



Soviet-era science, translated into English

PHYSICS

1957

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-195701.62254>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

PHYSICS

I. G. Ismailzade

X-Ray Study of the Influence of Uniaxial Pressure on the Structure of Polycrystalline Barium Titanate

(Presented by Academician N. V. Belov, 12 III 1957)

The magnitude of the dielectric permittivity of barium titanate changes appreciably under the action of various physical factors, one of which is pressure. The influence of hydrostatic pressure on the dielectric properties of barium titanate was first studied by B. M. Vul and L. F. Vereshchagin ⁽¹⁾. They showed that at room temperature its dielectric permittivity increases with increasing pressure. The influence of hydrostatic pressure on the Curie point of a single crystal of barium titanate was studied by Merz ⁽²⁾, who found a linear shift of the Curie point toward lower temperatures at a rate of $5.8 \cdot 10^{-3}$ deg/atm.

The action of mechanical pressure (compression) perpendicular to the electrode surfaces of BaTiO₃ ceramics was studied by Taraki, Sawaguchi, and Akioka ⁽³⁾. They showed that under these conditions the dielectric permittivity decreases with increasing pressure. Shirane and Sato ⁽⁴⁾ investigated the influence of hydrostatic and mechanical (uniaxial) pressures on the dielectric properties of BaTiO₃ ceramics and of solid solutions of BaTiO₃ and SrTiO₃. It was established that under uniaxial pressure (up to 600 kg/cm²), directed parallel to the electrode surfaces and perpendicular to them, in contrast to hydrostatic pressure, with increasing pressure below the Curie point the dielectric permittivity decreases, while above it increases. It was also found that with increasing uniaxial pressure the Curie temperature rises at a rate of $dT/dp = 4.0 \cdot 10^{-3}$ deg · cm²/kg. Later, the dependence of the dielectric properties of ferroelectric ceramics on uniaxial pressure was studied by E. V. Sinyakov and I. A. Izhak ⁽⁵⁾, who obtained analogous results.

In the present work we set ourselves the goal of carrying out a study of ferroelectrics under pressure.

The influence of uniaxial pressure of the order of 600–1000 kg/cm² on the structure of barium titanate is a subtle effect, and therefore the use of the ordinary photographic method of X-ray structural analysis is inadvisable. For this reason we carried out the study by the ionization method on a URS-50-I X-ray apparatus. We constructed a simple X-ray goniometric head that makes it possible to subject the specimen under study to compression in the direction of

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

the axis of the head. The pressure is produced by means of a lever system with an arm ratio of 1 : 10. The accuracy of pressure measurement is approximately 3–5%. The head makes it possible to move the substance under study in two mutually perpendicular directions.

The barium titanate specimen was prepared in the form of a polished rectangular plate with a cross-sectional area of 2 mm². The dimensions of the plate were measured with the aid of a measuring microscope.

All X-ray photographs were taken with filtered copper radiation under exactly identical conditions: with a stabilized anode current of 6 mA and an accelerating voltage of 36 kV (room temperature).

To obtain high accuracy, each diffraction maximum was recorded point by point. At definite intervals of the reflection angle θ , the number of pulses in 15 and 32 sec was measured. At each angle, 5–10 measurements were made, and for constructing the diffraction maxima the arithmetic mean value of the pulses over 15 sec (for the (110) reflection) and 32 sec was taken.

Fig. 1. Diffraction maximum of BaTiO₃ from (110) + (011) without pressure (1) and under a pressure of 1000 kg/cm² (2)

Fig. 2. Diffraction maxima of BaTiO₃ from (002) and (200) without pressure (1) and under a pressure of 1000 kg/cm² (2)

All maxima were recorded four times in the following order: without pressure, under pressure, without pressure, under pressure. In each case, for each condition, respectively the same results were obtained.

Table 1

Increment of the angle θ (in minutes)

Pressure	(110) + (011)	(200)	(002)	(301)	(103)	(224)
700 kg/cm ²	−1.0	+1.0	−1.5	+1.5	−2.5	−4.0
1000 kg/cm ²	−2.0	+1.5	−2.5	—	—	—

Thus, diffraction maxima were constructed for the planes (110) + (011), (200),

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

(002), (103), (301), and (224) without pressure and under a uniaxial pressure of 700 kg/cm², and, for the planes (110) + (011), (200), and (002), also under a pressure of 1000 kg/cm² (Figs. 1-4). The results of comparing the curves obtained are given in Table 1.

It is seen from the table that:

1. In the reflections from the (200) and (301) planes, under the influence of pressure the diffraction maxima shift toward larger angles, whereas the maxima (002), (103), and (224) shift toward smaller angles θ .
2. With increasing pressure, the absolute values of the displacements of the maxima increase.

Fig. 3. Diffraction maxima of BaTiO₃ from (103) and (301) without pressure (1) and under a pressure of 700 kg/cm² (2)

Fig. 4. Diffraction maximum of BaTiO₃ from (224) without pressure (1) and under a pressure of 700 kg/cm² (2)

The displacement of the diffraction maxima (200) and (301) toward larger angles θ indicates that, under the influence of uniaxial pressure, the period a in the barium titanate lattice decreases somewhat. The displacement of the maxima (002) and (103) toward smaller angles, on the contrary, is due to an increase in the period c . The increments of the periods Δa and Δc were calculated using the expression:

Table 2

Pressure, kg/cm ²	$\Delta a =$		$a, \text{ \AA}$	$\Delta c, \text{ \AA}$		$c, \text{ \AA}$	c/a
	$\Delta b, \text{ \AA}$ from (200)	$\Delta b, \text{ \AA}$ from (301) and (103)		$\Delta c, \text{ \AA}$ from (002)	$\Delta c, \text{ \AA}$ from (301) and (103)		
—	—	—	3.9935	—	—	4.0325	1.0098
700	-0.0026	-0.002	3.9915	+0.0042	+0.004	4.0365	1.0113
1000	-0.004	—	3.9895	+0.006	—	4.0385	1.0123

$$\Delta\theta = -\frac{\lambda^2}{4 \sin \theta \cos \theta} \left[\frac{h^2 + k^2}{a^3} \Delta a + \frac{l^2}{c^3} \Delta c \right] \quad (1)$$

and are given in Table 2.

Thus, in the BaTiO₃ lattice, under the influence of uniaxial pressure, the periods a and b decrease, whereas the period c increases. This leads to an increase in the tetragonality of the lattice, c/a .

The influence of uniaxial pressure on the structure of barium titanate can be clarified on the basis of the expression for the free energy of the system.

It is known that the differential of the free energy is equal to

$$dF = -p dv - S dT. \quad (2)$$

For the isothermal process that takes place in our case:

$$p = -\left(\frac{dF}{dv}\right)_T, \quad \left(\frac{dp}{dv}\right)_T = -\left(\frac{d^2F}{dv^2}\right)_T, \quad \left(\frac{dp}{dv}\right)_T < 0. \quad (3)$$

Since $dp > 0$, it follows that $dv < 0$, i.e., in the general case, at constant temperature, under the action of uniaxial pressure the increment in the volume of the unit cell will be negative. For a tetragonal cell

$$\Delta v = 2ac \Delta a + a^2 \Delta c < 0$$

or

$$|\Delta a| \geq \frac{a\Delta c}{2c}. \quad (4)$$

For BaTiO₃ it may be assumed that $a \simeq c$; then $|\Delta a| \geq \Delta c/2$, i.e., the smallest absolute value of the increment of the period $a(b)$ is equal to $\Delta c/2$, which corresponds to $\Delta v = 0$.

As the data obtained by us show (Table 2), within the errors of the experiment this case apparently occurs in our measurements. Thus it may be said that under uniaxial pressure of the order of 700-1000 kg/cm², at room temperature, the volume of the unit cell of polycrystalline BaTiO₃ practically does not change, whereas the tetragonality of the lattice, c/a , increases.

The displacement of the Curie point under uniaxial compression toward higher temperatures^(4,5) is due to the increase in the tetragonality c/a of the barium titanate lattice. Indeed, an increase in the period c and a decrease in the periods a and b hinders the transition to the cubic lattice; i.e., under uniaxial pressure

a higher temperature is required for the phase transition from the tetragonal lattice to the cubic one.

The author expresses his gratitude to Prof. L. S. Mayants for discussion of the results and valuable advice.

Institute of Petroleum
Academy of Sciences of the Azerbaijan SSR

Received
6 VII 1957

REFERENCES

1. B. M. Vul, L. F. Vereshchagin, DAN, 48, No. 9, 662 (1945).
2. W. J. Merz, Phys. Rev., 78, 52 (1950).
3. Y. Takagi, E. Sawaguchi, T. Akioka, J. Phys. Soc. Japan, 3, 270 (1948).
4. G. Shirane, K. Sato, J. Phys. Soc. Japan, 6, 20 (1950).
5. E. V. Sinyakov, I. A. Izhak, DAN, 100, No. 2, 243 (1955).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.