## High Dielectric Permittivity Behavior in Cu-Doped CaTiO<sub>3</sub>

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Cu-doped CaTiO<sub>3</sub>-based polycrystalline ceramics have been prepared by the conventional solid-state sintering. Our results indicate that the dielectric constant can be enhanced greatly by increasing the Cu-doped content, which show weak frequency and temperature dependence. The fitted activation energy is almost same (~0.10 eV) as the Cu-doped content is 0.4–0.6, which may be ascribed to the first ionization of the oxygen vacancies. The origin of the high dielectric permittivity observed in these Ca<sub>1-x</sub>Cu<sub>x</sub>TiO<sub>3</sub>-based ceramics should be attributed to the interfacial polarization mechanism, and can be well described by the percolation theory with  $f_c \approx 0.27$  and  $s \approx 0.74$ .

With the miniaturization and integration of electronic devices, high-permittivity dielectric materials have attracted considerable attention for both scientific understanding and their numerous technological applications such as capacitors and memory devices.<sup>1</sup> Usually, high-dielectric properties are observed in the perovskite ferroelectric or relaxor oxides, e.g., Pb(Zr,Ti)O3 and Pb(Mg,Nb)O3.2,3 However, both kinds of materials show strong temperature dependence due to the ferroelectric phase transition, and most of such perovskite oxides contain Ba/Pb, which are indispensable to modern electronic devices. Surface and internal barrier layer capacitors based on semiconductive perovskite such as (Ba,Sr)TiO<sub>3</sub> ceramics have also been attractive.<sup>4</sup> However, these capacitors are of poor reproducibility and complex processing (involving high temperatures, reducing atmospheres, and limited diffusion of oxygen and dopant ions along the grain boundaries), and inherit a strong variation in electrical properties with temperature and frequency, which is unfavorable for many applications.

Recently, a lead-free perovskite-like oxide  $CaCu_3Ti_4O_{12}$  (CCTO),<sup>5,6</sup> and Li, Ti co-doped NiO (LTNO)<sup>7,8</sup> ceramics have been reported to possess an extraordinarily high dielectric constant of ~10<sup>4</sup>-10<sup>5</sup> at room temperature, which is almost constant over a wide temperature and frequency range. However, both of CCTO and LTNO materials have not yet been obtained applications because of their large dielectric loss around room temperature (>0.10 at 1 kHZ). Therefore, creation of dielectric materials with a lead-free, high dielectric constant, low loss tangent, and good stability in wide temperature and frequency ranges are highly desired.

In this work, we prepared Cu-doped CaTiO<sub>3</sub> polycrystalline ceramics, and observed high dielectric permittivity, and low loss tangent behavior. The dielectric constant can be tuned by the addition of Cu, and shows good temperature and frequency stability. Our results indicate that it is a promising material for capacitors and memory devices.

CaCO<sub>3</sub>, CuO, and TiO<sub>2</sub> powders were used as the raw materials (all reagents are analytical purity), and  $Ca_{1-x}Cu_xTiO_3$ ceramics (x = 0, 0.1, 0.4, 0.5, and 0.6, abbreviated as CTO-0,CTO-1, CTO-2, CTO-3, and CTO-4, respectively) were prepared by a solid-state reaction sintering method. The starting materials were weighted as the above nominal composition and milled for 6 h. The dried mixture powders were presintered at 900°C for 2 h, and then the precursor powders were pressed to green pellets (12 mm in diameter) with polyvinyl alcohol binder. Finally, the pellets were sintered at 1100°C for 3 h in air. The phase compositions of these as-sintered samples were measured by the X-ray diffraction (XRD) equipment (Rigaku D-Max 3A, Suginami-ku, Tokyo, Japan, CuKa radiation). Scanning electron microscopy (SEM) equipped with X-ray energy-dispersive spectrometer (EDS) and electron back scatter diffraction (EBSD) was used to study the microstructure and the composition of the samples. The ceramic samples were polished and pasted by silver paste on both sides, and then treated at 600°C for 30 min to form the electrodes. The dielectric response of the specimens was measured using a HP 4194A gain-phase analyzer (Santa Clara, CA) over a frequency range from 100 Hz to 1 MHz and at an oscillation voltage of 1 V. These measurements were performed in the temperature range from -120 to 350 K. Each measured temperature was kept constant with an accuracy of  $\pm 1$  K.

Figure 1 show XRD patterns of the CTO-based samples, which indicate that two main phases CTO and CCTO can be observed. The relative intensity of the characteristic peaks of the CCTO phase increases with the doped concentration of Cu. SEM images and related EDS analysis results (not shown here) also show that ceramics are composed of CTO and CCTO grain particles.

As shown in Fig. 2, with the addition of a little amount of Cu in the pure CTO ceramic, the dielectric constant increases obviously, especially for CTO-4 ceramic, and can be enhanced up to about 40 times higher than that of pure CTO ceramics at 1 kHz. Of interest to note, the dielectric losses still remain low (<3% at 1 kHz), and show weak frequency dependence for various CTO-based ceramic samples. Another intriguing feature of the Cu-doped CTO-based samples is the very weak dependence of the dielectric constants on temperature as shown in Fig. 3, and these samples show excellent temperature stability on the dielectric property over a wide-temperature range, which is of technological importance for applications in a reproducible electronic device.

In order to further understand the physical nature of the dielectric behavior in this CTO system mentioned above, we measured the frequency dependence of dielectric permittivity at various temperatures shown in Fig. 4(a). Generally, the

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Fig. 1. X-ray diffraction patterns of various Cu-doped CaTiO\_3 ceramic samples. CCTO,  $CaCu_3Ti_4O_{12}$ .

dielectric relaxation can be represented by a Debye relaxation relation as the following<sup>9</sup>:

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

$$\epsilon'(\omega) = \epsilon_{\infty} + \frac{\epsilon_{s} - \epsilon_{\infty}}{1 + (\omega \tau)^{2}}$$
(2)

where  $\varepsilon'$  is the real part of the dielectric constant,  $\varepsilon''$  is the imaginary part of dielectric constant,  $\omega$  is the angular frequency,  $\varepsilon_0$  and  $\varepsilon_{\infty}$  are static dielectric constant and permanent dielectric constant, respectively,  $\tau$  is the relaxation time.

Therefore, the relaxation time can be obtained from the fitted dielectric permittivity curves by Eq. (2). As shown in the inset of Fig. 4(b), the rapid decrease of  $\tau$  with increasing temperature can be observed, which is suggestive of an increasing dipole density and a faster polarization process. Actually, the variation of relaxation time  $\tau$  with 1/T can be fitted with the Arrhenius law:

$$\tau = \tau_0 \exp(E_{\rm a}/k_{\rm B}T) \tag{3}$$



Fig. 2. Frequency dependence of dielectric constant of various samples. CCTO, CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>.



**Fig. 3.** Temperature dependence of the dielectric constant and dielectric loss for various  $Ca_{1-x}Cu_x TiO_3$ -based ceramic samples.

where  $E_{\rm a}$  is the activation energy,  $\tau_0$  represents the preexponential factor, and  $k_{\rm B}$  is the Boltzmann constant.

As shown in Fig. 4(b), a good linear regression of  $\log \tau \text{ vs } 1/T$  can be obtained, which yields  $E_a = 0.101 \text{ eV}$ . Similarly, we can also get the other two samples' activation energy ( $E_a$ ) = 0.103 eV



**Fig. 4.** (a) Frequency dependence of for CTO-based ceramics measured at different temperatures. The solid lines represent the calculated values by a Debye model. (b) The log of the relaxation time  $\tau$  vs 1/T. The symbols are the experimental points and solid lines are the fitted line by Eq. (3). CTO,  $Ca_{1-x}Cu_xTiO_3$ .

and 0.100 eV for CTO-2 and CTO-4, respectively. As reported previously,  $^{10-12}$  in the perovskite oxides, the activation energy for the first ionization of oxygen vacancies is about 0.10 eV, near our fitted activation energy for the conduction in the measured temperature region, which indicates that the first ionization of the oxygen vacancies should be responsible for the conduction for the CCTO of this system.

It is generally believed that pure CTO is an incipient ferroelectric with orthorhombic (space group Pcmn) structure in a broad temperature range, and its dielectric constant is about 100 at room temperature. However, as shown in Fig. 3, the dielectric constant of the CCTO-CTO composite ceramics increases with CCTO concentration. For example, the dielectric constant of the CTO-4 ceramic (CCTO volume ratio  $\sim 30\%$ ) is about 40 times higher than that of the pure CTO ceramic. Why the addition of Cu can improve the dielectric properties greatly in these CTObased ceramics? Actually, a lot of previous experiments demonstrated that CCTO ceramic is electrically heterogeneous and consists of semiconducting or conducting grains with insulating grain boundaries.<sup>13,14</sup> Two plausible models were also established to explain CCTO semiconducting grain, one based on oxygen loss, and the other based on cation nonstoichiometry.<sup>15</sup> Formation of CCTO semiconducting grain is explained by Cu oxidation process. During the heating process,  $Cu^{2+}$  becomes unstable and reduced to  $Cu^{1+}$ , so  $Ti^{4+}$  substitute in Cu site to maintain oxidation state of this Cu site. Therefore, the ionic formula of CCTO can be expressed as  $Ca^{2+}(Cu_{1-3x}^{2+}Cu_{2x}^{1+})$  $Ti_x^{4+}$ <sub>3</sub> $Ti_4^{4+}O_{12}$  at high temperature. And during the cooling process, Cu<sup>1+</sup> is oxidized to Cu<sup>2+</sup>. In this time, electrons move into Ti 3*d* band and finally forms  $Ca^{2+}(Cu_{1-x}^{2+}Ti_{x}^{4+})_{3}$  $(Ti_{6x}^{3+}Ti_{4-6x}^{4+})O_{12}$  in low temperature. So Ti<sup>3+</sup> represents charge carier and exhibits semiconductive grain<sup>16,17</sup> (as shown in Fig. 6). Recently, Chung *et al.*<sup>18</sup> measured directly the local conduction behaviors in the CCTO ceramic by probe force microscopy, and found that CCTO grains have high conductivity at room temperature (~several hundreds  $\Omega \cdot cm$ ). Therefore, such a large increase in the dielectric constant should be caused by the existence of a large number of high-conductivity CCTO particles in parallel and in very close proximity, but blocked by the insulating CTO phase. Some researchers have described the dielectric behavior of the composite system with a conducting phase dispersed in an insulating matrix. The dielectric behavior in these composites can be well described by percolation theory  $^{19-21}$  by the following equation:

$$\varepsilon = \varepsilon_0 \left( \frac{f_{\rm c} - f_{\rm filler}}{f_{\rm c}} \right)^{-s} \tag{4}$$



**Fig. 5.** Dielectric constant of CTO-based ceramic samples as a function of volume fraction of CCTO with logarithmic plot of Eq. (1). The inset is the fitted line of  $\lg vs \lg(f_c - f_{CCTO})$ . CCTO, CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>.



Fig. 6. The XPS patterns of the C–CTO-3 sample. (a) Cu (b)Ti. CTO,  $Ca_{1-x}Cu_xTiO_3$ .

where  $\varepsilon$  is the dielectric constant of CTO–CCTO composites,  $\varepsilon_0$  is dielectric constant of CTO,  $f_{\text{filler}}$  is the volume fraction of the conductive CCTO particles,  $f_c$  is the percolation threshold, and s is a critical exponent.

As shown in Fig. 5, a best fit of Eq. (4) to our experimental data near the percolation threshold is performed. The results indicate that the experimental values of the dielectric constant are in good agreement with Eq. (4), with  $f_c \approx 0.27$  and  $s \approx 0.74$ . Such a large increase in the dielectric constant is caused by the existence of a large number of conducting CCTO particles in parallel and in very close proximity, but blocked by thin barriers of the dielectric CTO material. Normally, the interfacial polarization will contribute on the high-dielectric behavior for a material consisting of two phases (one is insulating and another is conductive).<sup>22,23</sup> Therefore, this high dielectric behavior in Cudoped CTO ceramics is also associated with interfacial polarization. As the conductive CCTO volume fraction is low, the CCTO particles are dispersed into the CTO ceramic matrix, and thus the dielectric behavior of theses CCTO-CTO composites is dominated by the CTO ceramic matrix. With increasing the CCTO volume fraction, the CCTO particles form large particle clusters and even continuous clusters, and thus percolation effects will be effective. As the composition becomes almost pure CCTO phase, the dielectric constant can reach 17550 at 1 kHz, which means that percolation effects will become the boundary-layer capacitor effects as  $f_c \rightarrow 1$ .

In conclusion, Cu-doped CaTiO<sub>3</sub>-based polycrystalline ceramics exhibit high dielectric permittivity and low-loss tangent behavior. Analysis of the ceramic microstructure and composition analyses indicate that the obtained ceramics are composed of two phases, i.e., CTO and CCTO. The dielectric constant is almost independent on temperature and frequency in a wide range. The observed high-dielectric behavior can be explained by the percolation effects and interfacial polarization. The results indicate that such CTO-based ceramics will provide potential application for microelectronic devices.

## References

<sup>1</sup>S. M. Spearing, "Materials Issues in Microelectromechanical Systems (MEMS)," *Acta. Mater.*, **48**, 179–96 (2000).

<sup>2</sup>J. Carreaud, C. Bogicevic, B. Dkhil, and J. M. Kiat, "Dielectric Evidences of Core-Shell-like Effects in Nanosized Relaxor PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub>," *Appl. Phys. Lett.*, **92**, 242902 (2008).

<sup>3</sup>B. G. Kim, S. M. Cho, T. Y. Kim, and H. M. Jang, "Giant Dielectric Permittivity Observed in Pb-Based Perovskite Ferroelectrics," *Phys. Rev. Lett.*, 86, 3404–6 (2001).
<sup>4</sup>N. Setter and R. Waser, "Electroceramic Materials," *Acta. Mater.*, 48, 151–78

<sup>4</sup>N. Setter and R. Waser, "Electroceramic Materials," *Acta. Mater.*, **48**, 151–78 (2000).

<sup>5</sup>A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, and S. M. Shapiro, "Giant Dielectric Constant Response in a Copper-Titanate," *Solid State Commun.*, **115**, 217–20 (2000).

<sup>6</sup>C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramirez, "Optical Response of High-Dielectric-Constant Perovskite-Related Oxide," *Science*, **293**, 673–6 (2001).

<sup>7</sup>J. Wu, C.-W. Nan, Y.-H. Lin, and Y. Deng, "Giant Dielectric Permittivity Observed in Li and Ti Doped NiO," *Phys. Rev. Lett.*, **89**, 217601 (2002).

<sup>8</sup>Y.-H Lin, M. Li, C.-W Nan, J. F. Li, J. Wu, and J. L. He, "Grain and Grain Boundary Effects in High-Permittivity Dielectric NiO-Based Ceramics," *Appl. Phys. Lett.*, **89**, 032907 (2006).

<sup>9</sup>J. R. Macdonald, *Impendance Spectroscopy*, pp. 191–205. John Wiley & Sons Inc., New York, 1987. <sup>10</sup>J. Daniels, K. H. Hardtl, D. Hennings, and R. Wernicke, "Defect Chemistry

<sup>10</sup>J. Daniels, K. H. Hardtl, D. Hennings, and R. Wernicke, "Defect Chemistry and Electrical Conductivity of Doped Barium Titanate Ceramics," *Philips Res. Rep.*, **31**, 487–543 (1976). <sup>11</sup>C. C. Wang and L. W. Zhang, "Oxygen-Vacancy-Related Dielectric Anomaly in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>: Post-Sintering Annealing Studies," *Phys. Rev. B*, 74, 024106 (2006).

<sup>12</sup>Z. Wang, X. M. Chen, L. Ni, Y. Y. Liu, and X. Q. Liu, "Dielectric Relaxations in Ba(Fe<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub> Giant Dielectric Constant Ceramics," *Appl. Phys. Lett.*, **90**, 102905 (2007).

<sup>13</sup>D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West, "CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>: One-Step Internal Barrier Layer Capacitor," *Appl. Phys. Lett.*, **80**, 2153–5 (2002). <sup>14</sup>Y.-H. Lin, J. Cai, M. Li, C.-W. Nan, and J. He, "Grain Boundary Behavior in

<sup>14</sup>Y.-H. Lin, J. Cai, M. Li, C.-W. Nan, and J. He, "Grain Boundary Behavior in Varistor-Capacitor TiO<sub>2</sub>-Rich CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> Ceramics," *J. Appl. Lett.*, **103**, 074111 (2008).

<sup>15</sup>M. Li, A. Feteira, D. C. Sinclair, and A. R. West, "Influence of Mn Doping on the Semiconducting Properties of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> Ceramics," *Appl. Phys. Lett.*, **88**, 232903 (2006). <sup>16</sup>J. Li, M. A. Subramanian, H. D. Rosenfeld, C. Y. Jones, B. H. Toby, and A.

<sup>16</sup>J. Li, M. A. Subramanian, H. D. Rosenfeld, C. Y. Jones, B. H. Toby, and A. W. Sleight, "Clues to the Giant Dielectric Constant of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> in the Defect Structure of SrCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>," *Chem. Mater.*, **25** [16] 5223–5 (2004).

<sup>17</sup>J. Li, A. W. Sleight, and M. A. Subramanian, "Evidence for Internal Resistive Barriers in a Crystal of the Giant Dielectric Constant Material: CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>," *Solid State Commun.*, **135**, 260–2 (2005).

<sup>18</sup>S.-Y. Chung, I.-D. Kim, and S.-J. L. Kang, "Strong Nonlinear Current–Voltage Behaviour in Perovskite-Derivative Calcium Copper Titanate," *Nat. Mater.*, **3**, 774–8 (2004).

<sup>19</sup>C.-W. Nan, "Physics of Inorganic Inhomogeneous Materials," *Prog. Mater. Sci.*, **37**, 1–116 (1993).

<sup>20</sup>D. M. Grannan, J. C. Garland, and D. B. Tanner, "Critical Behavior of the Dielectric Constant of a Random Composite near the Percolation Threshold," *Phys. Rev. lett.*, **46**, 375–8 (1981).
<sup>21</sup>C. Pecharroman, F. Esteban-Bategon, and J. S. Moya, "New Percolative

<sup>21</sup>C. Pecharroman, F. Esteban-Bategon, and J. S. Moya, "New Percolative BaTiO<sub>3</sub>-Ni Composites with a High and Frequency-Independent Dielectric Constant ( $\varepsilon_r = 80000$ )," *Adv. Mater.*, **13**, 1541–4 (2001).

<sup>22</sup>V. V. Novikovl and K. W. Wojciechowski, "Frequency Dependences of Dielectric Properties of Metal-Insulator Composites," *Phys. Solid State*, **44**, 2055–62 (2002).

(2002). <sup>23</sup>C. Wang, Q. F. Fang, and Z. G. Zhu, "Enhanced Dielectric Properties of Low-Temperature Sintered SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>/Ag Composites," *Appl. Phys. Lett.*, **80**, 3578–80 (2002). □