

attribute this resistivity to the Rutherford scattering by impurity ions<sup>10</sup> of concentration  $N_s = n + N_0$ , where  $n$  is the concentration of the conduction carriers and  $N_0$  is provided by the loss of electrons from donor levels to lower lying acceptor levels. This model requires that the concentrations of donors and acceptors in a high resistivity sample should be nearly equal. This condition is not necessarily satisfied in practice. Such an assumption is not needed, however, if it is considered that in germanium, due to a small activation energy  $E_a'$ , a large number of carriers are found in the conducting impurity band described above, so that an equal number of ions are provided which can act as scattering centers. The resistivity curves may therefore be explained satisfactorily on the basis of a single type of impurity.

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### X-Ray Study of the Phase Transition in Lead Titanate

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IN a preceding note,<sup>1</sup> we have reported that the solid solution of  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  has the same type of crystal structure as that of  $\text{BaTiO}_3$ , and its tetragonality increases with lead contents, accompanying the rise of Curie temperature. Lead titanate has a larger tetragonality and a higher Curie temperature (ca. 490°C) compared with those of  $\text{BaTiO}_3$ . It may be expected that this crystal also transforms to cubic structure at the Curie point as in the case<sup>2</sup> of  $\text{BaTiO}_3$ . To examine this behavior precisely, we have performed an x-ray study on the temperature change of lattice parameters.

We used the ceramic specimens prepared by sintering the mixture of  $\text{PbO}$  and  $\text{TiO}_2$  at about 1100°C. These ceramics were pulverized to fine powder and sealed in a very thin capillary tube made of hard glass (diameter=0.5 mm). The Debye photographs were taken at temperatures from 30 to 535°C, using  $\text{CuK}\alpha$ -radiation.

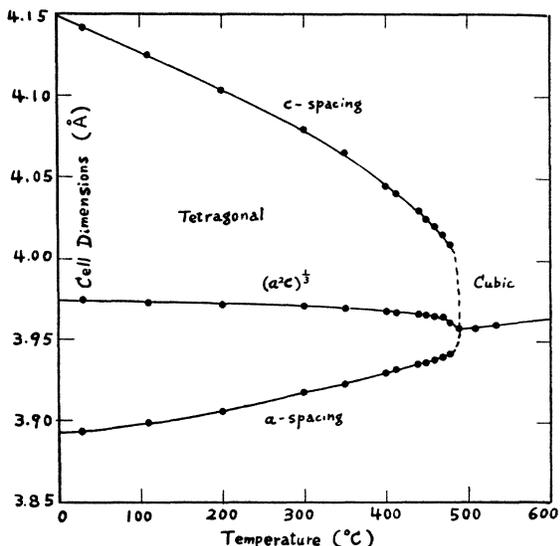


FIG. 1. Lattice parameters as a function of temperature.

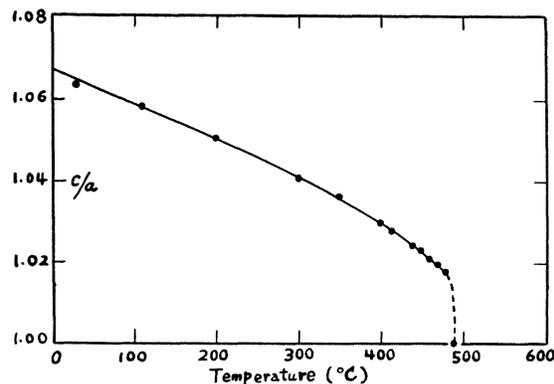


FIG. 2. Axial ratio as a function of temperature.

tion. The camera length is 55.5 mm. The precise lattice constants and the axial ratio were calculated mainly from (143) and (134) lines on photographs taken by the back reflection method. These results are shown in Figs. 1 and 2.

The photograph at 30°C clearly shows the tetragonal structure with  $a=3.894\text{Å}$ ,  $c=4.140\text{Å}$ , and  $c/a=1.063$ . These results are in agreement with those of other authors.<sup>3</sup> When the temperature is raised, this axial ratio decreases gradually until the structure changes to a cubic lattice at about 490°C, in accordance with our permittivity measurement. At 535°C, the lattice constant  $a=3.960\text{Å}$ .

It is remarkable that, as is shown in Fig. 3, the volume of unit cell does not increase but decreases slightly with the temperature rise, and during the transitional region it diminishes nearly discontinuously by the amount  $\Delta v/v=4.4 \times 10^{-3}$ ; i.e.,  $0.27\text{Å}^3$  per unit cell. It seems reasonable to suppose that the thermal expansion of  $\text{BaTiO}_3$ -type ferroelectrics is a superposition of the normal expansion and abnormal contraction which is caused by the temperature change of polarization. It seems that in this crystal the latter effect is large enough to cover the former. The volume expansion coefficient of this crystal is given approximately by  $\alpha=-1.6 \times 10^{-5}/\text{deg.}$  in the tetragonal region, and  $\alpha=2.5 \times 10^{-5}/\text{deg.}$  in the cubic region. A preliminary dilatometric measurement is in good agreement with the x-ray data.

After all, it will probably be said that the phase transition in  $\text{PbTiO}_3$  is of the barium titanate type, but is more drastic in several points. In addition, we have measured the permittivity at temperatures from -170 to 550°C, and found only one transition, in contrast with  $\text{BaTiO}_3$ , which shows three transitions in this temperature range. We are now studying the anomalous specific heat at this transition. Detailed results will be reported shortly in the *Journal of the Physical Society of Japan*.

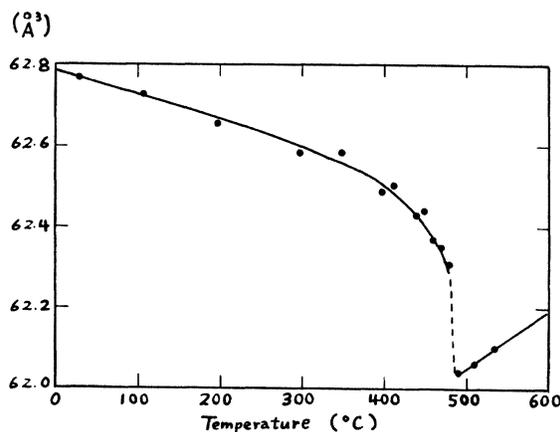


FIG. 3. Unit cell volume as a function of temperature.

The authors wish to express their sincere thanks to Professor S. Miyake and Professor Y. Takagi for their encouragement in the course of this work.

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### Domain Structure of Tungsten Trioxide

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IT has been found recently that tungsten trioxide,  $\text{WO}_3$ , behaves like a ferroelectric.<sup>1</sup> The dielectric constants of sintered ceramics or monocrystals are high compared with those of ordinary solid materials, being 100 to 300 at low temperature and of the order of  $10^3$  at room temperature. Though the tartrate, dihydrogenphosphate, and barium titanate are found to be analogous to a ferromagnetic, for example, to obey the Curie-Weiss law and to show the multiple domain structure, it is not certain whether  $\text{WO}_3$  corresponds to this case.

The present authors obtained single crystals of  $\text{WO}_3$  from the melt and were able to observe the details of the multiple domain structure which exhibits phenomena similar to those of  $\text{BaTiO}_3$ .<sup>2</sup> Optical and x-ray observation showed that the crystal has a pseudo-orthorhombic symmetry;  $a = 7.278\text{\AA}$ ,  $b = 7.460\text{\AA}$ ,  $c = 3.838\text{\AA}$ , and  $\beta \sim 90^\circ$  which coincide with the values reported earlier.<sup>3</sup> The flat plate of monocrystal obtained was usually smaller than  $1 \times 1 \times 0.1$  mm<sup>3</sup> in dimensions, with the orthorhombic  $c$ -axis parallel to the shortest edge. In many cases each crystal is composed of multiple domains divided by parallel stripes which are oriented at an angle  $45^\circ$  to the plate edges, or sometimes parallel to them.

In some cases, however, the crystal appears almost transparent with faint lines. These domain patterns, which are very like the twinned structure of  $\text{BaTiO}_3$ , are shown in Fig. 1a.

A microscopic inspection reveals that the neighboring twin components show pleochroism when observed by rotating the microscopic stage. When the direction of vibration of the polarized light coincides with one of the plate edges of the monocrystal, the contrast between light and dark fields is largest. This indicates the orthogonality of  $X'$ -directions for the neighboring twins.

Between crossed Nicols, an extinction effect is observed at positions at which one of the plate edges coincides with the directions of vibration of the polarized light. That is, the  $a$ - (or  $b$ -) axis in one domain component is perpendicular to the  $a$ - (or  $b$ -) axis in the neighboring components. In addition, there exist many fine striations parallel to the plate edges, which are nearly orthogonal with each other for neighboring twins (Fig. 1a). The angle between them is about  $88^\circ 30'$  and is equal to that between planes  $(110)$  and  $(\bar{1}\bar{1}0)$ , numerically equal to  $2 \tan(b/a) = 88^\circ 36'$ . Therefore, twinning occurs about  $\{110\}$  planes. These fine striations are considered to

be a kind of the crystal habit which specify the  $a$ - or  $b$ -axis in the orthorhombic lattice.

Wedge-shaped domains like those of  $\text{BaTiO}_3$  are also observed (Fig. 1b). In addition there exists fork- or scissors-shaped domains which are variable in shape, corresponding to the stress existing in the crystal. The breadth of the parallel components is about 0.01 to 0.004 mm, which is comparable to those of  $\text{BaTiO}_3$ .

When an unidirectional pressure is applied along one of the plate edges, some twins grow in volume by a migration of the twin boundary and wedge-shaped domains disappear gradually. At a fairly large pressure, irreversible boundary migration occurs, giving a crystal without domains. Temperature and electric field seemed to have no distinct effect upon the domain pattern.

X-ray studies of the powder samples and single crystals indicate that there exists no remarkable change in reflections above room temperature, except slight change in intensity above  $120^\circ\text{C}$  in the region of high Bragg angle.

It seems that there is no phase change like that of  $\text{BaTiO}_3$  for which a transition occurs from a low symmetry type to a high symmetry one at the Curie temperature.

The details of the investigation will be reported elsewhere.

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### Nuclear Magnetic Moment of $\text{S}^{33}$

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SEVERAL attempts have been made<sup>1-4</sup> to determine the nuclear magnetic moment of  $\text{S}^{33}$  by the Zeeman effect on the microwave rotational spectra of  $\text{OCS}^{33}$ . Jen<sup>1,2</sup> first set for  $\mu(\text{S}^{33})$  a broad range between 0.6 and 0.9 n.m., but there has not been good agreement on a more exact value. The difficulties encountered appeared to lie principally in the low intensities of the hyperfine lines at the low natural abundance of  $\text{S}^{33}$  and the uncertainty of the sign of the  $\text{OCS}$  rotational  $g$ -factor.

Recently, a sample of sulfur containing an isotopic abundance of 5.54 percent of  $\text{S}^{33}$  (7.5 times natural abundance), loaned by the Isotopes Division of the AEC, has made possible a re-examination of the problem under much more favorable conditions. The present paper is the result of a joint effort by the authors to reach essential agreement for the final result on  $\mu(\text{S}^{33})$  as measured independently with different experimental methods. Eshbach and Hillger<sup>4</sup> used a short section of wave guide employing Stark modulation and applied a magnetic field to the whole length of the wave guide. Jen<sup>5</sup> used a resonant cavity, which is placed between the pole pieces of an electromagnet. In spite of difference in their techniques, the authors have obtained substantially the same result for  $\mu(\text{S}^{33})$ .

The hyperfine structure of the  $\text{OCS}^{33} J=1 \rightarrow 2$  rotational transition was first studied by Townes and Geschwind,<sup>6</sup> who measured the nuclear quadrupole coupling and determined the nuclear spin,  $I(\text{S}^{33})$ , as  $3/2$ . The spin assignment has been confirmed by the present studies. The Zeeman splitting for each of the hyperfine lines has been examined in detail for both the  $\pi$ - and  $\sigma$ -transitions.

The strongest line in the spectrum at zero field represents the joint contribution of two coincident transitions:  $F=3/2 \rightarrow 5/2$ , and  $F=5/2 \rightarrow 7/2$ . The Zeeman components of this line are too numerous to be clearly resolved. The variation of intensity of this line as a function of the magnetic field was used in some preliminary experiments<sup>2,4</sup> for the determination of  $\mu(\text{S}^{33})$ . The results obtained in this manner are now superseded by much more accurate results derived from the well-resolved splittings of the hyperfine lines.

The Zeeman splittings of the following hyperfine lines have been examined:  $F=1/2 \rightarrow 3/2$ ,  $5/2 \rightarrow 5/2$ ,  $1/2 \rightarrow 1/2$ ,  $3/2 \rightarrow 3/2$ , and

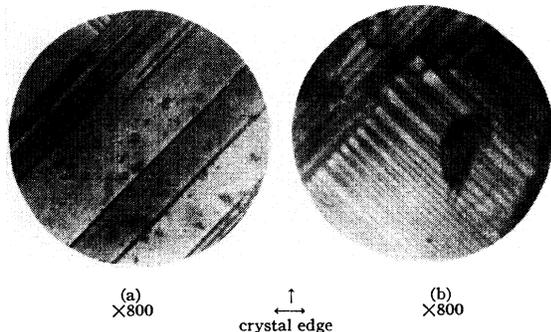


FIG. 1. Multiple domain structure of  $\text{WO}_3$ . (a) Domains divided by parallel stripes. (b) Wedge-shaped domains.