JOURNAL OF SOLID STATE CHEMISTRY 12, 84–91 (1975)

Defect Ferroelectrics of Type $Pb_{1-x}TiO_{3-x}$

S. SHIRASAKI, K. TAKAHASHI, AND H. YAMAMURA

National Institute for Researches in Inorganic Materials, Sakura-Mura, Niihari-Gun, Ibaraki, Japan

K. KAKEGAWA AND J. MORI

Faculty of Engineering, Chiba University, Chiba, Japan

Received October 26, 1973

A series of new ferroelectric substances of type $Pb_{1-x}TiO_{3-x}$ or $Pb_{1-x}Na_yTiO_{3-x+(y/2)}$ with perovskite-type structure was prepared by simple solid state reaction among powdered mixtures of PbO, TiO_2, and in a several cases, Na_2CO_3, with TiO_2 in an excess. The defect materials are characterized in terms of inhomogeneously distributed vacancies, $\square_{Pb}$ and $\square_{O}$ at the respective equivalent lattice positions. Their ferroelectric properties are discussed in relation to those of the same type of materials precipitated aqueously and followed by firing at elevated temperatures

1. Introduction

$PbTiO_3$ is a typical ferroelectric material with perovskite-type structure, its Curie temperature being 490°C and its tetragonal strain being 0.064 at room temperature. Polycrystalline $PbTiO_3$ is generally prepared by solid–solid reaction between an equimolar mixture of TiO_2 and PbO at elevated temperatures. It has so far been believed that even the reaction between any mixtures other than the equimolar one forms stoichiometric $PbTiO_3$, in which one reactant in an excess remains unreacted. In accordance with the above idea, Fushimi and Iida (*1*) in their phase equilibrium study in the system PbO–TiO_2–ZrO_2, and Koizumi (*2*) in his study in the system PbO–TiO_2–Nb_2O_5 did not refer to the existence of nonstoichiometry in $PbTiO_3$.

On the other hand, several possibilities of deviation from stoichiometry in perovskite compounds of type $A^{2+}B^{4+}O_3$ have been reported. Arend et al. (*3*) indicated the occurrence of deviation from stoichiometry in $BaTiO_{3-x}$ of magnitude $x < 0.1$. Harwood and Klasens (*4*) studied the dependence of lattice parameters on the heat-treatment temperature of $BaTiO_3$, and suggested the change of the lattice parameters to be due to imperfections in the lattice. Atkin and Fulrath (*5*) studying point defects of lead zirconate–titanates indicated that the crystals became deficient in Pb and O when they were fired at elevated temperatures. Holman and Fulrath (*6*) studying intrinsic nonstoichiometry in single phase $Pb(Zr_{0.5} \cdot Ti_{0.5})O_3$ by thermogravimetry showed that the width of the single phase region was at most 2.48 mole % PbO at 1100°C. Our previous studies (7–9) indicated the possible occurrence of substantial amounts of Pb and O vacancies in polycrystalline lead titanates precipitated aqueously and followed by firing at temperatures of < 1120°C.

The present report concerns the possible formation, solely by simple solid state reaction, of ferroelectric substances of type $Pb_{1-x}TiO_{3-x}$ or $Pb_{1-x}Na_yTiO_{3-x+(y/2)}$ with a perovskite-type structure. Efforts were made to verify the presence of Pb and O vacancies in the materials. Their basic ferroelectric properties are discussed in relation to those

Printed in Great Britain

of the same types of materials obtained through aqueous synthesis.

2. Experimental

Source materials G.R. PbO and TiO_2 of the Coso Chemicals Company were used. Solid solid reaction at 900°C were carried out by varying the mixed mole ratio of PbO, TiO_2, and Na_2CO_3 in 1.0:1.0:0.0, 0.9:1.0:0.0, 0.7:1.0:0.0, and 0.41:1.0:0.11 to obtain four types of polycrystalline specimens A_D, B_D, C_D, and D_D, respectively.

Noncrystalline material was precipitated by adding aqueous titanium tetrachloride ($TiCl_4:H_2O = 1:3$ by volume) to a strongly basic solution of lead acetate [$Pb(CH_3CO_2)_2 \cdot 3H_2O:NaOH:H_2O$ = 38 g:120 g:100 cc] with thorough stirring; a large amount of Pb^{2+} remained unreacted in solution when the precipitation reaction terminated. The resultant precipitate was filtered, washed with water until free from any adsorbed Na^+ and Pb^{2+}, and then oven-dried at 120°C. Two titanate compositions were prepared by varying the amount of Ti-solution added to Pb-solution in Ti:Pb mole ratios of 3:350 (specimen type A_N) and 3:70 (type B_N). The amorphous specimen A_N was heated at 1200°C and 800°C to prepare polycrystalline specimens A_W and B_W, respectively; specimen B_N was also fired at 800°C to get specimen C_W.

Elements Na, Pb, and Ti were analyzed chemically for the as-dried material A_N and B_N, which were soluble in 6 N HNO_3. The Na content was determined spectrographically. An acidic solution of cupron (α-benzoinoxime) was added to the specimen solution to precipitate quantitatively a yellowish precipitate of cupron–Ti complex, leaving cupron–Pb complex in solution. The resultant precipitate was filtered, washed with diluted acid until removal of all adsorbed cupron–Pb complex and then ignited at 700°C for 10 hr for the determination of Ti content as TiO_2. The collected solution of cupron–Pb complex was titrated with a standard EDTA solution to ascertain the Pb content. The quantities of adsorbed water in the amorphous materials A_N and B_N were estimated from their weight losses occurred up to 550°C.

Five types of specimens A_D, B_D, D_D, B_W, and C_W displayed only perovskite phase X-ray lines. Specimens C_D and A_W, however, were in the coexistence of very small amounts of rutile-type TiO_2 with the host phase. The free rutile was determined quantitatively by X-ray diffraction. A specimen (perovskite plus free rutile), rutile powder mixtures with a several mixed ratios were prepared, and their integrated intensity ratios between the perovskite {111} and rutile {101} reflections were determined planimetrically. A plot of the former ratio vs the latter one was made to determine the quantity of the free rutile in the specimen of interest from an integrated intensity ratio extrapolated to zero mixed ratio.

Bulk density of powdered materials was picnometrically measured to compare with two kinds of densities, one calculated from their composition and unit-cell volume with a postulated defect structure, and another calculated under assuming the simple coexistence of $PbTiO_3$ (theor. density = 7.52), rutile (theor. density = 3.84), and in some cases, Na_2O (theor. density = 2.27), which are possible reaction products from the mixed powdered reactants, PbO, TiO_2 and Na_2CO_3, with TiO_2 in an excess.

Experiments were also designed to determine whether each composition was microscopically uniform. For this purpose the composition dependence of lattice constants in the cubic paraelectric phase at 550°C for all the materials concerned was first examined. Then the magnitude of fluctuation of interplanar spacings $\Delta d/d$, at 550°C was determined by observing the reflection angle θ, and the diffraction line broadening β, relative to a silicon standard according to the equation $\Delta d/d = \beta \cos\theta/\sin\theta$.

To insure X-ray diffractometrically the presence of Pb and O vacancies, the integrated intensities were computer calculated to compare with the observed ones. The fundamental equation for the relative intensity of powder pattern lines is represented by

$$I = F^2 \cdot S \cdot A \cdot P((1 + \cos^2\theta)/\sin^2\theta \cdot \cos\theta) \times \exp(-2B_{\text{eff}} \cdot \sin^2\theta/\lambda^2), \quad (1)$$

where I = relative integrated intensity (arbitrary unit), F = structure factor, S = scale factor, A = absorption factor, P = multiplicity factor, B_{eff} = effective temperature factor and θ = Bragg angle. The structure factor for the *hkl* reflection of a crystal containing lattice defects is

$$F = \sum_{1}^{N} (f_n + \Delta f_n' + \mathrm{i}\Delta f_n'')\cdot r_n \times \exp(2\pi i(u_n h + v_n k + w_n 1)], \quad (2)$$

where u_n, v_n, and w_n are the fractional coordinate of atom n, r_n is the site occupancy fraction of atom n, f_n is the atomic scattering factor of atom n, and $\Delta f_n'$ and $i\Delta f_n''$ are the correction terms for the anomalous dispersion. Among these factors, F, P and Lorentz factor are calculable. For the calculations, a crystal containing random array of Pb and O vacancies is assumed in accordance with the experimental evidence for the materials. The X-ray diffraction patterns were recorded with Cu*Kα* radiation and Ni filter under the conditions of scanning speed = 1/2°2θ/min, time constant = 4 sec, voltage = 15 kV and current = 8 mA.

High temperature X-ray diffraction technique was used to study the ferroelectric to paraelectric phase transition of the titanates. Diffraction lines {200} and {111} of perovskite phase of the materials were traced at fixed temperatures between room temperature and 900°C with a silicon internal standard, and then the tetragonal distortion c/a, was calculated as a function of temperature, from which curves Curie temperatures were read. The use of low angle lines seemed appropriate for the measurements. This is because the high angle lines more or less had their line broadening as a result of composition fluctuation of the materials, due to which the estimation accuracy of the lattice constants were rather low. Six-times measurements of (c/a)-1 at room temperature, by the use of reflections {200} and {111}, for example for specimen C_D gave 1.057 ± 0.002 whose error range involved inside an open square plot (see Fig. 3).

Results and Discussion

X-ray diffraction showed speimens B_D, D_D, and of course A_D, to be perovskite-phase only, suggesting possible occurrence of Pb-deficiency in the perovskite lattice. In C_D yielded from a mixture of PbO : TiO$_2$ = 0.7 : 1.0, a very small amount of isolated rutile (3.14 wt%) coexisted with the host phase. Its quantity, however, made it safe to go to Pb-deficiency in the host of C_D (Table I). For the occurrence of Pb-deficiency, two ways of solid state reaction schemes are postulated

$$(1-x)\mathrm{PbO} + (1+x')\mathrm{TiO_2} \rightarrow x'\mathrm{TiO_2} + \mathrm{Pb_{1-x}TiO_{3-x}} \quad (3)$$

$$(1-x)\mathrm{PbO} + (1+x')\mathrm{TiO_2} + (x/2)\mathrm{O_2} \rightarrow x'\mathrm{TiO_2} + \mathrm{Pb_{1-x}} \oplus \mathrm{TiO_3} \quad (4)$$

where $\oplus$ is the positive hole. The thermogravimetry of any source mixtures chosen in

TABLE I

COMPOSITIONS AND THEIR FLUCTUATIONS FOR TWO SERIES OF "DRY" AND "WET" SPECIMENS

		Chemical formula $\mathrm{Pb_{1-x}Na_yTiO_{3-x+(y/2)}}$		Pb-vacancy concentration	$\Delta d/d$	Composition range
Specimen type	$1-x$	y	$3-x+(y/3)$	$x-y$	(°)	$\Delta(1-x)$
A_D	1.00	0.00	3.00	0.00	0.000	1.00–1.00
B_D	0.90	0.00	2.90	0.10	0.022	0.80–1.00
C_D	0.77	0.00	2.77	0.23	0.047	0.60–0.98
D_D	0.41	0.21	2.57	0.38	0.085	0.36–0.78
A_W	0.78	0.00_8	2.78	0.22	0.024	0.93–0.78
B_W	0.70	0.00_8	2.70	0.29	0.031	0.83–0.58
C_W	0.27	0.51	2.61	0.22	0.038	0.56–0.13

the present study revealed no measurable weight gain during the course of the solid state reaction. Chemical formula possibility of $Pb_{1-x}TiO_3$ may therefore be ruled out. In monophasic specimen D_D yielded from a mixture of $PbO:TiO_2:Na_2CO_3 = 0.41:1.0:0.11$, monovalent Na^+ may enter the A sites of $A^{2+}B^{4+}O_3$ perovskite, since ionic radius of Na^+ (1.42 Å for ninefold sites) is closer to that of Pb^{2+} (1.67 Å for twelve fold sites) than that of Ti^{4+} (0.745 Å for four fold sites). The expression as composition $Pb_{1-x}TiO_{3-x}$ or $Pb_{1-x}Na_yTiO_{3-x+(y/2)}$ for the reaction products may be appropriate (Table I); the values x, and y for specimens A_D, B_D and D_D were calculated from their corresponding mixed ratios of $PbO:TiO_2:Na_2CO_3$. The value x for C_D were determined by removing the isolated quantity of TiO_2 from the host.

A similar situation could be seen in a series of "wet" specimens. Specimens B_W and C_W both fired at 800°C were monophasic perovskite. The TG and DTA of as-dried materials A_N and B_N showed that the loss of adsorbed water was complete at 250°C; thereafter no ignition losses were detected up to 1100°C, where vaporization of PbO began. Thus it was concluded that the compositions of the single-phase polycrystalline materials, B_W and C_W were the same as those of the corresponding amorphous materials after the adsorbed water was removed. The results of chemical analyses of the as-dried noncrystalline materials A_N and B_N are listed in Table II. To test whether any types of perovskite compounds were actually formed, the calculations were done using the results of the chemical analyses. Two formulas I and II for each specimen type were calculated according to whether Pb and Na contents or the Ti and Na contents, respectively, were used in the calculations. These two fit chemical formulae $Pb_{1-x}Na_yTiO_{3-x+(y/2)}$ with nearly the same values of x and y for B_W and C_W. Table I shows chemical formula I for the two specimens. In specimen A_W, however, an isolated rutile occurred with the host phase. Comparison of A_W and B_W suggests that the present materials containing defects decompose at high temperatures according to

TABLE II

CHEMICAL ANALYSES OF NONCRYSTALLINE TITANATES A_N AND B_N

Specimen type	Constituent (wt %)			
	PbO	TiO_2	Na_2O	H_2O
A_N	66.8	33.7	0.00098	6.80
B_N	35.6	51.0	0.10	10.73

$$Pb_{1-x}TiO_{3-x} \rightarrow [(1-x)/(1-x')]Pb_{1-x'} \times TiO_{3-x'} + [(x-x')/(1-x')]TiO_2 \quad (5)$$

where $x > x'$. In this view, the defect structure can be seen as metastable existence. The composition of the host of A_W was thus calculated by taking the quantity of rutile coexited into consideration.

It is believed that the Pb and O deficiencies are present as vacancies because of the close-packed arrangement of Pb and O in the $PbTiO_3$ crystal. To clarify this the densities of the materials were determined picnometrically, and compared with two kinds of the calculated densities, one calculated from their composition and unit-cell valumes a^2c on the basis of Pb and O vacancies, another calculated with assuming simple coexistence of $PbTiO_3$, TiO_2 and in several cases, Na_2O, which can be possible solid state reaction products from the powdered mixtures chosen in the present study (Fig. 1). Remarks will be necessary for the errors in picnometric density measurements. The repeated measurements (6 times) for specimen A_D, $PbTiO_3$, led to 7.62 ± 0.04 as its density, which is somewhat higher than the calculated one (= 7.52); the origin of the discrepancy is not clear. Therefore all the observed values (Fig. 1) are shown after as-observed values are multipled by a factor 0.9868 (= 7.52/7.62). Figure 1 shows that the experimental values are in good agreement with the calculated values carried out on the basis of Pb and O vacancies. Pb and O vacancy model is therefore considered appropriate throughout "wet" and "dry" specimens. Thus we can give the number of Pb vacancies in the crystals in terms of x-y (Table I). Table I shows that PbO deficient $PbTiO_3$ could be

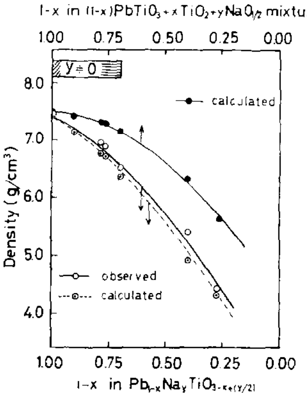

FIG. 1. Observed and calculated densities as a function of composition. --⊙-- indicates calculated density on the basis of Pb and O vacancies, and —●— calculated density on the basis of simple coexistence of $PbTiO_3$, TiO_2, and Na_2O.

crystallized without any dopants for values below at least $x = 0.23$ in $Pb_{1-x}TiO_{3-x}$.

To ensure more concretely the presence of Pb and O vacancies in the materials, observed integrated intensities relative to integrated intensity of reflection {110}, I_{obsd}, were compared with their values I_{calcd} involving calculable structure factor, multiplicity factor and Lorentz factor in the form of Eq. (6).

$$\ln(I_{obsd}/I_{calcd}) = \ln S + \ln A - 2B_{eff}(\sin\theta/\lambda)^2. \qquad (6)$$

Efforts were made for specimens A_D and C_D. The results show in Fig. 2. As seen there, the extent of data scatters for both materials is comparable, indicating that a model of randomly distributed Pb and O vacancies is reasonable for specimen C_D. The slopes of two straight lines drawn are somewhat different, which lead to two different values of effective temperature factor ($B_{eff} = 0.80$ Å^2 for A_D, $B_{eff} = 1.51$ Å^2 for C_D). It seems reasonable to expect larger amplitude of thermal vibration of concerned species of specimen containing larger amounts of vacancies.

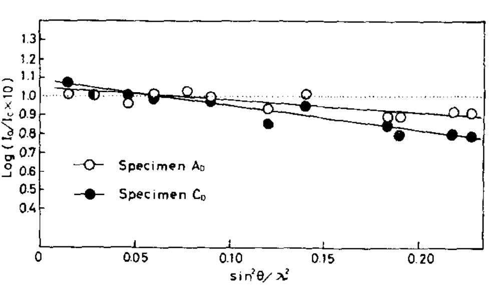

FIG. 2. Plots of log (I_{obsd}/I_{calcd}) vs $\sin^2\theta/\lambda^2$ for two "dry" specimens A_D and C_D.

Care should also be taken for as-obtained values of I_{obsd} and I_{calcd} as well as for Eq. (6) plots. Among various reflections, special care should be directed to reflections {100} and {110}. Faces {101} and {110} of tetragonal perovskite phase involve Pb and Ti atoms, due to which the reflections from both atoms intensify one another. Faces {100} and (001), on the other hand, have the respective two kinds of faces, one involving Pb and O atoms, and another, Ti and O atoms, in which the two kinds of reflections act so as to weaken their intensities on one another. Therefore, the integrated intensity ratio between reflections {101} plus (110) and {100} plus (001) should be sensitive to the presence of defects, especially of Pb vacancies. Actually as-obtained values of I_{calcd} and I_{obsd} were 0.404 and and 0.410, respectively, for A_D, while 0.276 and 0.333, respectively, for C_D. It should be noted that I_{obsd} values for the two materials is appreciably different in accordance with a large difference of I_{calcd} values for two materials.

This fact gives a strong evidence for the occurrence of Pb and O vacancies in specimen C_D. Unfortunately agreement between the I_{obsd} and I_{calcd} is not necessarily good. Undoubtedly this stems from large temperature factor of C_D as is understandable from Fig. 2.

The variation of tetragonal distortion, c/a, with temperature for "wet" and "dry" specimens is illustrated in Fig. 3, along with data of ceramic $PbTiO_3$ obtained by Shirane and Hoshino (*10*). The data points of A_D and the ceramic $PbTiO_3$ coincide over the temperature range tested, and their ferroelectric–paraelectric transition undergoes sharply at 490°C, their Curie temperature. The tetragonal distortion of the titanates containing lattice defects, on the other hand, decreases slowly with increasing temperature as the respective Curie temperatures are

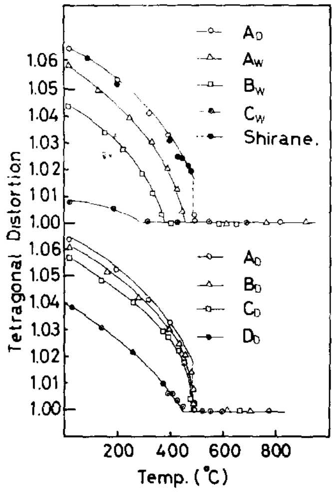

FIG. 3. Tetragonal distortion as a function of temperature for two series of materials.

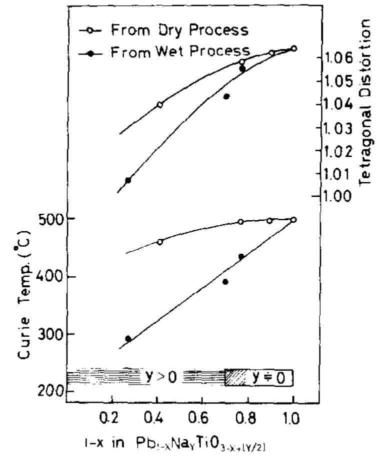

FIG. 4. Composition dependences of Curie temperature and of tetragonal distortion for two series of materials.

approached (diffused transition). At any rate all of them can be regarded as ferroelectrics at at least room temperature, which results from the occurrence of tetragonal lattice strain. It should be noted that Curie temperatures of specimens A_D through D_D are roughly constant, whereas that those for "wet" specimens are distributed over a rather wide temperature range, depending on the value of x in $Pb_{1-x}TiO_{3-x}$ or $Pb_{1-x}Na_yTiO_{3-x+(y/2)}$. The variations of the tetragonal distortion at room temperature and of Curie temperature with composition are independently shown in Fig. 4 for the two series of materials. For each series, there is a general trend such that an increase of compositional parameter x follows a decrease of T_c and c/a, although their decreasing tendency differs from one series to another. The general trend can be qualitatively interpreted as follows. In studying the relative polarization of the constituent ions in $BaTiO_3$, Slater indicated that polarization is almost entirely contributed by the Ti and O ions, where the O ions are those lying along lines parallel to the direction of polarization. This effect shows that spontaneous polarization occurs as a result of strong interaction between the Ti and O ions, which build linear chains of dipoles which all point in the same direction. When the origin is taken at a point along the tetragonal axis such that the oxygen network remains fixed, the structural features of $PbTiO_3$ and $BaTiO_3$ are similar. There is little doubt that lack of O ions, which is characteristic of crystals containing lattice defects, causes weakening of the interaction of Ti and O. Thus, the strength of spontaneous polarization and therefore the magnitude of tetragonal strain, which are both closely related to the strength of this interaction, may decrease with increasing x or x-y. In contrast with the above way of the interpretation of the anomalous properties of T_c and c/a, significant particle size effects on "anomalous" dielectric properties of perovskite compounds, especially of $BaTiO_3$, have been pronounced (*11*, *12*). In the previous reports (*9*), on the same type of defective titanates obtained through aqueous synthesis, however, no correlation between tetragonal distortion and crystallite size was found. Here it should be emphasized that temperature elevation allows simultaneously particle size and/or crystallite size to grow and the degree of Pb and O deficiencies to reduce. In view of this consideration, particle-size dependence of ferroelectric properties such as Tc, c/a, and permittivity may be often fortuitous.

A very important point is that one overall composition can have at least two different values of c/a and of Tc (Fig. 4). In order to account for such preparing history-sensitive properties, we first notice that the titanates containing lattice defects, exhibit more or less diffused transition. Ferroelectric–paraelectric phase transition which is not abrupt but extends over a temperature interval has previously been encountered in perovskite-type solid solution series such as $Ba(Ti{\cdot}Sn)O_3$ *(13)*, $Pb(Ni_{1/3}{\cdot}Nb_{2/3})O_3$ *(14)*, $Pb(Mg_{1/3}{\cdot}Nb_{2/3})O_3$ *(14)*, $Ba(Nb_{1.5}{\cdot}Zr_{0.25})O_{5.25}$ *(15)*, and $Pb(Sc_{1/2}{\cdot}Ta_{1/2})O_3$ *(16)*; these literatures have suggested that the presence of compositional fluctuation in these materials causes the diffused transition. The description as $(Pb_{1-x}{\cdot}\square_{Pb\,x})$ Ti $(O_{3-x}{\cdot}\square_{O\,x})$ instead of $Pb_{1-x}TiO_{3-x}$ enables the materials containing defects to see as a solid solution. One might expect the occurrence of compositional fluctuations in the present materials as well. Effort was therefore made to evaluate the compositional fluctuations as follows. Figure 5 shows the 1–x dependence of lattice constant a at paraelectric phase at 550°C. It is evident that the lattice constant depends on the overall value of $1-x$ throughout the two series of specimens. Therefore, if the individual crystal is inhomogeneous in composition, X-ray line broadening is to be expected. Thus, $\Delta d/d$ can be used as a measure of the magnitude of fluctuation in composition; care should be taken that any contribution from X-ray line broadening due to crystallite size reduction does not involve in the value $\Delta d/d$ *(17)*. The values of $\Delta d/d$ were thus calculated from the slopes of straight line plots of $\beta{\cdot}\cos\theta$ vs $\sin\theta$, and are shown in the sixth column of Table I. The data indicate stoichiometric crystal A_D to be homogeneous over the volume, whereas the other crystals containing defects to be inhomogeneous, as expected. The $\Delta d/d$ values were used with the data of Fig. 5 (determined at the same temperature as $\Delta d/d$) to express compositional fluctuations in terms of $\Delta(1-x)$. The calculated values of the upper- and lower-limit compositions for all the materials concerned are given in the last column of Table I. It is beleived that an inhomogeneous distribution of the Pb and O vacancies at the respective equivalent positions makes a major contribution to the compositional fluctuations. Comparison between $\Delta d/d$ values of C_D and A_W indicates that at a fixed overall composition, the titanate containing defects prepared by solid–solid reaction has a wider fluctuation in composition compared with "wet" titanate. The large degree of inhomogeneity for "dry" materials may be due to failure of the diffusion process to go to an equilibrium during the formation of the materials. The possible existence of two different values $\Delta d/d$ for nearly the same number of the vacancies (C_D, A_W) also indicates the $\Delta d/d$ value to be attributed to fluctuation in composition, as described, not to be inhomogeneous strain which may be caused by the presence of the vacancies.

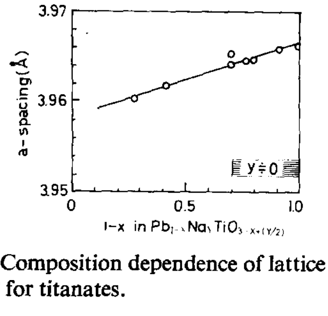

FIG. 5. Composition dependence of lattice constant a at 550°C for titanates.

It is clear that ferroelectric behaviors of the crystals containing defects depend not only on their overall composition but on the magnitude of fluctuation in their compositions. The Curie temperature measured experimentally should be taken as the one for the upper-limit composition, irrespective of the order of the transition. The Curie temperature was thus plotted against the upper-limit composition and against the overall composition for two series of materials (Fig. 6). The relation between Tc and the upper-limit composition is adjustable by a single curve. This relation can also be taken as the one between Tc and the composition of assumed materials containing defects such that no fluctuation in compositions occurs.

It needs to interpret the fact that one overall composition can have two different values of c/a at room temperature (Fig. 4). Let's again consider the assumed crystals having no fluctuation in composition. For such crystals it is postulated that upon increase of compositional parameter x, a curve of c/a vs temperature for specimen A_D not only solely moves toward lower temperature side,

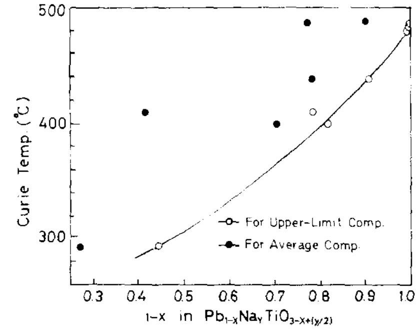

FIG. 6. Curie temperature vs upper-limit composition and vs average composition for two series of materials.

but also sharply reduce in the magnitude of c/a; the Curie temperature is given by the data in Fig. 6. If this assumption is valid, an actual defective material with a larger inhomogeneity can give rise to a larger tetragonal distortion compared with that with a less inhomogeneity, when the two have the same overall composition.

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