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THE CRYSTAL STRUCTURE OF TIN OXIDE AT HIGH PRESSURE

In the first communication (1) it was shown that SnO, at high pressure and room temperature, undergoes a reversible phase transition. It was suggested that the high-pressure phase SnOII crystallizes in the fluorite structural type, and on this basis an estimate was made of the compressibility of both phases.

A repeated X-ray study of SnO at high pressure confirmed the presence of a polymorphic reversible transformation under these conditions. Improvement of the experimental technique made it possible to markedly improve the quality of the X-ray patterns. The most important changes proved to be the use of filtered radiation ($\mathrm{Mo}K_\alpha$), a reduction of the diameter of the sample under study to ~ 0.17 mm. In carrying out the experiments, LiF was added to SnO; it served as an internal pressure manometer and at the same time substantially reduced the absorption of X-rays by the sample. In the first work (1), NaCl was used for the same purpose; replacing it with LiF was caused by the undesirable superposition of the strongest reflections of SnOII and NaCl. The pressure was estimated from the compressibility of LiF (2).

Table 1

Interplanar spacings in SnOII at $p = 90$ kbar, space group C_{2v}^7—$Pm2n$, $a = 3.82$ Å, $b = 3.61$ Å, $c = 4.30$ Å, $z = 2$

hkl	I_{obs}	d_{obs}	d_{calc}	I_{calc}
101	s.	2.90	2.86	80
011	s.	2.78	2.76	100
110	v. s.	2.63	2.62	96
111	v. w.	2.24	2.24	11
002	v. w.	2.12	2.15	20
200	med. w.	1.95	1.91	26
020	v. w.	1.80	1.80	12
201	w.	1.75	1.75	3

Fig. 1. Scheme of X-ray diffraction patterns of SnOI (A, $p = 1$ bar) and SnOII (B, $p = 90$ kbar)

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hkl	I_{obs}	d_{obs}	d_{calc}	I_{calc}
021	med.	1.66	1.66	2
112	med.	1.66	1.66	35
211	med.	1.572	1.572	40
121	med.	1.521	1.525	43
202	v. w.	1.426	1.428	13
022	w.	1.382	1.381	8
220	med. w.	1.311	1.314	11

As was noted (1), the influence of pressure is manifested first of all in the first reflections: the line (101) becomes noticeably broadened and then splits into two; the line (110) becomes considerably stronger. However, when recorded with filtered radiation the splitting of (101) proved to be smaller; apparently, in the absence of a filter it was artificially increased owing to the superposition of the β-reflection from (110).

At $p > 60$ kbar, splitting of the reflections (200), (201), (211), and (202) is observed on the X-ray patterns of SnOII. Since only lines with $h \neq k$ split, the natural supposition arises that during the phase transition a rhombic distortion of the SnOI structure occurs. Indeed, as shown in Fig. 1 and in Table 1, the X-ray pattern of the SnOII phase can be indexed on the basis of an orthorhombic cell with parameters $a = 3.82$ Å, $b = 3.61$ Å, $c = 4.30$ Å, $Z = 2$ at $p = 90$ kbar.

Figure 2 presents the dependence of the parameters and volume of the unit cell on pressure, which shows that the distortion of the crystalline structure of SnOI is a first-order polymorphic transition. Evidence is provided by the jump on the curve $c(p)$: at $p = 15$—17 kbar, $\Delta c/c = 2.5\%$. The volume jump is very small ($\Delta v/v = 1.5\%$) owing to the fact that the orthorhombic distortion of the tetragonal cell of SnOI occurs

by means of two deformations of opposite sign—extension and compression, as is seen from the relation

$$a_{\text{rhomb}} = a_{\text{tetr}} + \Delta_1; \qquad b_{\text{rhomb}} = a_{\text{tetr}} - \Delta_2; \qquad c_{\text{rhomb}} = c_{\text{tetr}} - \Delta_3. \tag{1}$$

The data obtained show that in the pressure interval 15-120 kbar the volume decreases by $\sim 15\%$, b and c by ~ 8-9%, while a remains practically unchanged.

Fig. 2. Dependence of the parameters (in Å) and volume (in $Å^3$) of the unit cell of tin oxide on pressure

Figure 2: Fig. 2. Dependence of the parameters (in Å) and volume (in $Å^3$) of the unit cell of tin oxide on pressure

Figure 3

Figure 3: Figure 3

Fig. 1. Scheme of X-ray diffraction patterns of SnOI (**A**, $p = 1$ bar) and SnOII (**B**, $p = 90$ kbar)

On the basis of the results obtained, an attempt was made to establish the arrangement of atoms in the SnOII structure.

It should be noted that, in contrast to the tetragonal oxides of tin and lead (^{3}), the rhombic modifications SnOII and yellow PbO (^{4}) crystallize in different structural types.

Fig. 2. Dependence of the parameters (in Å) and volume (in $Å^3$) of the unit cell of tin oxide on pressure

Among the reflections observed on the X-ray patterns of the new phase (Table 1), all $(hk0)$ with $h + k \neq 2n$ are absent; therefore the SnOII structure can be assigned to one of two space groups, D_{2h}^{13}–$Pmmn$ or C_{2v}^{7}–$Pm2n$, which are subgroups of D_{4h}^{7}–$P4/nmm$. Both groups allow the structural motif characteristic of the low-pressure phase SnOI to be retained in SnOII, which corresponds to the slight change in the intensity of the diffraction pattern (Fig. 1). In this case two possibilities arise for the arrangement of atoms in the rhombic cell: 1) in the group D_{2h}^{13}–$Pmmn$, tin atoms may occupy the twofold positions $2(c) : 0\,{}^1/2z;\ {}^1/20\bar{z}$, oxygen atoms $2(a) : 00z;\ {}^1/2\,{}^1/2\bar{z}$; and 2) in the group C_{2v}^{7}–$Pm2n$, the tin and oxygen atoms must be in the single twofold position $(2a) : 0yz;\ {}^1/2,\ {}^1/2 + y,\ \bar{z}$.

Since a quantitative estimate of the intensities of the reflections I_{hkl} from the SnOII X-ray patterns is practically impossible, in choosing the model the following qualitative relationships between I_{hkl} were taken into account: 1) $I_{101} \simeq I_{011} \simeq I_{110}$–very strong, 2) $I_{112} \simeq I_{211}$–medium, 3) $I_{111} \ll I_{201}$–weak.

If scattering by the oxygen atoms is neglected, conditions 1-3 will be satisfied when the tin atoms are displaced along the z axis by $\sim \pm 0.05$ Å from the initial position. However, taking into account the influence of the oxygen atoms in position $00z$, condition (1) is violated, and in order to preserve it the O atoms must be shifted along the y and z axes.

Thus, the best agreement with experiment can be achieved if tin and oxygen occupy the positions: $\mathrm{Sn} : 0{}^1/_2z,\ {}^1/_20\bar{z}$ with $z \simeq 0.2$ and

Fig. 3. Projections of SnOII: **A**—onto the (001) plane and —onto the (010) plane. —projection of the cubic sphalerite structure. The dashed lines mark projections of the doubled unit cell; the fractions denote atomic coordinates along the axes z (**A**) and y ( )

O : $0\,{}^{1}/_{4}\,{}^{3}/_{4}$; ${}^{1}/_{2}\,{}^{3}/_{4}\,{}^{1}/_{4}$. In this case the SnOII structure may be assigned to the group C_{2v}^{7}—$Pm2n$, and, consequently, the center of inversion disappears at the phase transition.

The chosen model corresponds to the SnOII structure shown in Figs. 3**A** and 3 . In the new SnOII phase, the distorted closest cubic packing of tin atoms is retained, but the order in which the tetrahedral voids are filled by atoms changes. If in tetragonal SnOI the tetrahedra occupied by oxygen alternated in the structure according to the motif: filled layer–empty layer, determining the layered character of the structure (5), then in rhombic SnOII the occupied tetrahedra are distributed uniformly throughout the volume, and thus in each layer half of the tetrahedra are filled. It follows from this that at the phase transition the shape of the coordination polyhedron for tin changes: the tetragonal pyramid is replaced by a rhombic tetrahedron.

Table 2

Interatomic distances in SnOI and SnOII (in Å)

SnOI	SnOII
4(Sn—O) 2.21	2(Sn—O) 2.12
Sn—Sn 3.53	Sn—O 2.14
	Sn—O 2.54
	Sn—Sn 3.14
Sn—Sn 3.72	Sn—Sn 3.68
O—O 2.70	O—O 3.40

Thus, the SnOII structure approaches a rhombically distorted structural type of sphalerite (Fig. 3), to which the following arrangement of atoms would correspond: Sn : $0\,{}^{1}/_{2}\,{}^{1}/_{4}$; ${}^{1}/_{2}\,0\,{}^{3}/_{4}$ and O : $0\,{}^{1}/_{4}\,{}^{3}/_{4}$; ${}^{1}/_{2}\,{}^{3}/_{4}\,{}^{1}/_{4}$. The interatomic distances in the SnOI and SnOII phases (Table 2) indicate that the SnO_4 tetrahedron is strongly distorted: one Sn–O distance, 2.54 Å, is much greater than the other 2(Sn—O): 2.12 and 2.14 Å. However, the Sn–Sn and O–O distances (Table 2) show that the edge lengths of the SnO_4 and OSn_4 tetrahedra have similar values, which also supports the analogy with the sphalerite structure.

In the present work the behavior of SnO was investigated under the simultaneous action of high temperature up to 400° and pressure up to $\sim$ 90 kbar. It is known that, on heating to 370° (^{6}) and $p = 1$ atm, SnO decomposes with the release of β-Sn according to the equation

$$2SnO \rightarrow SnO_2 + \beta\text{-}Sn_2 \tag{2}$$

The experiments were carried out in a high-pressure chamber calibrated by the electrical-resistance discontinuities of Bi, Tl, and Ba ([7]). A platinum ampoule with SnO was placed in a graphite heater. It was found that decomposition occurs throughout the pressure interval studied; however, the effect of pressure on the decomposition temperature was not evaluated quantitatively. The decomposition of SnO was recorded from the sharp increase in conductivity (a consequence of the release of β-Sn) and on the basis of X-ray analysis of the products of the experiment.

Taking into account the existence of a phase transition at $p > 15$ kbar and at 25°, and the procedure used in the experiments (first the load was applied, and then the heating was switched on), one may conclude that the decomposition of SnO at high temperature is observed for both modifications, SnOI and SnOII. Thus, up to pressures of ~ 100 kbar it is not possible to change the coordination number in the crystal structure of tin monoxide, which indicates the considerable stability of fourfold coordination for divalent tin.

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