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Effects of Processing Conditions on the Dielectric Properties of $CaCu_3Ti_4O_{12}$

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Abstract. There have been a number of recent reports of anomalously large permittivities ($\varepsilon_r \approx 10^4$) in the material $CaCu_3Ti_4O_{12}$. The dielectric spectra is characterized by a large, relatively temperature independent permittivity near room temperature which exhibits a dielectric relaxation above 100 K. The crystal structure of $CaCu_3Ti_4O_{12}$ can be described as pseudo-perovskite with a cubic unit cell with a lattice constant of 7.391 Å. The ubiquitous occurrence of this dielectric behavior in ceramics, single crystals, and thin films suggests that the polarization is not related to a simple conducting grain/insulating grain boundary-type system. While the precise origin of the dielectric response is not entirely clear, in this work it is shown that processing conditions have a significant influence on the room temperature dielectric properties. Specifically, the permittivity and loss exhibit a strong dependence on the oxygen partial pressure and sintering time. In fact, studies of the effects of sintering time and supporting evidence from capacitance-voltage measurements conclusively show that there is no direct relationship between the permittivity and grain size, as is the case in classical boundary layer systems. Lastly, with aliovalent doping the room temperature dielectric properties can be optimized to provide a high permittivity ($\varepsilon_r \sim 8{,}000$) dielectric with relatively low loss ($\tan \delta < 0.05$ at 1 kHz).

Keywords: dielectric materials, space charge, perovskite, Maxwell-Wagner

Introduction

In electroceramic technology, there is an ever-present desire for miniaturization and improved performance metrics. The distorted perovskite $CaCu_3Ti_4O_{12}$ has been shown to have an anomalously large dielectric permittivity over a broad temperature range with a small temperature coefficient. These large permittivities have been observed in polycrystalline, single crystal, and epitaxial thin films [1–10]. Considering the fact that there has been no evidence of ferroelectricity, this permittivity value is highly unusual. While the true origin of the dielectric behavior has not been fully explained, in this work the influence of processing conditions on the dielectric behavior has been examined.

$CaCu_3Ti_4O_{12}$ has a pseudo-perovskite crystal structure with a cubic unit cell with a lattice constant of 7.391 Å. In the ideal perovskite structure, with the formula $A^{XII}B^{VI}O_3$, the A-cation is in 12-coordination. However, to accommodate lower cation coordination, the TiO_6 octahedra distort so as to create a square planar coordination for three-quarters of the A-sites. This lowers the symmetry from point group $m3m$ to $m3$.

The dielectric spectra of polycrystalline $CaCu_3Ti_4O_{12}$ is characterized by a permittivity approaching 10^4 at room temperature. In the vicinity of room temperature the permittivity of $CaCu_3Ti_4O_{12}$ is nearly temperature independent, which is uncommon amongst high-K dielectrics. Often, the origin of the high permittivity is ferroelectricity or relaxor ferroelectricity which both show a peak of permittivity as a function of temperature. The material exhibits two relaxations, one above room temperature and one near 150 K. Below the low temperature relaxation, the

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permittivity decreases two to three orders of magnitude to approximately $\varepsilon_r \approx 100$. At room temperature, the permittivity decreases at frequencies above 100 kHz.

There have been many models proposed to explain this unique dielectric behavior, including both intrinsic and extrinsic mechanisms [3–6, 9, 10]. Both neutron and high resolution X-ray diffraction have been employed at low temperatures but no evidence of any kind of structural transition has been identified [1, 2]. The lack of a structural transition and the centrosymmetric $m3$ point group suggests that ferroelectricity cannot be responsible for such large permittivities. The frequency dependence of the permittivity in $CaCu_3Ti_4O_{12}$ does share some similarity with relaxor ferroelectric systems [3]. However, a common feature of relaxor systems is the presence of a solid solution of cations (e.g. $Pb(Mg,Nb)O_3$) which are randomly distributed. However, because of strong Jahn-Teller effects the Cu and Ca ions on the A-site in $CaCu_3Ti_4O_{12}$ are well ordered [11]. Furthermore, Raman and infrared reflection studies did not indicate any lattice anomalies. In general, the modes observed in the spectra were in well agreement with the calculated ones, and the additional mode observed in the low temperatures was assigned to the presence of domains of different atomic arrangement [12, 13]. From first-principles calculations, the lattice contributions to the permittivity using simple Clausius-Mosotti and more rigorous density functional methods are found to be drastically lower than the permittivity of the material [6, 14]. All these results strengthen the explanation for the origin of the high permittivity is, at least in part, extrinsic mechanisms.

Typically, permittivity values on this scale are associated with space charge polarization in polycrystalline specimens. However, as previously mentioned these high values were also obtained in single crystals and thin films of $CaCu_3Ti_4O_{12}$ [3, 7, 8]. Sinclair et al. suggested an internal boundary layer mechanism which is composed of conducting grains and insulating grain boundaries, which may be formed by limited reoxidation during cooling [4, 9]. The impedance data accurately fits an electrically heterogeneous system, however the exact nature of this heterogeneity has not been established. The data for single crystals and thin films suggest that the heterogeneity cannot be explained by a simple conducting grain/insulating grain boundary system. Furthermore, if space charge is indeed responsible for the colossal permittivity, it is unclear why isostructural (and in some cases isovalent) compounds that contain Cu, e.g. $CdCu_3Ti_4O_{12}$ and $CaCu_3Ge_4O_{12}$ have comparatively low permittivities of $\varepsilon_r = 410$ and 34 respectively [1, 5]. Subramanian et al. observed the presence of twinning in the microstructure and proposed a twin boundary suggesting that these twin boundaries may create barrier layer capacitance [1]. Twinning was also found in thin film $CaCu_3Ti_4O_{12}$ [7]. It is also interesting to note it was observed that the isostructural compound $CdCu_3Ti_4O_{12}$ has a reduced degree of twinning compared to $CaCu_3Ti_4O_{12}$ [15].

In this work, the effects of sintering time and oxygen anneals on the dielectric properties were investigated. It was observed that altering the defect equilibrium through aliovalent doping had significant influence on the dielectric behavior of the material.

Experimental

Polycrystalline samples of $CaCu_3Ti_4O_{12}$ were synthesized using conventional solid state ceramic processing techniques. The reagent powders of $CaCO_3$, CuO, TiO_2, and Nb_2O_5 were all 99.9% pure. Furthermore, the powders were tested for loss on ignition and the batch composition was compensated accordingly. The batch was milled in ethanol using a vibratory mill. The batch was then calcined in air at 1000 °C for 24 hours. After vibratory milling a second time, approximately 5 wt% organic binder is added to the calcined powders and powders were then pressed into 12.7 mm diameter pellets by cold uniaxial pressing. All of the pellets were sintered in air at 1100 °C for different sintering times. Finally, some of them were annealed at 800 °C for 24 hours in a controlled atmosphere furnace under oxygen partial pressures ranging from 0.001 to 1.0 atm. X-ray diffraction (XRD) was utilized to monitor phase evolution and changes in lattice parameter. Densities of the pellets were determined using the Archimedes method. The samples were sputtered with gold electrodes and the dielectric properties were measured with an HP-4174A LCR meter in an environmental chamber. Grain size measurements were conducted on thermally etched cross-sections using the SEM. In addition, the magnetic moment was measured using a SQUID magnetometer on a sintered polycrystalline sample.

Results and Discussion

The evolution of space charge polarization within a system such as $CaCu_3Ti_4O_{12}$ requires mobile charged species, and some form of internal interface or barrier.

Our preliminary studies have focused on identifying the influence of processing conditions on these parameters with the aim of shedding light on the polarization mechanism. To date, there are no proven links between structural features and the dielectric response of $CaCu_3Ti_4O_{12}$. Adams et al. proposed a direct link between grain size and permittivity (as the Maxwell-Wagner model would predict) based on two sets of samples obtained by varying the sintering time; a fine grained ($t_{grain} \sim 5\,\mu m$) and large grained ($t_{grain} > 100\,\mu m$) microstructure [9]. They noted a dramatic increase in permittivity with the coarse grained sample as validation of the idea that grain boundaries serve as the mitigating internal boundary for space charge polarization. In contrast to these results, in Figs. 1 and 2 the authors show through varying the sintering time that while the permittivity increases with sintering time, it is not directly correlated to grain size. Considering these discrepancies, there must be compositional differences compared to the Adams results. It is not uncommon to observe large grains on the order of 100 μm in TiO_2-rich titanate perovskites. In addition, the powders used in this study were only 99.9% pure compared to 99.99% pure for the samples prepared by Adams. This may be significant because impurities can inhibit or enhance grain growth in perovskites. Regardless, interpretation of these data and the single crystal measurements of Subramanian indicate that the source of the internal barriers is not restricted to grain boundaries [1].

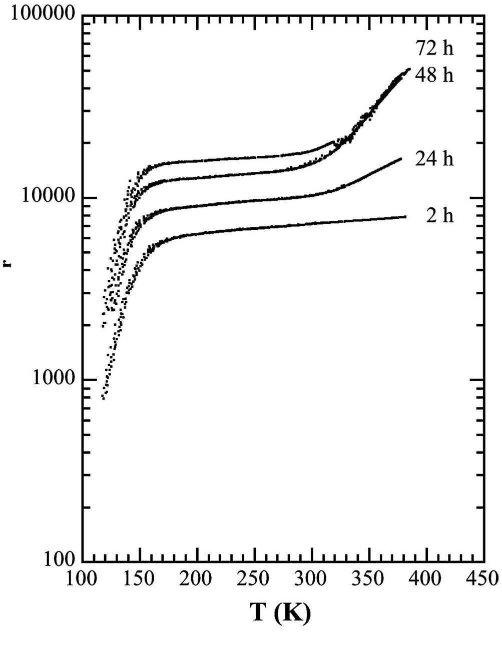

Fig. 1. Permittivity at 10 kHz for $CaCu_3Ti_4O_{12}$ ceramics sintered at 1100°C between 2 and 72 h.

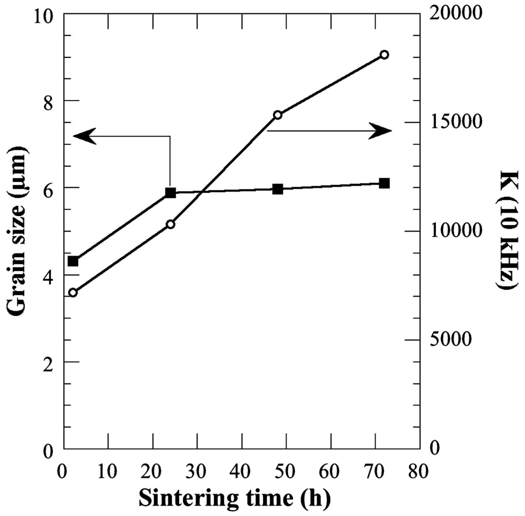

Fig. 2. Grain size and permittivity (at 10 kHz) as a function of sintering time.

In classical barrier layer capacitor materials such as $SrTiO_3$, the large permittivity values exhibit a strong bias dependence due to the effects of barrier lowering. However, measurement of the capacitance as a function of voltage for undoped and Nb-doped $CaCu_3Ti_4O_{12}$ ceramics showed that for both compositions the bias dependence is minimal ($\leq$1%). From the result we can infer that the potential drop across each barrier must be negligibly small. This, together with the data in Fig. 2 is another strong indication that the polarization mechanisms must be tied to features on a scale finer than the grain size.

Through a series of oxygen pressure dependent anneals, the effects of pO_2 were examined. XRD showed no secondary phases formed and no significant change in the lattice parameter. Furthermore, there was no change in the density of the samples or the grain size. As shown in Fig. 3, increasing the pO_2 in post-anneal had the effect of increasing the permittivity above room temperature. A minimal change in low temperature relaxation was observed. The dramatic rise in permittivity with increasing pO_2 is similar to observations seen in systems where p-type charge carriers are generated through interactions with the ambient. Additionally, it was observed that the permittivity was

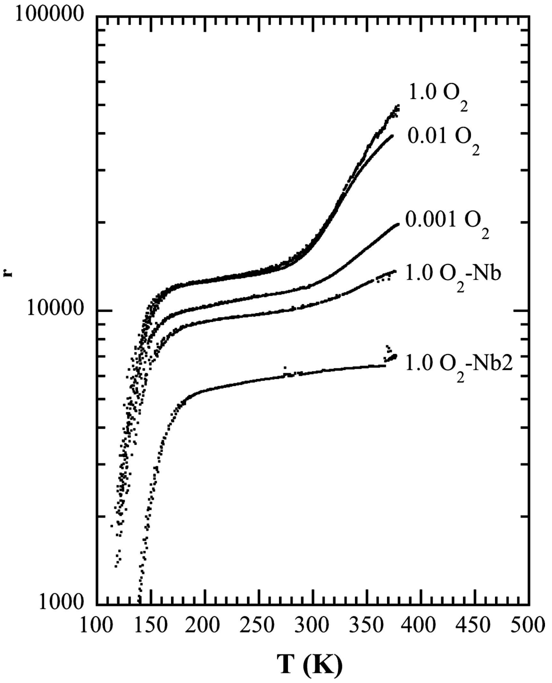

Fig. 3. Permittivity versus temperature for $CaCu_3Ti_4O_{12}$ annealed at 800 °C for 24 hours in various oxygen partial pressures. In addition, two samples annealed in 1.0 atm O_2 with Nb-doping is also shown (Nb= $CaCu_3Ti_{3.992}Nb_{0.008}O_{12}$, Nb2 = $CaCu_3Ti_{3.984}Nb_{0.016}O_{12}$).

dramatically affected by donor doping by substituting pentavalent Nb for Ti with the chemical formulae $CaCu_3Ti_{3.992}Nb_{0.008}O_{12}$ and $CaCu_3Ti_{3.984}Nb_{0.016}O_{12}$. As can be seen in Fig. 3, Nb-doped samples annealed in 1.0 atm pO_2 had a greatly decreased high temperature permittivity and consequently a considerably lower tan δ.

The defect chemistry of $CaCu_3Ti_4O_{12}$ is not known, however in many perovskites cation and anion vacancies are often the dominant species. The oxygen stoichiometry, and thus the oxygen vacancy concentration, is established through equilibrium with the environment. Cation vacancies may arise in systems with a volatile element. It is known that Cu-containing oxides can experience CuO volatilization at temperatures close to the processing temperatures in this study. However, Subramanian et al. synthesized Cu-deficient CCT compositions and noted a marked reduction in the permittivity [1]. Defects may also be derived from site occupancy modifications and the formation of defect complexes. Regardless of the exact nature of the defect species in $CaCu_3Ti_4O_{12}$, the pO_2-dependent permittivity and the effects of donor doping suggest that the permittivity can be controlled by modifying the defect equilibrium.

This result is consistent with predictions derived from the Maxwell-Wagner model. For a two layer system, if it is assumed that the permittivities of the layer 1 (boundary layer) and the layer 2 (grain) are equal (i.e. $\varepsilon_1 = \varepsilon_2 = \varepsilon_i$), the permittivity is given by a Debye-like relaxation [16]:

$$\varepsilon = \frac{\varepsilon_s + \varepsilon_\infty \tau_\varepsilon^2 \omega^2}{1 + \varepsilon_\infty \tau_\varepsilon^2 \omega^2} \tag{1}$$

where ε_s is the static permittivity, ε_∞ is the high frequency permittivity, ω is the angular frequency and τ is given by:

$$\tau_\varepsilon = \varepsilon_0 \varepsilon_i \rho_2 \frac{(d_1 + d_2)}{d_1} \tag{2}$$

where d_1 and d_2 are the thicknesses of layer 1 and layer 2 respectively, and ρ_2 is the resistivity of layer 2. If it is also assumed that the boundary layer has a high resistance, $d_1\rho_1 \gg d_2\rho_2$, the low frequency permittivity is:

$$\varepsilon_s = \varepsilon_i \frac{(d_1 + d_2)}{d_1} \tag{3}$$

From Eq. (1) we can deduce that a decrease in the intragranular resistance should result in a decrease in permittivity. It is important to note that the addition of Nb did not affect the grain size. The grain size was observed to change slightly due to variations in processing conditions, but within a narrow range between 4–7 μm for all of the samples.

From the room temperature dielectric data, the high frequency permittivity is approximately $\varepsilon_\infty \sim 100$. Using Maxwell-Wagner equations the room temperature permittivity of 10^4 can be calculated by taking $d_2/d_1 \sim 10^2$. Since grain size cannot account for this high permittivity, it may be due to a change in the resistivity of the grain or a change in the boundary layer thickness.

Figure 4 displays the capacitance as a function of inverse thickness. The intercept is very close to the origin, which suggests that the interfacial capacitance, *e.g.* due to the contacts, does not have a significant influence on our results. This result is consistent with the findings from the capacitance versus voltage data.

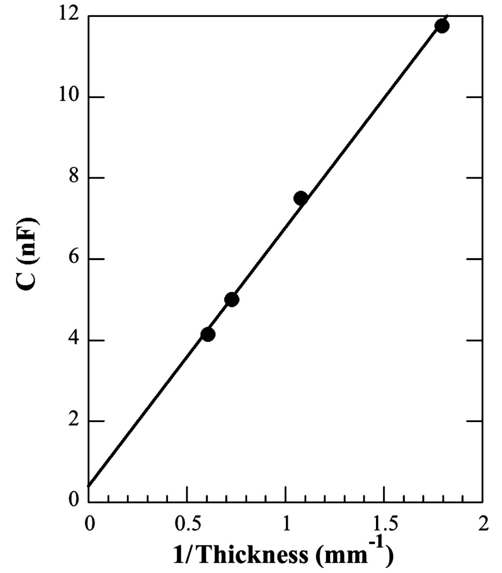

Fig. 4. Capacitance as a function of inverse thickness for undoped $CaCu_3Ti_4O_{12}$.

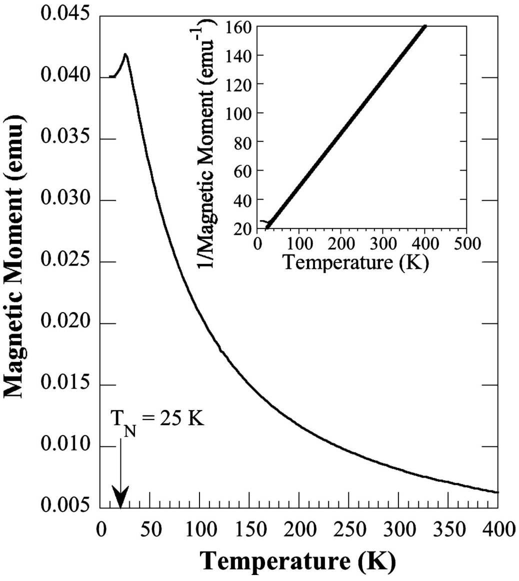

Fig. 5. The magnetic moment of $CaCu_3Ti_4O_{12}$ (24 h sinter) measured at 10 kOe (DC). The inset shows linear behavior in the inverse magnetic moment versus temperature.

Tenorite CuO shows similar relaxations near the same temperature range due to magnetic ordering transitions [18]. However, as depicted in Fig. 5 for $CaCu_3Ti_4O_{12}$, while there is evidence of an antiferromagnetic transition at 25 K (confirming the data of Kim et al. [19]) there are no magnetic ordering transitions in the vicinity of the dielectric anomaly.

Table 1. Dielectric properties of various samples at room temperature at $f = 10$ kHz.

Sample	ε_r	tan δ
$CaCu_3Ti_4O_{12}$ (2 h sinter)	6,700	0.051
$CaCu_3Ti_4O_{12}$ (24 h sinter)	9,700	0.128
$CaCu_3Ti_4O_{12}$ (oxygen anneal)	16,300	0.447
$CaCu_3Ti_{3.984}Nb_{0.016}O_{12}$ (oxygen anneal)	6,200	0.050

Table 2. Dielectric properties of $CaCu_3Ti_{3.984}Nb_{0.016}O_{12}$ at room temperature.

f	ε_r	tan δ
100 Hz	6,700	0.091
1 kHz	6,400	0.033
10 kHz	6,200	0.050
100 kHz	5,500	0.19

Finally, the room temperature dielectric properties of undoped and Nb-doped $CaCu_3Ti_4O_{12}$ are summarized in Tables 1 and 2. While the time constant of the space charge polarization mechanism prevents application of $CaCu_3Ti_4O_{12}$ for high frequency applications, the material exhibits excellent dielectric properties below 100 kHz. Given that the dielectric properties of the material are inherently temperature independent and the preliminary results show that the permittivity is not a strong function of bias, with further property optimization this material is a promising candidate for high capacitance density applications.

Conclusions

It was shown that the dielectric behavior of $CaCu_3Ti_4O_{12}$ is strongly influenced by processing parameters. An increase in the sintering time resulted in a dramatic increase in the room temperature permittivity. However, that increase in permittivity was not correlated to an increase in grain size. Furthermore, the room temperature capacitance was found to be independent of bias. This suggests that the classic grain boundary layer capacitor model is not appropriate for the dielectric response of $CaCu_3Ti_4O_{12}$. The dielectric properties were also found to be strongly dependent upon the pO_2 in post-anneals at 800 °C suggesting that charge carriers can be generated through electrically active defects. Thus, donor doping (Nb) was shown to be effective in controlling the dielectric properties with $\varepsilon_r = 8{,}000$ and a tan $\delta = 0.04$ at 1 kHz for $CaCu_3Ti_{3.984}Nb_{0.016}O_{12}$.

References

1. M.A. Subramanian, D. Li, N. Duan, B.A. Reisner, and A.W. Sleight, *J. Solid State Chem.*, **151**, 323 (2000).
2. A.P. Ramirez, M.A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, and S.M. Shapiro, *Solid State Comm.*, **115**, 217 (2000).
3. C.C. Homes, T. Vogt, S.M. Shapiro, S. Wakimoto, and A.P. Ramirez, *Science*, **293**, 673 (2001).
4. D.C. Sinclair, T.B. Adams, F.D. Morrison, and A.R. West, *Appl. Phys. Lett.*, **80**, 2153 (2002).
5. M.A. Subramanian and A.W. Sleight, *Solid State Sci.*, **4**, 347 (2002).
6. L. He, J.B. Neaton, M.H. Cohen, D. Vanderbilt, and C.C. Homes, *Phys. Rev. B*, **65**, 214112 (2002).
7. Y. Lin, Y.B. Chen, T. Garret, S.W. Liu, C.L. Chen, L. Chen, R.P. Bontchev, A. Jacobson, J.C. Jiang, E.I. Meletis, J. Horwitz, and H.D. Wu, *Appl. Phys. Lett.*, **81**, 631 (2002).
8. W. Si, E.M. Cruz, P.D. Johnson, P.W. Barnes, P. Woodward, and A.P. Ramirez, *Appl. Phys. Lett.*, **81**, 2056 (2002).
9. T.B. Adams, D.C. Sinclair, and A.R. West, *Adv. Mater.*, **14**, 1321 (2002).
10. P. Lunkenheimer, V. Bobnar, A.V. Pronin, A.I. Ritus, A.A. Volkov, and A. Loidl, *Phys. Rev. B*, **66**, 052105 (2002).
11. S.M. Moussa and B.J. Kennedy, *Mater. Res. Bull.*, **36**, 2525 (2001).
12. N. Kolev, R.P. Bontchev, A.J. Jacobson, V.N. Popov, V.G. Hadjiev, A.P. Litvinchuk, and M.N. Iliev, *Phys. Rev. B*, **66**, 132102 (2002).
13. A.P. Litvinchuk, C.L. Chen, N. Kolev, V.N. Popov, V.G. Hadjiev, M.N. Iliev, R.P. Bontchev, and A.J. Jacobson, *Phys. Stat. Sol.* (a), **195**, 453 (2003).
14. L. He, J.B. Neaton, D. Vanderbilt, and M.H. Cohen, *Phys. Rev. B*, **67**, 012103 (2003).
15. C.C. Homes, T. Vogt, S.M. Shapiro, S. Wakimoto, M.A. Subramanian, and A.P. Ramirez, *Phys. Rev. B*, **67**, 092106 (2003).
16. J. Volger, in *Progress in Semiconductors*; *Vol. 4*, edited by A. F. Gibson (Wiley, New York, 1960), p. 207.
17. R.K. Sharma, N.H. Chan, and D.M. Smyth, *J. Am. Ceram. Soc.*, **64**, 448 (1981).
18. X.-G. Zheng, C.-N. Xu, E. Tanaka, Y. Tomokiyo, H. Yamada, Y. Soejima, Y. Yamamura, and T. Tsuji, *J. Phys. Soc. Jpn.*, **70**, 1054 (2001).
19. Y.J. Kim, S. Wakimoto, S.M. Shapiro, P.M. Gehring, and A.P. Ramirez, *Solid State Comm.*, **121**, 625 (2002).
20. S. Aygün, X. Tan, J.P. Maria, and D.P. Cann, "Defect contributions to the anomalous permittivity in $CaCu_3Ti_4O_{12}$ ceramics," *Proceedings of the 204*th *Electrochemical Society Meeting, Orlando, Florida, October 2003*, (in press).