CaCu$_3$Ti$_4$O$_{12}$/CaTiO$_3$ Composite Dielectrics: A Ba/Pb-free Ceramics with High Dielectric Constants

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We have measured dielectric properties of Ca$_{1+x}$Cu$_{3-x}$Ti$_4$O$_{12}$ ($x = 0, 0.1, 0.5, 1, 1.5, 2, 2.9$ and $3$), and have found that Ca$_2$Cu$_2$Ti$_4$O$_{12}$ (a composite of CaCu$_3$Ti$_4$O$_{12}$ and CaTiO$_3$) exhibits a high dielectric constant of 1800 with a low dissipation factor of 0.02 below 100 kHz from 220 to 300 K. These are comparable to (or even better than) those of the Pb/Ba-based ceramics, which could be attributed to a barrier layer of CaTiO$_3$ on the surface of the CaCu$_3$Ti$_4$O$_{12}$ grains. The composite dielectric ceramics reported here are environmentally benign as they do not contain Ba/Pb.

FIG. 1: X-ray diffraction patterns of Ca$_2$Cu$_2$Ti$_4$O$_{12}$ and Ca$_{3.9}$Cu$_{0.1}$Ti$_4$O$_{12}$ at room temperature. Inset shows the crystal structure of CaCu$_3$Ti$_4$O$_{12}$.

It is widely known that high-dielectric ceramic capacitors primarily composed of Ba/Pb-based perovskite oxides are indispensable to modern electronic devices. These oxides have made a great contribution to development of electronics since their discoveries in forties—fifties [1, 2]. As seen in a recent discovery of Pb-free piezoelectrics by Saito et al. [3, 4], there increase pressing needs to use environmentally-friendly materials. Ceramic capacitors should also be replaced with Pb/Ba-free ones, if possible.

One can imagine that a good ceramic capacitor should have a large dielectric constant $\varepsilon'$. This is, however, not a sufficient condition; it should also require a low dielectric loss $\varepsilon''$ (or a low dissipation factor $\tan\delta = \varepsilon''/\varepsilon'$, which is related to loss of stored electricity), and a flat temperature dependence of $\varepsilon'$. At present, Ba/Pb-based perovskite oxides (e.g. BaTiO$_3$ and Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$) are widely used as capacitor materials, and exhibit a high $\varepsilon'$ (1000-20000) with a low $\tan\delta$ (0.01-0.2). Unfortunately, $\varepsilon'$ of BaTiO$_3$ changes rapidly around the ferroelectric transition temperature (278 K and 400 K), which does not satisfy the weak temperature dependence near room temperature. Although Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ does not show clear ferroelectric transition, $\varepsilon'$ of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ also changes rapidly around 250 K. To reduce the rapid change, various composites with other materials (e.g. CaTiO$_3$, PbTiO$_3$, BaZrO$_3$ and PbZrO$_3$) have been examined [4, 5].

Subramanian et al. [6] discovered that ceramic samples of CaCu$_3$Ti$_4$O$_{12}$ have a very large $\varepsilon'$ of 10000, which is nearly constant over a wide temperature range from 100 to 400 K below 1 MHz [5]. This is quite promising for ceramic capacitors, and it has attracted many researchers’ interests from both technological [5, 6] and scientific [7, 8, 9, 10, 11, 12] points of view. However, CaCu$_3$Ti$_4$O$_{12}$ has not yet been applied because of the large $\tan\delta$ of 0.15 around room temperature.

In a previous work [12, 13], we reported remarkable substitution effects in CaCu$_3$Ti$_4$O$_{12}$, where only 2 % substitution of Mn for Cu reduces $\varepsilon'$ from 10000 down to 100. We further attempted to improve the dielectric properties of CaCu$_3$Ti$_4$O$_{12}$ by partial substitution for Ca, Cu and Ti. Though some of the solid solutions exhibited higher $\varepsilon'$, almost all the compounds showed poorer dielectric performance because of their high $\tan\delta$. Thus, as a next move, we expected that a certain kind of two-phase composite could improve the dielectric properties. Eventually, we have found that a composite of CaCu$_3$Ti$_4$O$_{12}$ (high $\varepsilon'$) and CaTiO$_3$ (low $\tan\delta$) yields high dielectric performance. Here, we present that a composite of CaCu$_3$Ti$_4$O$_{12}$ : CaTiO$_3 = 2 : 1$ (the nominal composition is Ca$_2$Cu$_2$Ti$_4$O$_{12}$) exhibits a high $\varepsilon'$ (1800) with a low $\tan\delta$ (0.02) below 100 kHz, which is nearly constant from 220 to 300 K.

Polycrystalline samples of Ca$_{1+x}$Cu$_{3-x}$Ti$_4$O$_{12}$ ($x = 0, 0.1, 0.5, 1, 1.5, 2, 2.9$ and $3$) were prepared by a solid-state reaction. Stoichiometric amounts of CaCO$_3$, CuO
CaCu where all the peaks are indexed as a composite of CT-1. In a frequency range from $10^2$ to $10^6$ Hz and a temperature range from 220 to 300 K, a large $\varepsilon'$ of 1800 is almost independent of temperature. It should be emphasized that $\tan \delta$ remains at a low value of less than 0.02 in the same frequency and temperature ranges. This value is one order of magnitude smaller than that of CCTO. Below about 220 K, $\varepsilon'$ rapidly decrease, and $\tan \delta$ shows a large peak, which are explained in terms of dielectric relaxation [10].

Now we compare CCT-CT-1 with other ceramic capacitors. Figure 3 shows $\varepsilon'$ and $\tan \delta$ for some famous ceramic materials. These materials are classified into two large categories according to values of their $\varepsilon'$ and $\tan \delta$. The one category is for temperature compensating capacitor, and the other one is for high dielectric capacitor. The latter is further classified into X5R, X7R, Z5U and Y5V of EIA (Electronic Industries Association in USA) stan-
FIG. 4: Room-temperature dielectric properties of (1-
\(y\))CaTiO\(_3\) + \(y\)Ca\(_{1/4}\)Cu\(_{3/4}\)TiO\(_3\) at 100 kHz.

standards (For the detailed regulations, see figure caption.). These categories are roughly represented by dotted rectangles in Fig. 3. The dielectric performance of CCT-CT-1 is in the X5R/X7R standards, which is comparable with those of Samples B (BaTiO\(_3\)) and C (Pb(Sc\(_1/2\))Ta\(_1/2\)O\(_3\)). In particular, temperature variation of \(\varepsilon\)' of CCT-CT-1 is +1.0 % at 1 kHz from 218 K (-55 °C) to 300 K (+27 °C), which is the smallest value in X5R/X7R, and is even superior to that of sample A (CTO). Samples F-I in Fig. 3 represent dielectric properties of partially substituted samples for Ca, Cu and Ti in CCTO. They have the large tan\(\delta\) in common, which suggests that the good dielectric properties of CCT-CT-1 are unlikely to come from simple substitution effects.

Let us discuss an origin of the large \(\varepsilon\)' and the low tan\(\delta\) of CCT-CT-1. Figure 4 shows the room-temperature dielectric properties of (1-
\(y\))CaTiO\(_3\) + \(y\)Ca\(_{1/4}\)Cu\(_{3/4}\)TiO\(_3\) at 100 kHz, where \(y\) represents a volume fraction of CCTO (\(y = 0.66\) corresponds to CCT-CT-1). \(\varepsilon_{\text{cal}}\) shown by the dotted curve is a calculation from Lichtenecker’s logarithmic law written by

\[
\ln \varepsilon_{\text{cal}}' = y \ln \varepsilon_{\text{CCTO}}' + (1 - y) \ln \varepsilon_{\text{CTO}}',
\]

where \(\varepsilon_{\text{CCTO}}\) and \(\varepsilon_{\text{CTO}}\) represent dielectric constants of CCTO and CTO, respectively. Obviously, the experimental data are in excellent agreement with \(\varepsilon_{\text{cal}}\).

Equation (1) was first suggested by Lichtenecker in 1926, and has been used by many researchers. In fact, it well explains dielectric properties of various composites, such as BaTiO\(_3\)/CaTiO\(_3\), BaTiO\(_3\)/BaTiO\(_3\)-gel, aluminum powder/epoxy resin, and human blood. According to Zakri et al., the necessary conditions of Eq. (1) are: (i) ingredients in the mixture are not dissolved in the solvent, and (ii) in a two-component case, one component is uniformly distributed as fine particles in the background of the other one. We readily see that CCT-CT-1 satisfies the first condition, because CTO and CTO make no solid solution as mentioned earlier. In a microscopic point of view, this means that Ca ions do not occupy the Cu site in CCTO, and hence the surface of the CCTO grain should be covered with CTO in CCT-CT-1, which suggests that CTO acts as a barrier layer. Some systems such as BaTiO\(_3\)-CeO\(_2\) and BaTiO\(_3\)-Nb\(_2\)O\(_5\)-Ce\(_2\)O\(_4\), and BaTiO\(_3\)-CdBi\(_2\)Nb\(_2\)O\(_9\) obeys Eq. (1), in which the BaTiO\(_3\) grain takes the so-called “core-shell” structure. We expect that a similar core-shell structure will exist in CCT-CT-1, which should be verified in a further study.

Preliminarily, we took scanning-electron-microscope images to evaluate the size and distribution of the grains in CCT-CT-1. They showed homogeneous distribution of the CTO grains, which satisfies the second condition for Eq. (1). The grain size of CTO was 2 – 3 \(\mu\)m, which was significantly smaller than a typical grain size (several dozen \(\mu\)m) of normally prepared CTO. Such a small grain size of CTO shows a high dielectric constant (2000-2500) with remarkably flat temperature dependence, which can be another origin for the high performance of CCT-CT-1.

Finally we will make some comments on remaining issues. (i) We found that CCT-CT-1 showed no piezoelectricity. This is reasonable, because it shows no ferroelectric transition, which is advantageous for reduction mechanical damages in ac operation. (ii) A sintering temperature of CCT-CT-1 is 1090 °C, which is significantly lower than that of BaTiO\(_3\) (typically 1350 °C). This indicates that CCT-CT-1 can save considerable costs and energies, which is another environmentally-friendly feature. (iii) CCT-CT-1 is highly stable. After 20000 h, \(\varepsilon\)' and tan\(\delta\) remain intact within +4 % and +13 %, respectively, which is still in the range of the X5R/X7R standards.

In summary, we have prepared a set of ceramic samples of Ca\(_{1+x}\)Cu\(_{3-x}\)Ti\(_4\)O\(_{12}\) (\(x = 0, 0.1, 0.5, 1, 1.5, 2, 2.9\) and 3), and measured the dielectric properties. They are found to be composites of CaCu\(_{3}\)Ti\(_4\)O\(_{12}\) and CaTiO\(_3\), whose dielectric constant obeys Lichtenecker’s logarithmic law. This means that the CaCu\(_{3}\)Ti\(_4\)O\(_{12}\) grains distribute homogeneously in the CaTiO\(_3\) matrix, in which CaTiO\(_3\) can act as a barrier layer. For \(x = 1\), the dielectric constant reaches as large as 1800 with a small loss of tan\(\delta\) <2% below 100 kHz in a wide temperature range from 220 to 300 K. These are the best values among dielectric ceramics in the X5R/X7R standards. Although the dielectric constant is highly dependent on frequency, we hope that it will be applied in a complimentary way to existing ceramics.

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[1] M. E. Lines, and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford University Press, London, 2000).
[2] G. A. Smolenskii, V. A. Isupov, A. I. Agranovskaya, and S. N. Popov, Sov. Phys.-Solid State 2, 2584 (1961).
[3] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, Nature 432, 84 (2004).
[4] Landolt-Börnstein, *Ferroelectric oxides*, Group III, Crystal and Solid State Physics, Volume 16a (Springer, Berlin, 1981).
[5] D. Hennings, and H. Schreinemacher, Mater. Res. Bull. 12, 1221 (1977).
[6] M. A. Subramanian, D. Li, N. Duan, B. A. Reisner, and A. W. Sleight, J. Solid State Chem. 151, 323 (2000).
[7] A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, and S. M. Shapiro, Solid State Commun. 115, 217 (2000).
[8] D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West, Appl. Phys. Lett. 80, 2153 (2002).
[9] W. Si, E. M. Cruz, P. D. Johnson, P. W. Barnes, P. Woodward, and A. P. Ramirez, Appl. Phys. Lett. 81, 2056 (2002).
[10] C. C. Home, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramirez, Science 293, 673 (2001).
[11] A. Koitzsch, G. Blumberg, A. Gozar, B. Dennis, A. P. Ramirez, S. Trebst, and S. Wakimoto, Phys. Rev. B 65, 052406 (2002).
[12] L. He, J. B. Neaton, M. H. Cohen, D. Vanderbilt, and C. C. Homes, Phys. Rev B 65, 214112 (2002).
[13] W. Kobayashi, and I. Terasaki, Physica B 329-333, 771 (2003).
[14] B. Bochu, M. N. Deschizeaux, and J. C. Joubert, J. Solid State Chem. 29, 291 (1979).
[15] K. Lichtenecker, Phys. Z. 27, 115 (1926).
[16] D. H. Yoon, J. Zhang, and B. I. Lee, Mater. Res. Bull. 38, 765 (2003).
[17] Y. Baziard, S. Breton, S. Toutain, and A. Gourdenne, Eur. Polym. J. 24, 521 (1988).
[18] S. Kisdnasamy, and P. S. Neelakantaswamy, Electron. Lett. 20, 291 (1984).
[19] T. Zakri, J. P. Laurent, and M. Vauclin, J. Phys. D31, 1589 (1998).
[20] Y. Park, and H. G. Kim, Ceram. Int. 23, 329 (1997).
[21] Y. Yuan, S. Zhang, and W. You, Mater. Lett. 58, 1959 (2004).
[22] D. Hennings, and G. Rosenstein, J. Am. Ceram. Soc. 67, 249 (1984).
[23] Y. L. Zhao, G. W. Pan, Q. B. Ren, Y. G. Cao, L. X. Feng, and Z. K. Jiao, Thin Solid Films 445, 7 (2003).