A novel route to lower the dielectric loss in CaCu$_3$Ti$_4$O$_{12}$ ceramics

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Based upon a widely-accepted internal-barrier-layer-capacitance (IBLC) model, the dielectric loss in the giant-dielectric-constant CaCu$_3$Ti$_4$O$_{12}$ (CCTO) material is expected to decrease as the conductivity of the CCTO grains/subgrains increases. In this letter, we report that this idea was successfully realized through the La-for-Ca substitution in the CCTO ceramics. The impedance spectroscopy analysis gives the evidence.

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The perovskite-like material CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has attracted much attention during the last few years due to its extraordinary dielectric properties. It exhibits very high value of low-frequency dielectric constant ($\varepsilon_r \sim 10,000$) over a wide temperature range (100 - 500 K), while the crystal structure remains cubic and centric above 35 K.$^1, 2$ Furthermore, the dielectric constant is almost temperature independent from 100 K to 400 K, which is desirable for many micro-electronic applications. However, the dissipation factor of the material is relatively too high. For the ceramic$^1$ and thin-film$^3$ samples at room temperature, the typical value of tan$\delta$ is about 0.1 at 1 kHz.

As we know, the dielectric loss is closely related with the mechanism of the dielectric response. Subramanian et al.$^4$ initially proposed that the dielectric constant of CCTO might be enhanced by a barrier layer mechanism, assuming that there was a naturally-formed inhomogeneous microstructure such as twin boundaries. Later, Sinclair et al.$^5$ confirmed this idea by the impedance spectroscopy measurement which demonstrated that the CCTO ceramics were electrically heterogeneous and consisted of semiconducting grains with insulating grain boundaries. Very recently, by using micro-contact current-voltage measurements Chung et al.$^6$ found a strong non-linear current-voltage behaviour in the undoped CCTO ceramics, suggesting an electrostatic barrier at the grain boundaries. Nevertheless, the insulating barrier should not be only the grain boundaries but also some kinds of extended planar defects inside the grains, because exceptionally high $\varepsilon_r$ was observed in CCTO crystals.$^6, 7$ On the whole, the IBLC model with the Maxwell-Wagner relaxation is widely accepted$^3, 4, 10, 11$ as the primary mechanism for the appearance of giant dielectric constant in CCTO and its related compounds.

Based on the IBLC model, the dielectric loss mainly originates from the conductivity of the CCTO conducting crystalline grains/subgrains as well as that of the insulating barriers. The conductance of the barriers leads to the leakage loss. On the other hand, the alternate current within the conducting region also produces a dissipation as the Joule heat. Unlike the leakage loss that can be suppressed by increasing the resistance of the barriers, the dissipation loss from the conducting regions is expected to decrease as the conductance of the CCTO grains/subgrains increases. Therefore, we performed a partial substitution of divalent Ca$^{2+}$ by the trivalent La$^{3+}$ in order to increase the conductivity of the grains/subgrains. Our result demonstrates that the dielectric loss of the CCTO ceramics was remarkably lowered by the La substitution, while the giant dielectric property still remains.

Ceramic samples of Ca$_{1-x}$La$_x$Cu$_3$Ti$_4$O$_{12}$ ($x = 0, 0.1, 0.2, 0.3$ and $0.4$) were prepared by a conventional solid-state reaction. The starting materials were high purity (99.99%) CaCO$_3$, CuO, La$_2$O$_3$ and TiO$_2$. They were weighed according to the stoichiometric ratios and mixed thoroughly in an agate mortar. The mixture was calcined at 1223 K for 12 h in air. Then the calcined powder was reground and pressed into disks of 10 mm in diameter and 2 mm in thickness. The disks were sintered in air at about 1333 K for 24 h and furnace-cooled to room temperature. The sintered temperature varied a little for different samples to obtain similar density and grain size. The scanning electron microscopy images (not shown here) for the samples’ cross sections indicated that the samples had the similar morphology and grain size (about 5 $\mu$m). This observation ensures the comparability for the sample’s dielectric properties.

The dielectric property was measured using an Agilent 4284A precision LCR meter. The capacitance $C_p$ and the dissipation factor $D$ (i.e., tan$\delta$) of the parallel-plate capacitor made of the disk sample were directly measured at an ac voltage of 1 V in the frequency range of 20 to $10^6$ Hz and the temperature range of 80 - 300 K. The $\varepsilon_r$ value was easily obtained from $C_p$ and the sample’s size (the thickness and the area of the electrodes). The complex impedance was obtained by the equation $Z^* = 1/(i\omega C^*)$, where $C^* = C_p - i\Delta C_p$ and $\omega = 2\pi f$.

Figure 1 shows the powder x-ray diffraction (XRD) results for the samples of Ca$_{1-x}$La$_x$Cu$_3$Ti$_4$O$_{12}$. Except for $x = 0.4$, all the XRD peaks of each sample can be well indexed using a body-centered cubic lattice with $a \sim 0.74$
FIG. 1: Powder XRD results of Ca$_{1-x}$La$_x$Cu$_3$Ti$_4$O$_{12}$ ceramic samples. The top right inset is an expanded view of the XRD patterns around 2θ = 61.4°, showing the shift of the (422) peaks. The top left one shows the lattice constant as a function of $x$.

nm. The lattice constant, obtained by a least-squares fit with the consideration of zero-shift, increases monotonically with increasing $x$ (see the inset), confirming that La does enter the lattice. When $x \geq 0.3$, the lattice constant tends to saturate, suggesting the La-for-Ca solubility limit at $x \sim 0.3$. This result is in agreement with the observation that the sample of $x = 0.4$ contains small amount of secondary phase marked by an asterisk. The increase of the lattice constant is probably due to the fact that La$^{3+}$ has larger ionic radius than Ca$^{2+}$ does. Besides, the possible formation of larger Ti$^{3+}$ (compared with Ti$^{4+}$) due to the substitution might also play a role for expanding the lattice. One notes that the x-ray photoemission spectroscopy indicated the existence of Ti$^{3+}$ in CCTO.[12]

Figure 2 shows the temperature and frequency dependences of the dielectric constant and the loss tangent for the Ca$_{1-x}$La$_x$Cu$_3$Ti$_4$O$_{12}$ monophasic ceramics. As can be seen, all the samples show giant dielectric constant of $\varepsilon_r \geq 3000$ in broad temperature and frequency ranges though the dielectric constant decreases to some extent with the La substitution. In addition, the La-substituted samples have the temperature-independent $\varepsilon_r$ down to lower temperature and up to higher frequency. The striking effect of the La substitution comes from the decrease of tanδ. As can be seen in figure 2(b), the tanδ values in the whole measured temperature range are decreased by the La substitution. At the low-frequency substituting level up to $x = 0.1$, this effect is rather remarkable. While from $x = 0.1$ to $x = 0.2$, the magnitude of the decrease becomes smaller. And for samples of $x = 0.2$ and 0.3, the dielectric loss is nearly identical. Compared back with the parent CCTO sample, the dissipation factor of the $x = 0.2$ sample is decreased by 3 to 5 times. The frequency dependence of tanδ shown in figure 2(d) indicates that the most prominent decrease of tanδ occurs at the intermediate frequencies. For example, the tanδ value at 1 kHz is decreased from $\sim 0.1$ to $\sim 0.015$ as the La substitutes for Ca at $x = 0.2$.

To understand the La substitution effect on the dielectric loss, let us first derive the expression of tanδ under the IBLC mechanism. Considered the case of single barrier, for simplicity, the CCTO system can be modelled by an equivalent circuit consisting of two parallel $RC$ elements connected in series. The two parallel $RC$ units represent semiconducting regions ($R_{sc}$,$C_{sc}$) and insulating barriers ($R_{ins}$,$C_{ins}$), respectively. One may easily write out the expression of the total complex impedance as,

$$Z^* = \frac{R_{sc}}{1 + i\omega R_{sc} C_{sc}} + \frac{R_{ins}}{1 + i\omega R_{ins} C_{ins}}.$$  \hspace{1cm} (1)

From the above equation, the complex admittance, known as the reciprocal of $Z^*$, can be derived. Since $R_{ins} \gg R_{sc}$ and $C_{ins} \gg C_{sc}$ in the CCTO system,[4] the real part of the admittance (i.e., the conductance $G$) can be simplified as,

$$G = \frac{1 + \omega^2 R_{sc}^2 R_{ins} C_{ins}^2}{R_{ins} + \omega^2 R_{sc}^2 R_{ins} C_{ins}^2}.$$  \hspace{1cm} (2)

Noted that $\omega R_{sc} C_{ins} \ll 1$ is basically satisfied in our measured frequency range, and $C_{ins} \approx C_p$, the loss tangent (tanδ = $G/|\omega C_p|$) is then approximately to be,

$$\tan\delta = \frac{1}{\omega R_{ins} C_p} + \omega R_{sc} C_p.$$  \hspace{1cm} (3)

Eq. (3) qualitatively agrees with the experimental result shown in figure 2(d). At low frequencies, the first term is important. Thus tanδ decreases with $f$. At high frequencies, however, the second term becomes predominant. As a result, tanδ increases almost linearly with the frequency for all the samples when $f \geq 10^6$.

Eq. (3) clearly shows that tanδ can be lowered by either increasing $R_{ins}$ or decreasing $R_{sc}$. Then, which
of the semiconducting region ($Z''$) as a function of La content. The lines are the fitted curves using the Cole-Cole empirical relation. The top left inset shows an enlarged view for the high frequency data close to the origin. The top left inset plots the resistance of the semiconducting region ($R_{sc}$) and that of the insulating barriers ($R_{ins}$) as a function of La content.

Fortunately, the $R_{sc}$ and $R_{ins}$ values can be obtained by an impedance spectroscopy analysis. As shown in the top right inset of figure 3, the non-zero intercept on the $Z'$ axis at very low frequency. Since the experimental impedance data at 270 K only cover a part of the arcs for the limit of the measured frequency range, $R_{ins}$ was then determined by a data fitting and extrapolation using the well-known Cole-Cole empirical relation.

As can be seen in the top left inset of figure 3, $R_{sc}$ does decrease with the La substitution. Furthermore, the decrease is very sharp at the low $x$ value, and it becomes mild when $x \geq 0.2$. This is in conformity with the decrease of tanδ in figure 2(b) (Note that the second term of tanδ in Eq. (3) predominates at 10 kHz). On the other hand, $R_{ins}$ does not change so much with increasing $x$. It is also noted that the decrease of $C_p$ (or $\varepsilon_r$) cannot explain the large magnitude of the drop in tanδ. Therefore, we conclude that the notable decrease of tanδ by the La substitution is mainly due to the decrease in resistivity of the CCTO grains/subgrains. The La-for-Ca substitution is expected to induce excess electrons due to the charge compensation effect, which basically explains the decrease of $R_{sc}$.

One may note that tanδ at low frequencies does not decrease so much (figure 2(d)). The sample of $x = 0.3$ shows even higher tanδ than that of the parent compound at 20 Hz, primarily due to the lower $R_{ins}$ value. To decrease the low-frequency tanδ, the direct route is to increase the resistivity of the barriers. Very recently, we succeeded in increasing $R_{ins}$ (and thus decreasing tanδ) by incorporating additional CaTiO$_3$. The decrease of tanδ was also reported in the CaCu$_3$Ti$_4$O$_{12}$/CaTiO$_3$ diphasic samples. It is expected that the combination of the two routes may further optimize the dielectric property in the CCTO material.

In summary, we have developed a novel route to improve the dielectric properties of the CCTO material based on the IBLC model. By the La-for-Ca substitution in CCTO the loss tangent was suppressed remarkably while the giant dielectric constant still remains. The impedance spectroscopy analysis shows that the conductivity of the semiconducting regions increases substantially with the La substitution while the internal barriers remain highly resistive, leading to the notable decrease in the loss tangent. We hope that the present work will be able to promote the CCTO-related materials to practical applications.

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[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 Commun. 115, 217 (2000).
[3] W. Si, E. M. Cruz, P. D. Johnson, P. W. Barnes, P. Woodward, and A. P. Ramirez, Appl. Phys. Lett. 81, 2056 (2002).
[4] D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West, Appl. Phys. Lett. 80, 2153 (2002).
[5] S. Y. Chung, I. D. Kim, and S. J. L. Kang, Nature Mater. 3, 774 (2004).
[6] C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramirez, Science 293, 673 (2001).
[7] J. Li, A. W. Sleight, and M. A. Subramanian, Solid State Commun. 135, 260 (2005).
[8] P. Lunkenheimer, V. Bobnar, A. V. Pronin, A. I. Ritus, A. A. Volkov, and A. I. Ritus, Phys. Rev. B 66, 052105 (2002).
[9] M. H. Cohen, J. B. Neaton, L. X. He, and D. Vanderbilt, J. Appl. Phys. 94, 3299 (2003).
[10] C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, M. A. Subramanian, and A. P. Ramirez, Phys. Rev. B 67, 092106 (2003).
[11] J. J. Liu, C. G. Duan, W. G. Yin, W. N. Mei, R. W. Smith, and J. R. Hardy, Phys. Rev. B 70, 144106 (2004).
[12] L. Zhang and Z. J. Tang, Phys. Rev. B 70, 174306 (2004).
[13] Y. Y. Yan, L. Jin, L. X. Feng, and G. H. Cao, submitted.
[14] W. Kobayashi and I. Terasaki, Appl. Phys. Lett. 87, 032902(2005).