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X-ray and optical studies on phase transition of $PbTiO_3$ at low temperatures

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Accurate measurements of the lattice parameters and the anisotropy of the optical susceptibilities, i.e., optical birefringence and activity of $PbTiO_3$ were made in the low-temperature region by using a special x-ray strainmeter and a newly developed polarimeter. It was found that $PbTiO_3$ undergoes a phase transition at $-90\,^{\circ}C$ between C_{4v} and C_{2v} point groups. This transition is different from the corresponding transition of $BaTiO_3$ in that the transition is of second order and the direction of polarization is unchanged. Lattice and optical anisotropies featuring the C_{2v} phase are smaller than those ever found in other perovskite-type crystals.

I. INTRODUCTION

Lead titanate $PbTiO_3$ is isomorphic with $BaTiO_3$ in its crystal structure, and undergoes a similar ferroelectric phase transition at $T_c = 490\,^{\circ}C$ (Ref. 1) where the symmetry changes from the cubic O_h^1 ($Pm3m$, paraelectric) to tetragonal C_{4v}^1 ($P4cc$, ferroelectric) space groups.[2] However, it has been believed that the successive phase transitions to other crystal modifications with the space groups C_{2v}^{14} ($Amm2$) and C_{3v}^5 ($R3m$), which are realized in $BaTiO_3$, do not occur in this crystal. As this fact is important for elucidating the origin of the ferroelectricity in perovskite-type crystals much work was formerly directed to find evidence of the occurrence of other phase transitions in the low-temperature region. The first report concerning this problem was given by Kobayashi and Ueda. They found a phase transition to take place at approximately $-100\,^{\circ}C$ by the x-ray powder diffraction method,[3] and another at approximately $-150\,^{\circ}C$ by dielectric measurements.[4] The existence of these low-temperature phase transitions was partly confirmed afterwards by Ikegami, Ueda, and Miyazawa[5] with the use of x-ray and thermal studies.

In the decade after 1970, advanced apparatuses were applied to study phase transitions of $PbTiO_3$, and the progress of growing techniques of single crystals[6–8] promoted this tendency. Remeika and Glass[9] obtained no evidence of other phase transitions by dielectric and piezoelectric measurements. Doshi, Glass, and Novotny[10] suggested the possibility of the occurrence of other transitions by their perturbed γ-γ directional correlation measurements. Glazer and Mabud[11] did not find any sign of the occurrence of low-temperature phase transitions in their neutron powder profiles, but they detected anomalous small humps of the isotropic temperature factors of the constituent atoms around $-100\,^{\circ}C$, which could be conceived as the proximity of a transition at this temperature. Mabud and Glazer[12] subsequently made x-ray dilatometric and optical measurements on single crystals, and drew the conclusion that there do not exist any structural changes in the low-temperature region.

We believe that this problem has not yet been settled although the majority of the recent reports rejects the occurrence of other transitions. One of the most serious difficulties that made the problem so annoying seemed to lie in the difficulty of preparing good single-domain crystals. We feel it necessary to make very precise measurements of temperature changes of the lattice parameters and the anisotropy of the optical susceptibilities, i.e., optical birefringence and activity in the low-temperature range. For this aim we prepared purely single-domain crystals at first and applied the precise x-ray strainmeter[13,14] and the newly developed optical polarimeter [high accuracy universal polarimeter (HAUP)] (Refs. 15 and 16) to these specimens.

II. SPECIMEN PREPARATION

We modified Fesenko's method[8] for growing single crystals of $PbTiO_3$. When a 30-ml platinum crucible was used, the best result was yielded when the molar ratios $[B_2O_3:PbO:PbTiO_3] = 3.2:7.5:1$ were adopted. The crucible containing about 6.1 g of $PbTiO_3$ was heated at about $800\,^{\circ}C$ for 24 h in an electric furnace and then cooled to $530\,^{\circ}C$ by the cooling rate of $3\,^{\circ}C/h$. At this temperature the crucible was turned over for pouring off the liquid and cooled again to room temperature. As an advantage of this method, we could grow small but perfect single-domain crystals with a dendritic $\{100\}$ form, which were suitable for x-ray and optical experiments.

III. LATTICE PARAMETER MEASUREMENTS

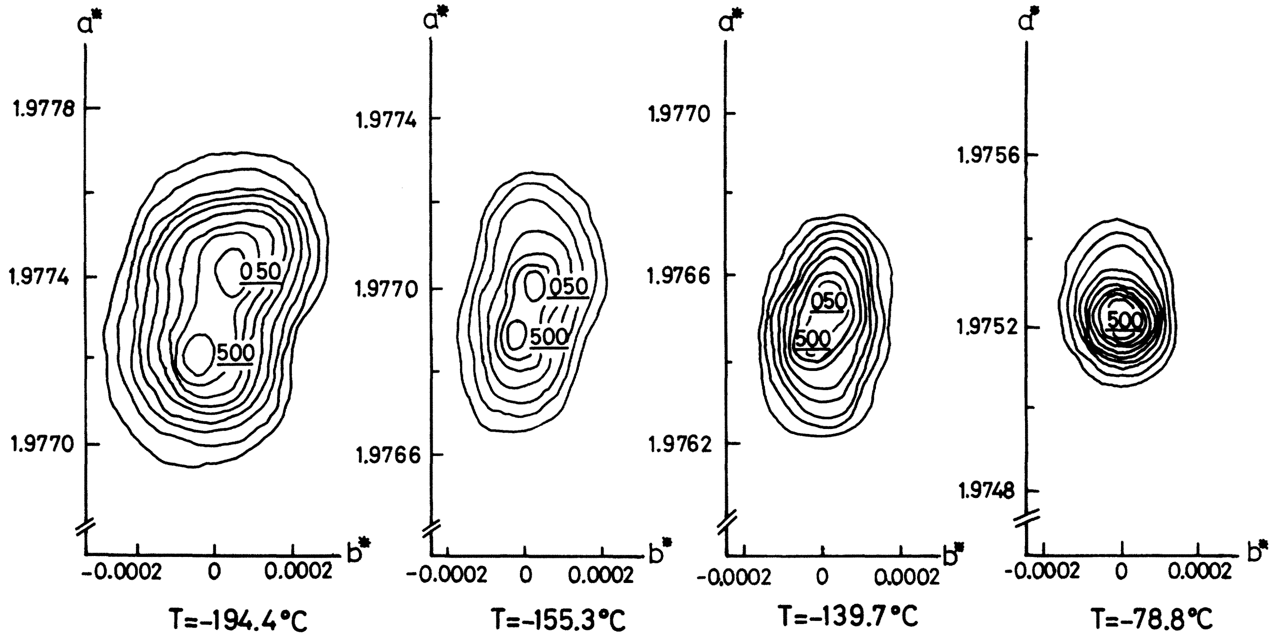
X-ray diffractometries were made of specimens that oscillate around the c and b axes in the temperature range between room temperature and −194 °C. The x-ray strainmeter was a special spectrometer consisting of two main parts, a Si monochromator, which was located 1112 mm apart from the specimen, and a counter 2017 mm apart from the specimen. By this arrangement the horizontal divergence of the monochromatic Cu$K\alpha_1$ beams could be limited to 4.69″, and the purity of the wavelength becomes 9.0×10^{-5}. Besides, to increase the resolution for reading the reflection positions, the two-dimensional reciprocal-lattice method[17,18] was adopted as were cases in our previous work. Then the accuracy for the lattice parameter measurements attained 5.3×10^{-7} at $\theta=81°$.

For the c-axis oscillation diffractometry, a (100) plate crystal with 0.13×0.15 mm^2 area and 0.053 mm thick [(100) direction] was mounted on a goniometer head, and the specimen was cooled by a conduction-type cryostat within the accuracy of ±0.005 K. The spectra used for the measurements were 500 ($\theta=81°$), 050 (81°), and 430 (81°).

The a and b parameters were determined by the two different procedures. First, we obtained them by measuring separately the spacings of 500 and 050 spectra reflected from (100) and (010) planes of the specimen. Second, we made good use of the fact that 500 reflection became occasionally doublets, as shown in Fig. 1, when the specimen was cooled for a long time below −90 °C. This fact was clearly interpreted as due to the formation of twinnings of the two individuals having the c axes as the common direction, since the doublets approach each other with increasing temperature, and coalesce into a single reflection at −90 °C. Therefore, the accompanying reflection must be 050, and we could obtain the spacings of both spectra immediately from a single intensity map. Systematic errors for measuring the positions of the spectra due to the absorption of x rays and to the eccentric rotation of the specimen were removed by the usual extrapolation corrections[19] which were made at room temperatures −34 °C and −50 °C. The refraction effect of x-rays was also corrected. The results obtained by these two methods were found perfectly coincident.

With decreasing temperature the a and b parameters coincide until −90 °C, but begin to split from that temperature. The amount of the splitting was extremely small, e.g., 4.5×10^{-4} Å at −194 °C, but unequivocally resolved within the accuracy of our method. Thus it was found that the crystal transforms into another phase at −90 °C; the phase is defined as a low-temperature phase and the temperature as T_1 in what follows. The axial ratio a/b is expressed in Fig. 2(a) as a function of temperature, its deviation from unity being 1.3×10^{-4} at −194 °C. Thus the lattice anisotropy in the (001) plane of the low-temperature phase of $PbTiO_3$ is extremely small, and this would be the reason why it has been overlooked in previous investigations. Axial angles γ at various temperatures were evaluated from the spacings of 430 spectra together with the measured a and b parameters. The temperature dependence of γ is indicated in Fig. 3 where it is seen that it remains 90° below T_1.

Let us compare temperature dependences of lattice parameters a and b of $PbTiO_3$ with those of $BaTiO_3$ which were measured by Kay and Vousden.[20] In the case of $BaTiO_3$ the spontaneous polarization P_s changes from [001] to [101] (or [011]) directions below the transition temperature T_1 accompanying a pure shear in the (010) [or (100)] plane. Thus a special monoclinic cell is formed with orthorhombic symmetry, where the elongated a parameter becomes equal to the c parameter while the b parameter contracts discontinuously. Axial ratios a/b of $BaTiO_3$, which are approximately 2 orders of magnitude larger



T=-194.4 °C T=-155.3 °C T=-139.7 °C T=-78.8 °C

FIG. 1. Two-dimensional x-ray intensity contours of the 500 and 050 spectra issued from a twinned specimen.

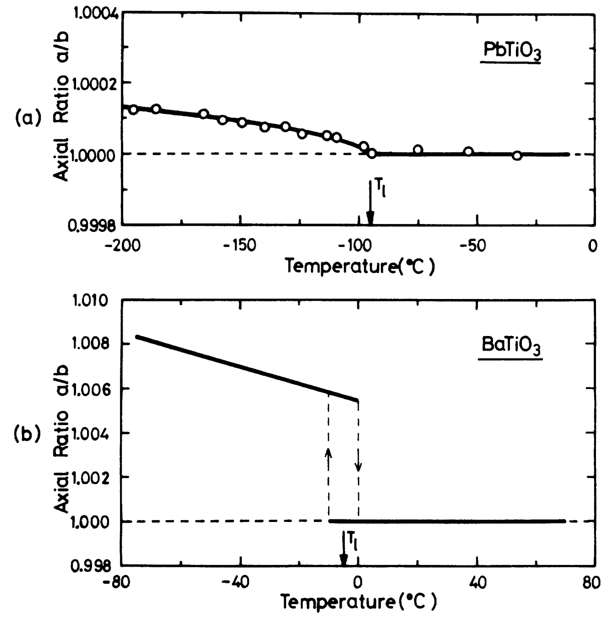


FIG. 2. Temperature dependences of the axial ratios a/b of $PbTiO_3$ and $BaTiO_3$. (a) represents the case of $PbTiO_3$ and (b) that of $BaTiO_3$ [after Kay and Vousden (Ref. 20)].

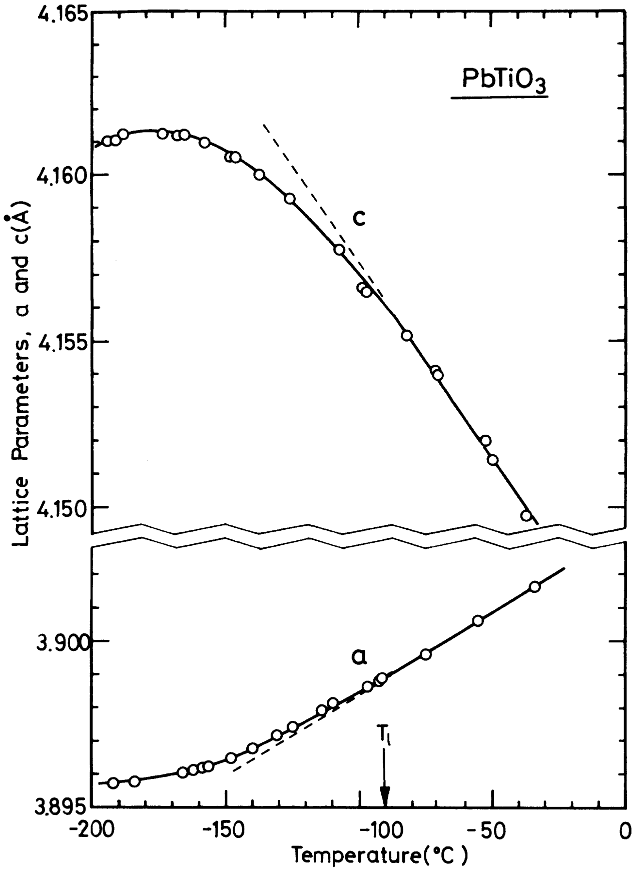


FIG. 4. Temperature dependences of lattice parameters a and c of $PbTiO_3$.

than those of $PbTiO_3$, are indicated in Fig. 2(b). From this experiment it can be suspected that the pure shear deformation in the (010) plane, found in $BaTiO_3$, does not take place in $PbTiO_3$.

A (001) plate crystal with 0.45×0.04 mm^2 area and 0.061 mm thick ([001] direction) was used for the b axis oscillation diffractometry, the used spectra being 005 (68°), 403 (75°), and $\bar{4}03$ (75°). Temperature dependences of the a and c parameters are shown in Fig. 4 and of β in Fig. 3. The c parameter does not change discontinuously, but only its temperature dependence changes discontinuously at T_I. On the other hand, in the case of $BaTiO_3$, the c parameter discontinuously contracts and becomes equal to the a parameter when the pure shear takes place in the (010) plane, as shown in Fig. 5(a), or the a parameter contracts differently from the c parameter when the pure shear takes place in the (100) plane, as indicated in Fig. 5(b). The present experiment clearly indicates that $BaTiO_3$-type shears do not occur in $PbTiO_3$. The constan-

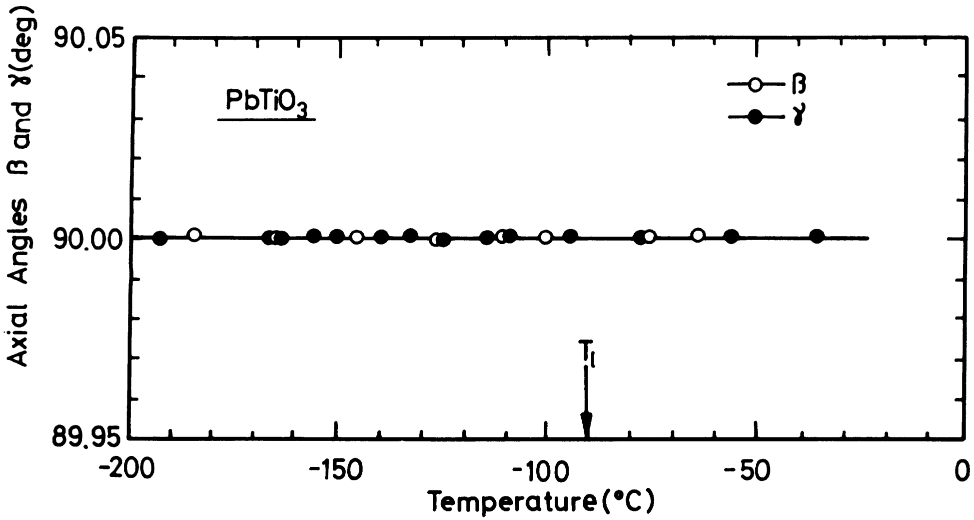


FIG. 3. Temperature dependences of axial angles β and γ of $PbTiO_3$.

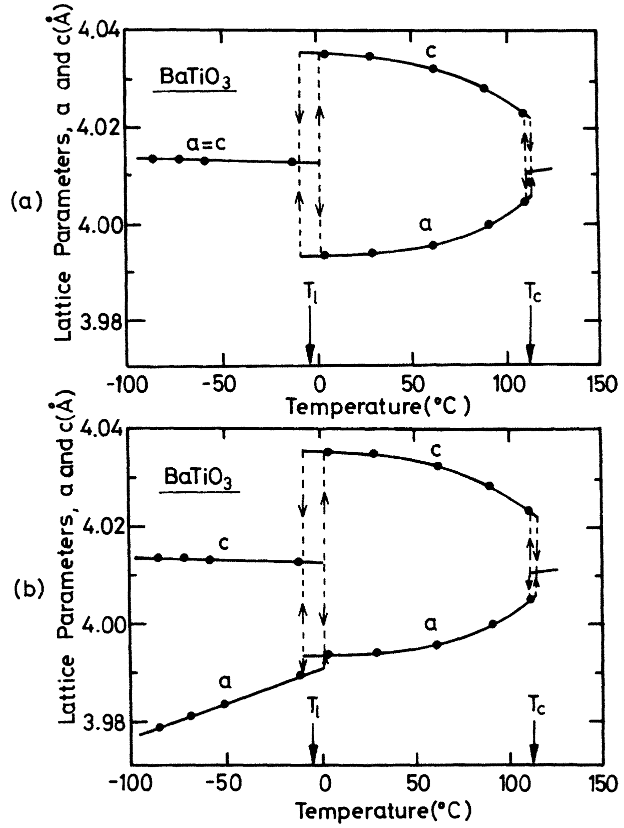


FIG. 5. Temperature dependences of lattice parameters a and c of BaTiO$_3$ [after Kay and Vousden (Ref. 20)]. (a) represents the case where the pure shear takes place in the (010) plane and (b) the case where it takes place in the (100) plane.

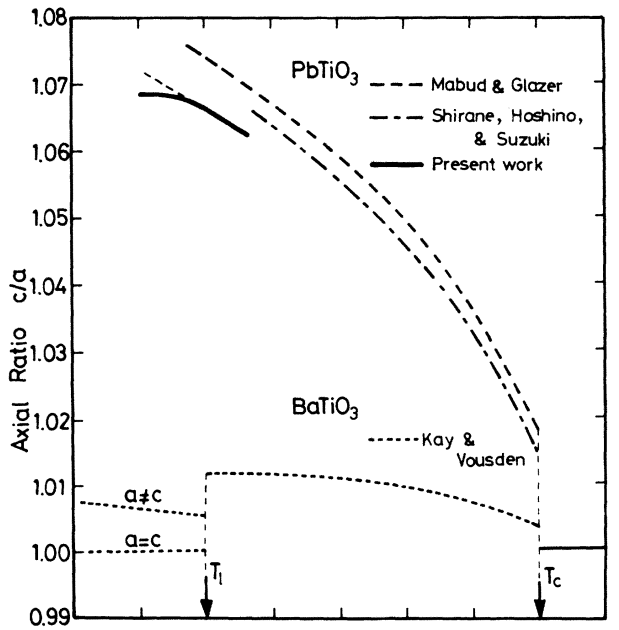


FIG. 6. Axial ratio c/a of PbTiO$_3$ and BaTiO$_3$ as a function of the reduced temperature $(T-T_1)/(T_c-T_1)$.

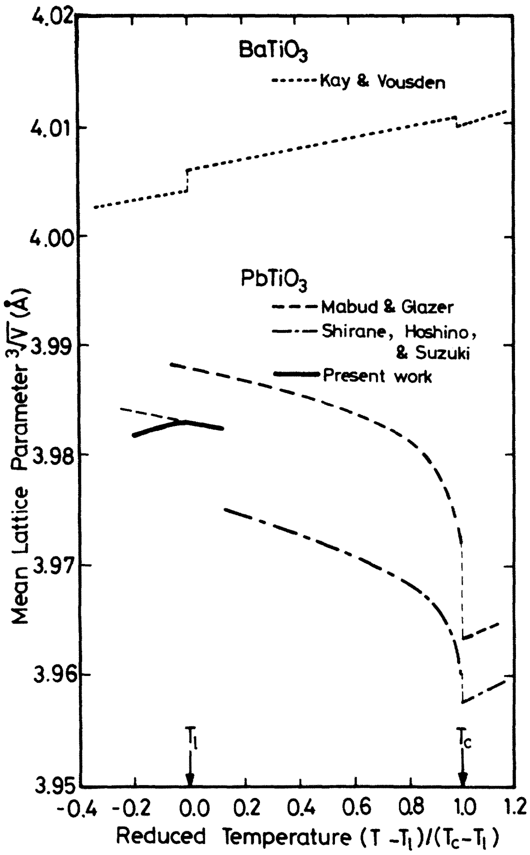


FIG. 7. Mean lattice parameters $(v)^{1/3}$ of PbTiO$_3$ and BaTiO$_3$ as a function of the reduced temperature $(T-T_c)/(T_c-T_1)$.

cy of β found 90° below T_1 becomes the direct evidence of this fact. It is worthwhile to note that the rate of increase of the c parameter diminishes below T_1 with decreasing temperature, levels off at approximately $-180\,^{\circ}\mathrm{C}$, and begins to decrease afterwards. The axial ratio c/a and the mean lattice parameter $(V)^{1/3}$ (V is lattice volume) are expressed in Figs. 6 and 7, respectively, as functions of the reduced temperature $(T-T_1)/(T_c-T_1)$, where comparisons are made with results of other authors[12,21] and with the same quantities of BaTiO$_3$.

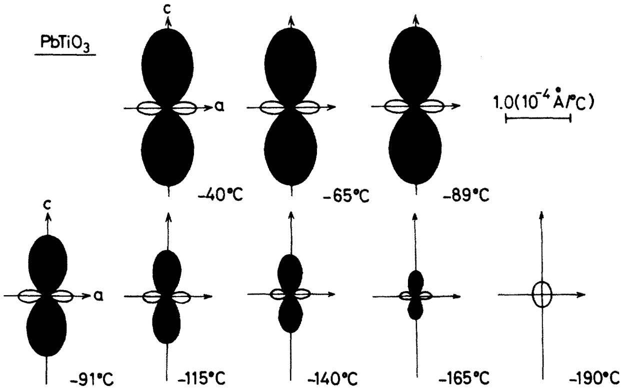


FIG. 8. Polar diagram representation of thermal strains of PbTiO$_3$ along the a and c axes, as a function of temperature.

The change of thermal strains of $PbTiO_3$ along the a and c axes is depicted in Fig. 8 by the polar diagram representation, where the white ovoids represent positive thermal expansions and the black ovoids negative ones. In the tetragonal region thermal expansions are almost constant along the two directions, while in the low-temperature phase, discernible changes take place especially along the c axis. Temperature changes of the linear thermal expansion coefficients α_a, α_b, and α_c, and the volume expansion coefficient β_v are expressed in Fig. 9(a). They are constant in the tetragonal region, but manifest discontinuous changes at T_1, indicating that the transition is of second order. As has been stated above, α_c changes from negative to positive signs at about $-180\,^\circ C$. It is also noticeable that β_v changes its sign at T_1. These characteristics of the thermal expansions of $PbTiO_3$ are quite different from those of $BaTiO_3$, which are shown in Fig. 9(b).

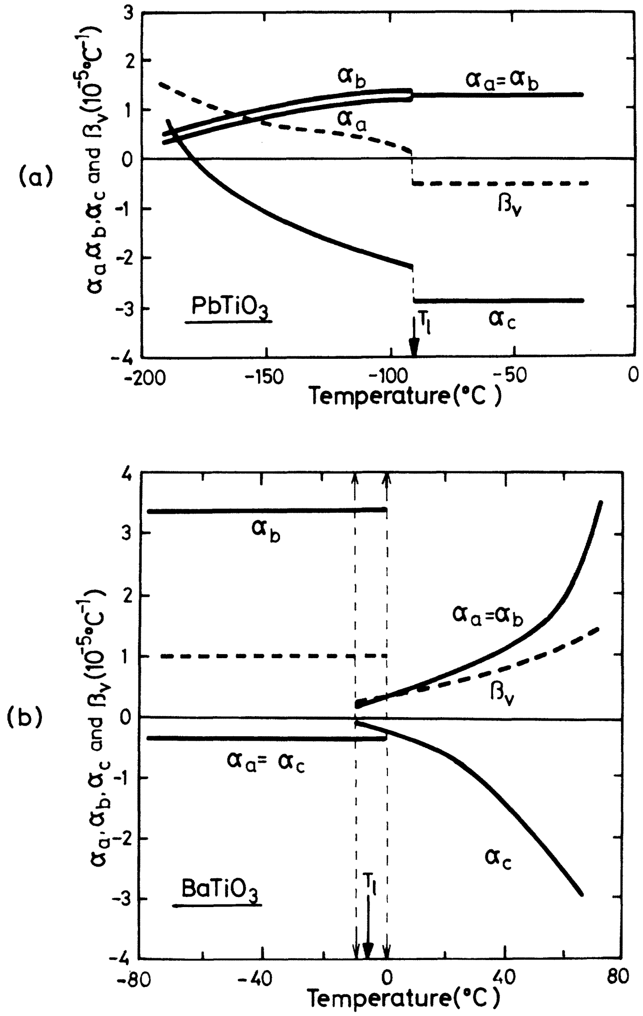


FIG. 9. Temperature dependences of the linear thermal expansion coefficients $\alpha_a,\alpha_b,\alpha_c$ (solid lines) and the volume thermal expansion coefficient β_v (dashed lines) of $PbTiO_3$ and $BaTiO_3$. (a) represents the case of $PbTiO_3$ and (b) that of $BaTiO_3$ [after Kay and Vousden (Ref. 20)].

Present measurements of the lattice constants disclosed that there exists a second-order phase transition in $PbTiO_3$ at $-90\,^\circ C$. However, the changes of the lattice parameters due to the transition are smaller than those ever found in other perovskite-type crystals. This represents a characteristic feature of the low-temperature phase transition of $PbTiO_3$. To examine whether superlattice spectra can be found in the low-temperature phase, we took ($hk0$) and ($h0l$) Weissenberg photographs at $-110\,^\circ C$, but could not find such reflections.

IV. OPTICAL SUSCEPTIBILITY MEASUREMENTS

Shirane, Pepinsky, and Frazer[2] measured the birefringence $\Delta n_{ac}=n_a-n_c$ (n_a is the refractive index along the a axis, n_c along the c axis) of $PbTiO_3$ in the tetragonal region, and first pointed out an unusual temperature dependence. The wavelength dispersion of Δn_{ac} was studied by Kobayashi and Yamada.[22] Recently, this property was measured again by Mabud and Glazer.[12] However, it seems to us that no experimental evidence was reported as to the temperature change of optical anisotropy except for Forsbergh.[23] He remarked that Δn_{ac} at the liquid-air and liquid-helium temperatures were on the order of $\frac{1}{2}$ and $\frac{1}{3}$ of the room-temperature value, respectively. A reason preventing the low-temperature measurements of optical properties of $PbTiO_3$ might also be the difficulty of preparing good single-domain specimens. We measured the birefringence and optical activity of $PbTiO_3$ in the low-temperature region by using our {100} dendritic crystals.

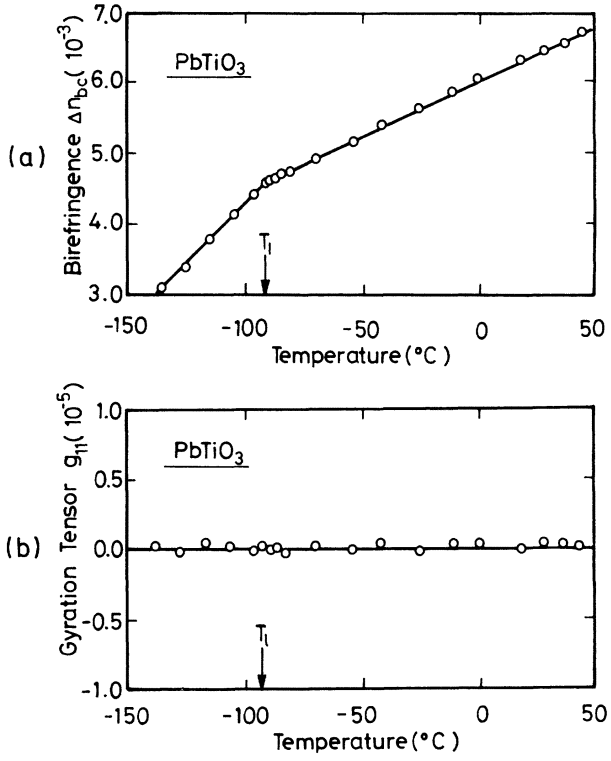


FIG. 10. Temperature dependences of optical anisotropies of $PbTiO_3$. (a) represents birefringence Δn_{bc} and (b) gyration tensor g_{11}.

In order to measure the birefringence and gyration along the [100] direction, we applied HAUP to the same (100) plate specimen as used in the x-ray diffractometry. As we reported details of the principles of HAUP in Ref. 15, we use here some characteristic terms without descriptions. We first determined the position of the characteristic angle θ_0 at each temperature. Then we set up the reading systems of θ' and performed two-dimensional measurements. Temperature dependences of Δn_{bc} and gyration tensor g_{11} of $PbTiO_3$ for the wavelength $\lambda = 632.8$ nm are shown in Figs. 10(a) and 10(b). The former agrees with our previous results measured by the Senarmont method.[24] The temperature derivative changes discontinuously at $-90\,°C$, manifesting the occurrence of the phase transition. However, g_{11} is always zero. Δn_{bc} of the present measurements is consistently connected with that of our previous measurements in the higher-temperature region,[22] as shown in Fig. 11(a). On the other hand, Kay and Vousden[20] observed the discontinuous change of Δn_{bc} of $BaTiO_3$ with an abrupt change of the extinction position (symmetrical extinction) below T_1, as illustrated in Fig. 11(b).

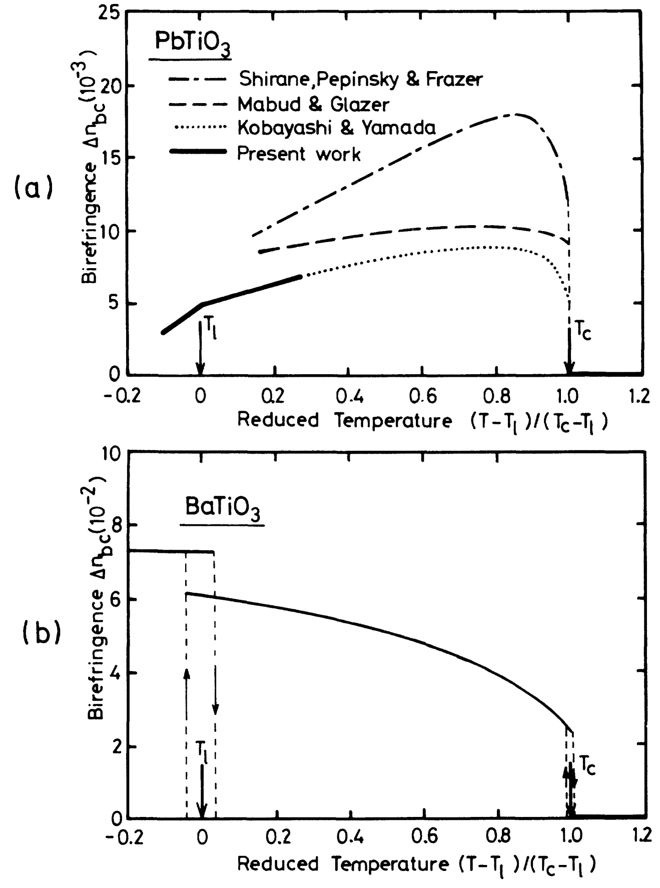


FIG. 11. Birefringence Δn_{bc} of $PbTiO_3$ and $BaTiO_3$ as a function of the reduced temperature $(T-T_1)/(T_c-T_1)$. (a) represents the case of $PbTiO_3$ and (b) that of $BaTiO_3$ [after Kay and Vousden (Ref. 20)].

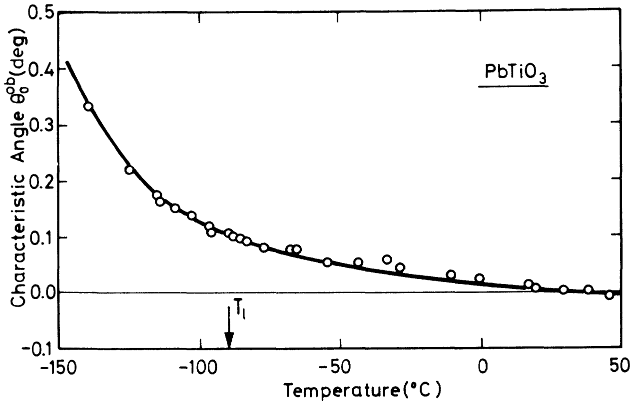


FIG. 12. Temperature dependences of the observed characteristic angle $\theta_0^{\rm ob}$ and the calculated angle θ_0 (solid line) of $PbTiO_3$.

Here we can definitely answer the problem whether the indicatrix rotates around the a axis below T_1. An observed characteristic angle $\theta_0^{\rm ob}$ at T should be written as

$$\theta_0^{\rm ob} = \theta_0 + \phi(T) \, , \tag{1}$$

where $\phi(T)$ represents the rotation angle of the indicatrix at T. In Fig. 12, θ_0^{ob} and θ_0 (solid line), which are calculated from the measured Δn_{bc}, are plotted against the temperature. It can be seen that they perfectly coincide and thus $\phi(T)$ is zero throughout this temperature range. This is direct evidence that the indicatrix does not rotate around the a axis at all, and equivalently a pure shear in the (100) plane does not take place in $PbTiO_3$.

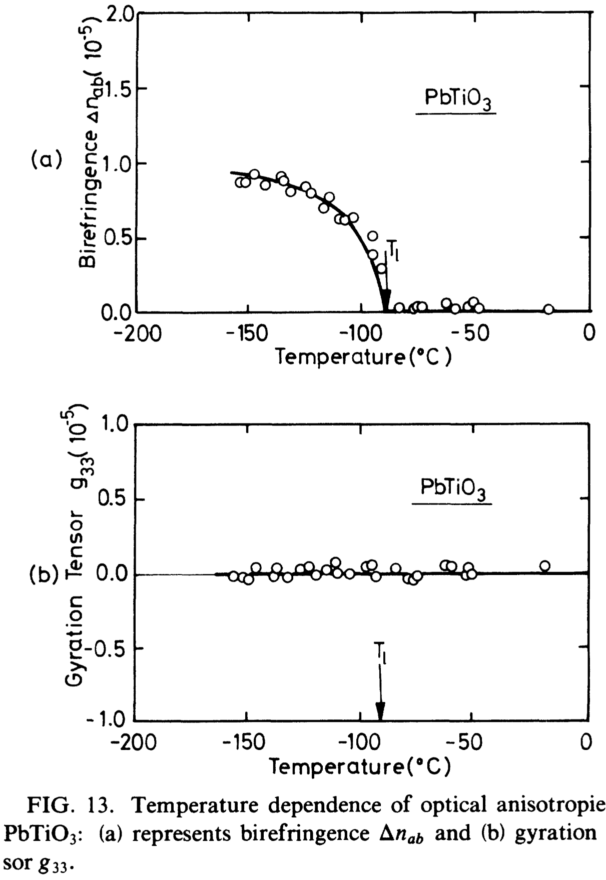


FIG. 13. Temperature dependence of optical anisotropies of $PbTiO_3$: (a) represents birefringence Δn_{ab} and (b) gyration tensor g_{33}.

Measurement of Δn_{ab} and gyration tensor g_{33} were performed also by using HAUP, the specimen being (001) plate crystals used for x-ray experiments. The temperature dependences are depicted in Fig. 13(a) for Δn_{ab} and in Fig. 13(b) for g_{33}. We found that extremely small birefringences Δn_{ab} on the order of 10^{-6} appear but gyrations do not take place in the low-temperature phase. It has already been established that the indicatrix does not rotate around the a or b axis below T_1. Therefore, Δn_{ab} can be ascribed to the lattice anisotropy in the (001) plane of the low-temperature phase.

V. CRYSTAL SYMMETRY OF THE LOW-TEMPERATURE PHASE

Summing up the present x-ray and optic experiments, the most prominent feature of the low-temperature phase of $PbTiO_3$, compared with $BaTiO_3$, is that the pure shear does not take place in the (100) or (010) planes. This clearly indicates that the Bravais lattice of the low-temperature phase is parallel to that of the tetragonal phase. Besides, we measured small anisotropy in the (001) plane and knew that the principal axes of the optical indicatrix are always parallel to the crystallographic axes. Then it follows that the crystal system must be orthorhombic.

The next problem is to determine the point group of the orthorhombic phase of $PbTiO_3$. Among the three point groups belonging to the orthorhombic system, D_{2h} is centrosymmetrical and accordingly nonpiezoelectric. Ikegami, Ueda, and Miyazawa[5] reported that $PbTiO_3$ is piezoelectric down to $-190\,^{\circ}\mathrm{C}$, so this group must be excluded as one of the candidates. In the remaining two groups, D_2 and C_{2v}, there exist directions where optical activity can be observed. The gyration surface of D_2 resembles a general ovaloid with the principal axes parallel to the crystallographic axes, so every direction can be optically active. On the other hand, the gyration surface of C_{2v} consists of four ovoid regions, so the optical activities are inhibited along [100], [010], and [001] directions. The HAUP observations revealed that the crystal is not optically active along [100] and [001] directions. Therefore, it would be reasonable to assign the point group of the low-temperature phase of $PbTiO_3$ as C_{2v}. Although the point group of the low-temperature form of $PbTiO_3$ is the same as that of $BaTiO_3$, their crystallographic orientations are quite different: In $PbTiO_3$ the polar axis is still directed along the [001] direction, while in $BaTiO_3$ it is changed into [101] or [011] directions.

The three ferroelectric phases in $BaTiO_3$, viz., C_{4v}, C_{2v}, C_v phases, are stabilized by the successive minima of the free-energy function, which is expanded by an order parameter P_s and three symmetry parameters belonging to a triply degenerated T_{1u} irreducible representation of the O_h group.[25,26] However, we found that the transition mechanism between C_{4v} and C_{2v} phases in $PbTiO_3$ is different from the corresponding transition in $BaTiO_3$; the Bravais lattices of both phases are parallel in $PbTiO_3$, but not in $BaTiO_3$ as stated before. Besides, it has been clarified that the transition is of second order and various unusual structural and optical properties are realized. Thus the low-temperature phase transition of $PbTiO_3$ offers an interesting problem to the crystal physics of perovskite-type crystals.

ACKNOWLEDGMENT

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