Dielectric Dispersion in PZT Ceramics

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The dielectric dispersion in PZT ceramics that have compositions nearby the morphotropic phase boundary is observed by the frequency and temperature dependence of complex permittivity. The dispersion is assigned to the damping of the vibration of ferroelectric domain walls. The mobility of domain walls is derived and from the composition dependence, correspondence with the crystalline structure is discussed.
Key words: Dielectric dispersion, PZT, Domain wall, mobility, Morphotropic phase boundary

1. INTRODUCTION

Ferroelectric materials such as $BaTiO_3$ (BT) and $Pb(Zr, Ti)O_3$ (PZT) are known to show strong Debye type dielectric dispersion at the microwave frequencies for more than 40 years. Since then, many dielectric measurements have been performed on BT, PZT and other oxide ceramic ferroelectrics and some models that explain the mechanism of the dispersion have been proposed. It has been found that the temperature dependence of relaxiation temperature is small for these oxides[1]. For BT, it has been proposed that that the hopping of off center Ti atoms play an important role[2]. On the other hand, it is known that when an AC electric field is applied on a ferroelectric material, the ferroelectric domain walls inside the material vibrate. From this fact, is has been presumed that the motion of the domain walls effect the dispersion phenomenon strongly. A model which attributes the sound emission by domain walls to the origin of the dispersion has also been proposed[3]. However, the relation between the configuration of domain walls and the mechanism of dispersion has not yet been clarified clearly enough.

PZT is a solid solution of $PbZrO_3$ and $PbTiO_3$ which both have a perovskite crystalline structure, while the former shows a rhombohedral symmetry and the latter a tetragonal one, respectively. At room temperature, the symmetry changes at the composition around Zr/Ti=53/47, which is called the morphotropic phase boundary (MPB). It had been believed that the MPB is a single line on the phase diagram and no dual phase region exists, but recently, the existence of this region seems to be postulated[4].

The aim of our paper is to study the temperature and frequency dependence of complex permittivity of PZT ceramics with compositions nearby MPB and investigate how the mobility of domain walls is related to the configuration of ferroelectric domains.

2. Experimental

The preparation of the $Pb(Zr_xTi_{1-x})O_3$ ceramic specimens were carried out by a conventional mixed oxide technique where the source materials were PbO (99.98%), ZrO_2 (99.99%) and TiO_2 (99.95%). Specimens with the compositions of x=0.50, 0.53, 0.55 and 0.60 were prepared. Suitable mixture of oxides were weighed and mixed and then pressed to form a column of 10mm diameter and 4 to 8mm thick. The column was calcined at 1173K for 2 hours in air. The reacted column was ground to powder and then again pressed into a column and then put into an alumina crucible, and sintered at 1473K for 2 hours in

$PbO+PbZrO_3+O_2$ atmosphere. Powder X ray diffraction of the sintered specimens were measured in order to check the formation of perovskite single phase. From the ratio of the peak area derived from decomposing the (200) peaks into the rhombohedral and tetragonal components, the ratio of the two phases were determined. The grain size was approximately 10μm for all the compositions.

0.6mm thick disks were cut out from the column and platinum with a thickness of 100nm was sputtered on the circular sides as electrodes. The specimens were poled with an electric field of 5MV/m for 10 minutes at room temperature. An unpoled specimen (x=0.6) was also prepared in order to investigate the effect of poling.

The permittivity measurements were carried out with a Hewlett Packard HP4192A impedance analyzer. The specimen was attached to a specially designed sample holder which was connected to the analyzer, and the holder was placed in a furnace. The temperature was scanned from room temperature up to a temperature approximately 150K above Curie temperature for each specimen, and the frequency dependence was of complex permittivity was measured at the desired temperature during heating and cooling by scanning the frequency between 1MHz and 1.8GHz. The oscillation level was 1V peak to peak.

3. Results

The composition dependence of the ratio of rhombohedral and tetragonal phases is shown in Fig.1. Both phases coexist at the composition range between x=0.50 and 0.55. It is confirmed from complementary measurements that this coexistence range does not change by modifying the calcining or sintering condition as long as the other conditions are the same. This seems to support the suggetion that the dual phase region intrinsically exists[4]. Furthermore, according to the asymmetrical shape of the curves, the tetragonal phase seems to be a slightly more favorable phase in the dual phase region.

In Figure 2, the frequency dependence of complex permittivity is shown for the poled specimen having a composition of x=0.55 measured at the temperature of 660K. This temperature is the Curie temperature for this composition. In (a) and (b), the frequency dependence of the real and imaginary part of the complex permittivity is shown, respectively. (c) is the Cole-Cole plot from the same data. A typical Debye type dispersion is seen. The frequency where the value of the real part equals to the middle point of the step, and where the imaginary part takes the maximum value,
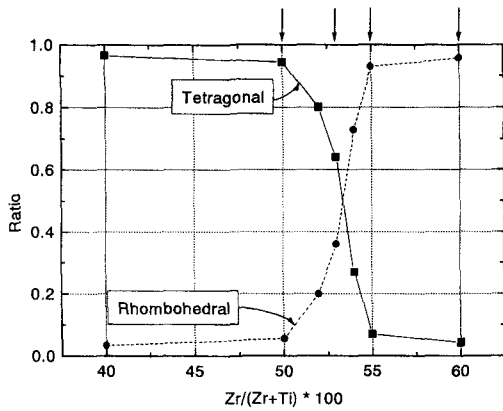
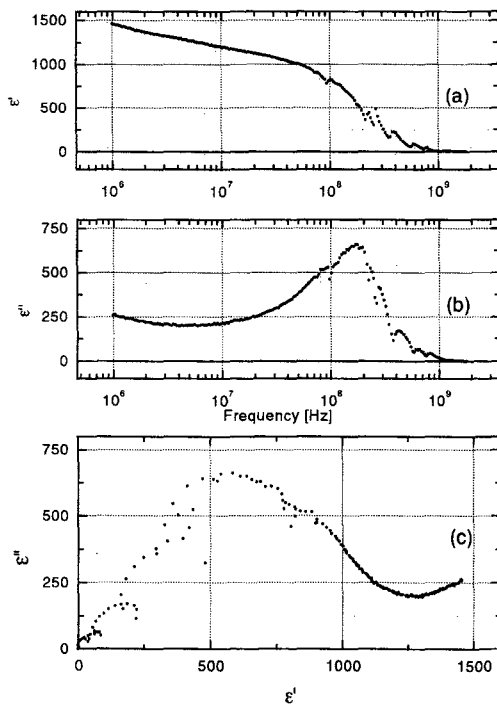Fig. 1   The composition dependence of the ratio of rhombohedral and tetragonal phases.

Fig. 2   A dielectric dispersion observed for poled PZT with a composition of x=0.55 measured at the temperature of 660K. (a) and (b) are the dependence of real and imaginary part, respectively. (c) is the Cole-Cole plot from the same data.

corresponds to the relaxation frequency. The slope of the diameter of the half circle of the Cole-Cole plot indicates how the relaxation frequency is distributed. However, from these plots, it is difficult to determine these values precisely. In order to estimate the frequency quantitatively, curve fittings were performed on the frequency dependence curves of the real and imaginary parts. The applied functions are,

$$y_1 = \left(A_1 - A_2\right) / \left[1 + \exp\left\{\left(x - x_0\right)/ w\right\}\right]$$

and,

$$y_2 = \left(A_1 - A_2\right) \exp\left\{\left(x - x_0\right)/ 2w\right\} / \left[1 + \exp\left\{\left(x - x_0\right)/ w\right\}\right]$$

for the real and imaginary part, respectively. Here, A_1 and A_2 are the values of the real part before and after the dispersion step ($\varepsilon(0)$ and $\varepsilon(\infty)$), y_1 and y_2 are the real and imaginary part of the complex permittivity, x is the independent variant corresponding to the frequency by,

$$x = \left(\ln f - 6\ln 10\right) \times 200 / \ln\left(1.8 \times 10^3\right) + 1$$

where f in the frequency. x_0 corresponds to the relaxation frequency by the same function. w indicates how the frequency is distributed is assigneed as degree of distribution. These functions are modifications of the Debye's dispersion functions by introducing the distribution w. The result of fitting the data of Fig. 2 is shown in Fig. 3. From these curve fittings, 4 sets of data for $\varepsilon(0)$, $\varepsilon(\infty)$, relaxation frequency and degree of distribution can be obtained for one temperature; those are from the real and imaginary part during both heating and cooling
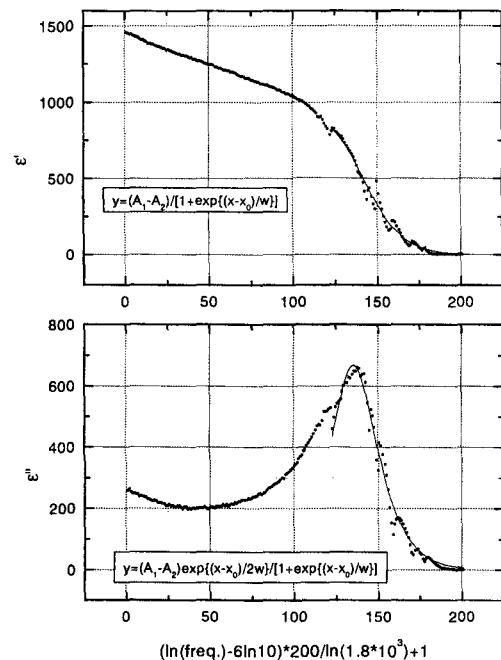

Fig. 3   Results of fitting the data of Fig. 2.

The temperature dependence of relaxation frequency, relaxation time which is the reciprocal of the frequency, and the degree of distribution for the poled specimen with x=0.55 are shown in Fig. 4. Although the absolute values differ between the 4 sets, the tendencies are common. The relaxation frequency and the degree of distribution take minima at the Curie temperature.

In Fig.5, the data of the temperature dependence of relaxation frequency is arranged on an Arrhenius plot. From the slope of the high temperature side, the activation energy for the dispersion was derived to be 0.15±0.05eV. According to the accuracy and
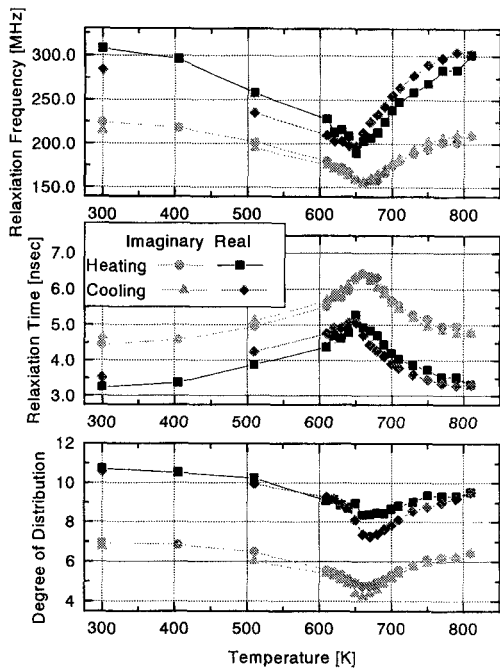
Fig. 4   Temperature dependence of relaxation frequency, relation time and degree of distribution.
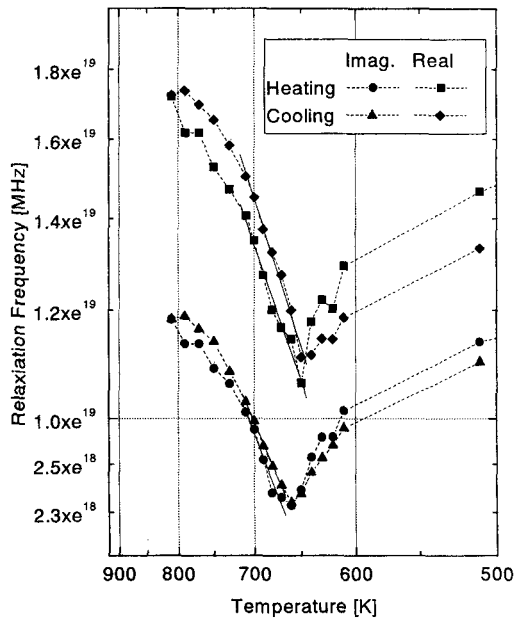

Fig. 5   Temperature dependence of the relaxation frequencies arranged on a Arrhenius plot
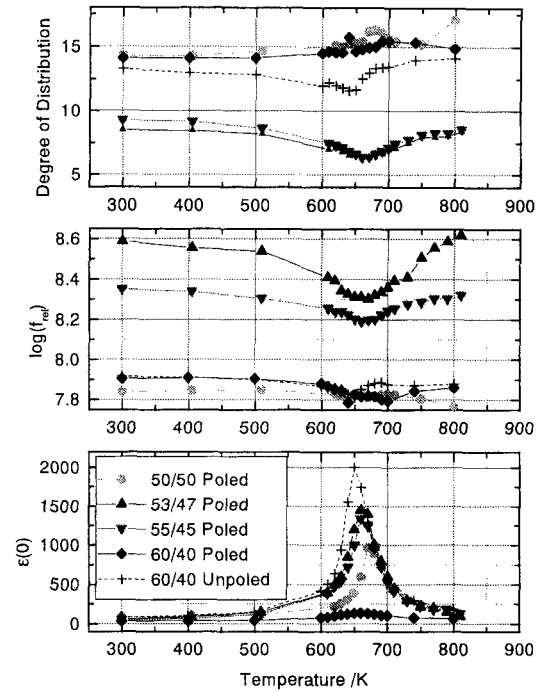

Fig. 6   Temperature dependence of degree of distribution, relaxation frequency and $\varepsilon(0)$ for the poled specimens with the composition or x=0.50, 0.53, 0.55 and 0.60 together with the ones for unpoled x=0.60

avoidance of the thermal effect, the data from the imaginary part during heating will be used for the following discussion.

The temperature dependence of degree of distribution, relaxation frequency in a logarithm scale and $\varepsilon(0)$ for the poled specimens with the compositions of x=0.50, 0.53, 0.55 and 0.60 together with those of unpoled x=0.60 are

shown on Fig. 6. The temperature where $\varepsilon(0)$ takes the maximum value are the Curie temperature for each specimen. All of the specimens show similar tendencies as those that were mentioned for the poled x=0.55 specimen; the degree of distribution and relaxation frequency show minima at the Curie temperature.

However, there seems to be large differences between each specimen. The composition dependence of the relaxation frequency and degree of distribution measured at room temperature and at Curie temperature for each specimen are shown on Fig. 7.   As was seen in Fig. 1, at the composition range between x=0.50 and 0.55, the rhombohedral and tetragonal phases coexist. And within this same range, the relaxation frequency is large and the degree of distribution is small.   On the other hand, the effect of temperature is smaller than that of composition.   It is presumed that the coexistence of the two phases plays an important role for the increase in the relaxation frequency and decrease in the degree of distribution.   For an additional interesting thing, the degree of distribution increased as the specimen was poled.   It seems to be a contradictory, as by poling the local polarizations in the ferroelectric phase are more aligned in a similar direction so the environment should be more uniform.   This problem still leaves room for discussion

Figure 8 shows the composition dependence of the activation energy derived from the Arrhenius plots of the relaxation frequency.   The energy is also larger at the composition range where the two phases coexist, while the energy for the rhombohedral phase seems to be larger than that for the tetragonal phase.   Furthermore, by poling, the energy decreases drastically.
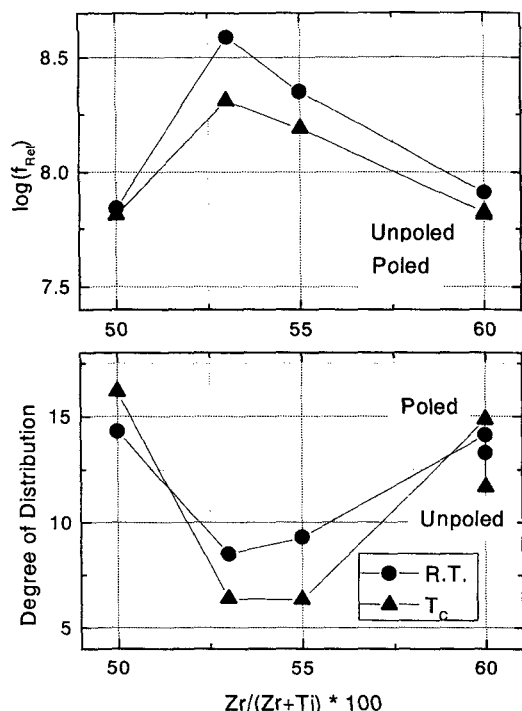
Fig. 7　Composition dependence of relaxation frequency and degree of distribution measured at room temperature and at Curie temperature.
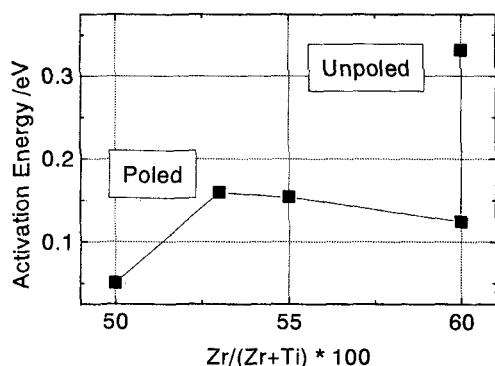

Fig. 8　Composition dependence of the activation energy of dielectric dispersion.

4. Discussion

As was mentioned previously, the dielectric dispersion which is observed in the microwave region is assigned to the damping of the vibration of the ferroelectric domain walls in the phase. While the frequency of the externally applied AC field is low, the domain wall vibrates so that the domains that have the polarization directed favorable to the instantaneous field grow. As the frequency increases, the vibration of the wall cannot catch up with the external field at a characteristic frequency. That frequency is the relaxation frequency. Therefore, when the relaxation frequency is large, it means that the mobility of the domain walls in the phase is high, and vice versa. When the degree of distribution is large, it means that the environment where the walls are located at has a wide distribution throughout the specimen. When the degree is small, all of the walls in the specimen are

placed at sites that have a similar environment.

As the temperature approaches the Curie temperature in the ferroelectric phase, the relaxation frequency and degree of distribution decrease. These mean that the mobility of the domain walls are suppressed and the environment becomes more uniform. As the oscillating amplitude of the external AC field is constant, the increase of permittivity will induce an increase of the part of polarization enhanced by the AC field, and also in the resulting strain. This is presumed to be the reason why the walls become less mobile. Furthermore, as the strain increases, the types of domain walls which can vibrate become less. Therefore the distribution of the environment becomes narrower and the relaxation frequency becomes less scattered in the specimen. Once the Curie temperature is passed, the vibration can be explained as a thermally activated state. That is the vibration of the interface of ferroelectric clusters which form a short range order in a paraelectric matrix.

Ferroelectric domains have a strong correlation with the crystalline structure. At the composition range where rhombohedral and tetragonal phases coexist, the freedom of the direction in which the wall vibrates will increase. Furthermore, as the composition is closer to MPB, the distortion in both phases will decrease. These mean that the mobility of the walls will increase. Also as the freedom increases, the strain will be averaged between the two phases. So the difference in the local structure around the wall will be less and the environment will be more unified. These are presumed to be the reasons why the relaxation frequency is high and the degree of distribution is low at the composition range where the two phases coexist. It should also be noted that the temperature dependencies of the relaxation frequency and degree of distribution are much smaller that those from composition.

When the temperature is higher than the Curie temperature for the specimens in which the two phases coexist, rhombohedral and tetragonal clusters will coexist in the paraelectric matrix. It is assumed that the total distortion applied to the paraelectric matrix surrounding the clusters when the interfaces vibrate will be larger compared with when only one type of clusters exist. If this is the case, the activation energy will be higher for the specimens in which the two phases coexist. The interface of the tetragonal cluster seems to be more mobile than that of a rhombohedral one. When the specimen is poled, the polarization will be aligned in a more uniformed direction. Therefore the vibration of the walls will be less disturbed. This explains the activation energy being less for the poled specimen than the unpoled one.

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