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Coexistence of normal and diffuse ferroelectric-paraelectric phase transitions in (Pb,La)TiO$_3$ ceramics

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Distinct evidence for the coexistence of a normal ferroelectric-paraelectric phase transition (NPT) at the Curie temperature and a diffuse phase transition (DPT) above the Curie temperature has been discovered in small-grained, nearly fully dense $Pb_{1-x}La_{2x/3}TiO_3$ ($x=0.10$) ceramics. It is found that the dielectric properties showed a strong dependence on the chemical composition of the materials and that these two types of phase transitions no longer coexisted in ceramics with $x=0.05$, with only a DPT around the Curie temperature. This observation of the coexistence of these two kinds of phase transitions may provide a clue to understanding the mechanism of DPT's which are observed in various ferroelectric materials.

It is well known that complex perovskite ferroelectric compounds, such as (Pb,La)TiO$_3$ or Pb(Mg,Nb)O$_3$, *A*-site and/or *B*-site ions of which are substituted by unlike elements alone or combinations of elements with different valencies, exhibit a broad peak of dielectric constant in their dielectric constant-temperature characteristics around their Curie temperature, which seems to be due to phase transitions with distributed Curie temperature.[1-3] The dielectric property in the materials of this kind with diffuse phase transition (DPT) is characterized by a significant frequency dependence of dielectric constant in the Curie temperature range associated with a considerable shift of its peak temperature with frequency. These dielectric properties due to DPT can be compared with ones attributed to normal ferroelectric-paraelectric phase transition (NPT), which are characterized by a sharp dielectric constant peak at the Curie temperature showing little frequency dependence, so that the difference between the mechanisms of DPT and NPT is clearly demonstrated. From the points of view of both the utilization of DPT and understanding the mechanism,[4-6] ferroelectric and dielectric properties have been extensively studied on various complex perovskite compounds with DPT, which are often called relaxor ferroelectrics. Since Smolensky *et al.*[1] first intensively studied DPT in ferroelectric materials, several models have been proposed to interpret this phenomenon. The plausible models which have been accepted as appropriate ones well interpreting the DPT phenomenon, are compositional fluctuation models assuming the existence of isolated polar regions surrounded by nonpolar regions[2] or unit-cell-scale local variations.[5] Other distinguishable models are a submicroscopic dipole aggregate model[7] and a glassy polarization model[8] on the basis of randomly oriented local polarization. The former model was used to interpret the ferroelectric behavior in a barium zirconium metaniobate single crystal with no distinct Curie temperature, the phase transition in this model being considered to be higher than second order. No distinct evidence for the existence of any of compositional fluctuations, dipole aggregates, or glassy polarization have, however, been found so far in relaxor-type ferroelectrics. The mechanism of DPT still remains to be cleared.

The authors have discovered a distinct evidence for the coexistence of a NPT with a sharp peak of dielectric constant at the Curie temperature and a DPT with a broad one above the Curie temperature in ferroelectric $Pb_{1-x}La_{2x/3}TiO_3$ ($x=0.10$) ceramics. The dielectric properties obtained for the materials and an interpretation of this phenomenon on the basis of a new idea are presented in this paper.

Ferroelectric $Pb_{1-x}La_{2x/3}TiO_3$ ceramics used in this study were prepared using a conventional procedure for preparation of ceramics, but special attention was directed at densifying the ceramics to be nearly full dense without the formation of any phases other than (Pb,La)TiO$_3$ and controlling the grain size of the materials. A brief description of the procedure is given here. $PbTiO(C_2O_4)_2\cdot 4H_2O$ (Central Glass Co. Tokyo, $>99.9\%$ purity), La_2O_3 (Mitsuwa Chem. Co., Osaka, $>99.9\%$ purity), TiO_2 and MnO_2 (both from Kojundo Chem. Co., Osaka, $>99.9\%$ purity) were used as the starting materials. Exactly required amounts of these materials were well mixed, ball milled, and calcined at 800 °C for 3 h in air to produce starting powders with the compositions of $0.99Pb_{1-x}La_{2x/3}TiO_3+0.01MnO_2$ with $x=0.05$ and 0.10 (samples prepared from these powders are referred to as PLT5 and PLT10, respectively, hereafter). The ball milling was conducted using ethyl alcohol and 2-mm-diam ZrO_2 balls as grinding media. The obtained powders were pressed into pellets (10 mm in diameter and ≈ 1.5 mm thick) and then sintered under two different conditions of 1100 °C for 3 h and 1225 °C for 10 h to change the average grain size (AGS) of the obtained materials.

The average grain size of a sample was determined by the intercept method using scanning electron micrographs taken on polished and thermally etched surfaces of the sample, where the measured value was multiplied by 1.5 to get the correct value of the average grain size.[9]

TABLE I. Specifications of the samples used in this study.

Sample	Sintering Temp. (C)	Sintering Time (h)	RSD (%)	AGS (μm)	Lattice constant (Å) a	Lattice constant (Å) c
PLT5-1	1100	3	99.4	0.37	3.917	4.069
PLT10-1	1100	3	99.9	0.30	3.922	4.046
PLT10-2	1225	10	97.3	1.14	3.915	4.058

The lattice constants (a and c) of the materials prepared were determined at room temperature using x-ray diffractometry (XRD) on the polished surfaces of the ceramic samples. The relative sintered density (RSD) of a sample was obtained as the ratio of the observed apparent density to its theoretical value. The theoretical density of the materials was calculated using lattice constants obtained by XRD by taking into account the amounts of vacancies assumed to be existing at the A site of the perovskite lattice,[4] but without taking into account of the addition of MnO_2. The specifications of all the samples used in this study are given in Table I.

Measurements of dielectric constants and dissipation factors (tanδ) were conducted using a vector impedance analyzer (YHP, Tokyo, 4192A) in the temperature range from room temperature to 600 °C on the obtained samples with fired silver-paste electrodes, where frequencies ranging from 100 Hz to 100 kHz were used for the measurements. To examine the thermal aging effect on the obtained dielectric properties, the measurements were carried out both by heating and by cooling at a rate of 1 °C/min, and it was confirmed that no considerable thermal hysteresis was observed in all the obtained dielectric properties. Thus, the results presented here are all those taken on heating.

Figure 1 shows plots of both dielectric constants and dissipation factors as functions of temperature obtained for the PLT10-1 sample at several frequencies. Figures 2 and 3 show the dielectric constant and dissipation factor temperature characteristics, respectively, obtained for the PLT10-2 sample, taken in the frequency range of 100 Hz to 100 kHz. The dielectric constant temperature characteristic of the PLT10-2 sample is obvious to be composed of three parts of it, with a sharp peak and a broad peak followed by a steep increase of the dielectric constant. It is also evident that the two kinds of peaks in the dielectric constant temperature characteristics for both samples, PLT10-1 and PLT10-2, correspond to NPT for the first peak and DPT for the second, which appeared at and above the Curie temperature, respectively. Steep rises of both dielectric constants and dissipation factors are likely to be attributed to the contribution of vacancies rapidly increasing in concentration with increasing temperature. From the comparison between the behavior patterns of the temperature dependence of both dielectric constants and dissipation factors in these two samples, one may recognize several interesting features of the dielectric properties in the materials.

(1) In both samples, PLT10-1 and PLT10-2, sharp peaks of the dielectric constant for NPT appeared at exactly the same temperature of 378 °C, which corresponds to the Curie temperature of the materials with no shift with frequency. The temperature of the second peak of dielectric constant due to DPT, on the other hand, shows a significant shift to higher temperature with increasing frequency, behavior patterns of the peak temperature shifts being exactly the same for the two samples.

(2) The peak value of dielectric constant at the Curie

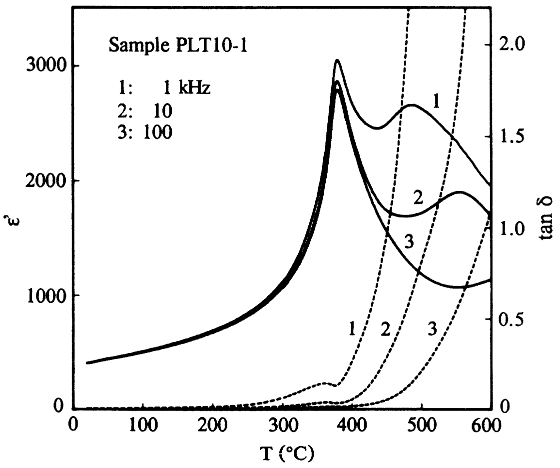

FIG. 1. Plots of dielectric constants (solid line) and dissipation factors (tanδ) (dotted line) as functions of temperature for the PLT10-1 sample.

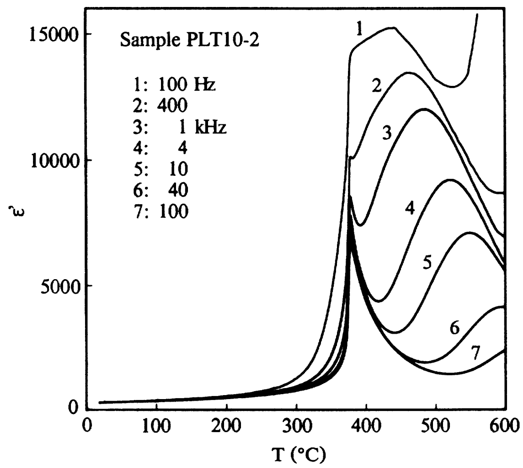

FIG. 2. Temperature dependence of dielectric constants at various frequencies for the PLT10-2 sample.

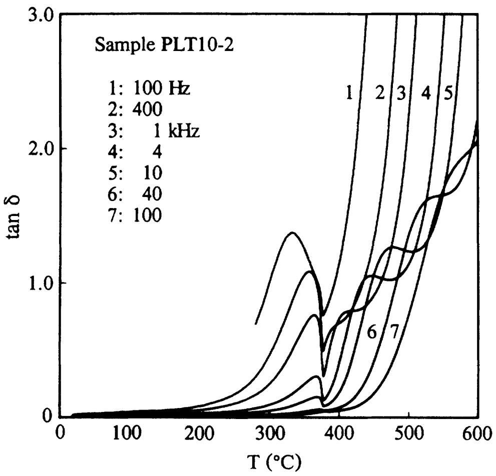

FIG. 3. Temperature dependence of dissipation factor at various frequencies for the PLT10-2 sample.

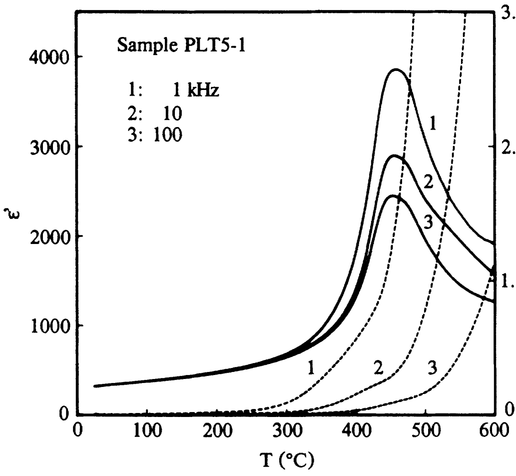

FIG. 4. Plots of dielectric constants (solid line) and dissipation factors (dotted line) as functions of temperature for the PLT5-1 sample.

temperature shows a little frequency dependence for both of the samples, while the value of the second peak of dielectric constant is found to significantly decrease with an increase in frequency.

(3) The broadness of both peaks of dielectric constant attributed to NPT and DPT is much more remarkable in the PLT10-1 sample than in the PLT10-2 sample. This may result from the difference in either the grain size or lattice constants (see Table I) of the two samples.

(4) It is found that the dielectric constant temperature characteristics for NPT in both of the samples can be described by the Curie-Weiss law, whereas those for DPT obey the equation $1/\varepsilon' = A + B(T - T_m)^2$, where T_m is its peak temperature, which has been well known as the equation best describing the properties of DPT.[2]

(5) The dissipation factor in the PLT10-2 sample (Fig. 3) shows a distinct anomalous peak above the Curie temperature, which is obviously attributed to the existence of a DPT.

Another interesting feature of the temperature dependence of the dielectric constant was found in the characteristic for the PLT5-1 sample, as shown in Fig. 4. This figure shows that the dielectric constant temperature characteristic in the PLT5-1 sample is featured by only one peak getting broader and smaller with increasing frequency, being described substantially by the Curie-Weiss law. The peak temperature of the dielectric constant at 460 °C, corresponding to the Curie temperature of the PLT5-1 sample, shows no shift with frequency.

These dielectric relaxation properties with the interesting features described above may be interpreted on the basis of a new idea concerning the origin of polarization in these materials. The new idea is based on the assumption that the size of ferroelectric domains and their alignment morphology are strongly influenced by the morphology of presence of either dissimilar ions or vacancies incorporated in the crystal lattice of a ferroelectric material. The ferroelectricity in the present samples is the case modified by vacancies incorporated by the addition of La for Pb in $PbTiO_3$. Although the domain size effect on the dielectric relaxation properties in a ferroelectric material has not been sufficiently understood, one may expect that the dielectric constant peak for NPT at the Curie temperature becomes broader and smaller in its peak value as the domain size (similarly the grain size) decreases.[10] If further allowed to assume that there exists a critical domain size for NPT and that domains with a size smaller than the critical size (probably on the order of several hundreds Å) retain a spontaneous polarization up to a little higher temperature over the Curie temperature for NPT, we can interpret semiquantitatively all the features of the dielectric properties observed in the present materials mentioned above. In this model, incorporated vacancies are supposed to aggregate at local positions a certain distance apart from each other, and, consequently, they play a role severing ferroelectric domains with large sizes into small domains with sizes under the critical size for NPT which undergo a phase transition in the manner of the so-called DPT. To interpret the difference between the dielectric constant temperature characteristics in the two samples of PLT10-1 and PLT5-1 according to this model, we have to make another assumption that the concentration of vacancies existing in samples of PLT10 is just appropriate to yield a twofold structure of the domain size morphology providing both NPT and DPT, but that, in the PLT5-1 sample, it is deficient to significantly modify the domain size morphology.

Based on this model, the behavior pattern of the additional dielectric constant peak likely due to DPT appearing in both of the PLT10-1 and PLT10-2 samples is well understood in terms of the displacement shift of vacancies responding to the outer ac field, by which the orientation of domains is effectively strengthed. The contribution of vacancies to the strengthening of polarization may be demonstrated by the fact that both the dielectric constant and dissipation factor in the present samples steeply increased at temperatures above the Curie temperature.

The displacement shift of vacancies is naturally considered to be a thermally activated rate process providing a dielectric relaxation including the term of $\exp(-E_a/kT)$, where E_a is the activation energy for the process. This may interpret the experimental fact that the frequency dependence of the peak temperature (T_m) of the dielectric constant for DPT shown in Fig. 2 can be expressed by a well-acknowledged equation for DPT,

$$f = f_0 \exp(-E_a/kT_m) ,$$

over a limited temperature range, where f is the frequency of an ac field used and f_0 is a constant. It is, however, worth nothing that the relationship between f and T_m can be more appropriately expressed by the equation

$$f = f_0\{\exp[-E_a(1/T_m - 1/T_0)/k - 1]\} ,$$

that is,

$$\log_{10}(f + f_0) = -E_a(1/T_m - 1/T_0)/2.3k + \log_{10} f_0 ,$$

over a much wider temperature range, as shown in Fig. 5, where T_0 is T_m at $f=0$. From the plot of Fig. 5, T_0 is found to be 413 °C, f_0 being taken as 50 Hz in this plot, though the physical meaning of f_0 is not known. Since this temperature of T_0 is a little higher than the actual Curie temperature T_c of samples of PLT10 (by 35 °C), it may thus be possible to consider T_0 as another Curie temperature at which the polarization of domains with a size less than the critical size for NPT completely establishes by the assist of the cooperating movement of vacancies.

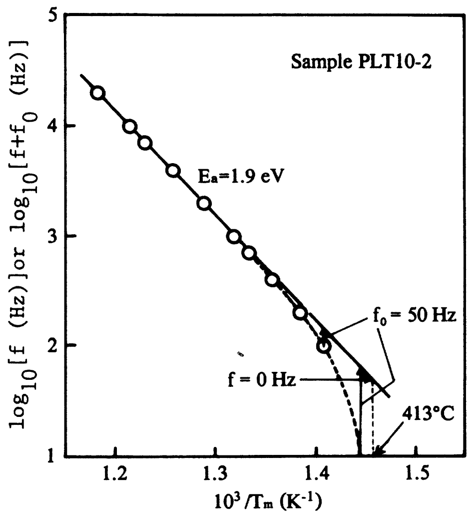

FIG. 5. The relationship between measuring field frequency and the peak temperature of the dielectric constant for DPT in the PLT10-2 sample, represented in forms of $\log_{10} f$ against $1/T_m$ (dashed line with open circles observed), and $\log_{10}(f + f_0)$ against $(1/T_m - 1/T_0)$ (straight line calculated from the dashed line).

In conclusion, a distinct evidence for the coexistence of NPT and DPT was discovered in the dielectric constant temperature characteristics of $(Pb_{1-x}La_{2x/3})TiO_3$ ($x=0.10$) ferroelectrics. To interpret the dielectric behavior for DPT, a new model was presented in this work which is based on the idea that vacancies or dissimilar ions incorporated in the crystal lattice play a decisive role in yielding domains with sizes under the critical size for NPT. A twofold structure of ferroelectric domains with two sizes above and under the critical size for NPT is built in samples of PLT10, providing the ferroelectricity with both NPT and DPT. The possibility of the compositional fluctuation model to interpret dielectric relaxation phenomena for DPT is definitely denied in this study, whereas both the dipole aggregate model[7] and the glassy polarization model[8] cannot simply be discarded. This is because these two models and the new model proposed by the authors all seem to well interpret dielectric properties for DPT at present. Further investigation on both the compositional and grain-size dependence of the dielectric relaxation phenomenon for DPT and the condition under which it disappears, just as seen in the characteristics of the PLT5-1 sample shown in Fig. 4, is in progress.

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[1] G. A. Smolensky and A. I. Agranovskaya, Fiz. Tverd. Tela (Leningrad) **1**, 1562 (1960) [Sov. Phys.—Solid State **1**, 1429 (1960)].
[2] V. V. Kirillov and V. A. Isupov, Ferroelectrics **5**, 3 (1973).
[3] N. Setter and L. E. Cross, J. Appl. Phys. **51**, 4356 (1980).
[4] D. Hennings and K. H. Härdtl, Phys. Status Solidi **3**, 465 (1970).
[5] G. Burns and F. H. Dacol, Phys. Rev. B **28**, 2527 (1983).
[6] T. Tsurumi and Y. Hoshino, J. Am. Ceram. Soc. **72**, 278 (1989).
[7] G. Goodman, J. Am. Ceram. Soc. **43**, 105 (1960).
[8] G. Burns and F. H. Dacol, Phys. Rev. B **30**, 4012 (1984).
[9] M. I. Mendelson, J. Am. Ceram. Soc. **52**, 443 (1969).
[10] K. Keizer and A. J. Burggraaf, Phys. Status Solidi **24**, 561 (1974).