



Diffuse Dielectric Anomaly in Ferroelectric Materials

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Abstract. It has not been clear whether the diffuse dielectric anomaly by Debye-type dielectric relaxation is extrinsic or intrinsic in origin although it has been frequently found in ferroelectric materials regardless of their structures and ferroelectric properties. We experimentally investigated the extrinsic nature of the diffuse dielectric anomaly in ferroelectric oxides and sulfide such as BaTiO₃, Pb_{0.9}La_{0.1}TiO₃, and SnP₂S₆. The advanced fitting method using the modified Debye relaxation equation was introduced in order to explain the temperature dependent behavior of the diffuse dielectric anomaly. It was confirmed that the diffuse dielectric anomaly was a competitive phenomenon between the dielectric relaxation and the electrical conduction of the relaxing species. It was also proved that the activation energy of the dielectric relaxation should be always higher than the conductivity activation energy of the relaxing species in the diffuse dielectric anomaly.

Keywords: dielectric relaxation, ferroelectric, Debye relaxation, electrical conductivity

1. Introduction

The diffuse dielectric anomaly has been known as an interesting phenomenon in various kinds of ferroelectric materials because of its similar temperature dependence to the diffuse phase transition [1–10]. It has been generally regarded as a defect-related dielectric relaxation phenomenon, which does not have any practical relationship with the phase transition of ferroelectric materials [4, 5]. Bidault et al. [4] have collected a number of data in order to clarify whether the diffuse dielectric anomaly found at 400–700°C is an intrinsic or an extrinsic phenomenon in various kinds of perovskite oxides. Although they experimentally reported that the activation energy of dielectric relaxation in the diffuse dielectric anomaly is quantitatively similar to the conductivity activation energy of the sample in perovskite-type ferroelectric oxides, they did not give a definite explanation. Similar results have been also reported in Bi-doped SrTiO₃ by Ang et al. [5]. They suggested that the dielectric relaxation which originates the diffuse dielectric anomaly is a common phenomenon at the temperature range of 400–700°C in perovskite-type oxides containing titania.

However, we have found that the diffuse dielectric anomaly is not observed in Pb_{0.9}La_{0.1}Ti_{0.4}Zr_{0.6}O₃ and Pb_{1-x}La_xTiO₃ ceramics, which was sintered in an oxidized atmosphere, although they are included in the perovskite oxide group [11]. Especially, the similar diffuse dielectric anomaly is also found in sulfide ferroelectric material such Sn₂P₂S₆ single crystal, of which the structure is quite different from the perovskite oxides [7]. It implies that the diffuse dielectric anomaly is not a unique dielectric relaxation phenomenon which is found only in perovskite structure. It has still remains unclear what conditions are related with the diffuse dielectric anomaly in ferroelectric materials.

In most cases, the Debye relaxation equation has been very useful for describing the frequency dependence of the diffuse dielectric anomaly [4]. The fitting process is generally performed in the frequency space at a given temperature in order to find the activation energy of the dielectric relaxation. However, the Debye relaxation equation is not proper for explaining the temperature dependent behavior of the diffuse dielectric anomaly, considering that this equation is originally driven in the time response function of the electric polarization [12–14]. Recently, we have

experimentally described the temperature dependence of the diffuse dielectric anomaly at high temperature region of 400–700°C in $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ ceramics with the simply modified form of Debye relaxation equation [8]. We have suggested that another exponential term should be involved into the ideal Debye relaxation equation to explain the temperature dependence of the diffuse dielectric anomaly, although its theoretical origin is not clear [9, 10].

The main objective of this study is the clear understanding on the diffuse dielectric anomaly, which is found in ferroelectric materials. We first discuss whether the diffuse dielectric anomaly is extrinsic or intrinsic on the basis of experimental results. We suggest an advanced fitting method for describing the temperature dependent behavior of the diffuse dielectric anomaly by establishing the relationship between the dielectric relaxation and the electrical conduction of the relaxing species.

2. Experimental Procedure

We have chosen three kinds of model systems such as BaTiO_3 , $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$, and $\text{Sn}_2\text{P}_2\text{S}_6$, which are known for their typical dielectric relaxation peaks as a function of temperature. BaTiO_3 is a representative ferroelectric oxide of perovskite structure. This system has the phase transition of the first order at $T_c = 407$ K [4]. The diffuse dielectric anomaly of BaTiO_3 has been already reported in the temperature range of 800–1000 K by Stumpe et al. [1]. The ceramic and the single crystal of BaTiO_3 were prepared for the dielectric measurement. BaTiO_3 ceramic samples were prepared by the solid state sintering method. They were sintered at 1300°C for 30 minutes in air. The single crystal of BaTiO_3 was fabricated by the solid state single crystal growth method (SSCG) [15, 16]. The details of the growth process of BaTiO_3 single crystal have been published elsewhere [9]. Both sides of the samples were electroded with silver paste and fired at 600°C for 30 minutes.

Another system is the $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ ceramics, which is also included in the perovskite-type ferroelectric oxide group. This system has the phase transition of the first order at around $T_c = 600$ K [8, 17]. Kuwabara et al. [2], and Bidault et al. [4] have found that this system has the diffuse dielectric anomaly within the temperature range of 600–900 K. The ceramic samples of $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ were fabricated by the solid state sin-

tering method. The calcined PbZrO_3 powder was used as an agent for maintaining the Pb-rich sintering atmosphere. The two kinds of $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ samples, which were in the as-sintered state and in the annealed state after the sintering, were prepared for the comparison. The sintering condition was 3 hours at 1150°C, and the annealing was 3 hours at 900°C, where the atmosphere was maintained in air. They were electroded with silver paste and fired at 600°C for 30 minutes.

The other system is the $\text{Sn}_2\text{P}_2\text{S}_6$ (SPS) single crystal, which belongs to the class of sulfide ferroelectrics. This crystal undergoes ferroelectric phase transition of the second order at $T_c = 339$ K, and the crystal symmetry is monoclinic P_c in the ferroelectric phase [18, 19]. The diffuse dielectric anomaly was found at the temperature region of 300–600 K in the case of the single crystal of SPS, which was grown by the chemical vapor transport method [7]. In this study, two types of yellow-colored SPS single crystals with a dimension of $5 \times 5 \times 1$ mm³ were prepared by the chemical vapor transport method and the Bridgeman technique, respectively. These samples were grown in the Institute of Solid State Physics and Chemistry of Uzhgorod State University [7, 20]. Gold was deposited for the electrode with the sputtering method.

The X-ray diffraction analysis confirmed that all of the samples used for the measurement were monophasic under the detection limit of the equipment. Both sides of all the samples were polished to the thickness of 500 μm for the measurement of dielectric properties except the SPS single crystals. The dielectric constants of the samples were measured in the frequency range of 1 kHz–1 MHz with a HP4194 Impedance Gain/Phase analyzer in the temperature region of 300–1000 K with the heating rate of 1°/min.

3. Discussion and Results

3.1. Effect of Processing Parameters on the Diffuse Dielectric Anomaly in Ferroelectric Materials

Figure 1 shows the real and the imaginary parts of dielectric constants versus temperature at various frequencies in BaTiO_3 ceramics and single crystals. The measuring frequency is in the range of 1 kHz–1 MHz. The sharp dielectric anomaly by the ferroelectric-to-paraelectric phase transition appeared near 400 K in both samples as shown in Figs. 1(a) and (c). The diffuse dielectric anomaly is also found in both kinds

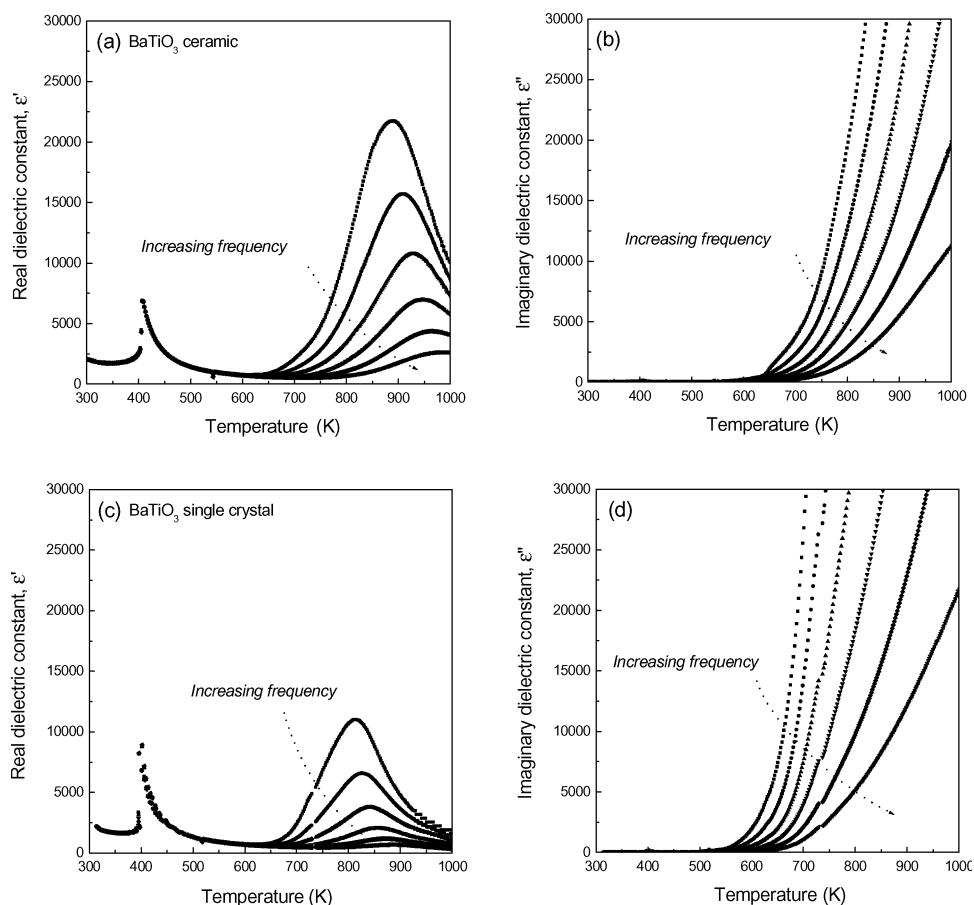


Fig. 1. Temperature dependence of dielectric constants at various frequencies of (a) and (b) BaTiO₃ ceramics, and (c) and (d) BaTiO₃ single crystals. The measuring frequencies are in the range of 1 kHz–1 MHz.

of samples in the temperature range of 600–1000 K. The diffuse dielectric anomaly in the single crystal of BaTiO₃ has been already reported by Stumpe et al. [1] and Bidault et al. [4]. The amplitude of the diffuse dielectric anomaly at the same frequency is higher in the ceramic of BaTiO₃ than the single crystal in this study.

Meanwhile, the imaginary part of dielectric constant monotonously increases over 600 K in both kinds of samples. It is due to the electrical conduction of the sample, σ/ω [4, 14]. Figures 1(b) and (d) show that the temperature dependence of the imaginary part of dielectric constant in both samples is relatively similar to each other. However, it should be noted that there should be a relaxation peak in the imaginary part of dielectric constant, considering that the diffuse dielectric anomaly is the Debye-type dielectric relaxation phenomenon [7]. This result implies that the electrical

conductivity of the sample seems to be related with the diffuse dielectric anomaly in the real part of dielectric constant.

Figure 2 shows the temperature dependence of the real and the imaginary parts of dielectric constants in Pb_{0.9}La_{0.1}TiO₃ ceramics. Figures 2(a) and (b) represent the dielectric data of the as-sintered sample, and Fig. 2(c) and (d) shows the dielectric data of the annealed sample after the sintering. The sharp dielectric anomaly of the phase transition occurs in the real part of dielectric constant near 620 K in the case of Pb_{0.9}La_{0.1}TiO₃ ceramics. As shown in Fig. 2(a), the diffuse dielectric anomaly is also found over the Curie temperature. However, Fig. 2(c) shows that the diffuse dielectric anomaly clearly disappears after annealing treatment, while the sharp anomaly of the phase transition in the real part of dielectric constant remains

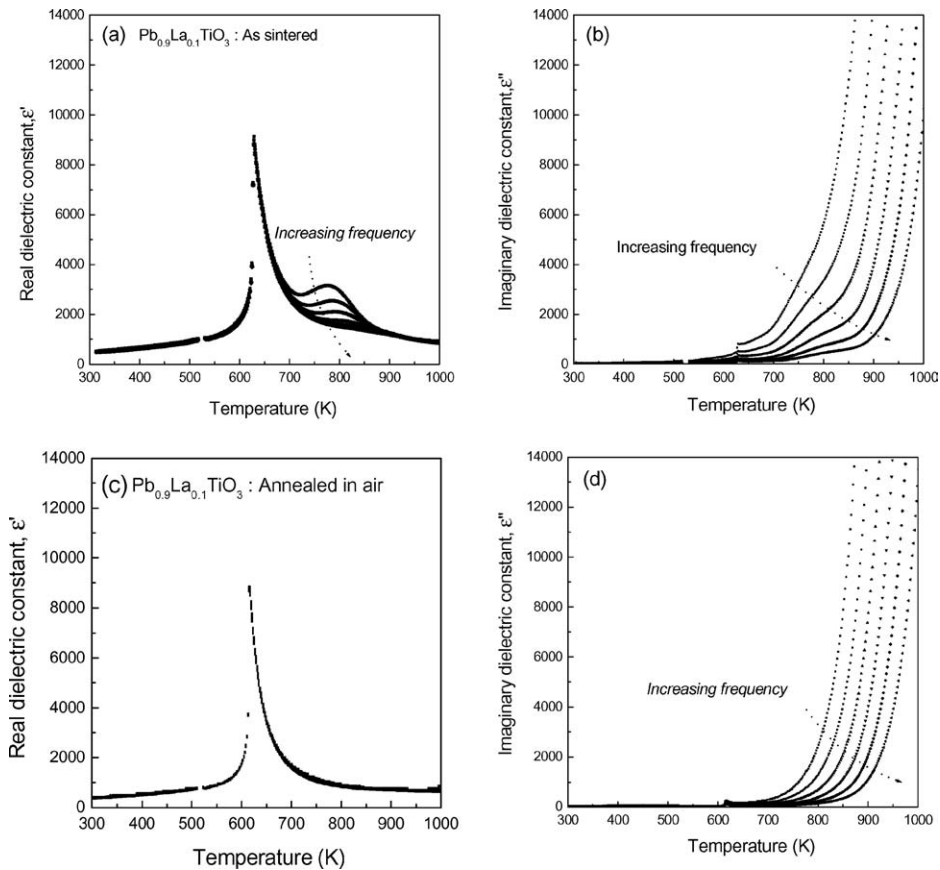


Fig. 2. Temperature dependence of dielectric constants at various frequencies of (a) and (b) as sintered $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ ceramic, and (c) and (d) the annealed $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ ceramic after sintering. The measuring frequencies are in the range of 1 kHz–1 MHz.

consistent. Especially, it is noticeable that the temperature dependence of the imaginary part of dielectric constant is not varied apparently as was different from the result in BaTiO_3 . This result implies that the intensive increase of the imaginary part of dielectric constant, which means the electrical conductivity in the sample, is not related with the diffuse dielectric anomaly. It also proves that the diffuse dielectric anomaly is very sensitive to the annealing treatment after sintering in the case of $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ ceramics.

According to Bidault et al. [4], the origin of the diffuse dielectric anomaly, which is found at 700–1000 K in perovskite oxides, is the same regardless of their composition. It is believed that oxygen vacancies is closely related to this diffuse dielectric anomaly in perovskite-type ferroelectric oxides [4, 5]. However, the diffuse dielectric anomaly is not observed in the annealed sample, although the diffuse dielectric anomaly is regarded

as a common feature in the case of La-doped PbTiO_3 ceramics regardless of La content when they are sintered in air [2, 4, 8]. It has been reported that the vacancy distribution easily changes with the sintering condition such as temperature, time, impurity content, and sintering atmosphere in La-doped PbTiO_3 system [17]. Consequently, it is considered that oxygen vacancies are compensated by the heat treatment in the case of $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ ceramics. Inferring from these experimental results, it becomes clear that the diffuse dielectric anomaly is an extrinsic phenomenon. The diffuse dielectric anomaly should not be affected by any of processing parameters if it is intrinsically found in all kinds of perovskite oxides which contain titania, which was suggested by Ang et al. [5].

Figure 3 represents the variation of dielectric constants in the SPS single crystals in the temperature range of 250–550 K. Figures 3(a) and (b) are the

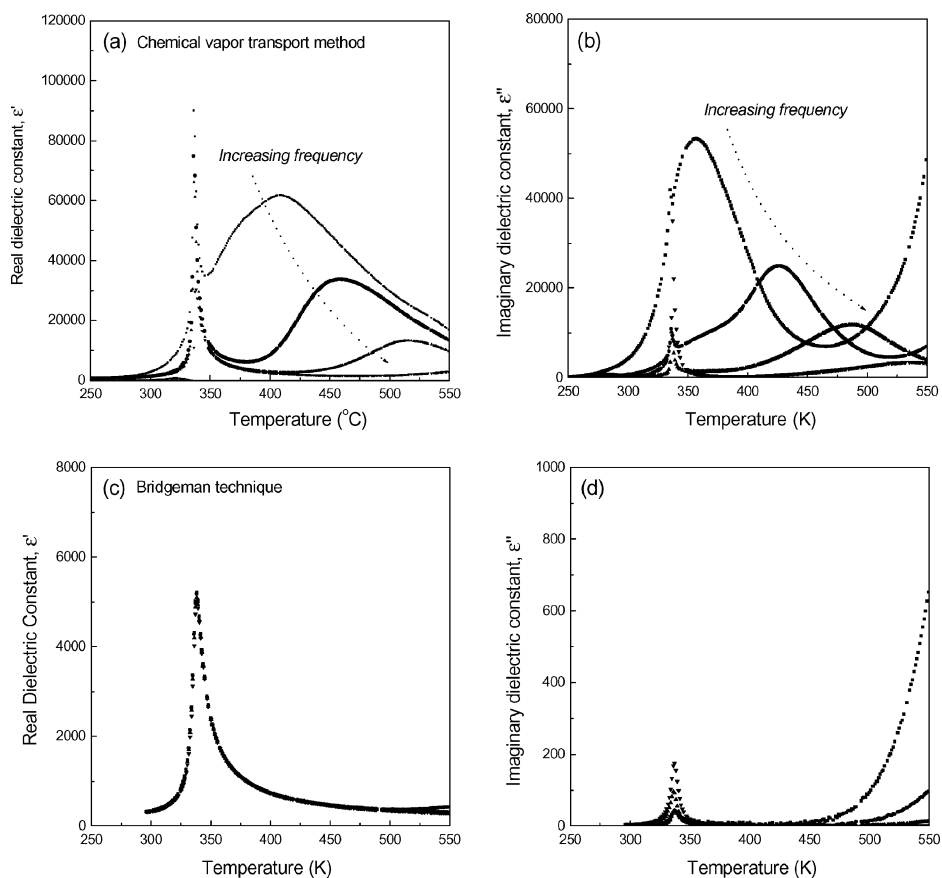


Fig. 3. Temperature dependence of dielectric constants at various frequencies of (a) and (b) $\text{Sn}_2\text{P}_2\text{S}_6$ single crystals which was grown by the chemical vapor transport method, and (c) and (d) $\text{Sn}_2\text{P}_2\text{S}_6$ single crystals which was grown by the Bridgeman technique. The measuring frequencies are in the range of 1 kHz–1 MHz.

dielectric data from the SPS crystal which was grown by the chemical vapor transport method and Fig. 3(c) and (d) are those from the crystal of the same composition which was grown by the Bridgeman technique. The dielectric data were not obtained over 600 K due to the thermal decomposition of the crystals. The dielectric anomaly by the phase transition was observed at 340 K in both kinds of crystals, which is in a quantitative consistence with the previous studies [7].

As shown in Fig. 3(a), the diffuse dielectric anomaly is observed at the wide temperature region near the Curie temperature, convoluted with the phase transition in the real part of dielectric constant. The dielectric relaxation peak by the diffuse dielectric anomaly is found in the imaginary part of dielectric constant instead of the intensive increase as was observed in BaTiO_3 and $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$. It confirms that the diffuse dielectric

anomaly is a dielectric relaxation phenomenon, which is not related with the electrical conduction of the sample [5].

In the case the SPS crystals of the Bridgeman technique, there is no diffuse dielectric anomaly as shown in Fig. 3(c). All the experimental conditions for the SPS samples are exactly the same before the measurement except the crystal growth method. The dielectric relaxation peak in the imaginary part of dielectric constant was also disappeared. This result strongly confirms the extrinsic nature of the diffuse dielectric anomaly. Sulfur and Phosphorous are volatile elements in the SPS single crystal. Therefore, it is considered that the diffuse dielectric anomaly of the SPS crystals is related with S and P vacancies, which is formed during the crystal growth process. In the case of the chemical vapor transport method, the SPS single crystal is obtained from

the gas phase reaction, while the single crystal seed grows from the molten solution in the conventional Bridgeman technique [19]. This result implies that defects are much easily involved in the chemical vapor transport method than the Bridgeman technique for fabricating the SPS single crystals.

3.2. Temperature Dependent Behavior of the Diffuse Dielectric Anomaly in Ferroelectric Materials

It has been generally believed that the diffuse dielectric anomaly is a dielectric relaxation phenomenon, of which the frequency dependence is well described by the Debye relaxation equation [4–6, 8–10]. Equation (1) shows the modified form of Debye relaxation equation for the fitting process, when the distribution of the relaxation time and the electrical conductivity of the sample are considered [4]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)^\beta} - i\frac{\sigma}{\omega}, \quad (1)$$

where ε_s is the static permittivity, ε_∞ is the permittivity at high frequency, ω is the angular frequency, $\tau = \tau_0 \exp(E_\tau/k_B T)$ is the mean relaxation time, σ is the electrical conductivity of the sample, and β is the angle deviation parameter when there is a distribution of the relaxation time [5]. The relaxation strength, $\Delta\varepsilon$ is defined as $\varepsilon_s - \varepsilon_\infty$, which is generally regarded as a constant in the fitting process [4, 5]. The activation energy of the dielectric relaxation behavior, E_τ is obtained from the frequency fitting process using the Debye relaxation equation. Although there has been little dielectric information on this kind of dielectric relaxation in the case of sulfide ferroelectric materials, numerous data on the activation energy of the dielectric relaxation have been reported at various temperature regions in perovskite-type ferroelectric oxides such as BaTiO₃, SrTiO₃, PbLaTiO₃ ceramics and single crystals, [4–6, 8, 9, 21–24] and other structured ferroelectric oxides such as KTaNbO₃ [25], Cd₂Nb₂O₇ [26], La₂Mo₂O₉ [27].

Figure 4 schematically represents the temperature dependence of the dielectric relaxation behavior according to the Debye relaxation equation. The real part of dielectric constant should be saturated to the value of ε_s when the relaxation time, τ is the only adjustable parameter and the relaxation strength, $\Delta\varepsilon$ is constant as was assumed in the Debye relaxation equation. In

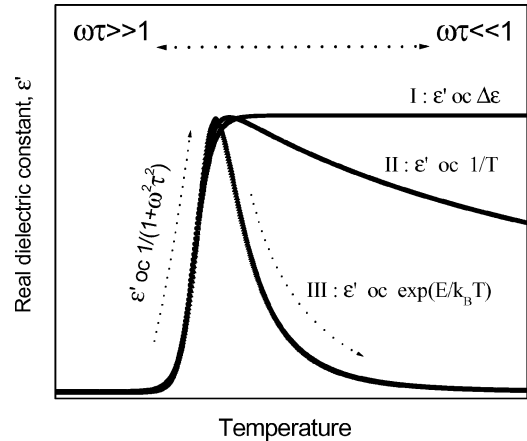


Fig. 4. Schematic diagrams of the temperature dependent behavior of the dielectric relaxation following the Debye relaxation equation, where the relaxation time and the relaxation strength are regarded as fitting parameters.

the case of the dipolar relaxation which is occurred by defects in the lattice, the relaxation strength, $\Delta\varepsilon$ is generally expressed by the following equation [13, 14]:

$$\Delta\varepsilon = N_d \mu^2 / 3k_B T, \quad (2)$$

where N_d is the number of defect dipoles, μ is the dipole moment, k_B is the Boltzman constant, and T is the absolute temperature. In this case, the dielectric relaxation peak becomes more asymmetric because the relaxation strength decreased in proportion with the inverse temperature. In the Debye relaxation equation, the increasing factor with the temperature is an exponential term, $\exp(2E_\tau/k_B T)$, which is included in the relaxation time. Therefore, the figure implies that an exponentially decreasing factor should be involved to the Debye relaxation equation in order to describe the temperature dependence of the diffuse dielectric anomaly.

As already mentioned above, the diffuse dielectric anomaly is involved by defects, which is extrinsically formed in the sample preparation process. Therefore, it is considered that the relaxing species, which originates the diffuse dielectric anomaly, is closely related with defects such as vacancies, free electrons, or substituted ions. For example, the diffuse dielectric anomaly which is found at 700–1000 K in perovskite oxides is closely related with oxygen vacancies in the lattice [4]. According to Ang et al. [5], it was suggested that the dielectric relaxation is originated from the short range thermal motion of oxygen vacancies. However,

it should be noted that the role of conducting carriers by oxygen vacancies should be also considered in this case when the electrical field is applied. The relaxing species, which was formed by defects such as an oxygen vacancy, can be conducting carriers in the point of the electrical conduction. However, it is not considered that the relaxing species contributes to the dielectric polarization and the electrical conduction simultaneously. Instead, the dielectric polarization in an ac electric field is distinguished from the electrical conduction by the phase difference as the following relationship [12, 13].

$$\sigma^* = i\omega\varepsilon^*, \quad (3)$$

where σ^* is the complex conductivity, and ε^* is the complex dielectric constant. The complex conductivity is expressed in a similar form to the dielectric relaxation equation [28]:

$$\sigma^* = \frac{\sigma_{dc}}{1 - i\omega\tau_c} \quad (4)$$

where σ_{dc} is the dc electrical conductivity, and τ_c is the conductivity relaxation time of free carriers. Equation (4) is originally induced in a metal where free electrons are dominant. In this study, it is assumed that this relationship is valid in the system where the relaxing species are easily activated by the electric field and become mobile enough under the ac electric field. In this case, σ_{dc} is the dc electrical conductivity of the relaxing species.

Equation (5) explains that the electrical response of the relaxing species in the ac electric field is related to the dielectric relaxation and the electrical conduction simultaneously.

$$\frac{\sigma_{dc}}{1 - i\omega\tau_c} = \frac{i\omega\Delta\varepsilon}{1 + i\omega\tau_p}, \quad (5)$$

where τ_p is the dielectric relaxation time, which is discriminated from the conductivity relaxation time, τ_c . A simple comparison defines the relaxation strength term with the multiplication of the dielectric relaxation time and the electrical conductivity of the relaxing species as following equation.

$$\Delta\varepsilon = \tau_p \cdot \sigma_{dc} = \frac{1}{\omega^2} \cdot \frac{\sigma_{dc}}{\tau_c} \quad (6)$$

Equation (7) describes the resulting dielectric relax-

ation equation.

$$\begin{aligned} \varepsilon^* &= \varepsilon' - i\varepsilon'' - i\frac{\sigma}{\omega} \\ &= \frac{\tau_p \cdot \sigma_{dc}}{1 + \omega^2\tau_p^2} - i\frac{\omega\tau_p^2 \cdot \sigma_{dc}}{1 + \omega^2\tau_p^2} - i\frac{\sigma_{avg}}{\omega}, \end{aligned} \quad (7)$$

where $\tau_p = \tau_{p0} \exp(E_\tau/k_B T)$ is the dielectric relaxation time, and $\sigma_{dc} = \sigma_o \exp(-E_\sigma/k_B T)$ is the electrical conductivity of the relaxing species itself, and $\sigma_{avg} = \sigma_{o,avg} \exp(-E_{\sigma,avg}/k_B T)$ is the average electrical conductivity of the sample. It should be noted that σ_{avg} is different from σ_{dc} . The electrical conductivity of the sample, σ_{avg} includes all contributions of charge carriers, and depends on the conduction mechanism of the dominant charge carrier in the sample. Consequently, the variation of the relaxation strength is modified to the exponential term as the following equation.

$$\begin{aligned} \varepsilon^* &= \frac{\tau_{p0} \cdot \sigma_o}{1 + i\omega\tau_p} \exp\left(\frac{E_\tau - E_\sigma}{k_B T}\right) - i\frac{\sigma_{avg}}{\omega} \\ &= \frac{\varepsilon_\Delta \exp(E_\varepsilon/k_B T)}{1 + i\omega\tau_p} - i\frac{\sigma}{\omega}, \end{aligned} \quad (8)$$

where $\varepsilon_\Delta = \tau_{p0} \cdot \sigma_o$ is a constant related with the amplitude of the diffuse dielectric anomaly, and $E_\varepsilon = E_\tau - E_\sigma$ is defined as the activation energy for the relaxation strength variation. This equation is different from Eq. (1) in that the relaxation strength, $\Delta\varepsilon$ changes exponentially with the temperature. Also, it is noticeable that the activation energy of the relaxation strength is induced as the difference between the two kinds of activation energies: the dielectric relaxation and the electrical conduction of the relaxing species. The activation energy of the electrical conduction by the relaxing species, E_σ is expected to depend on the conduction mechanism of the relaxing species itself.

Figure 5 shows the measured dielectric data and the fitting results on the temperature dependence of the diffuse dielectric anomaly in BaTiO₃ ceramic, Pb_{0.9}La_{0.1}TiO₃ ceramic, and SPS single crystals. Table 1 lists the fitting parameters used in the modified Debye fitting process using Eq. (8). There are four kinds of adjustable parameters such as τ_p , ε_Δ , $E_\varepsilon (= E_\tau - E_\sigma)$, and σ_{avg} in the modified fitting process, while the relaxation time, τ_p is only used in the conventional Debye fitting process [4–6, 2–27]. These parameters characterize the diffuse dielectric anomaly in the real and the imaginary parts of dielectric constants as a function of

Table 1. Parameters used in the modified Debye fitting method. (In the case of $\text{Sn}_2\text{P}_2\text{S}_6$, $E_{\sigma, \text{avg}}$ is not used in the fitting.)

Sample	ϵ_{Δ}	E_{τ} (eV)	E_{σ} (eV)	$E_{\sigma, \text{avg}}$ (eV)	β
BaTiO_3	0.038	1.52	0.52	1.12	0.90
$\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$	0.0098	1.55	0.70	1.45	0.92
$\text{Sn}_2\text{P}_2\text{S}_6$	25	0.63	0.33	–	0.90

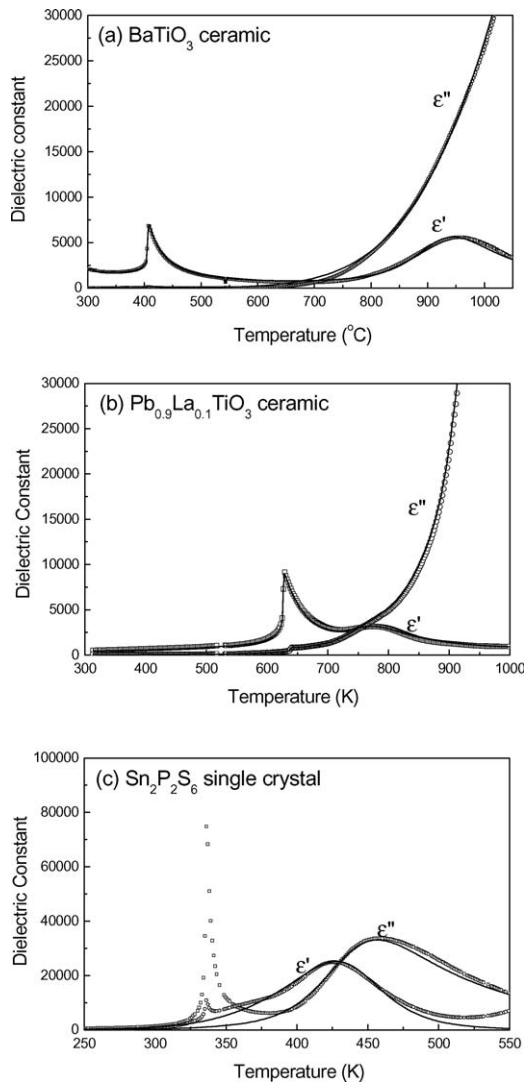


Fig. 5. Temperature dependences of the real and the imaginary part of dielectric constants measured in (a) BaTiO_3 ceramic at 100 kHz, (b) $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ ceramic at 1 kHz, and (c) $\text{Sn}_2\text{P}_2\text{S}_6$ single crystal at 10 kHz. Points are measured data and solid lines are fit results by the modified Debye relaxation equation.

temperature. The peak position of the diffuse dielectric anomaly in the real part of the dielectric constant is set by the competition of two kinds of activation energies, E_{τ} and E_{σ} . ϵ_{Δ} is related to the amplitude of the dielectric relaxation peak in the temperature plot. The activation energy for the dielectric relaxation E_{τ} is confirmed by the conventional frequency fitting process [8]. It should be noted that the average conductivity of the sample, σ_{avg} is only used for fitting the variation of the imaginary part of dielectric constant [12]. The dielectric data measured at 1 MHz was used as background value, ϵ_{∞} . Through matching the temperature dependent behavior of the diffuse dielectric anomaly with the modified Debye relaxation equation, the conductivity activation energy of the relaxing species, E_{σ} is obtained.

In this study, the temperature dependent behavior of the diffuse dielectric anomaly is clearly described in both the real and the imaginary part of the dielectric constants as shown in Fig. 5. In the case of BaTiO_3 and $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ ceramics, the imaginary part of the dielectric constant monotonously increases, which is due to the electrical conduction term of the sample, $\sigma_{\text{avg}}/\omega$. This result indicates that the conductivity activation energy of the relaxing species, E_{σ} is originally different from the average conductivity activation energy of the sample, $E_{\sigma, \text{avg}}$. It also implies that the diffuse dielectric anomaly in the real part of dielectric constant is related to the electrical conduction of the relaxing species, not to the electrical conduction of the sample. In the case of SPS single crystals, the fitting was possible without the contribution of the electrical conductivity of the sample, σ_{avg} .

According to the previous studies [4, 5], one of the most important experimental facts was that the activation energy of the dielectric relaxation, E_{τ} was in a quantitative agreement with the conductivity activation energy of the sample, $E_{\sigma, \text{avg}}$ which was measured in the same temperature region. In the case of $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ ceramics, two kinds of activation energies seem to be quantitatively agreeable as shown in Table 1, which has been already reported by Bidault et al. [4]. However, in the case of BaTiO_3 ceramics, they are not similar to each other. In the case of the diffuse dielectric anomaly of the SPS crystal, the conductivity activation energy of the sample, $E_{\sigma, \text{avg}}$ is not involved. It should be noted that the conductivity activation energy of the relaxing species, E_{σ} is not measured by experimental method, but is calculated from the fitting process in this study. Consequently, it is confirmed that the diffuse dielectric anomaly is the competitive phenomenon between

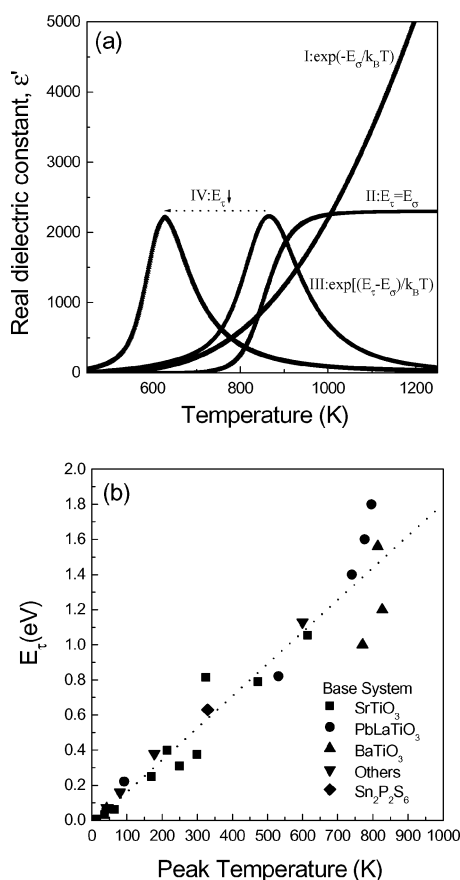


Fig. 6. (a) Schematically simulated results by the modified Debye fitting process on the temperature dependent behaviors of Debye-type dielectric relaxation in the real part of the dielectric constant which is found in ferroelectric materials, and (b) the activation energy of the dielectric relaxation vs. the peak temperature of the diffuse dielectric anomaly [4–6, 8–11, 21–27].

the dielectric relaxation and the electrical conduction of the relaxing species, which is not related with the electrical conductivity of the sample.

Figure 6(a) schematically describes various types of temperature dependent behaviors of the dielectric relaxation in the real part of the dielectric constant according to the modified Debye relaxation equation as was suggested in this study. The fitting parameters were based on the case of BaTiO₃ ceramics. In the case of the imaginary part of the dielectric constant, $E_{\sigma, \text{avg}}$ will also become effective as shown in Fig. 5. The case I of the intensive increase in the real part of the dielectric constant implies that the activation energy of the dielectric relaxation, E_τ is zero. This means that there is no inhibiting barrier for the dielectric polar-

ization. In this case, the dielectric relaxation behavior is not observed as the diffuse dielectric anomaly and the dielectric constant diverges with the temperature as shown in Fig. 6(a). The case II describes the situation where the activation energy of the dielectric relaxation is quantitatively the same with the conductivity activation energy of the relaxing species. In this case, the ideal Debye relaxation equation is valid in the temperature plot. Although the similar dielectric relaxation behavior like this case has been reported in K₂ZnCl₄ single crystal [9], it is considered to be unusual case [29].

The case III represents the situation where the diffuse dielectric anomaly, which is similar to the diffuse phase transition, is observed. This case describes that the activation energy of the dielectric relaxation, E_τ should be always higher than the conductivity activation energy of the relaxing species, E_σ . The maximum peak temperature of the diffuse dielectric anomaly in the real part of the dielectric constant lowers in temperature as the activation energy of the dielectric relaxation becomes smaller as shown in the case IV. Figure 6(b) represents the relationship between the activation energy of the dielectric relaxation and the peak temperature of the diffuse dielectric anomaly measured at 1 kHz, which have been reported in the previous studies [4–6, 8–11, 21–27]. It is noticeable that the figure shows almost the linear relationship between the activation energy of the dielectric relaxation and the peak temperature of the diffuse dielectric anomaly. This result indicates that the higher activation energy of the dielectric relaxation is obtained as the diffuse dielectric anomaly occurs at the higher temperature region. It also confirms that the modification of the Debye relaxation equation is quite useful for describing the temperature dependence of the diffuse dielectric anomaly in ferroelectric materials.

4. Conclusions

The diffuse dielectric anomaly was investigated in ferroelectric materials such as BaTiO₃, Pb_{0.9}La_{0.1}TiO₃ and Sn₂P₂S₆ single crystals. The extrinsic nature of the diffuse dielectric anomaly was experimentally confirmed. The modified Debye relaxation equation was induced from the assumption that the relaxing species, which is extrinsically formed in the lattice, can contribute to both of the dielectric polarization and the electrical conduction. The advanced fitting method using

the modified Debye relaxation equation successfully described the temperature dependent behavior of the diffuse dielectric anomaly. It was also confirmed that the diffuse dielectric anomaly was a competitive phenomenon between the dielectric relaxation and the electrical conduction of the relaxing species.

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