

# Effects of $\text{ZrO}_2$ additions on the dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

Eric A. Patterson

Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50010

Seunghwa Kwon, Chien-Chih Huang, and David P. Cann<sup>a)</sup>

Department of Mechanical Engineering, Oregon State University, Corvallis, Oregon 97331

(Received 20 June 2005; accepted 26 September 2005; published online 28 October 2005)

The dielectric spectra of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is characterized by a large permittivity ( $\epsilon_r > 10\,000$ ) with only a weak dependence on temperature over the temperature range 200–400 K. In this work, doping with 0.1–1.0 wt %  $\text{ZrO}_2$  has been shown to dramatically reduce the dielectric loss. At 0.5 wt %  $\text{ZrO}_2$ ,  $\tan \delta$  remains below 0.05 over the frequency range 50 Hz–30 kHz and is just 0.065 at 100 kHz. While there is some diminution of the permittivity ( $\epsilon_r \approx 5000$  at 10 kHz) Zr-doped ceramics, exhibited very little bias dependence ( $\Delta C/C_0 < 1.0\%$  up to 40 V). In summary, results suggest that  $\text{ZrO}_2$  doping is an effective method for maintaining a high permittivity and low loss over a broad range in temperature, bias, and frequency. © 2005 American Institute of Physics. [DOI: 10.1063/1.2126142]

The exceptionally high room temperature permittivity of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ( $\epsilon_r \approx 12\,000$ ) was discovered in 2000 by Subramanian *et al.*<sup>1</sup> This has been confirmed by others in single crystals and epitaxial thin films as well as in polycrystalline ceramics.<sup>2–6</sup> Another interesting feature of the dielectric response is the temperature independent permittivity in the vicinity of room temperature. At temperatures below 150 K and at frequencies above 100 kHz the permittivity drops to levels more typical of an ionocovalent solid.<sup>7</sup> The polarization mechanism that yields the high permittivity in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is not definitively known, but the magnitude and frequency dependence of the permittivity is consistent with a space charge polarization mechanism.

The crystal structure of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is a pseudoperovskite with a cubic unit cell with a lattice parameter of 7.391 Å. The Ca and Cu cations occupy crystallographically distinct A sites with a coordination of 12 and 4, respectively. The Ti cation is in octahedral coordination, with a heavily distorted Ti–O–Ti bond angle of 141°.

This work will investigate the effects of cation doping on  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ceramics with the aim of improving its dielectric loss characteristics. There are many examples in the literature illustrating the effects of dopants in perovskite-based dielectrics. As one example, it is commonly observed that the addition of 0.5–2 mol %  $\text{MnO}_2$  to  $\text{BaTiO}_3$  results in a dramatic reduction in the dielectric loss.<sup>8</sup> Many other examples exist in the literature that demonstrate that doping is an effective means of improving the dielectric properties of perovskite materials.<sup>9–12</sup>

The effects of doping on dielectric properties for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  have not been widely investigated. Doping with 2% Mn was found to decrease the permittivity from  $\epsilon_r \sim 10\,000$  down to little more than 100 over the temperature range of 4.2–300 K.<sup>13</sup> In prior work, the effects of an aliovalent dopant ( $\text{Nb}^{5+}$ ) directly substituting for Ti was explored with two different compositions with the chemical formulas  $\text{CaCu}_3\text{Ti}_{3.992}\text{Nb}_{0.008}\text{O}_{12}$  and  $\text{CaCu}_3\text{Ti}_{3.984}\text{Nb}_{0.016}\text{O}_{12}$ .<sup>14</sup> At the higher concentration of Nb, the room

temperature dielectric loss values were decreased by an order of magnitude at 10 kHz to 0.05. However, this was accompanied by a decrease in room temperature permittivity. In this work, the effects of the isovalent dopant  $\text{ZrO}_2$  on the dielectric properties of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  were investigated.

Polycrystalline samples of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  were synthesized using conventional solid state ceramic processing techniques. Powders of  $\text{CaCO}_3$ , CuO,  $\text{TiO}_2$ , and  $\text{Nb}_2\text{O}_5$  were tested for loss on ignition and the batch composition was compensated accordingly. Powders of  $\text{ZrO}_2$  were added to stoichiometric  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  at the calcination stage in concentrations of 0.1, 0.5, and 1.0 wt %. Each batch was milled in ethanol using a vibratory mill and then calcined in air at 1000 °C for 24 h. After vibratory milling a second time, approximately 5 wt % organic binder was added to the calcined powders and the 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 1 h. X-ray diffraction

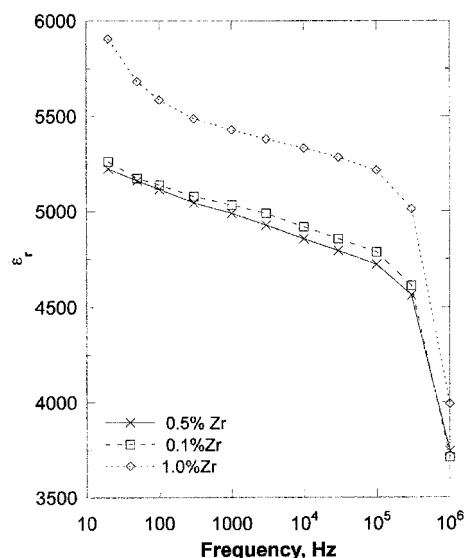


FIG. 1. Permittivity vs frequency for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  with 0.1, 0.5, and 1.0% Zr.

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: cann@engr.orst.edu

TABLE I. Dielectric Properties of  $\text{ZrO}_2$ -doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ceramics.

Frequency (kHz)	Permittivity				Loss tangent			
	Undoped	0.1% Zr	0.5% Zr	1.0% Zr	Undoped	0.1% Zr	0.5% Zr	1.0% Zr
0.1	10 900	5140	5120	5590	0.16	0.031	0.025	0.065
1	9550	5030	4990	5430	0.084	0.016	0.018	0.019
10	8660	4920	4860	5330	0.060	0.022	0.023	0.018
100	8150	4790	4720	5220	0.060	0.065	0.063	0.065

(XRD) was utilized to monitor phase evolution and changes in lattice parameter. The density of the pellets was determined using the Archimedes method. The samples were sputtered with gold electrodes and the dielectric properties were measured with an HP-4284A LCR meter utilizing an environmental chamber for the temperature measurements. Impedance spectra were obtained on ceramic specimens utilizing an HP 4194A impedance analyzer. Finally, microstructural analysis was performed on thermally etched cross sections of the sintered ceramics.

The room temperature dielectric properties of Zr-doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  are shown in Table I. In Fig. 1, the permittivity versus frequency is plotted for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  with 0.1, 0.5, and 1.0 wt %  $\text{ZrO}_2$  added. The permittivity of the samples was reduced by a factor of 2 ( $\epsilon_r \sim 4900$ –5300) compared to undoped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ( $\epsilon_r \sim 10\,000$ ). In Fig. 2, the loss tangent is plotted against frequency for the three different doping levels of  $\text{ZrO}_2$ . It is shown that the lowest value of dielectric loss obtained was 0.0158 for 0.1 wt %  $\text{ZrO}_2$  at 1 kHz. However, the 0.5%  $\text{ZrO}_2$ -doped composition exhibited dielectric losses below 0.05 over a wide frequency range from 50 Hz to 30 kHz.

In Fig. 3, the data for the capacitance as a function of voltage for 0.5 wt %  $\text{ZrO}_2$ -doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is shown. The bias dependence was negligible with less than 0.8% change in capacitance for each of the three measurement frequencies. In  $\text{SrTiO}_3$ , a prototypical barrier layer capacitor material, the effects of barrier lowering causes the large per-

mittivity value to exhibit a strong bias dependence. From the data in Fig. 3, it can be inferred that the potential drop across each barrier was insignificantly small. More testing at high voltages is necessary to determine whether these properties extend to high electric fields.

The temperature dependence of the permittivity and loss tangent for 0.5 wt %  $\text{ZrO}_2$ -doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is plotted in Fig. 4. Above the dielectric relaxation at  $T \sim 150$  K, the permittivity was nearly temperature independent up to 400 K. Over the temperature range of  $-30$ – $85^\circ\text{C}$  the change in permittivity is less than  $\pm 3\%$ . While the  $\text{ZrO}_2$  doping effectively reduced the dielectric loss over a wide range in temperature and frequency, it also lowered the room temperature permittivity. The doping also significantly lowered the rise in the loss tangent at higher temperatures, for both 10 and 100 kHz. This is often indicative of an enhanced resistivity.

The XRD data confirmed a modest decrease in lattice parameter with the addition of  $\text{ZrO}_2$  up to a concentration of 0.5 wt %  $\text{ZrO}_2$  (with a  $\sim 0.2\%$  decrease in  $a_0$ ). Higher concentrations of  $\text{ZrO}_2$  did not result in any noticeable shift in lattice parameter, suggesting that the added  $\text{ZrO}_2$  is most likely present in the microstructure either in the grain boundaries or as a second phase. While no second phase was observed in the XRD data, this is not surprising given the typical detection limits of the technique. Another important point is that the grain size remained at a constant value of approximately  $5\,\mu\text{m}$  independent of the  $\text{ZrO}_2$  concentration. Thus the change in the dielectric properties of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is apparently not correlated with any significant change in the

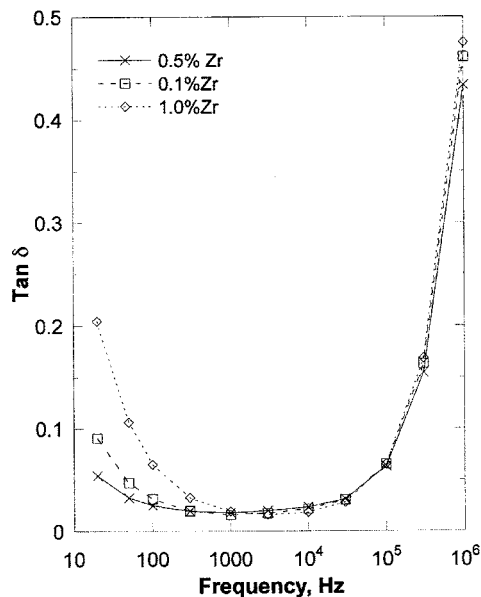


FIG. 2. Dielectric loss of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  for 0.1, 0.5, and 1.0% Zr doping levels.

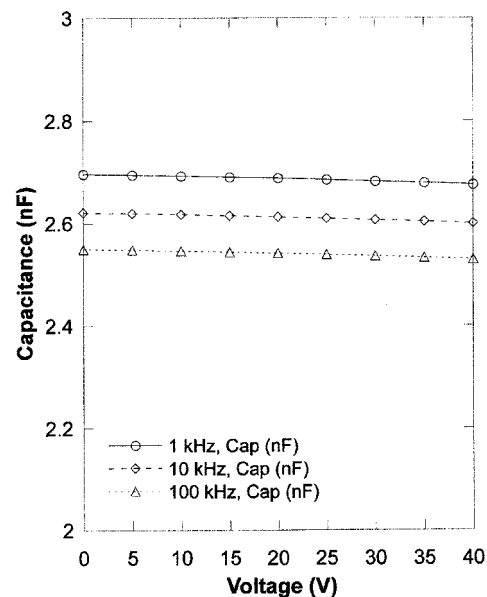


FIG. 3. Measurement of the capacitance as a function of applied V for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  with 0.5% Zr added.

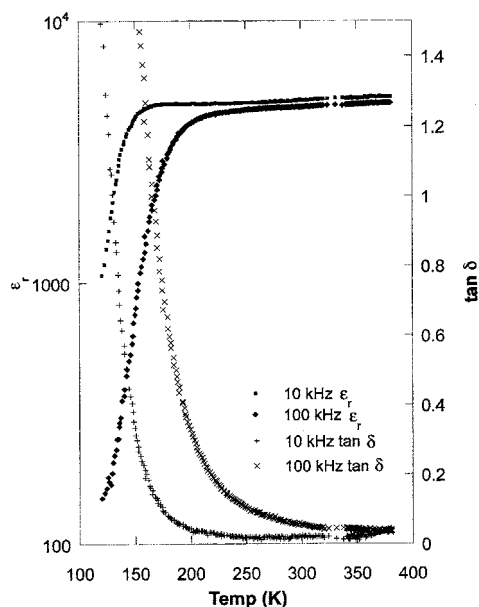


FIG. 4. Dielectric constant and  $\tan \delta$  for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  with 0.5% Zr added at 10 and 100 kHz.

crystal structure or microstructure. This suggests that it is most likely that the  $\text{ZrO}_2$  doping is modifying the defect equilibrium. The dramatic decrease in the low frequency loss could be indicative of an increase in the grain boundary resistivity. The presence of  $\text{ZrO}_2$  in the grain boundaries could be responsible for this effect. To further explore this possibility, room temperature impedance spectroscopy measurements were conducted on undoped and 0.5 wt %  $\text{ZrO}_2$ -doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ceramics. The results indicated an order of magnitude increase in the static resistivity in the doped

samples compared to the undoped samples. This finding is consistent with an enhanced grain boundary resistivity due to the presence of  $\text{ZrO}_2$  at the grain boundaries.

While the space charge polarization mechanism inhibits application of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  for high frequency applications, the material exhibits excellent dielectric properties below 100 kHz. With 0.5 wt %  $\text{ZrO}_2$  added,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  exhibits a permittivity in excess of 4900 and a dielectric loss below 0.05 over the frequency range 50 Hz–30 kHz. Given that these dielectric properties are largely independent of temperature and bias, this material is a promising candidate for high capacitance density applications.

<sup>1</sup>M. A. Subramanian, D. Li, N. Duan, B. A. Reisner, and A. W. Sleight, *J. Solid State Chem.* **151**, 323 (2000).

<sup>2</sup>A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, and S. M. Shapiro, *Solid State Commun.* **115**, 217 (2000).

<sup>3</sup>C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramirez, *Science* **293**, 673 (2001).

<sup>4</sup>D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West, *Appl. Phys. Lett.* **80**, 2153 (2002).

<sup>5</sup>M. A. Subramanian and A. W. Sleight, *Solid State Sci.* **4**, 347 (2002).

<sup>6</sup>L. He, J. B. Neaton, M. H. Cohen, D. Vanderbilt, and C. C. Homes, *Phys. Rev. B* **65**, 214112 (2002).

<sup>7</sup>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).

<sup>8</sup>L. M. Arunachalam, D. Chakravorty, and E. C. Subbarao, *Bull. Mater. Sci.* **9**, 165 (1987).

<sup>9</sup>G. Chiodelli, V. Massarotti, D. Capsoni, M. Bini, C. B. Azzoni, M. C. Mozzati, and P. Lupotto, *Solid State Commun.* **132**, 241 (2004).

<sup>10</sup>Y. Li, X. Yao, and L. Zhang, *Ceram. Int.* **30**, 1325 (2004).

<sup>11</sup>W. Li, J. Qi, Y. Wang, L. Li, and Z. Gui, *Mater. Lett.* **57**, 1 (2002).

<sup>12</sup>D. D. Gulwade, S. M. Bobade, A. R. Kulkarni, and P. Gopalan, *J. Appl. Phys.* **97**, 074106 (2005).

<sup>13</sup>W. Kobayashi and I. Terasaki, *Physica B* **329–333**, 771 (2003).

<sup>14</sup>D. P. Cann, S. Aygün, X. Tan, and J. P. Maria, *J. Electroceram.* (in press).