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Dielectric properties and Maxwell-Wagner relaxation of compounds $ACu_3Ti_4O_{12}$ (A=Ca, $Bi_{2/3}$, $Y_{2/3}$, $La_{2/3}$)

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We have studied the frequency and temperature dependences of permittivity and impedance of the compounds $ACu_3Ti_4O_{12}$ (A=Ca, $Bi_{2/3}$, $Y_{2/3}$, $La_{2/3}$) in the ranges of 10^{-1}–10^6 Hz and −150–200 °C. All compounds investigated display similar dielectric properties. Specifically, they all have a Debye-like relaxation and their dielectric constants are independent of frequency and temperature over a wide range. They all have two electrical responses in impedance formalism, indicating that there are two distinct contributions. We attribute them to grains and grain boundaries in the ceramic samples and explain the dielectric behaviors by Maxwell-Wagner relaxation arising at the interfaces between grains and their boundaries. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2125117]

I. INTRODUCTION

The giant dielectric constant material $CaCu_3Ti_4O_{12}$ (CCTO) has recently attracted much attention because of its intriguing mechanism and potential technical applications. CCTO shows an extremely high dielectric constant (up to 10^5) at room temperature.[1,2] Many other materials also have a large dielectric constant, e.g., $Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO),[3] Li- or Ti-doped NiO,[4] $Cu_2Ta_4O_{12}$,[5] $AFe_{1/2}B_{1/2}O_3$ (A=Ba, Sr, Ca; B=Na, Ta, Sb),[6] and $LaMnO_3$.[7] All these large dielectric constant materials have similar dielectric behavior, i.e., they all exhibit a Debye-like relaxation and their dielectric constants are nearly independent of frequency and temperature well below the relaxation frequency. For example, the giant dielectric constant of CCTO is invariant in the ranges of dc–10^6 Hz and 100–600 K.[1,2] Usually large dielectric constants are found in ferroelectric materials and are related to atomic displacements within a noncentrosymmetrical structure. However, CCTO is nonferroelectric and has no structural changes down to 35 K. Accordingly, the origin of the giant dielectric constant has been attributed to an extrinsic mechanism, e.g., the barrier layer capacitances, presumably at twin boundaries,[1] or at the interface between the sample and contacts,[7,8] or at grain boundaries.[3,9] Although there are still some disputes about where the barrier layer capacitances occur, nonlinear current-voltage behavior[10] of CCTO and measurements of transmission electron microscopy[11] (TEM) show that the grain boundaries play an important role in the electrical properties of CCTO.

Subramanian and Sleight measured the dielectric constant of the compounds in the $ACu_3M_4O_{12}$ system at room temperature and 10^5 Hz.[12] They found that more than ten compounds have dielectric constants larger than 1000. Because there are tremendous technical demands for large dielectric constant materials, it is worthwhile to systematically investigate the dielectric properties of the compounds in this system. We have already reported the temperature and frequency dependences of impedance, electric modulus, and permittivity of BCTO,[3] which is one of the compounds in this system. We found that BCTO has the same temperature and frequency dependences of the dielectric behavior as CCTO except with a smaller dielectric constant. We explained its large dielectric constant as arising from Maxwell-Wagner relaxation occurring at the interfaces of grains and grain boundaries. In this paper we report the results of $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO) and $La_{2/3}Cu_3Ti_4O_{12}$ (LCTO), together with the results of CCTO and BCTO, to provide more evidence of this mechanism for the large dielectric constant.

The compounds in the $ACu_3M_4O_{12}$ system crystallize as cubic perovskite-related structures in space-group $Im3$,[12] as shown in Fig. 1. For A=$Bi_{2/3}$, $Y_{2/3}$, $La_{2/3}$, the A sites are 1/3 vacant in order to achieve charge neutrality. The dielectric constants of CCTO, BCTO, YCTO, and LCTO were reported to be 10 286, 1871, 1743, and 418, respectively, at 25 °C and 10^5 Hz.[12]

In Sec. II of this article, we briefly describe the experimental method. In Sec. III, we report the dielectric behaviors of the samples investigated, then analyze their impedance to reveal electrical inhomogeneity in all the samples, and interpret the dielectric behaviors in terms of the Maxwell-Wagner relaxation. In Sec. IV, we present our conclusion.

II. EXPERIMENT

Polycrystalline samples of $ACu_3Ti_4O_{12}$ (A=Ca, $Bi_{2/3}$, $Y_{2/3}$, and $La_{2/3}$) were prepared by heating mixed stoichio-

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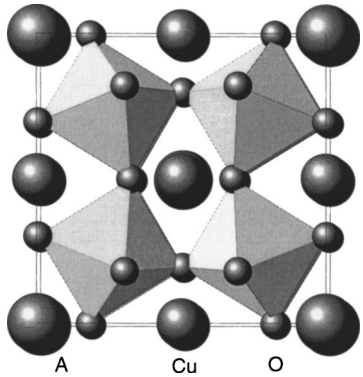

FIG. 1. Crystal structure of the compounds in $ACu_3Ti_4O_{12}$ system. For $A = Bi_{2/3}$, $Y_{2/3}$, and $La_{2/3}$, 1/3 of A sites are vacant. The Ti atoms sit at the center of the TiO_6 octahedra.

metric amounts of the chemicals $CaCO_3$ (Bi_2O_3, Y_2O_3, La_2O_3), CuO, and TiO_2 at 1000 °C for 20 h with intermediate grinding. The final samples were ground into powder and checked by x-ray diffraction to ensure they were single phase. Pellets of 10 mm diameter and 1.0 mm thickness were cold pressed and sintered at 1100 °C for 10 h.

The complex impedance was measured using a NOVOCONTROL Alpha high-resolution dielectric analyzer (Alpha-S) in the temperature range of −150–200 °C and the frequency range of 10^{-1}–10^6 Hz. Silver paint was used on the polished surfaces of the pellets as electrodes. The applied ac voltage was 1 V.

The complex impedance Z^* of the sample was obtained in the usual way, i.e., $Z^* = V^*/I^*$, where V^* and I^* are the applied voltage and the resulting current, respectively. Then the complex permittivity ε^* was calculated as follows:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{1}{i\omega C_0 Z^*}, \tag{1}$$

where ω is the angular frequency $\omega = 2\pi f$ and $i = \sqrt{-1}$. $C_0 = \varepsilon_0 S/d$ is the empty cell capacitance, where S is the sample area and d is the sample thickness.

III. RESULTS AND DISCUSSION

Figure 2 shows the frequency dependence of the permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ for the four investigated compounds at −150 °C. ε^* was obtained from the measured complex impedance Z^* using Eq. (1). In Fig. 2 we observe that each compound has a similar dielectric behavior. First, they all have a Debye-like relaxation, i.e., their ε' displays a step decrease at the frequency where ε'' shows a relaxation peak; second, ε' has little frequency dependence below the relaxation frequency; third, the relaxation peak in all samples shifts to higher frequency at higher temperature (not shown). The only difference they display is very different values of dielectric constant ε', e.g., at −150 °C and 1 Hz, ε' is 9340, 2150, 2009, and 558 for CCTO, BCTO, YCTO, and LCTO, respectively.

The Debye-like relaxation peaks in all samples (Fig. 2) can be fitted to the empirical Cole-Cole equation:[13]

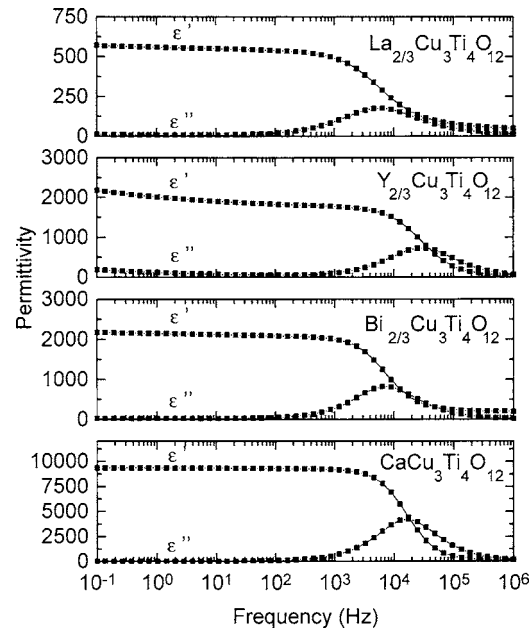

FIG. 2. Frequency dependence of permittivity ε^* at −150 °C.

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^\alpha}, \tag{2}$$

where ε_s and ε_∞ are the static and high-frequency limits of the dielectric constant, respectively, τ is the most probable relaxation time, and α is a constant with values between 0 and 1. For an ideal Debye relaxation $\alpha = 1$. $\alpha < 1$ implies that the relaxation has a distribution of relaxation times, leading to a broader peak shape than a Debye peak. At −150 °C the fitted α values are 0.96, 0.91, 0.90, and 0.80 for CCTO, BCTO, YCTO, and LCTO, respectively, indicating that LCTO has the widest relaxation peak. We also found that the fitted τ values at different temperatures follow the Arrhenius law:

$$\tau = \tau_0 e^{(E/k_B T)}, \tag{3}$$

where τ_0 is the prefactor, E is the activation energy for the relaxation, k_B is Boltzmann constant, and T is absolute temperature. In Fig. 3 we plot $\ln \tau$ vs $1/T$, in which the solid lines are the fitted results using Eq. (3). From the slopes of the fitted straight lines we obtain activation energies of the dielectric relaxations 0.093, 0.095, 0.088, and 0.103 eV for CCTO, BCTO, YCTO, and LCTO, respectively.

Figure 4 shows the temperature dependences of the dielectric permittivity ε' at different frequencies. For all samples, ε' exhibits a step increase with increasing temperature. In the temperature range of 0–150 °C, ε' depends only slightly on the temperature. These dielectric behaviors are similar to those in the reported large dielectric constant materials, such as CCTO,[1,2] Li- or Ti-doped NiO,[4] $AFe_{1/2}B_{1/2}O_3$ (A=Ba,Sr,Ca; B=Na,Ta,Sb),[6] and yttrium iron garnet.[14]

In order to interpret the dielectric properties, we first analyze the electrical properties of the samples. In Fig. 5 we present the frequency dependence of the imaginary part (Z'') of the impedance $Z^* = Z' - iZ''$ at −150 and 50 °C. At −150 °C all compounds have a very weak peak at about 10^5–10^6 Hz overlapping with the tail of a strong peak whose

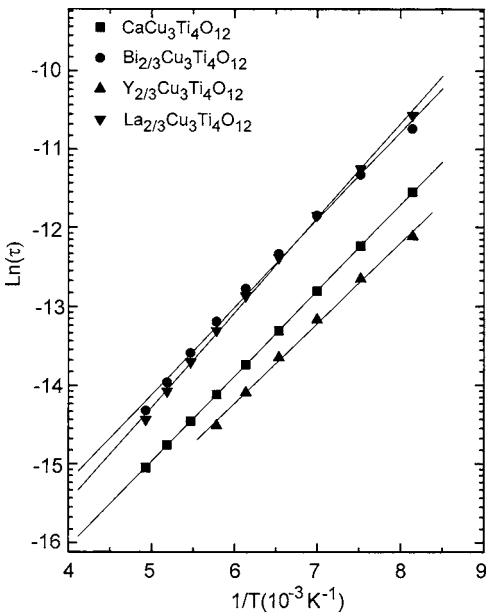

FIG. 3. Arrhenius plot of dielectric relaxation time τ.

peak frequency is too low to be measured. As the temperature increases, both weak and strong peaks shift to higher frequencies with decreased intensity, indicating that both electrical responses are thermally activated. When the temperature rises to 50 °C, the weak peak shifts out of the measured frequency range, while the strong peak emerges, as shown in Fig. 5(b).

Impedance data Z^* of a crystal usually are modeled by an ideal equivalent circuit consisting of resistors R and capacitors C. Usually there is more than one electrical response in heterogeneous systems. Since polycrystalline materials usually show grain-boundary impedance in addition to grain (bulk) effect, they can be represented by the equivalent circuit shown in Fig. 6.[15] The circuit consists of a series array of two subcircuits, one representing grain effects and the other representing grain boundaries. Each subcircuit is composed of a resistor and capacitor joined in parallel.

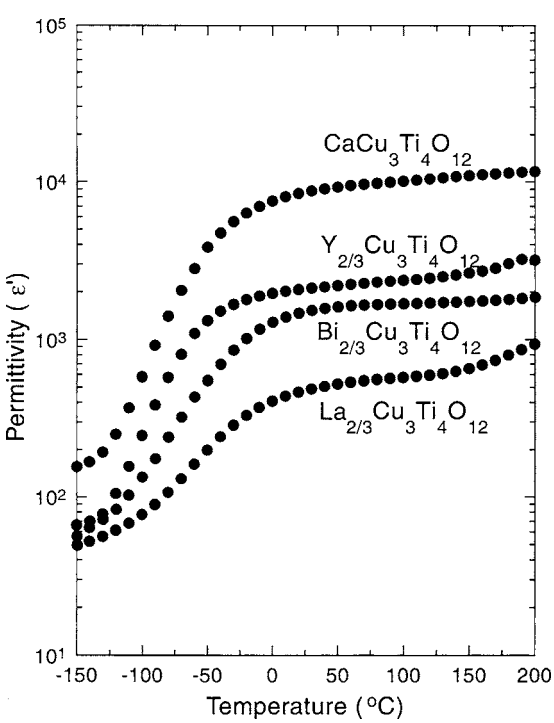

FIG. 4. Temperature dependence of permittivity ε' at frequency 10^6 Hz.

In general, the electrical response from the grain boundary is associated with larger resistance and capacitance than those of grains.[9,16] Its response frequency is thus much lower than that of grains, and it gives rise to a relatively strong peak in the impedance. We therefore attribute the weak responses in Fig. 5(a) to the grains and the strong responses in Fig. 5(b) to the grain boundaries. At −150 °C the strong responses and at 50 °C the weak responses are out of the measured frequency range.

For the samples that show grain and grain-boundary responses and are represented by the equivalent circuit in Fig. 6, the impedance can be calculated as[16]

$$Z^* = \frac{1}{R_g^{-1} + i\omega C_g} + \frac{1}{R_{\mathrm{gb}}^{-1} + i\omega C_{\mathrm{gb}}} = Z' - iZ'', \tag{4}$$

where

$$Z' = \frac{R_g}{1 + (\omega R_g C_g)^2} + \frac{R_{\mathrm{gb}}}{1 + (\omega R_{\mathrm{gb}} C_{\mathrm{gb}})^2} \tag{5}$$

and

$$Z'' = R_g\left[\frac{\omega R_g C_g}{1 + (\omega R_g C_g)^2}\right] + R_{\mathrm{gb}}\left[\frac{\omega R_{\mathrm{gb}} C_{\mathrm{gb}}}{1 + (\omega R_{\mathrm{gb}} C_{\mathrm{gb}})^2}\right], \tag{6}$$

where (R_g, R_{gb}) and (C_g, C_{gb}) are the resistances and capacitances of grains and grain boundaries, respectively.

Based on Eqs. (5) and (6) the responses from the grains and grain boundaries are located at $1/(2\pi R_g C_g)$ and $1/(2\pi R_{\mathrm{gb}} C_{\mathrm{gb}})$, respectively. The peak values of Z'' are proportional to the associated resistances. As shown in Fig. 5, at a certain temperature, the Z'' peak values from the grain-boundary responses are much larger than those of grain responses; therefore, for all the investigated samples, $R_{\mathrm{gb}} \gg R_g$.

To interpret the dielectric behavior, we calculated the permittivity ε^* of the equivalent circuit in Fig. 6 using Eqs. (1) and (4). The result can be presented in the following form:[7]

$$\varepsilon^*(\omega) = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + i\omega\tau} - i\frac{\sigma'}{\omega}, \tag{7}$$

where

$$\varepsilon'_\infty = \frac{1}{C_0}\frac{1}{(1/C_g) + (1/C_{\mathrm{gb}})}, \tag{8}$$

$$\varepsilon'_s = \frac{R_g^2 C_g + R_{\mathrm{gb}}^2 C_{\mathrm{gb}}}{C_0 (R_g + R_{\mathrm{gb}})^2}, \tag{9}$$

$$\sigma' = \frac{1}{C_0 (R_g + R_{\mathrm{gb}})}, \tag{10}$$

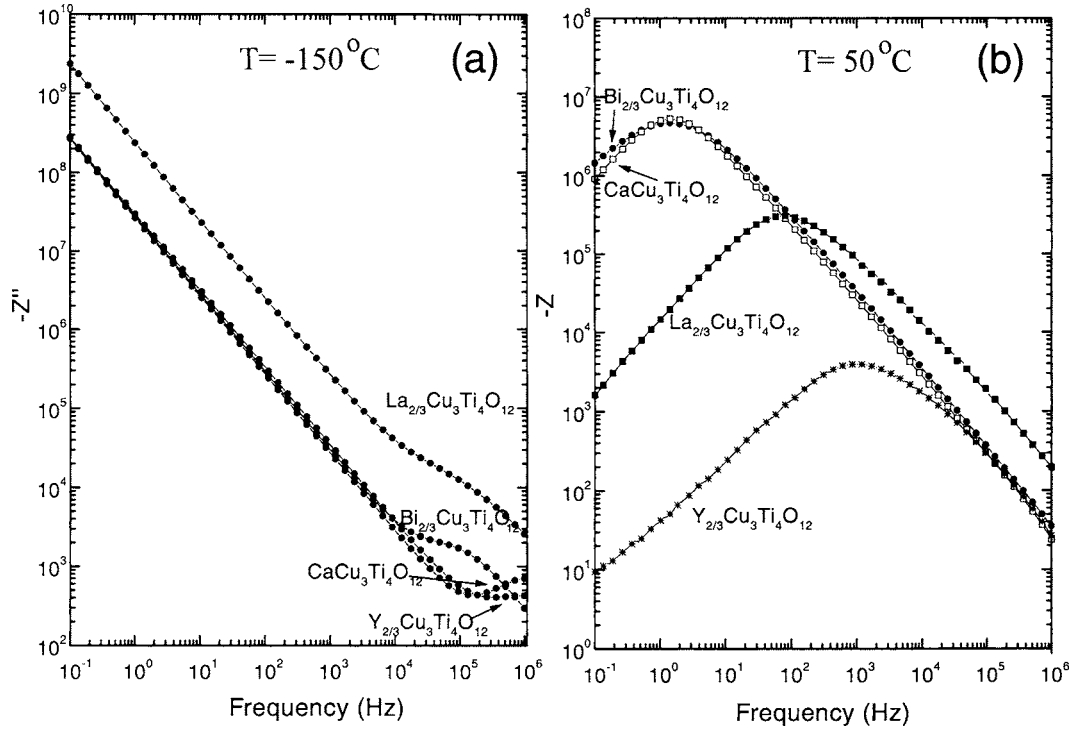

FIG. 5. Frequency dependence of imaginary part (Z'') of impedance Z^* (a) at −150 °C and (b) at 50 °C.

$$\tau = \frac{R_g R_{gb}(C_g + C_{gb})}{R_g + R_{gb}}, \tag{11}$$

where ε_s' and ε_∞' are the static and high-frequency permittivities, respectively, σ' is Ohmic conductivity, τ is the time constant, and C_0 is the empty cell capacitance.

Equation (7) is expressed in the form of a Debye relaxation with a conduction term. This means that even without any dipole involved the equivalent circuit in Fig. 6 gives rise to a relaxation spectrum similar to that of the Debye relaxation, which is referred to as Maxwell-Wagner relaxation, and often occurs in the heterogeneous systems in which the component dielectrics have different conductivities.[17] When an electric current passes through interfaces between two different dielectric media, because of their different conductivities, surface charges pile up at the interfaces and give rise to a Debye-like relaxation process under an external alternating voltage. A detected Debye-like relaxation response is therefore not necessarily the result of dipole relaxation in the system; sometimes it originates from the heterogeneity of the system. For example, grain boundaries and/or the electrodes applied to the sample can produce the effect. We attribute the observed peaks in Fig. 2 to the Maxwell-Wagner relaxation arisen from the interfaces between grains and grain boundaries.

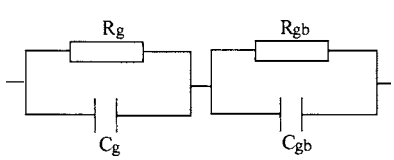

FIG. 6. Equivalent circuit used to represent the electrical properties of a ceramic sample that exhibits grain (R_g, C_g) and grain-boundary (R_{gb}, C_{gb}) effects.

As stated above, $R_{gb} \gg R_g$. The capacitance of grain boundaries (C_{gb}) is also much larger than that of grains (C_g).[3,9,16] The effective dielectric permittivity of the sample at frequencies much lower than the relaxation frequency $1/(2\pi\tau)$ can therefore be approximated from Eq. (9),

$$\varepsilon_s' \approx \frac{C_{gb}}{C_0}. \tag{12}$$

Thus ε_s' is determined only by the ratio between the grain-boundary capacitances C_{gb} and the vacuum capacitance of the sample C_0. Hence ε_s' is constant when C_{gb} is temperature and frequency independent. We indeed observed that BCTO has a constant C_{gb} in a wide temperature range,[3] so it shows a constant dielectric constant. Equation (12) also shows that a large C_{gb}/C_0 ratio leads to a large effective dielectric constant. We propose that the large different dielectric constants of all four compounds are caused by the differences in grain-boundary capacitances C_{gb}, i.e., the differences in microstructure of each ceramic sample.

Occasionally the Maxwell-Wagner effect at the interfaces between the sample and electrodes gives rise to a large contact capacitance and results in a large dielectric constant. However, the contact capacitance is not the principal cause of the large dielectric constants in CCTO and its related compounds. First, the experimental results have shown that changing the electrodes of ceramic CCTO has no effect on the dielectric constant.[18] Second, at room temperature and 10^5 Hz, the dielectric constants of the four investigated compounds obtained in our experiments are very close to the reported values.[12] Hence, we conclude that the electrode effect is minimal.

BCTO, YCTO, and LCTO all have 1/3 vacancies in their A sites. To date there is no experimental evidence that

A-site vacancies are directly related to the value of the dielectric constant. For example, $CdCu_3Ti_4O_{12}$ has the same crystal structure and has no vacancies in its lattice, but its dielectric constant is only 409 at 25 °C and 10^5 Hz.[12] However, it is possible that different *A*-site ions might give rise to different microstructures (grains and grain boundaries) of the ceramic samples and render different dielectric constants.

IV. CONCLUSION

We have investigated the temperature and frequency dependences of the permittivity and impedance of polycrystalline CCTO, BCTO, YCTO, and LCTO. We observed that there is a Debye-like relaxation in all samples and that their dielectric constants are independent of frequency and temperature below the relaxation frequency. We found that the samples are electrically inhomogeneous by analyzing their impedance, because two electrical responses were observed in all samples. We attribute them to grain and grain-boundary contributions. We explained the dielectric properties using the Maxwell-Wagner relaxation arising at the interfaces between the grains and their boundaries.

ACKNOWLEDGMENTS

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