# DEFECT LEAD TITANATES WITH DIVERSE CURIE TEMPERATURES

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A new type of ferroelectric defect lead titanates with perovskite type structure is proposed. Their Curie temperature varies between 295°C and 435°C, depending on the degree of nonstoichiometry, $x$, in their general formula of $Pb_{1-x}TiO_{3-x}$. A qualitative interpretation of anamalous Curie temperatures is given by the concept of 'rattling' lattice space available for $Ti^{4+}$ ions.

THE CURIE temperature of $PbTiO_3$ is considered as being settled, i.e. 490°C even if slightly different figures have been reported by by different investigators.[1,2] On the other hand, there has been a wide variety of barium titanates such as $BaTi_3O_7$, $Ba_2TiO_4$, $BaTi_2O_5$ and so on, in addition to $BaTiO_3$ of interest, whereas only a $PbTiO_3$ phase with peroskite structure as lead titanate has been known. This means that when the $PbTiO_3$ is formed by solid–solid reaction between PbO and $TiO_2$ at elevated temperatures, either reactant in an excess remains unreacted with the product $PbTiO_3$ without forming any other lead titanates. Furthermore, studies of any type of nonstoichiometry of the $PbTiO_4$ have not yet been available. Under such situations, the present communication presents a discovery of defect lead titanates with various Curie temperatures.

Sample B and sample C were obtained by firing a noncrystalline lead titanate at 1120°C and 800°C, both for 1 hr; the preparation of the noncrystalline lead titanate was undertaken by hydrolysis of titanium tetra-chloride solution into a basic solution of lead acetate, with the latter solution in a large excess. Sample D was also prepared by firing a noncrystalline lead titanate from another batch (with an equimolar ratio of the $Pb^{2+}$-solution to the $Ti^{4+}$-solution), at 700°C for 10 min.

Analysis of the X-ray powder patterns taken with $CuK_\alpha$ radiation indicated that all the polycrystalline samples thus obtained possess more or less tetragonal lattice strains (0.058 for sample B, 0.043 for sample C and 0.006 for sample D), at room temperature. Accordingly, all of them should be considered as a new type of ferroelectric substance with perovskite structure. The temperature dependence of the unit-cell parameters ($a$, $c$ and $\sqrt[3]{(a^2c)}$) is illustrated in Fig. 1, together with the data for a standard sample which was prepared by solid–solid reaction of an equimolar mixture of PbO and $TiO_2$, at 1000°C for 2 hr. As seen in Fig. 1, the Curie temperature varies from one sample to others, being 490°C (sample A), 435°C (sample B), 375°C (sample C) and 295°C (sample D) respectively; the first two reveal discontinuous volume changes at these temperatures, whereas the last two seem to show continuous volume change.

Qualitative interpretations on the anomalous Curie temperatures will be given below. One of the explanations of the origin of the anomaly may be attributed to a role played by surface distorted-layer onto the fine particles formed as
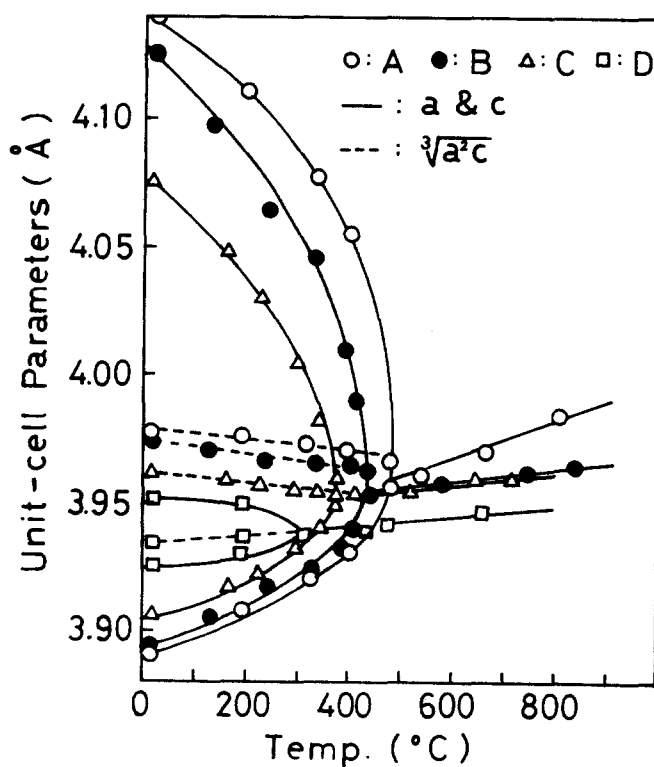
FIG. 1. The temperature dependence of Unit-cell parameters $(a, c$ and $\sqrt[3]{(a^2c)})$. All the parameters were determined with the aid of high-temperature X-ray diffractometer (Nihon–Denshi Co.). The convex parts in tetragonal phase show loci of $c$ spacing, while the concave parts, loci of $a$ spacing.
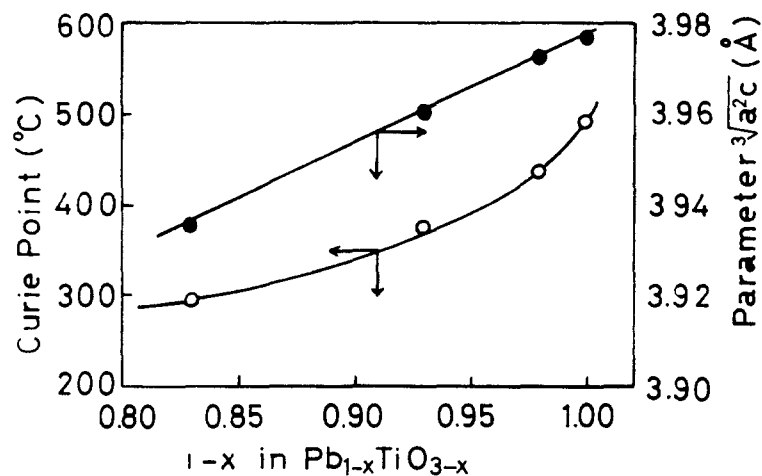
FIG. 2. The Curie temperature and the parameter $\sqrt[3]{(a^2c)}$ as a function of the degree of non-stoichiometry in lead titanates. The values of $\sqrt[3]{(a^2c)}$ only at room temperature are indicated. Care must be placed on the abscissa being given by the degree of stoichiometry, $1 - x$, in the $Pb_{1-x}TiO_{3-x}$.

a result of the wet process. The results of chemical and quantitative X-ray analysis of these samples (Table 1), however, are contrary to the above explanation. As seen in Table 1, samples B, C and D, all possess considerable amounts of lead- and oxygen-deficiencies, being given by a general formula of $Pb_{1-x}TiO_{3-x}$ or $(PbO)_{1-x} \cdot TiO_2$. It should be noted that there are different degrees of the nonstoichiometry between a noncrystalline lead titanate before firing and the corresponding polycristalline one after firing. It is concluded from repeated experiments that this difference arises from isolating small amounts of $TiO_2$ from the $Pb_{1-x}TiO_{3-x}$ during the course of the firing; undoubtedly, the progress of the firing process causes the degree of the nonstoichiometry to decrease. At any rate, it is surprising that even after firing at fairly high temperatures, sufficient amounts of the deficiencies can be introduced into the $PbTiO_3$ crystal while maintaining the perovskite type structure. In summary, we can successfully correlate the Curie point to the degree of the nonstoichiometry, $x$, after firing, as shown in Fig. 2.

Prior to further discussion, it is desirable to take note of a relatiosnhip between the values $\sqrt[3]{(a^2c)}$ and $x$, as given together in Fig. 2. This relation will be the same as saying that a lattice contraction takes place as a result of introducing both lead- and oxygen-deficiencies into the $PbTiO_3$ crystal; both deficiencies may exist as vacancies owing to the close-packed arrangement of $Pb^{2+}$ and $O^{2-}$ ions in the $PbTiO_3$ with the tolerance factor[3] $= 0.98$. On the other hand, there have been similar phenomena; i.e. it is well known that such a contraction occurs when $Pb^{2+}$ in $PbTiO_3$ is fully or partially replaced

with other cations such as $Sr^{2+}$, $Ca^{2+}$ abd $Cd^{2+}$, all having smaller ionic radii than that of $Pb^{2+}$. In all cases, the tolerance factor of resulting titanates must decrease successively with increasing amounts of the replacing cations. The foregoing facts allow us to believe that introduction of both vacancies into $PbTiO_3$ leads to over-all shrinking of the close-packed framework consisted of $Pb^{2+}$ and $O^{2-}$ ions. If so, this shrinking will be accompanied with a decrease of 'rattering' lattice space[4] available for $Ti^{4+}$ ions filling the interstitial positions of the framework. Consequently, the defect lead titanate, with increasing the value $x$, will have a tendency to go toward perovskite lattice with smaller tetragonal lattice strains from that with larger ones as a result of increasing suppression of spontaneous polarization. In an extreme case, cubic perovskite structure will be favorable. Thus, the Curie temperature will be lowered as the value $x$ increases. Throughout the above discussion, however, no remark is made on the effect of polarizability of the constituent ions.

Up to now, different measurements on a certain kind of ferroelectric phenomena have been reported by different investigators. Among these, a typical example has been on the transition energy and the accompanying entropy change during the transition from ferroelectric phase to paraelectric phase of $PbTiO_3$; G. Shirane et al.[1] found $\Delta E = 1150$ cal/mole and $\Delta S = 1.591$ cal/mole°C for the ceramic sample fired at 1100°C, whereas V.G. Bhide et al.[5] $\Delta E = 1550$ cal/mole and $\Delta S = 2.055$ cal/mole°C for the single crystal obtained with the aid of flux technique. Furthermore, the present study resulted in $\Delta E = 406$ cal/mole and $\Delta S =$

Table 1. The degrees of nonstoichiometry in noncrystalline lead titanates, and in the corresponding polycrystalline ones obtained by firing them. All the titanates could be expressed by a general formula of $Pb_{1-x}TiO_{3-x}$.

| Samples | $x$ in $Pb_{1-x}TiO_{3-x}$ | |
| --- | --- | --- |
| | in polycrystalline state | in noncrystalline state |
| A | 0.00 | — |
| B | 0.02 | 0.16 |
| C | 0.07 | 0.16 |
| D | 0.17 | 0.21 |

0.604 cal/mole°C for the standard sample A. On the basis of the present communication, this discrepancy may be also attributed to the difference of over-all deficiencies such as proposed above and/or of microscopic fluctuation of the deficiencies in the three samples of interest. The detailed study on these will be reported elsewhere.

## REFERENCES

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Ein neuer Typus vom ferroelektrischen defektiven Bleititanat mit Perowskityp–Struktur wird vorgeschlagen. Die Curiepunkt dieser Sustanz liegt im Bereich von 295°C bis 435°C und hängt von der Grade der Nonstöchiometrie, $x$, im $Pb_{1-x}TiO_{3-x}$. Die Ursache dieser anomalen Curie Temperaturen werden bei einem Standpunkt des 'ratternden' Gitterraum, den $Ti^{4+}$-Ionen benutzen können, qualitativ diskuriert.