O_4 , this line shows a substantially greater difference between calculated and observed value than any other line. Also, of eight lines whose calculated intensity is given as <1, it was the only one observed. It seems possible, then, that the 331 line reported for CdIn_2O_4 represents an impurity.

Trömel (1969) does not report a density value for orthorhombic Cd_2SnO_4 , and none is available for the cubic form discussed here. The unit-cell dimensions indicate that the

density of the cubic form is about 10% smaller than that of the orthorhombic form.

These results are presented as evidence for the existence of a spinel form of Cd_2SnO_4 . It is the only form of Cd_2SnO_4 that has been observed here for sputtered films. It has also been found in bulk samples, including one prepared at high-pressure and high-temperature conditions. No relation is known to exist between sputtering and the effects of high temperature and high pressure. Occurrence of the spinel form under these two sets of conditions appears to be coincidental.

The cadmium stannate preparations were made by Drs A. J. Nozik and G. Haacke, and I am indebted to them for many helpful discussions. I wish to thank Dr F. M. Lovell of the Lederle Laboratories Division, American Cyanamid Company, for carrying out the structure factor calculations.

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J. Appl. Cryst. (1978). **11**, 286–288

Lattice parameter and thermal expansion of ReO_3 between 291 and 464 K. By TZUEN-SHI CHANG and P. TRUCANO, *Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, USA*

(Received 11 July 1977; accepted 8 March 1978)

The Bond technique was used to measure the lattice parameter of the red transition-metal oxide, ReO_3 , as a function of temperature. At 298 K the lattice parameter is $3.7477(1)\text{Å}$. The thermal expansion is linear with temperature between 291 and 464 K and a linear coefficient of thermal expansion of $1.1(1) \times 10^{-6} \text{ K}^{-1}$ was fit to the data.

Introduction

ReO_3 is a red transition-metal oxide which crystallizes in space group $Pm3m$. The structure, which is closely related to the perovskite structures of the tungsten bronzes (Goodenough, 1971), is formed by Re atoms at the center of the unit cell and O atoms in face-centered positions. Crystals contain highly covalent bonds between Re and O atoms (Mattheiss, 1969) but show unusually high conductivities (Phillips & Shanks, 1971; Pearsall & Lee, 1974). The measured specific heat and magnetic susceptibility are in agreement with the free electron model (Zumsteg & Pearsall, 1974).

The crystals have been further characterized by X-ray photoelectron measurements (Wertheim, Mattheiss, Campagna & Pearsall, 1974), Hall constant results (Pearsall & Lee, 1974) and band structure calculations (Mattheiss, 1969), all of which are consistent with highly covalent bonding and a broadened $5d$ conduction band leading to high conductivity. Elastic stiffness measurements (Pearsall & Coldren, 1976) show that acoustic properties are dominated by strong Re–O bonds and a highly anisotropic shear propagation.

Measurements of the thermal expansion of ReO_3 were undertaken to provide an estimate of the importance of anharmonic effects in the crystal. To test the experimental

apparatus and procedures, measurements were also carried out on Si single crystals and compared with the results of other researchers.

Experimental

The ReO_3 single crystals were grown by Pearsall (1973), who used chemical vapor-transport techniques and found room-temperature resistivities of approximately $2 \times 10^{-6} \Omega \text{ cm}$ and an impurity content of less than 100 p.p.m. A crystal which had a (110) face with dimensions of $0.7 \times 0.3 \text{ mm}$, was chemically polished and used to measure the Bragg angle for the 330 reflection. The Si crystal was oriented, cut, and polished so that its (110) planes were parallel to a $1 \times 2 \text{ mm}$ diffracting surface. Undoped Lopex grade silicon with a dislocation density of less than 100 cm^{-2} , as reported by the manufacturer (Texas Instruments, Inc.), was used.

Bond's method for lattice parameter determination (Bond, 1960) with an extensively modified General Electric SPG Spectrometer was used to measure the lattice constants. Temperatures were controlled and measured to $\pm 1^\circ\text{C}$. Step scans through each peak with a step width of 0.005° and the midchord method (Bond, 1960) were used to determine the peak positions.

Table 1. ReO_3 lattice parameters vs temperature

θ_{uncorr} is the measured Bragg angle for the 330 reflection. a_{uncorr} and a_{corr} are the uncorrected and corrected lattice parameters, respectively, and α_T is the linear coefficient of thermal expansion. Errors are based on estimates of the uncertainty in measuring angles. See text for further discussion of errors.

$T(^{\circ}\text{C})$	θ_{uncorr}	$a_{\text{uncorr}}(\text{Å})$	$a_{\text{corr}}(\text{Å})$	$\alpha_T(\times 10^{-6} \text{ K}^{-1})$
17.5	60.698 (1)	3.74758 (4)	3.74768 (4)	1.1 (1)
21.5	60.697	3.74764	3.74774	1.1
44	60.695	3.74770	3.74780	1.1
63	60.692	3.74784	3.74794	1.1
82	60.690	3.74788	3.74798	1.1
109	60.687	3.74802	3.74812	1.1
140	60.684	3.74813	3.74823	1.1
164	60.682	3.74821	3.74831	1.1
167	60.680	3.74828	3.74838	1.1
191	60.677	3.74837	3.74847	1.1

Measurements of the Bragg angles for the 110 and 220 reflections resulted in the following values:

(110) 23	16.897 (1)	3.74801 (25)	3.74885 (25)
(220) 23	35.543 (1)	3.74795 (11)	3.74818 (11)