PHYSICS

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Abstract

Full Text

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X-RAY INVESTIGATION OF THE EFFECT OF HYDROSTATIC PRESSURE UP TO 18,000 kg/cm^2 ON THE STRUCTURE OF LEAD TITANATE

As is known, lead titanate crystallizes in the perovskite structure ([1]). At room temperature $PbTiO_3$ has a tetragonal structure with an axial ratio $c/a = 1.063$. At $T_K = 490°$ (Curie temperature ([2,3])) and $p = 1$ kg/cm^2, the crystal undergoes a first-order phase transition from the ferroelectric to the paraelectric state, which is accompanied by the transformation of the tetragonal cell into a cubic one. An analogous transition at $T_K = 120°$ and $p = 1$ kg/cm^2 is also exhibited by barium titanate ([4]). Hydrostatic pressure lowers the Curie temperature of $BaTiO_3$ ([5,6]). From the work of Merz ([5]) it follows that T_K decreases linearly with pressure, with $dT_K/dp = -5.8 \cdot 10^{-3}$ deg/atm.

Fig. 1. High-pressure X-ray camera

The present work is devoted to an X-ray investigation of the effect of hydrostatic pressure on the structure of lead titanate at room temperature. In comparison with barium titanate, $PbTiO_3$ possesses more sharply expressed ferroelectric properties and, consequently, is characterized by a large spontaneous polarization ([7]), strong distortion of the crystal lattice, significant displacements of the titanium and lead ions ([8,9]), a sharp change in the parameters, and a large jump in volume at the transition point ([2]). It may be expected that the influence of hydrostatic pressure on the transition will be more noticeable in the case of $PbTiO_3$. The application of diffraction analysis to the study of lead titanate is facilitated (in comparison with $BaTiO_3$) by the fact that the ratio c/a in this case is considerably

tively exceeds unity. The latter makes it possible to obtain a Debye diffraction pattern with good resolution. When photographing with copper radiation using a cassette with $d = 114$ mm, resolution is already achieved on the front lines, as

a result of which it proved possible to apply the usual method of X-ray analysis at high pressure.

The investigation was carried out in a high-pressure X-ray camera, shown in Fig. 1, differing from the camera described by us earlier ([10]) in the following design features of the high-pressure vessel (see the section schematically shown in Fig. 2): 1) the high-pressure vessel consists of two cylinders hot-pressed into one another—the inner one (1), made of ShKh-15 steel, $R_c = 56 \div 58$, and the outer one (2), made of 40Kh steel, $R_c = 40 \div 42$; 2) the specimen under study (3) is located in the channel of the fixed beryllium cone (4) under the action of the hydrostatic pressure of the liquid (6).

The specimens of lead titanate under study were obtained in the form of ceramic from the L. Ya. Karpov Physicochemical Institute*. The parameters of the starting substance were: $a = 3.903$ Å, $c = 4.154$ Å, $c/a = 1.064$. Photography was carried out at room temperature in the range 1—18 000 kg/cm^2 on a fine-focus tube with a copper anode ([11]). Figure 3 presents four radiographs, taken on one film at different pressures. The photographs show reflections (100), (110), (101), (111) (the lines (112) and (211), which usually appear on such radiographs, are absent in this case because of the small slit length of the high-pressure vessel; the strong line (200) is poorly visible owing to the superposition of diffraction from beryllium). The radiographs were measured on an IZA-2 comparator. The distances between the symmetric $2s$ lines were recorded with an accuracy of ± 0.05 mm. In the calculation, the usual correction for absorption by the cylindrical specimen was introduced. The parameters a, c, the ratio c/a, and the compressibility $\Delta c/c$ of $PbTiO_3$ are presented in Table 1 and in Fig. 4.

Fig. 2. Diagram of the high-pressure vessel. 1—inner cylinder; 2—outer cylinder; 3—specimen under study; 4—fixed beryllium cone; 5—electrode to which a manganese manometer is fastened; 6—liquid transmitting pressure; 7—diaphragm; 8—piston; 9—seal.

Table 1

p, kg/cm^2	c, Å	c/a	$\Delta c/c$, %, meas.	$\Delta c/c$, %, calc.	Δ	p, kg/cm^2	c, Å	c/a	$\Delta c/c$, %, meas.	$\Delta c/c$, %, calc.	Δ
1	4.154	1.064				13500	4.065	1.042	2.1	1.9	+0.2
3800	4.125	1.056	0.7	0.5	+0.2	14100	4.066	1.038	2.1	2.0	+0.1
5400	4.118	1.056	0.9	0.8	+0.1	14200	4.071	1.043	2.0	2.0	0
8000	4.101	1.050	1.3	1.1	+0.2	14200	4.075	1.041	1.9	2.0	−0.1
8200	4.102	1.050	1.2	1.2	0	14700	4.057	1.039	2.3	2.1	+0.2
9500	4.100	1.048	1.3	1.4	−0.1	15200	4.070	1.040	2.0	2.2	−0.2
10900	4.089	1.046	1.6	1.6	0	15400	4.057	1.036	2.3	2.2	+0.1
11700	4.083	1.042	1.7	1.7	0	16200	4.052	1.035	2.4	2.3	+0.1
12800	4.083	1.043	1.7	1.8	−0.1	16300	4.050	1.035	2.5	2.3	+0.2
13300	4.075	1.042	1.9	1.9	0	17800	4.051	1.035	2.5	2.5	0

Fig. 4. I —dependence of the parameters c and a on pressure; II —dependence of the ratio c/a on pressure; III —dependence of $\Delta c/c$ on pressure, corresponding to the equation $\Delta c/c = 14.3 \cdot 10^{-7} p$; experimental points are plotted

Figure 2: Fig. 4. I —dependence of the parameters c and a on pressure; II —dependence of the ratio c/a on pressure; III —dependence of $\Delta c/c$ on pressure, corresponding to the equation $\Delta c/c = 14.3 \cdot 10^{-7} p$; experimental points are plotted

* The authors express their gratitude to Yu. N. Venevtsev for providing the specimens.

It follows from the data obtained that, with increasing pressure, in the case of $PbTiO_3$ a decrease in the tetragonality of the cell is observed and, consequently, a lowering of the Curie point due to a considerable contraction of the parameter c and a small, but undoubtedly present, increase in the parameter a (at $p = 18\,000$ kg/cm^2, $\Delta c = -0.10$ Å, $\Delta a = +0.01$ Å). From the experimental data it follows that in the pressure interval 1–18 000 kg/cm^2 the dependence of $\Delta c/c$ on p is linear in character and can be represented in the form

$$\frac{\Delta c}{c} = 14.3 \cdot 10^{-7} p. \tag{1}$$

The values of $\Delta c/c$ calculated from formula (1) are given in Table 1. The change in the parameter c was recorded from the displacement of the (110) line. Measurements carried out independently by two investigators showed that in all experiments with $p > 10\,000$ kg/cm^2 the (110) line is displaced toward smaller angles; at $p = 15\,000$–$18\,000$ kg/cm^2, $\Delta(2s_{110}) = -0.2 \pm 0.05$ mm, which corresponds to $\Delta\theta = -0.05^\circ$. It is known [2] that, upon heating $PbTiO_3$ from room temperature to $T_K = 490^\circ$, the parameter c decreases monotonically, the parameter a increases, and the ratio c/a approaches unity. Thus, the change in the parameters with increasing pressure (at room temperature) qualitatively coincides with the change in its parameters as a function of temperature; hydrostatic pressure and high temperature act in this case in the same direction—decreasing the polarization. However, quantitatively, the effect of pressure and temperature on the change in the parameters of $PbTiO_3$ is not the same. The rates of change of the parameters differ from one another much more with increasing pressure than with increasing temperature. Thus, at $T = 480^\circ$, $\Delta c = -0.129$ Å, $\Delta a = 0.048$ Å, while at $p = 18\,000$ kg/cm^2, $\Delta c = -0.10$ Å, $\Delta a = +0.01$ Å.

Fig. 4. *I* —dependence of the parameters c and a on pressure; *II* —dependence of the ratio c/a on pressure; *III* —dependence of $\Delta c/c$ on pressure, corresponding to the equation $\Delta c/c = 14.3 \cdot 10^{-7} p$; experimental points are plotted.

It may be assumed that the compressibility of the ferroelectric phase of $PbTiO_3$ is the result of the superposition of normal compression and a deformation

associated with a decrease in polarization under pressure. Since the indicated deformation is a compression along the c axis and an extension along a (the polarization of $PbTiO_3$ is accompanied by extension along c and contraction along a), the considerable contraction of c and the small increase of a become understandable. The latter is the result of normal compression and anomalous expansion associated with polarization. If the analogy is continued and ···

To the article by S. S. Kabalkina and L. F. Vereshchagin, p. 818

Fig. 3. X-ray diffraction patterns of $PbTiO_3$, taken at different pressures on one film. 1 –$p = 1$ kg/cm^2 (before compression), 2 –$p = 11\,700$ kg/cm^2, 3 – $p = 10\,900$ kg/cm^2, 4 –$p = 1$ kg/cm^2 (after release of pressure)

To the article by S. M. Stishov and N. V. Belov, p. 951.

Fig. 1. Powder X-ray diffraction patterns: a –new dense modification of SiO_2, b –rutile TiO_2

To the article by D. K. Belyaev, I. I. Kiknadze, and A. I. Sherudilo, p. 958.

Fig. 1. Sections of the testis of a standard (a) and homosapphire (b) mink. Fixation at the beginning of March. Carnoy' s fixative. Staining with Heidenhain' s hematoxylin.

Assuming that $c/a = f(p)$ undergoes, in the transition region, a jump equal in magnitude to the jump $c/a = f(T) - 0.02$ ([2]), one can estimate the order of magnitude of dT_k/dp for $PbTiO_3$. Interpolating $c/a = f(p)$ (Fig. 4, II) to $c/a = 1.02$, which corresponds to $p = 27\,000$ kg/cm^2, we obtain $dT_k/dp = 18 \cdot 10^{-3}$ deg/atm.

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Note: Figure translations are in progress. See original paper for figures.