Dielectric relaxation in Pb$_{0.9}$La$_{0.1}$TiO$_3$ ceramics in the temperature range of 400–700 °C

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The dielectric properties of Pb$_{0.9}$La$_{0.1}$TiO$_3$ ceramics were investigated at intermediate frequencies ($10^2 \leq f \leq 10^8$ Hz) in the temperature range of 400–700 °C. The limitation of the application of Debye relaxation model was discussed to explain the temperature-dependent behavior of the dielectric relaxation. The dielectric relaxation strength was considered as an important fitting variable through the modified Debye equation. The diffuse dielectric anomaly was successfully described by introducing the exponential decay form for the relaxation strength in the modified Debye equation. © 2002 American Institute of Physics. [DOI: 10.1063/1.1430263]

It has been frequently reported that the dielectric relaxation behaviors at low frequencies (<10$^4$ Hz) are commonly observed in various perovskite oxide materials. It is known as the diffuse dielectric anomaly and observed in the temperature range of 400–700 °C, regardless of Curie temperature of the materials. Although it looks like the behavior of the diffuse phase transition, it has no relationship with the phase transition. Several models have been suggested in various perovskite-type oxide materials for this relaxation behavior. According to these studies, it is clear that the diffuse dielectric anomaly is an oxygen vacancy-related dielectric relaxation phenomenon.

In many cases of studying the dielectric relaxation behavior, the Debye equation has been a powerful fitting method.

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \left[ 1 + (i \omega \tau)^\beta \right].$$

(1)

The adjustable parameters are the relaxation time, $\tau$, and the relaxation strength, $\varepsilon_s - \varepsilon_\infty$. However, the relaxation time generally has been chosen as a main fitting parameter in the Debye equation, while the relaxation strength is regarded as constant. In this case, the dielectric constant should be saturated at $\varepsilon_s$ as the frequency decreases at a fixed temperature, or the temperature increases at a fixed frequency. The problem is that the dielectric relaxation behavior is observed as the type of the frequency-dependent diffuse peak in the real part of the dielectric constant. Therefore, the modified fitting method is suggested to understand the dielectric relaxation behavior of the diffuse dielectric anomaly more clearly in this study. We mainly discuss on the temperature-dependent behavior of the dielectric relaxation by concerning on the variation of the relaxation strength as other fitting parameters.

We have chosen 10 mol %La-doped PbTiO$_3$ ceramics system, of which the diffuse dielectric anomaly was typically observed in the temperature range of 400–700 °C. 10 mol %La-doped PbTiO$_3$ ceramic samples (Pb$_{0.9}$La$_{0.1}$TiO$_3$) were prepared by the mixed sintering method. The samples of 10 mm in diameter were sintered at 1150 °C for 10 h in Pb-rich atmosphere, where the calcined PbZrO$_3$ powder was used as an agent for maintaining the sintering atmosphere. The x-ray diffraction analysis confirmed that all of the samples used for the measurement were monophasic under the detection limit of the equipment. The relative density was about 97%. The samples were electroded with silver paste and fired at 600 °C for 30 min. The real and the imaginary capacitances were measured by an HP4192 Impedance Gain/Phase analyzer at temperature of 25–700 °C with the heating rate of 1°/min in the frequency range of 100 Hz–1 MHz.

Figure 1 describes a typical temperature dependence of the dielectric constant in Pb$_{0.9}$La$_{0.1}$TiO$_3$ ceramics in the temperature range of 200–700 °C. The dielectric anomaly by the phase transition is observed near 350 °C. Figure 1(a) shows that the diffuse dielectric anomaly is observed in the real part of the dielectric constant above Curie temperature, while Fig. 1(b) shows that the imaginary part intensively increases with the temperature, which is due to the conductivity. The results are coincident with the previous study.

Figure 2(a) shows the schematic diagram of the frequency-dependent behavior of the dielectric relaxation in the real part following the Debye relaxation equation when only the relaxation time is chosen as a fitting parameter. This process well describes the frequency-dependent relaxation behavior of the diffuse dielectric anomaly in the frequency plot. However, it is no longer available in the temperature plot. Figure 2(b) describes that the dielectric constant should be saturated as the temperature increases when the relaxation strength is constant. The relaxation strength should be modified to understand the temperature-dependent behavior of the diffuse dielectric anomaly. We first introduced the decay function for the relaxation strength, which is proportional to the inverse temperature, according to the dipolar relaxational polarization as shown in Fig. 2(b). However, the result did not show any good fit with the experimental results. The right-hand side of the diffuse dielectric anomaly peak needs more steep decay function. Therefore, a simple exponential decay form was introduced to correct the temperature-dependent behavior of the dielectric strength. Equation (2) represents the dielectric relaxation strength, which is expressed with the exponential term:

$$\Delta \varepsilon = \varepsilon_s - \varepsilon_\infty = \Delta \varepsilon_0 \exp\left(\frac{E_s}{k_B T}\right),$$

(2)
where $\Delta \varepsilon_0$ is defined as a constant, proportional to the number of the relaxing species.

Therefore, the modified fitting equation in the real part is expressed with the following form:

$$
e^* = \varepsilon_\infty + \Delta \varepsilon_0 \exp \left( \frac{E_t}{k_B T} \right) \left[ 1 + (i \omega \tau)^\beta \right]$$  \hspace{1cm} (3)

As already shown in Fig. 1(a), the diffuse dielectric anomaly by the dielectric relaxation and the dielectric anomaly by the phase transition are very close to each other in the temperature plot, which may get the fitting process into trouble in the case of Pb$_{0.9}$La$_{0.1}$TiO$_3$ ceramics. Therefore, the background was chosen as the dielectric data at 1 MHz because they have no frequency dependence and follows the Curie–Weiss behavior as shown in Fig. 1(a). This process needs an assumption that the diffuse dielectric anomaly by the dielectric relaxation and the dielectric anomaly by the phase transition are independent from each other. The fitting was done in the real part of the dielectric constant. The imaginary part failed to fit because the dielectric data showed the intensive monotonous increase in the imaginary part at low frequency, which is due to the contribution of the electrical conduction. It should be noted that the diffuse dielectric anomaly occurs in a highly conductive state, which is considered to be the difficulty of analysis on the high-temperature dielectric relaxation.

A typical frequency spectrum of Pb$_{0.9}$La$_{0.1}$TiO$_3$ ceramics separated from the ferroelectric contribution is displayed in Fig. 3(a) at several temperatures. Solid lines are fit results obtained from Eq. (3) with the relaxation strength fixed according to the conventional process. The parameters obtained in the fitting process, $\beta$, $\Delta \varepsilon$, $\varepsilon_\infty$, and $\tau$ are shown in Table I. Arrhenius plot gives $E_t = 1.60$ eV, and $\tau_0 = 1.2 \times 10^{-14}$ s, which was similar to the previous study in (Pb,La)TiO$_3$ ceramics.

The deconvoluted form of the diffuse dielectric anomaly of Pb$_{0.9}$La$_{0.1}$TiO$_3$ ceramics is shown in Fig. 3(b). Fit results obtained by using Eq. (3) are also displayed with the solid lines. The fitting parameters are summarized in Table II. It should be noted that the activation energy, $E_t$, shown in Table II is based on the fitted value obtained from the relationship between the relaxation time and the inverse temperature.

The fitted results match well with the experimental results as shown in Fig. 3(b). It should be especially noted that the asymmetry of the diffuse dielectric anomaly peak is well described by the modified fitting. The relaxation strength has the activation energy of 1.21 eV as shown in Table II. The fitting result proves that the diffuse dielectric anomaly is a competition effect between the dielectric relaxation behavior and the variation of relaxation strength. As mentioned earlier,

FIG. 1. Temperature dependence of (a) the real, and (b) the imaginary part of dielectric constants of Pb$_{0.9}$La$_{0.1}$TiO$_3$ ceramics as various frequencies.

FIG. 2. Schematic diagrams of the frequency and the temperature dependent behavior of the dielectric relaxation following the Debye relaxational equation where both of the relaxation time and the relaxation strength are regarded as fitting parameters.
TABLE I. Parameters obtained with the modified Debye fitting method for Pb$_{0.9}$La$_{0.1}$TiO$_3$ ceramics. Points are measured data and solid lines are fit results by the modified Debye equation suggested.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>β</th>
<th>Δε</th>
<th>ε∞</th>
<th>τ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>510</td>
<td>0.80</td>
<td>3100</td>
<td>100</td>
<td>1.2 × 10^{-4}</td>
</tr>
<tr>
<td>520</td>
<td>0.80</td>
<td>2590</td>
<td>120</td>
<td>9.3 × 10^{-5}</td>
</tr>
<tr>
<td>530</td>
<td>0.80</td>
<td>2150</td>
<td>140</td>
<td>7.1 × 10^{-5}</td>
</tr>
<tr>
<td>540</td>
<td>0.79</td>
<td>1750</td>
<td>140</td>
<td>5.3 × 10^{-5}</td>
</tr>
<tr>
<td>550</td>
<td>0.78</td>
<td>1370</td>
<td>140</td>
<td>3.7 × 10^{-5}</td>
</tr>
</tbody>
</table>

In the case of Bidault et al. data, $E_\varepsilon$ obtained in Pb$_{1-x}$La$_x$TiO$_3$ ceramics varies in the range of 1.17–1.40 eV. They have reported that the activation energy for the dielectric relaxation, $E_\varepsilon$, in the diffuse dielectric anomaly is similar to the conductivity activation energy, $E_\sigma$, which is in the range of 1.07–1.30 eV. However, it does not seem that $E_\varepsilon$ is related with $E_\sigma$ although they have a quantitative agreement. The dielectric relaxation is an opposite behavior to the electrical conduction according to the Debye relaxation model. Therefore, we suggest that the decreasing behavior of the relaxation strength is related with the temperature-dependent variation of the electrical conduction. It means that $E_\varepsilon$ should be related with the conductivity activation energy, $E_\sigma$, in origin. The conductivity activation energy, $E_\sigma$ of Pb$_{1-x}$La$_x$TiO$_3$ ceramics is also in quantitative agreement with $E_\varepsilon$ (1.21 eV) obtained in this study. The previous studies have usually focused on the activation energy, $E_\varepsilon$, assuming the relaxation strength is constant. However, we believe that the diffuse dielectric anomaly is a competition effect between the dielectric relaxation and the variation of the relaxation strength. We also suggest that the electrical conduction is related to the variation of the relaxation strength including the $E_\varepsilon$ term.

In conclusion, the dielectric relaxation strength should be considered as an important fitting parameter for the understanding of the temperature-dependent behavior of the diffuse dielectric anomaly observed in Pb$_{0.9}$La$_{0.1}$TiO$_3$ ceramic. The frequency and temperature dependence of the dielectric relaxation in the diffuse dielectric anomaly was successfully described by introducing the exponential temperature dependence into the relaxation strength in the modified Debye equation.

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