Rapid Communication

An anion substitution route to low loss colossal dielectric $CaCu_3Ti_4O_{12}$

Andrew E. Smith [a], T.G. Calvarese [b], A.W. Sleight [a], M.A. Subramanian [a,*]

[a] *Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, Oregon 97331-4003, USA*
[b] *DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0328, USA*

A R T I C L E   I N F O

A B S T R A C T

An anion substitution route was utilized for lowering the dielectric loss in $CaCu_3Ti_4O_{12}$ (CCTO) by partial replacement of oxygen by fluorine. This substitution reduced the dielectric loss, and retained a high dielectric constant that was essentially temperature independent from 25 to 200 °C. In particular, $CaCu_3Ti_4O_{11.7}F_{0.3}$ exhibited a giant dielectric constant over 6000 and low dielectric loss below 0.075 at 100 kHz within a temperature range of 25–200 °C. Fluorine analysis confirmed the presence of fluorine in all samples measured.

1. Introduction

Perovskite type oxides (ABO_3) have long been an important focus for development of new materials with high dielectric constants. With the discovery of the colossal dielectric constant in the body-centered cubic pseudo-perovskite $CaCu_3Ti_4O_{12}$ (CCTO), Fig. 1, there has been much interest in the source of such an unusually high dielectric constant, $\kappa = \sim12,000$, over a broad range of temperatures (300–600 K) without a phase transition. Unfortunately, the CCTO loss tangent of ~0.15 is high for present ceramic application requirements [1]. The best known high-κ dielectric material is barium titanate, $BaTiO_3$, which has a dielectric constant and loss favorable for application, $\kappa = \sim1500$ and $\tan\delta = \sim0.01$. There are several reports of cation substitution in CCTO. Substitution has included Co, Fe, Ni, Zr, Sc and Nb on the Ti site, and La on the Ca site [2–6]. Some reports indicate success in lowering the dielectric loss. For example, a loss of 0.015 was reported for $Ca_{0.8}La_{0.2}Cu_3Ti_4O_{12}$; however, the dielectric constant was also suppressed to 3000 [6]. Some compounds with the CCTO structure show a low loss tangent but not a giant dielectric constant [7]. In this communication, we present a novel route for decreasing the $\tan\delta$ of CCTO by anion substitution.

2. Experimental

The samples in this investigation were prepared by conventional solid state synthesis. Reactants were $CaCO_3$ (99%+,

Spectrum), CuO (99.9%+, Aldrich), CuF_2 (99.5%+, Alfa Aesar), and TiO_2 (99.9%+, Aldrich). Appropriate quantities were thoroughly mixed by grinding in an agate mortar. The mixed powder was first calcined in air at 900 °C for about 12 h, and then reground, pressed into pellets, and sintered in air at 1025 °C for 12 h. In both heating cycles, the ramping and cooling rates were 300 °C/h. X-ray powder diffraction (XRD) patterns were recorded with a Rigaku MiniFlex II diffractometer ($CuK\alpha$ radiation) in the range of 10–60° 2θ. In order to analyze the F content of the sample, the fluorine was first leached from the sample by means of sodium hydroxide fusion in a platinum crucible. This process was carried out in a closed Inconel vessel to avoid the fluorine loss. The percentage of fluorine was determined using a fluoride ion selective electrode. A sample of K_2NbO_3F was used as a reference and to check the accuracy of the measurements. Accuracy depends on F content and size of sample used. For dielectric constant and loss tangent measurements pellets of samples were polished, electroded with silver paint and then dried for 3–5 h at 100 °C. Measurements on the pellets utilized an HP-4275A LCR meter in the temperature range of 25–300 °C at a frequency of 100 kHz.

3. Results and discussion

Analysis of powder XRD patterns indicated that the substitution of fluorine for oxygen was successful for doping levels of $x = 0.05$–1.3. Attempted doping levels above $x = 1.3$ resulted in secondary phases, mainly CaF_2 and TiO_2. Fig. 2 shows XRD patterns for pure CCTO and doping levels of $x = 0.2$, 0.4, 0.6, and 0.8. The shift of peaks to lower 2θ values with increasing F content indicates an increase in the lattice constant of the cubic phase

* Corresponding author.
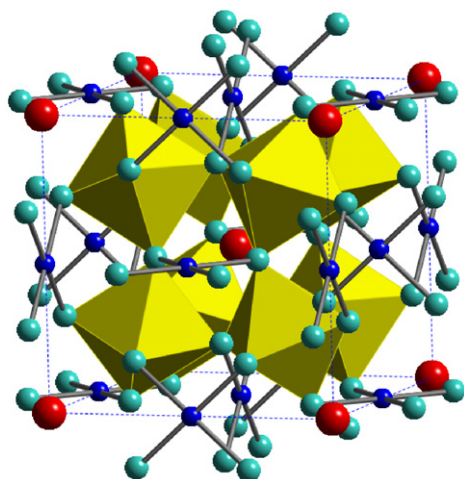 *E-mail address:* mas.subramanian@oregonstate.edu (M.A. Subramanian).

Fig. 1. Structure of the cubic pseudo-perovskite (Im3) $CaCu_3Ti_4O_{12}$ with TiO_6 octahedra, Cu in square planar coordination (small black spheres) about O (small light grey spheres) and Ca at the origin and cube center (medium size grey spheres).
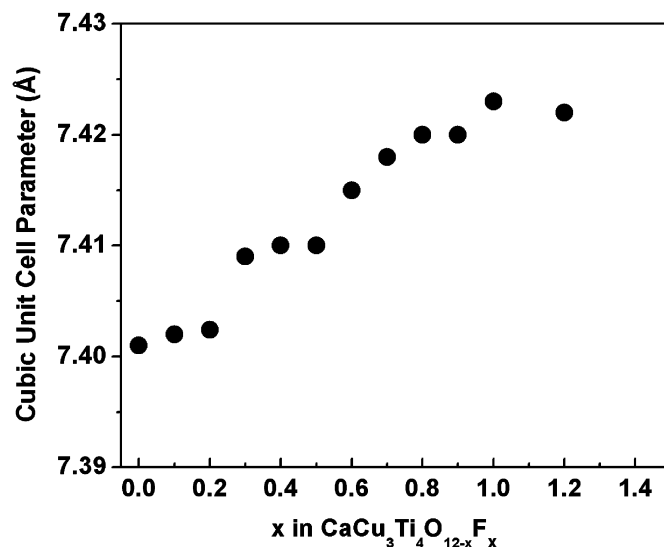

Fig. 3. Lattice parameter expansion as a result of fluorine substitution for oxygen, and the valence reduction of $Cu^{2+} \rightarrow Cu^{1+}$.
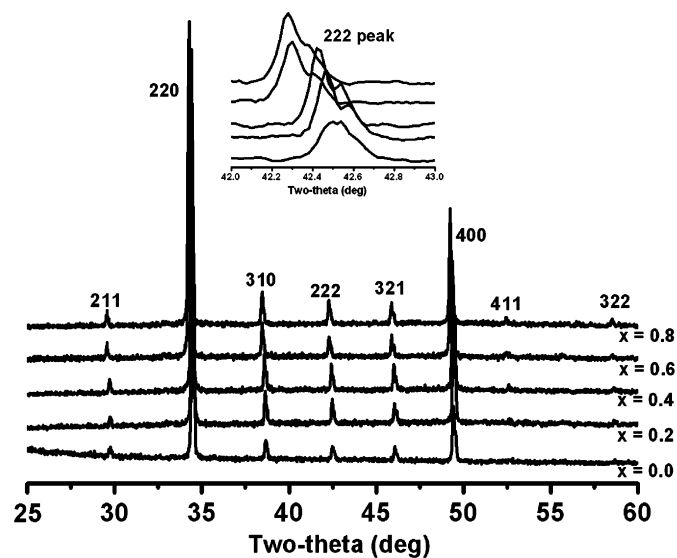

Fig. 2. Room temperature XRD powder patterns for $CaCu_3Ti_4O_{12-x}F_x$ samples where $x = 0$–0.8. The inset in the upper left corner is an expanded view of the shift in (222) peak around $2\theta = 42.5°$. Shoulders in the peaks are due to $CuK\alpha_2$ radiation.

Table 1
Fluorine content of selected samples.

Sample	Calc. (wt%)	Meas. (wt%)
$CaCu_3Ti_4O_{11.6}F_{0.4}$	1.23	1.1 ± 0.1
$CaCu_3Ti_4O_{11.4}F_{0.6}$	1.85	1.7 ± 0.2
$CaCu_3Ti_4O_{11.2}F_{0.8}$	2.46	2.3 ± 0.2
$CaCu_3Ti_4O_{11}F$	3.08	3.1 ± 0.1
$CaCu_3Ti_4O_{10.8}F_{1.2}$	3.67	3.6 ± 0.1
$K_2NbO_3F^*$	7.99	8.1 ± 0.1

(Fig. 2, inset). With the addition of F, increased grain (crystallite) size could be expected. This would account for the initial sharpening of the peaks upon F addition. The broadening that occurs with further F addition is most likely due to inhomogeneity
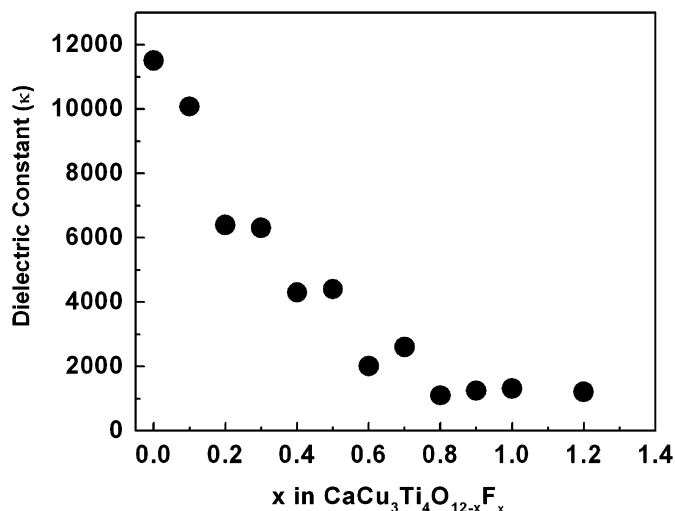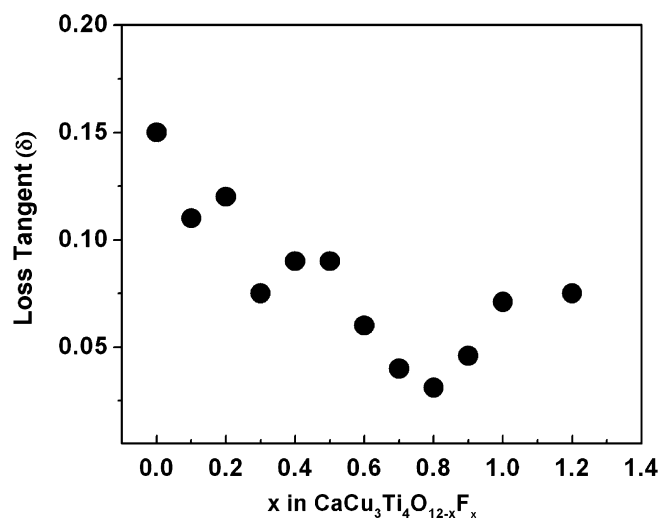

Fig. 4. Result of fluorine substitution on dielectric constant (K) and loss tangent ($\tan \delta$) for pure and F-doped $CaCu_3Ti_4O_{12-x}F_x$ where $x = 0$–1.2 measured at 25 °C at a frequency of 100 kHz.
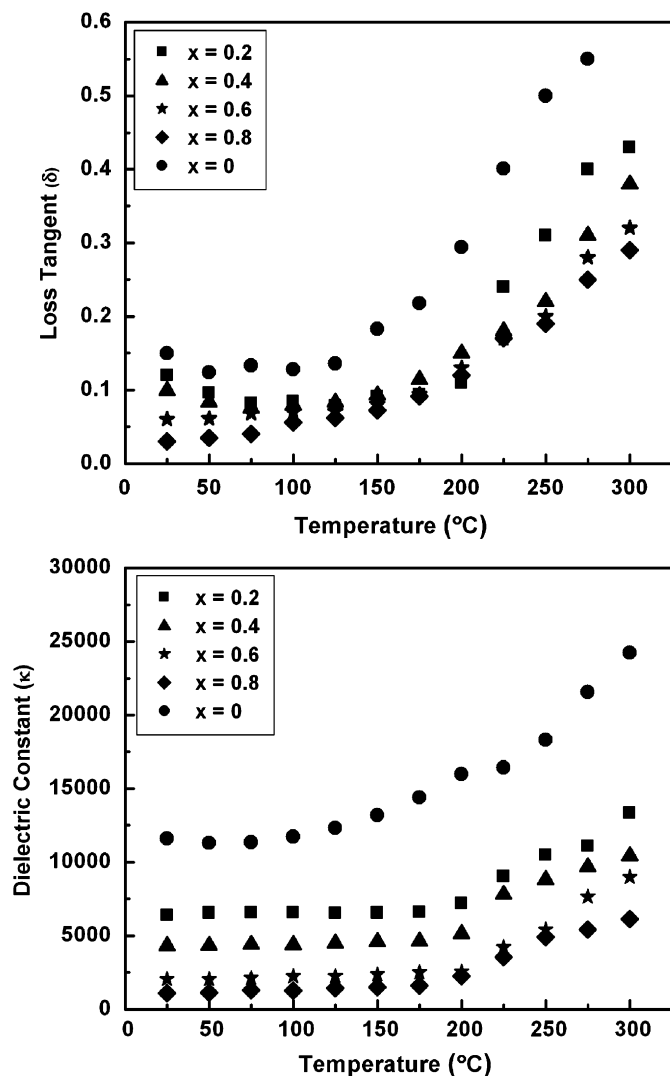
Fig. 5. Temperature dependence of the dielectric constant (K) and loss tangent (tan δ) for pure and F-doped $CaCu_3Ti_4O_{12-x}F_x$ at 100 kHz.

$\kappa = 10{,}080$ to 4404, and tan δ is decreased from 0.11 to 0.075. Taking into consideration both constant and loss, an optimal fluorine content is $x = 0.3$ where the dielectric constant is $\kappa = 6310$ and tan δ is 0.075.

The temperature dependence of the dielectric constant and loss tangent relationships for selected fluorine doped levels in $CaCu_3Ti_4O_{12-x}F_x$ is presented in Fig. 5. The dielectric constants remain essentially temperature independent for the various doping levels from 25 to 175 °C. This is an improvement over pure CCTO at 100 kHz where the dielectric constant increases steadily with tan δ throughout the full temperature range.

There is a consensus that the giant dielectric constant in CCTO is due to an internal barrier layer mechanism (IBLM). This mechanism normally applies to materials with conducting grains and insulating grain boundaries. However, in CCTO it has been shown that the giant dielectric constant is obtained within grains [1,6,10,11]. Thus, there must be insulating planar defects in these grains. Despite much effort, there is still no good definition of these defects. Dopants frequently concentrate at lattice defects. The F, thus, may be concentrating on the important planar defects in CCTO. This could increase the electrical resistivity of the internal barrier and decrease the dielectric loss. Movement of electrons from cation to cation through F is much more difficult than through O.

4. Conclusions

It has been shown in this study that anion substitution by fluorine in $CaCu_3Ti_4O_{12-x}F_x$ was successful, and that single phase samples were prepared for fluorine doping levels of $x < 1.3$. A lower dielectric loss tangent, tan $\delta = 0.075$, and a giant dielectric constant, $\kappa = 6310$, was obtained for a fluorine doped level of $x = 0.3$.

of the F (and Cu^{1+}) distribution, which apparently causes lattice strain [8]. The ionic radius difference between fluorine and oxygen is negligible [9]. The observed increase in the lattice constant (Fig. 3) is attributed to the conversion of Cu^{2+} to Cu^{1+} as F^{1-} is substituted for O^{2-}. Thus, the formula for these phases is represented as $CaCu^{2+}_{3-x}Cu^{1+}_xTi_4O^{2-}_{12-x}F^{1-}_x$. The F substitution was verified by chemical analysis (Table 1). The F content was always as expected within the error of the analysis. Any F loss that occurs during the calcination in air is negligible.

Fig. 4 shows the dielectric constant and the dielectric loss as a function of fluorine content in CCTO at 25 °C and 100 kHz. As fluorine doping increases, the dielectric constant and loss tangent decrease. As the fluorine doping increases from $x = 0.1$ to 0.5, a large dielectric constant is still observed but is decreased from

References

[1] M.A. Subramanian, D. Li, N. Duan, B.A. Reisner, A.W. Sleight, J. Solid State Chem. Rapid Commun. 151 (2000) 323–325.
[2] G. Chiodelli, V. Massarotti, D. Capsoni, M. Bini, C.B. Azzoni, M.C. Mozzati, P. Lupotto, J. Solid State Commun. 132 (2004) 241–246.
[3] O. Parkash, D. Kumar, A. Goyal, A. Agrawal, A. Mukherjee, S. Singh, P. Singh, J. Phys. D Appl. Phys. 41 (2008) 1–8.
[4] S.Y. Chung, S.I. Lee, J.H. Choi, S.Y. Choi, Appl. Phys. Lett. 89 (2006) 1–3.
[5] R.K. Grubbs, E.L. Venturini, P.G. Clem, J.J. Richardson, B.A. Tuttle, G.A. Samara, Phys. Rev. B 72 (2005) 1–11.
[6] L. Feng, X. Tang, Y. Yan, X. Chen, Z. Jiao, G. Cao, Phys. Status Solidi Rapid Res. Lett. 203 (4) (2006) 22–24.
[7] M.A. Subramanian, A.W. Sleight, J. Solid State Sci. 4 (2002) 347–351.
[8] P. Karen, P.M. Woodward, J. Solid State Chem. 141 (1998) 78–88.
[9] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751–767.
[10] S.W. Choi, S.H. Hong, Y.M. Kim, J. Am. Ceram. Soc. 90 (2007) 4009–4011.
[11] T.B. Adams, D.C. Sinclair, A.R. West, Adv. Mater. 14 (18) (2002) 1321–1323.