Physics

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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X-Ray Study of the Effect of Hydrostatic Pressure on the Structure of Barium Titanate

To study the nature and features of ferroelectric phenomena in barium titanate, it is necessary to investigate the effect of high pressure on its properties and structure. The effect of hydrostatic pressure on the Curie temperature (T_K) of a single crystal of $BaTiO_3$ was studied by Merz (^{1}), who found a linear shift of T_K toward lower temperatures at a rate of $5.8 \cdot 10^{-3}$ deg/atm. Similar results were obtained in a number of other works ($^{2-4}$).

The aim of the present work is to study the effect of hydrostatic pressure on the structure of barium titanate at room temperature. It is known that $BaTiO_3$ at room temperature has a tetragonal lattice with $c/a = 1.01$ (^{5}) and $T_K = 120°$. Since the value of c/a is close to unity, the splitting of lines on the Debye photograph associated with tetragonal distortion of the lattice is noticeable only in the region of large angles; the usual method of x-ray investigation at high pressures (^{6,7}) gives angles not exceeding 30-40°, and therefore cannot be used in this case. For this reason, a special attachment to a back-reflection camera (KROS) was constructed, making it possible to obtain reflection angles of 60-80° on x-ray photographs in the pressure range 1-6000 kg/cm^2.

Fig. 1. *a*—KROS x-ray camera with an attachment for photography at high pressures; *b*—diagram of the high-pressure vessel (attachment)

Figure 1a shows the KROS camera with an attachment for photographing specimens at high pressure. The latter is a high-pressure vessel, a section of which is shown schematically in Fig. 1b. The vessel body 1 is made of 45KhNMFA steel. The specimen under study 2 is placed in the channel of a beryllium cup 3, pressed into sleeve 4. Nut 5, with a conical opening for the entrance and exit of the x rays, serves to secure sleeve 4. The pressure is created by piston 7 (ShKh-15 steel), which is fixed in the working position by nut 6, resting on its shoulders. Aviation gasoline 8 serves as the pressure-transmitting medium. The pressure is measured with a manganin pressure gauge 9 mounted on electrode 10.

Fig. 2

Figure 2: Fig. 2

To establish the suitability of the new attachment for precision determination of parameters at high pressure, a study was made of the compressibility of aluminum; it seemed convenient to choose the latter as a standard, since its compressibility has repeatedly been measured by various physical methods. Figure 2 shows three X-ray photographs of aluminum taken on one film at different pressures. The measured values of the lattice constant and the compressibility coefficient of aluminum (at $p = 4400$ kg/cm^2: $a = 4.0409 \pm 0.0001$ Å,

$$k = \frac{1}{p}\frac{\Delta V}{V} = (13.2 \pm 0.2) \cdot 10^{-7} \text{ cm}^2/\text{kg})$$

agree sufficiently well with data of other authors, presented in Table 1.

Fig. 2. X-ray photographs of aluminum, taken at different pressures on one film:
I $-p = 1$ kg/cm^2,
II -4400 kg/cm^2,
III -1 kg/cm^2 after pressure release.

The study of barium titanate was carried out on ceramic specimens obtained from the L. Ya. Karpov Physico-Chemical Institute.* The ceramic was carefully ground in an agate mortar and the powder was placed in the high-pressure vessel.

The parameters of the initial substance were: $a = 3.993$ Å, $c = 4.032$ Å, $T_K = 118°$. The exposure was made at room temperature (λ_{Cu}) on a URS-55a X-ray unit. To determine the parameters of $BaTiO_3$ at high pressure, a group of lines with $h^2 + k^2 + l^2 = 26$ ($\theta = 77$-$80°$) was used. Figure 3 presents a scheme of three X-ray photographs (results of one of the experiments). The X-ray photographs were measured with a caliper on a negatoscope (measurement accuracy ±0.1 mm).

Table 1

Authors	Method of determination	$\frac{1}{p} \cdot \frac{\Delta V}{V} \cdot 10^{-7}$, $\frac{\text{cm}^2}{\text{kg}}$
Our data	X-ray	13.2
Bridgman (8)	Piston displacement	13.38
Jacobs (9)	X-ray	12.92
Voronov (10)	Pulse-ultrasonic	13.46

Figure 4 gives the parameters a, c, the ratio c/a, and the compressibilities $\Delta a/a$, $\Delta c/c$ of $BaTiO_3$ in the pressure interval 1-6000 kg/cm^2. All the dependences

Fig. 3

Figure 3: Fig. 3

shown in the figure may, in a first approximation, be regarded as linear. The results of the study show that, under the influence of hydrostatic pressure, the lattice parameters of barium titanate decrease at different rates (c decreases 3-4 times faster than a), which leads to a decrease in the ratio c/a.

Fig. 3. Scheme of three X-ray photographs of $BaTiO_3$, taken at different pressures on one film. $h^2 + k^2 + l^2 = 26$.
I $-p = 1$ kg/cm^2,
II -5500 kg/cm^2,
III -1 kg/cm^2 after pressure release.

Thus, the shift of the Curie point toward lower temperatures is accompanied by a decrease in the tetragonality of the lattice. The general course of the change in the parameters of $BaTiO_3$ with pressure is in qualitative agreement with the course of the change in the parameters of the solid solution $(Ba—Sr)TiO_3$ as a function of the $SrTiO_3$ content (^{11}). Table 2 gives the coefficients of linear compressibility of $BaTiO_3$, calculated from the elastic constants of two different single crystals (^{12}) and from the data of the present work.

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

Comparing our results with the results of a study of lead titanate (^{13}), we note a difference in the behavior of $BaTiO_3$ and $PbTiO_3$ at high pressure. Thus, it follows from Fig. 4 that the compressibility $\Delta c/c$ for $PbTiO_3$ is almost 4 times greater than $\Delta c/c$ for $BaTiO_3$.

The parameters a and c of barium titanate decrease with increasing pressure (Fig. 4); for lead titanate, under the same conditions, a increases slightly, while c decreases considerably. It may be considered that the compressibility of the ferroelectric phase in both cases is the result of the superposition of normal compression and of a deformation associated with a decrease in polarization under pressure; since the indicated deformation represents compression along c and extension along a, the unequal behavior described above of the parameter a for $PbTiO_3$ and $BaTiO_3$ should be attributed to a quantitative difference in the change of polarization with pressure.

Table 2

Source	$\frac{1}{p}\frac{\Delta a}{a} \cdot 10^{-7}\ \frac{\text{cm}^2}{\text{kg}}$	$\frac{1}{p}\frac{\Delta c}{c} \cdot 10^{-7}\ \frac{\text{cm}^2}{\text{kg}}$
Calculated from elastic constants (^{12}): Crystal No. 1	0.84	4.3

Fig. 4

Figure 4: Fig. 4

Source	$\frac{1}{p}\frac{\Delta a}{a} \cdot 10^{-7}\ \frac{\text{cm}^2}{\text{kg}}$	$\frac{1}{p}\frac{\Delta c}{c} \cdot 10^{-7}\ \frac{\text{cm}^2}{\text{kg}}$
Calculated from elastic constants (^{12}): Crystal No. 2	0.46	5.2
X-ray (present work)	1.9	4.0

Fig. 4. Dependence on pressure of the parameters c, a, of the ratio c/a, and of the ratios $\Delta c/c$ and $\Delta a/a$ for $BaTiO_3$. The dashed straight line is the dependence of $\Delta c/c$ for $PbTiO_3$.

In accordance with the data obtained for $a(p)$, it may be concluded that the extension of the lattice along a, accompanying the change in polarization, in the case of $PbTiO_3$ exceeds the normal compression, whereas in the case of $BaTiO_3$ it proves to be smaller than it. Thus, the influence of hydrostatic pressure on the structure is considerably stronger in the case of lead titanate than in the case of barium titanate.

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