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The Characteristics of Defect Lead Titanate

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$PbTiO_3$ and $BaTiO_3$ have been known as typical ferroelectric materials with perovskite-type structures, the former being characterized by a fairly high Curie temperature (490°C) and by the largest tetragonal lattice strain (0.063) among known perovskite-type ferroelectrics. On the other hand, although many sorts of barium titanate, such as $BaTi_3O_7$, $BaTi_2O_5$, and Ba_2TiO_4, besides the well-studied $BaTiO_3$, have been known, no phase other than $PbTiO_3$ has so far been found in the system of Pb–Ti–O. This means that, during the course of the solid-solid reaction between PbO and TiO_2 at elevated temperatures, one of the reactants present in an excess remains unreacted without forming any compounds other than a single product of $PbTiO_3$. Furthermore, neither an oxygen-excess nor an oxygen-deficient state in $PbTiO_3$ has been found. The present communication will discuss the basic chracterization of the defect lead titanate newly found.

Experimental

All the ceramic samples of defect lead titanate proposed here were prepared by firing noncrystalline lead titanate. The noncrystalline bodies were prepared by adding a titanium tetrachloride aqueous solution to a strongly basic aqueous solution (with the aid of NaOH) of lead acetate under following conditions: with an equimolar ratio of Ti^{4+} and Pb^{2+} quantities (sample A′), with Pb^{2+} in twice the molar quantity of Ti^{4+} (sample B′), and with the latter solution in a large excess (sample C′). All the precipitates thus obtained were thoroughly washed with water until they were free from Na^+. A portion of as-precipitated sample C′ was immersed into a basic aqueous solution of lead acetate for 10 hr and then washed with water (sample D′); the solution was formed by the dissolution of lead acetate into a slightly basic aqueous solution adjusted with the aid of acetic acid and ammonia water. Finally, the noncrystalline samples, A′, B′, C′, and D′ were all fired at 800°C for 1 hr in order to convert them satisfactorily into polycrystalline samples, A, B, C, and D respectively.

Results and Discussion

The results of the chemical analysis of these polycrystalline samples indicated that they all more or less possessed Pb- and oxygen-deficiencies; they can be characterized by the general formula of $(PbO)_x \cdot TiO_2$. Here, it was confirmed that no phases other than the perovskite one were observed, at least on X-ray powder patterns of the samples. The defective structures, however, should be understood as being metastable even if they are stable up to 800°C. A piece of experimental evidence to support the above statement was that all the samples of defect lead titanate, when heated at a considerably higher temperatures (for example, at 950°C) were changed to those with less deficiencies by successively isolating TiO_2 from the original samples.

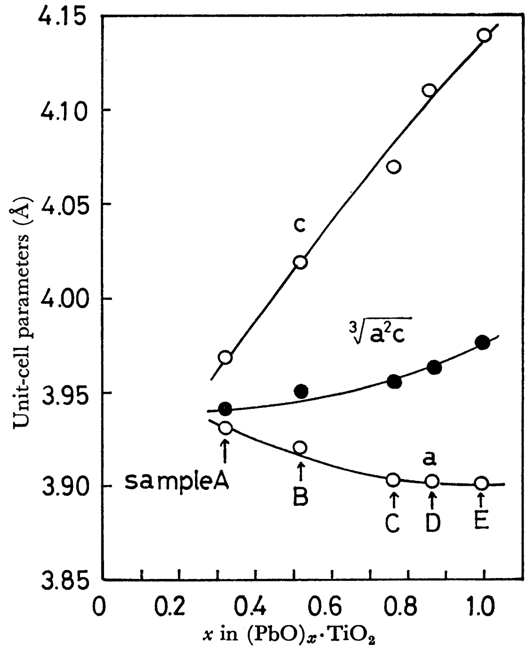

Fig. 1. Unit-cell parameters (a,c and $\sqrt[3]{a^2c}$) as a function of the value x in $(PbO)_x \cdot TiO_2$.

On the other hand, the unit-cell parameters (a,c and $\sqrt[3]{a^2c}$) of each tetragonal lattice varied from one sample to others, depending on the history of the preparation of the samples. The dependence of these parameters on the x value in $(PbO)_x \cdot TiO_2$ is obvious; Fig. 1 depicts this along with the data on a standard sample, E, which was prepared by the solid-solid reaction of an equimolar mixture of PbO and TiO_2 at 1000°C for 1 hr. As may be seen in Fig. 1, with an increase in the degree of the nonstoichiometry between constituent cations, a reducing tendency of $\sqrt[3]{a^2c}$ value is evident. In other words, this fact may be the same as saying that a contraction of the unit-cell volume of the defect lead titanate takes place as a result of the introduction Pb- and/or oxygen-vacancies into the $PbTiO_3$ crystal. It is surprising that considerable amounts of the deficiencies can be introduced into the $PbTiO_3$ crystal while maintaining the perovskite-type structure. At any rate, the present ceramic samples of defect lead titanate may be successfully taken as a new type of ferroelectric material, because they all more or less possess tetragonal lattice strains, $1-c/a$.

Further study was undetaken in order to determine whether or not the defect structures are uniform over the bulk. For this purpose, the degree of the fluctua-

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1) J. Mazur, *Nature*, **164**, 358 (1949).
2) W. H. Hall, *J. Inst. Met.*, **75**, 1129 (1949).

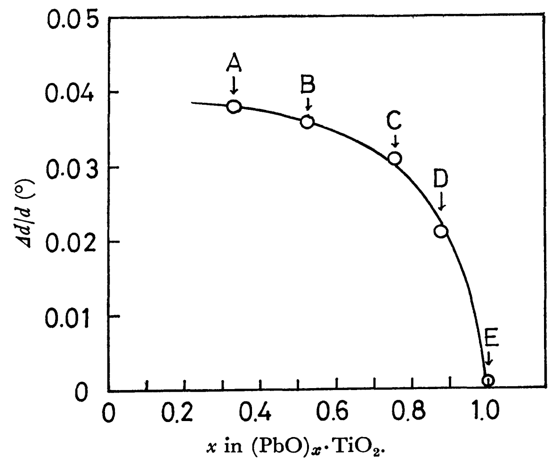

Fig. 2. The fluctuation of interplaner spacings in defect lead titanate.

tion of interplanar spacings, $\Delta d/d$, of each cubic lattice, which appeared when the substance was intentionally held at a temperature (550°C) above the Curie point of the samples, was calculated by observing the reflection angles, θ, and the pure X-ray diffraction broadening, β, with the aid of the relationship:[1,2]

$$\beta = -\frac{\Delta d}{d}\cdot\frac{\sin\theta}{\cos\theta}$$

Practically, when plotting $\beta\cdot\cos\theta$ against $\sin\theta$, the $\Delta d/d$ value was determined from the slope of the straight line obtained. The dependence of the $\Delta d/d$ ratio on the x value is evident, as is illustrated in Fig. 2. Here, from the fact of the presently-observed dependence on x of $\sqrt[3]{a^2c}$ at room temperature, one may expect a further dependence of $\sqrt[3]{a^3}$ or a at 550°C on x. If so, it seems resonable to believe that the fluctuation of interplanar spacings occurs mainly due to a fluctuation of the x value, *i.e.* due to a microscopic inhomogeneity of the defect structures.

In summary, the present lead titanate prepared through the wet process can be characterized by both Pb- and oxygen-deficient structures, and by their inhomogeneities, the degree of which increase with an increase in the over-all degree of the deficiencies.