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Abstract

Full Text

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PHYSICS

Corresponding Member of the Academy of Sciences of the USSR L. F. Vereshchagin, S. S. Kabalkina,
L. M. Lityagina

INVESTIGATION OF THE EFFECT OF HIGH PRESSURE ON THE STRUCTURE OF TIN OXIDE

Tin oxide SnO under normal conditions has a structure of the PbO type (ˆ1, ˆ2) with unit-cell parameters $a = 3.80$ Å; $c = 4.82$ Å; $c/a = 1.27$, space group $P4/nmm$, $Z = 2$. According to the same data, the oxygen atoms form square nets in the SnO structure; above or below the centers of the squares are tin atoms; as a result, each oxygen atom is at the center of a tetrahedron of tin atoms, and each tin atom occupies the apex of a tetragonal pyramid, at the base of which lies a square of oxygen atoms.

Thus, in the SnO structure one can distinguish packets, each of which consists of a flat net of oxygen atoms enclosed between two nets of tin atoms. The packets are bound to one another by weak van der Waals interactions and, consequently, the SnO structure is layered. The value of the interatomic distance Sn···O (2.21 Å) indicates that in the layer there is a superposition of ionic and covalent bonding.

Fig. 1. Scheme of X-ray diffraction patterns of SnO, taken at pressures: I –1 bar, II –60 kbar, III –1 bar after release of pressure.

The layered character of the structure and the low coordination of the atoms (although by Goldschmidt' s criterion the ratio of ionic radii in SnO coincides with the lower limit of stability of a structure with coordination 8) determined our interest in the behavior of tin oxide under high pressure.

In the present work an X-ray diffraction study of the structure of SnO was carried out at room temperature and high pressure up to 100 kbar. A special X-ray camera was used in the work ($^{3-}$4), the main part of which is a pellet of amorphous boron with a channel for the sample. Calibration of the camera with respect to pressure was carried out by recording jumps in the electrical resistance of bismuth during phase transitions at 25.4, 27, and 90 kbar ($^\frown$5), and also radiographically from the compressibility of NaCl; in the latter case the Bridgman data ($^\frown$6) were used. We estimate the error in determining the pressure as ±5 kbar. For the work, SnO of chemically pure grade was taken. X-ray photography was carried out with molybdenum radiation. In order to reduce absorption, the investigated samples were diluted with amorphous boron in the proportion $^2/_3$SnO $+^1/_3$B.

The experiments showed that at high pressure SnO undergoes a reversible phase transition. Figure 1 presents a scheme of three X-ray diffraction patterns of SnO taken on one film. On diffraction pattern II, obtained during photography while high pressure was acting on the sample, the lines of the initial phase (which we shall call SnO I) disappear and new ones appear, indicating a polymorphic transition under pressure. Upon removal of the pressure

we again obtain an X-ray pattern of the SnO I phase; the latter indicates that the high-pressure phase (we shall denote it SnO II) is unstable at atmospheric pressure, i.e., the phase transition is reversible.

In the X-ray patterns of the high-pressure phase (SnO II) there are 6 lines that are unambiguously indexed in the rutile-type structure. Table 1 presents data for the SnO II phase at $p = 60$ kbar.

Table 1

I	hkl	d_{meas}, Å	d_{calc}, Å	I	hkl	d_{meas}, Å	d_{calc}, Å
Medium	100	2.96	2.95	Weak	102	2.04	2.05
Medium	002	2.80	2.81	Weak	110	1.715	1.71
Strong	101	2.62	2.62	Weak	103	1.575	1.57

The cell parameters for SnO II are: $a = 3.42 \pm 0.02$ Å; $c = 5.62 + 0.04$ Å. From this one can calculate the bond lengths: Sn . . . Sn 3.42 Å and Sn . . . 0.2 Å. Consequently, the difference in the Sn . . . Sn distances (3.80; 3.70 and 3.51 Å) that exists in SnO I disappears, since the SnO II structure is a closest packing of tin atoms.

Fig. 2. Dependences of the parameters a, c, and c/a for the SnO I phase on pressure p

A detailed study of the effect of high pressure on the structure of SnO made it possible to estimate the compressibility of the low-pressure phase and the

Fig. 2. Dependences of the parameters a, c, and c/a for the SnO I phase on pressure p

Figure 2: Fig. 2. Dependences of the parameters a, c, and c/a for the SnO I phase on pressure p

volume jump at the phase transition. In this case, a small amount of NaCl was mixed into the sample as a standard for estimating the pressure from its compressibility. Figures 2 and 3 show the change in the cell parameters, the ratio c/a, and the volume V as functions of pressure.

As can be seen from Fig. 2, the parameters a and c decrease under pressure nonuniformly; more intense compression occurs in the direction of the c axis, and accordingly the ratio c/a decreases as p increases. The latter was to be expected, taking into account the layered character of the SnO I structure. The data obtained made it possible to estimate the coefficients of linear compressibility:

$$-\frac{1}{a_0}\frac{\Delta a}{\Delta p} = 3.3 \cdot 10^{-7}\ \text{bar}^{-1}, \quad -\frac{1}{c_0}\frac{\Delta c}{\Delta p} = 12.9 \cdot 10^{-7}\ \text{bar}^{-1}$$

and the volume jump at the transition $\Delta V/V = 7.0 \pm 5\%$ at $p = 40$ kbar.

The study showed that the phase transition in most cases occurs at a pressure of 40–50 kbar; however, in a number of experiments the transition was observed at significantly lower pressures (15–20 kbar).

The transition pressure in SnO is not strictly constant, which, apparently, may be connected either with kinetic features of the process or is a consequence of the influence of boron, which in this case may play the role of an impurity. Comparing the structures of SnO I and SnO II, one may conclude that, in the polymorphic transformation, the order of stacking of the layers and the arrangement of the nearest neighbors of the tin atom change.

Indeed, the distorted cubic packing of tin atoms [SnO I] transforms into the hexagonal closest packing of SnO II, while the coordination polyhedron—a tetragonal pyramid in SnO I—is replaced by a tetrahedron in [SnO II] (in SnO II the oxygen atoms occupy the vertices of the tetrahedron, at the center of which is the tin atom).

It follows from this that the transition SnO I → SnO II is, by Buerger's definition (^{7}), reconstructive, since in order for it to occur it is necessary to destroy the "old" Sn ... O bonds and form new ones; such transitions require a considerable expenditure of energy and are usually sluggish (^{7}). For a more complete characterization of the process it should be noted that the phase transition in SnO is "prepared" at fairly low pressures, still within the stability range of the initial phase. Long before the transition, the SnO I lines in the x-ray pattern become blurred; a noticeable redistribution of their intensities occurs, especially clearly expressed in the first reflections ((110) increases, (101) weakens noticeably). At the moment of transition the strongest SnO I line (101) broadens and splits into two SnO II lines with indices (100) and (002), while the (110) reflection gives the strongest SnO II line (101). The phase with the rutile structure, SnO II, is represented in the x-ray pattern by very broad and diffuse lines, which, apparently, may be caused by inhomogeneous deformation of individual grains of the specimen during the phase transition under pressure.

Fig. 3. Dependence of the volume V of the unit cell of the SnO I and SnO II phases on pressure p

By analogy with the results of previous investigations ([4,8]), it may be assumed that at higher pressure SnO will undergo the next polymorphic transition from a rutile-type structure to a NaCl-type structure.

Institute of High Pressure Physics
Academy of Sciences of the USSR

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