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RAPID COMMUNICATION

High Dielectric Constant in $ACu_3Ti_4O_{12}$ and $ACu_3Ti_3FeO_{12}$ Phases

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High dielectric constants have been found in oxides of the type $ACu_3Ti_4O_{12}$. The most exceptional behavior is exhibited by $CaCu_3Ti_4O_{12}$, which shows a dielectric constant at 1 kHz of about 12,000 that is nearly constant from room temperature to 300°C. The cubic structure of these materials is related to that of perovskite ($CaTiO_3$), but the TiO_6 octahedra are tilted to produce a square planar environment for Cu^{2+}. The $CaCu_3Ti_4O_{12}$ structure down to 35 K has been examined by neutron powder diffraction. The structure remains cubic and centric. Most compositions of the type $A_{2/3}Cu_3Ti_4O_{12}$ (A = trivalent rare earth or Bi) show dielectric constants above 1000. The dielectric properties of isostructural compounds of the type $ACu_3Ti_3FeO_{12}$ are also presented. © 2000 Academic Press

Oxides with the perovskite structure are well known for their ability to produce high dielectric constants; this had led to many important applications. However, dielectric constants higher than 1,000 have always been associated with ferroelectric or relaxor properties. In both cases, the dielectric constant shows a peak as a function of temperature. The resulting temperature dependence of the dielectric constant is undesirable for many applications. We report here on a class of compounds with a perovskite-related structure which have dielectric properties very different from those of ferroelectrics or relaxors. Their high dielectric constants show only a small dependence on temperature.

The compounds used in the present investigation were prepared by a conventional powder-sintering technique using starting materials with a purity of 99.9% or higher. Ln_2O_3 was heated to 1000°C before use. The materials were weighed according to the stoichiometric ratios and mixed thoroughly in an agate mortar. The mixed powder was calcined at 900–1000°C for 8 h. The calcined powder was reground and pressed into disks of 12.7 mm diameter/1–2 mm thickness. The discs were sintered in air at 1000–1200°C for 20 h. The ramping rate was 200°C/h and the cooling rate was 150°C/h. X-ray powder diffraction patterns were recorded with a Siemens D5000 diffractometer. The disc samples were polished to produce a flat uniform surface and electroded with silver paint. The painted samples were dried at 70–100°C overnight. Capacitance and loss tangent measurements were taken on an HP-4275A LCR meter in the temperature region from 25 to 500°C. For frequency dependence measurements, an HP-4284A LCR meter was used. (Certain trade names and company products are identified to adequately specify experimental procedures. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose).

The $ACu_3Ti_4O_{12}$ family of compounds has been known since 1967 (1). This family was expanded and accurate structures (Fig. 1) were determined in 1979 (2). Apparently, the dielectric properties of these compounds have not been previously examined. The dielectric constant and loss for $CaCu_3Ti_4O_{12}$ are shown as a function of temperature, T, in Fig. 2. The dielectric constant for $CaCu_3Ti_4O_{12}$ decreases with increasing frequency, to a value of 9200 at 1 MHz. The dielectric properties of 13 members of this family are presented in Table 1. Many have the formula $A_{2/3}Cu_3Ti_4O_{12}$, where A is a trivalent rare-earth cation. The $Bi_{2/3}Cu_3Ti_4O_{12}$ compound was first reported by Bryntse and Werner (3). Those of the composition $A^{3+}Cu_3Ti_3FeO_{12}$ (A = a rare earth) have been reported previously (4); we prepared $BiCu_3Ti_3FeO_{12}$ for the first time.

The structure of $CaCu_3Ti_4O_{12}$ was previously determined from neutron powder diffraction data (2). We have now refined the $CaCu_3Ti_4O_{12}$ structure in space group *Im3* (No. 204) at 100 and 35 K to investigate the possible

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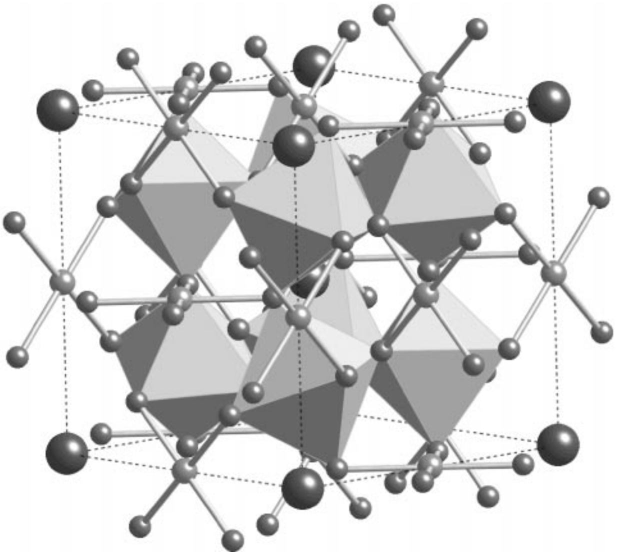

FIG. 1. Structure of $CaCu_3Ti_4O_{12}$ shown as TiO_6 octahedra, Cu atoms bonded to four oxygen atoms, and large Ca atoms without bonds.

occurrence of a ferroelectric phase transition. The refinements are based on neutron powder diffraction data collected at the NIST Center for Neutron Research on the BT-1 neutron powder diffractometer using a Cu(311) monochromator. Details of the results are shown in Table 2. There is no indication of any phase transition: the $CaCu_3Ti_4O_{12}$ structure remains cubic and centric down to 35 K. All thermal displacement factors are normal and decrease on cooling from 100 to 35 K.

The high dielectric constant in $BaTiO_3$, which peaks at its three ferroelectric transitions, is generally attributed to rattling of Ti^{4+} within its TiO_6 octahedron. The Ti–O distances in $CaTiO_3$ and $SrTiO_3$ (both isostructural with $BaTiO_3$) are 1.95 Å. The larger Ba^{2+} cation expands the structure, resulting in a Ti–O distance of 2.00 Å. The TiO_6 octahedron is now considered too large for Ti^{4+}, which rattles in the

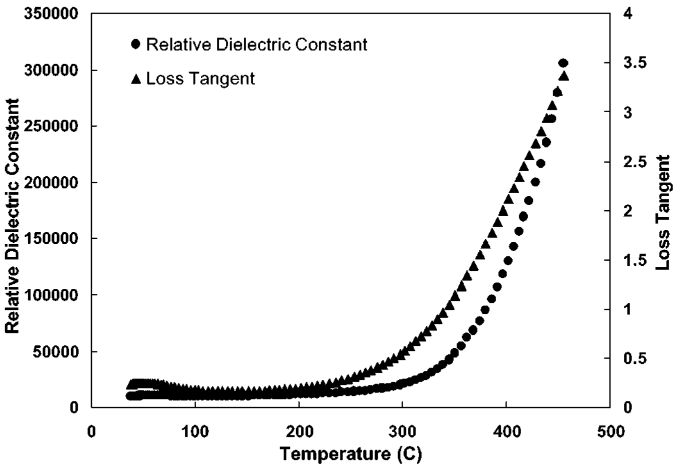

FIG. 2. Relative dielectric constant (*K*) and loss tangent (*D*) data for $CaCu_3Ti_4O_{12}$ at 1 MHz.

TABLE 1
Dielectric[a] and Cell Edge Data for $ACu_3M_4O_{12}$ Phases (at 25°C)

Compound	Relative dielectric constant (*K*)	Loss tangent (*D*)	*a* (Å at 25°C)
$CaCu_3Ti_4O_{12}$	10,286	0.067	7.391
$CdCu_3Ti_4O_{12}$	409	0.093	7.384
$La_{2/3}Cu_3Ti_4O_{12}$	418	0.060	7.427
$Sm_{2/3}Cu_3Ti_4O_{12}$	1,665	0.048	7.400
$Dy_{2/3}Cu_3Ti_4O_{12}$	1,633	0.040	7.386
$Y_{2/3}Cu_3Ti_4O_{12}$	1,743	0.049	7.383
$Bi_{2/3}Cu_3Ti_4O_{12}$	1,871	0.065	7.413
$BiCu_3Ti_3FeO_{12}$	692	0.082	7.445
$LaCu_3Ti_3FeO_{12}$	44	0.339	7.454
$NdCu_3Ti_3FeO_{12}$	52	0.325	7.426
$SmCu_3Ti_3FeO_{12}$	52	0.256	7.416
$GdCu_3Ti_3FeO_{12}$	94	0.327	7.409
$YCu_3Ti_3FeO_{12}$	33	0.308	7.394

[a] Measured at 100 KHz.

TABLE 2
$CaCu_3Ti_4O_{12}$ Structural Results[a]

	100 K	35 K
x (O)	0.30308(9)	0.30328(8)
y (O)	0.1790(1)	0.1790(1)
U_{11} (Ca)[b]	1.39(7)	0.89(6)
U_{11} (Cu)[c]	0.23(9)	0.14(8)
U_{22} (Cu)	0.68(7)	0.51(6)
U_{33} (Cu)	0.94(7)	0.31(6)
U_{11} (Ti)[d]	0.61(2)	0.35(2)
U_{12} (Ti)	0.07(4)	0.06(4)
U_{11} (O)[e]	0.78(3)	0.50(3)
U_{22} (O)	0.77(4)	0.56(4)
U_{33} (O)	0.45(4)	0.40(4)
U_{12} (O)	0.07(3)	0.02(2)
Ca–O	2.6024(7)	2.6006(6)
Ti–O	1.96115(2)	1.95890(2)
Cu–O	1.9675(7)	1.9642(6)
O–Ti–O	89.420(3)	89.479(3)
O–Ti–O	90.580(3)	90.521(3)
O–Ti–O	180.000	179.980(0)
O–Cu–O	95.46(4)	95.39(4)
O–Cu–O	85.54(4)	84.61(4)
a (Å)	7.39347(3)	7.38426(3)
R_{wp} (%)	6.45	5.8
R_p (%)	5.09	4.42
R_{F2} (%)	1.70	1.67
χ^2	2.26	5.98

[a] Ca: 0 0 0; Cu: 0 1/2 1/2; Ti: 1/4 1/4 1/4; O: *x y* 0.

[b] Ca: $U_{11} = U_{22} = U_{33}$; $U_{12} = U_{13} = U_{23} = 0$.

[c] Cu: $U_{12} = U_{13} = U_{23} = 0$.

[d] Ti: $U_{11} = U_{22} = U_{33}$; $U_{12} = U_{13} = U_{23}$.

[e] O: $U_{13} = U_{23} = 0$.

paraelectric state and is displaced from the center of the octahedron when $BaTiO_3$ becomes ferroelectric. The $CaCu_3Ti_4O_{12}$ structure is much more constrained than the usual perovskite structure. The TiO_6 octahedra have tilted to form a square planar arrangement around Cu^{2+}. If one assumes that both Ti–O and Cu–O distances are 1.96 Å and that the Ti–O octahedron is not distorted, one finds that the unit cell edge must be 7.383 Å and the Ca–O distance 2.61 Å. A small deviation of the O–Ti–O angles from 90° produces the experimentally determined values of $a = 7.391$ Å and Ca–O = 2.604 Å (2). This Ca–O distance is much less than the 2.72 Å value predicted based on the ionic radii (5). The situation is then similar to that in $BaTiO_3$, where the Ba–O distance of 2.84 Å is much less than the 2.99 Å predicted, based on the sum of ionic radii. Thus, in both $BaTiO_3$ and $CaCu_3Ti_3O_{12}$, the A^{2+} cation is in a site too small for it. As it pushes out to expand the lattice, it places the Ti–O bonds under tension and increases the polarizability of the TiO_6 octahedra.

In the cubic perovskite structure encountered in $BaTiO_3$ above 120°C, the Ti^{4+} cation is in a site of full cubic symmetry. With decreasing temperature, Ti^{4+} displaces toward one, then two, and finally three oxygen anions, to produce, respectively, the tetragonal, orthorhombic, and rhombohedral ferroelectric structures. The site symmetry for Ti^{4+} in $CaCu_3Ti_4O_{12}$ is much lower than that in cubic $BaTiO_3$; this greatly reduces the possibility of a ferroelectric phase transition based on the displacement of Ti^{4+} from the center of its octahedron. For example, the lack of a fourfold axis in the *Im3* space group for $CaCu_3Ti_4O_{12}$ eliminates the possibility of a transition to a tetragonal ferroelectric structure. The Ti^{4+} cations could displace off center, along their one threefold axis. However, this could not be a pure ferroelectric transition, because the displacements would actually occur along four different directions. Thus, we have in $CaCu_3Ti_4O_{12}$ a perovskite-type structure where polarizability and dielectric constant are enhanced by tension on the Ti–O bonds, but where a transition to a ferroelectric state is frustrated by the TiO_6 octahedra tilt structure that accommodates the square planar coordination of Cu^{2+}.

Although we can rationalize the high dielectric constant of $CaCu_3Ti_4O_{12}$ based on its atomic structure, there is good reason to suspect that the dielectric constant of this phase is enhanced by its microstructure. One consideration is the fact that other compounds (Table 1) with similar or larger cell edges have considerably lower dielectric constants. Furthermore, it known that addition of copper to $BaTiO_3$ or $SrTiO_3$ can lead to greatly enhanced dielectric constant through the barrier layer mechanism (6). We therefore prepared some samples of $CaCu_3Ti_4O_{12}$ that were copper deficient, which might be expected to preclude a copper rich phase at the grain boundaries. The copper deficiency does indeed result in a lower dielectric constant (Fig. 3), but the dielectric constant remains impressively high. The production of barrier layer capacitors normally requires complex processing (6). It would be remarkable if our straightforward preparation of $CaCu_3Ti_4O_{12}$ leads naturally to a microstructure that greatly enhances the dielectric constant by a barrier layer mechanism. A final resolution of this matter will require detailed studies on the microstructure of $CaCu_3Ti_4O_{12}$ ceramics or studies on single crystals of $CaCu_3Ti_4O_{12}$.

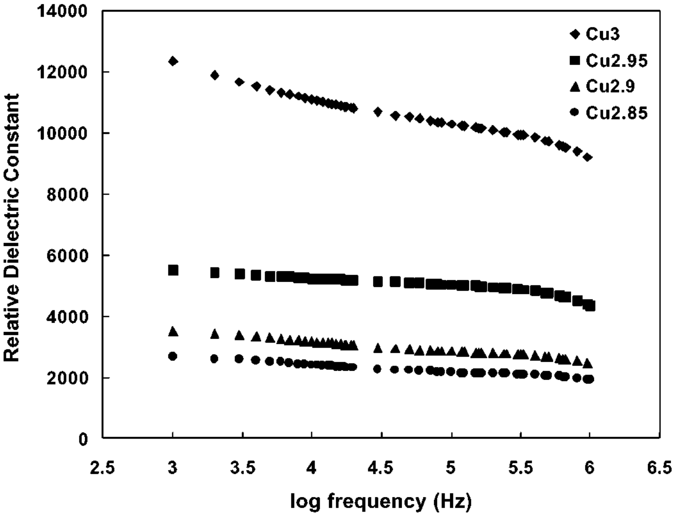

FIG. 3. Relative dielectric constant data for $CaCu_3Ti_4O_{12}$ showing the effect of Cu deficiency at room temperature.

Note added in proof. After this paper was accepted, single crystals of $CaCu_3Ti_4O_{12}$ were obtained from copper oxide flux. Single crystal X-ray diffraction studies confirmed the structure and stochiometry of $CaCu_3Ti_4O_{12}$. Several crystals were examined; all were twinned. The twinning was such that the Laue Group appeared to be $m\bar{3}m$ instead of $\bar{3}m$. The ratio of the two twin orientations was close to unity in all crystals. This suggests a high degree of twinning with small domains, because large domains would not likely give rise to a twin ratio of unity. The composition at the boundary between twins may well be different from that expected of a perfectly periodic lattice. These twin boundaries may then be acting a manner to create a barrier layer capacitance, thus offering a possible explanation for the dielectric properties reported here.

REFERENCES

1. A. Deschanvres, B. Raveau, and F. Tollemer, *Bull. Soc. Chim. Fr.*, 4077 (1967).
2. B. Bochu, M. N. Deschizeaux, and J. C. Joubert, *J. Solid State Chem.* **29,** 291 (1979).
3. I. Bryntse and P. Werner, *Mater. Res. Bull.* **25,** 477 (1990).
4. C. Meyer, Y. Gros, and B. Bochu, *Phys. Status Solidi A* **48,** 581 (1978).
5. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
6. C.-F. Yang, *Jpn. J. Appl. Phys.* **35,** 1806 (1996); **36,** 188 (1997).