Progress in High-Dielectric Constant Materials

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(Invited Paper)

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***Abstract*—The relative permittivity of a material is a scaling factor for capacitors and the devices based upon them; the larger the relative permittivity, the greater the degree of miniaturization, or potential for energy storage. Materials with a relative permittivity than that of silicon nitride (approximately 7) are referred to as high-dielectric constant materials. Values of about 100 are typical in titanium dioxide rutile. Values of about 10,000 are observed in barium titanate in the region of the ferroelectric transition, which while impressive, is not very useful due to the strong temperature dependence. The observation of a relative permittivity of over 100,000 in the calcium copper titanate material sparked considerable interest because it showed little temperature dependence between 100 and 600 K over most of the radio-frequency range. Further investigation revealed that this material appears to be naturally nanotextured and that the colossal permittivity was likely due to the surface and/or internal barrier layer capacitance effect, although the issue is not settled. Unfortunately, the dielectric losses in this class materials are relatively high. A new strategy to achieve high dielectric permittivity with low loss involves using localized lattice defect states through ambipolar co-doping; these intrinsic defect complexes give rise to strong dipoles that are responsible for a relative permittivity of 10,000 with exceptionally low dielectric losses over most of the radio frequency range and excellent thermal stability.**

***Index Terms*—Permittivity, dielectric loss, dielectric materials, spectroscopy.**

I. INTRODUCTION

The capacitor is a ubiquitous device that finds a broad range of applications from microelectronics to high-performance power applications. The capacitance of a parallel plate capacitor is simply,

$$C = \epsilon_{\rm r}\epsilon_0 A/d, \tag{1}$$

where A is the area of the plates separated by a distance d, $\epsilon_{\rm r}$ is the relative permittivity, and ϵ_0 is the permittivity of vacuum. The relative permittivity is related to the polarizability, which arises from structures with a permanent electric dipole moment that can change orientation in an applied electric field. In metals, the charge is delocalized, and $\epsilon_{\rm r} \ll 0$. In an insulator, the charge is localized and $\epsilon_{\rm r} > 0$. Materials with a relative permittivity greater than that of silicon nitride ($\epsilon_{\rm r} \simeq 7$), are referred to as high dielectric constant materials [1]. One strategy to increase the capacitance is to reduce the plate spacing; however, this type of geometric optimization has arguably reached its limits, and a better approach is to increase $\epsilon_{\rm r}$. Materials with $\epsilon_{\rm r} > 1000$ are generally related to either a ferroelectric that exhibits a dipole moment in the absence of a field, or to relaxor behavior (a ferroelectric response under high electric fields at a lower temperature, but with no spontaneous bulk polarization) [2]. In both cases, $\epsilon_{\rm r}$ is a strong function of temperature, making these materials unsuitable for devices. The largest stable values of the relative permittivity are generally observed in the titanium dioxide rutile, with $\epsilon_{\rm r} \simeq 250$. Doping Nb into TiO_2 ceramics is known to produce high values for $\epsilon_{\rm r}$; however, the dielectric loss is rather large [3].

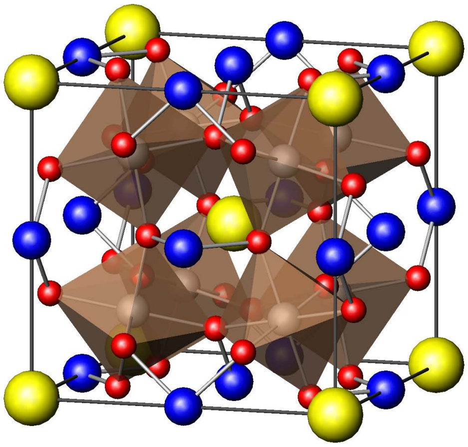

Fig. 1. The unit cell of body-centered cubic $CaCu_3Ti_4O_{12}$ in the $Im\bar{3}$ space group, which consists of two formula units. The Ti atoms sit at the center of the canted TiO_6 octahedra (the tilt angle is nominally 141°), with bridging Cu atoms (blue) bonded to the oxygens (red), and large Ca atoms (yellow) the corners and center of the unit cell.

Perovskites possess large values for $\epsilon_{\rm r}$, and so the observation of an extraordinarily high value for the relative permittivity of $\epsilon_{\rm r} \sim 10^5$ at room temperature in the body-centered cubic perovskite-related oxide $CaCu_3Ti_4O_{12}$, shown in Fig. 1, that was stable between 100 to 600 K [4]–[7] was greeted with considerable interest. First principles calculations found no direct evidence for an intrinsic lattice or electronic mechanism, suggesting an extrinsic effect [8]. Numerous experiments provide strong evidence that the high

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permittivity is likely due to Maxwell-Wagner-type extrinsic effects [9]; depletion layers form at the electrodes in single crystals, resulting in a surface barrier capacitance effect, and at intergrain boundaries in ceramics, resulting in an internal barrier layer capacitor effect [10], [11]. Regardless of the details of the mechanism (which is not entirely settled), a consequence of the extremely high value for $\epsilon_{\rm r}$ in calcium copper titanate, and all other high permittivity materials for that matter, is the correspondingly high value for the dielectric loss, which severely limits their use in electronic and energy storage devices. A possible solution to the problem of large dielectric loss in the high permittivity materials is the use of ambipolar co-doping in transition-metal oxides to create clusters of defect sites that form defect dipoles; these defect dipoles have large dipole moments and thus high permittivity, but the electrons are also localized to the clusters and are unable to hop between complexes, resulting in low dielectric loss.

We review the work on $CaCu_3Ti_4O_{12}$ as the motivation for the development of electron-pinned defect dipoles in rutile materials [12], which achieve high permittivity with exceptionally low dielectric loss.

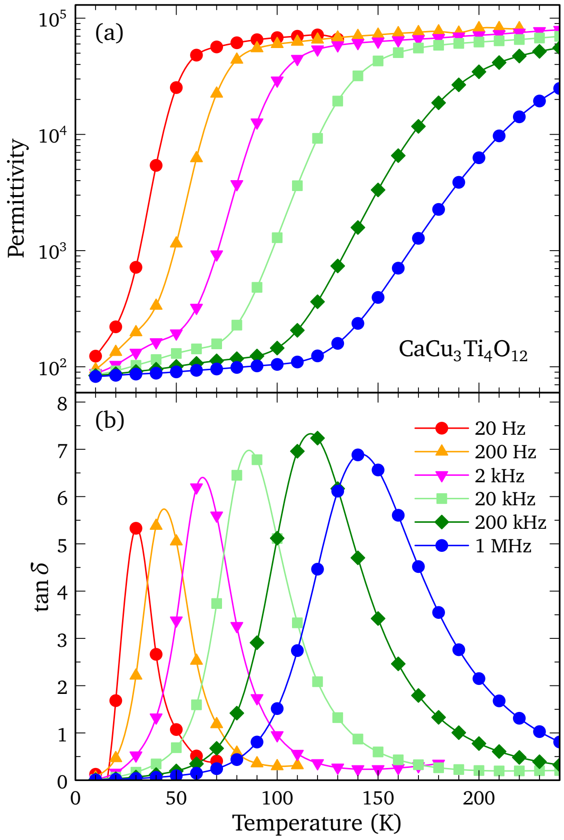

Fig. 2. (a) The temperature dependence of the dielectric permittivity ($\epsilon_{\rm r}$) of $CaCu_3Ti_4O_{12}$ at different frequencies between 20 Hz and 1 MHz. At 250 K, $\epsilon_{\rm r} \simeq 10^5$; however the permittivity decreases dramatically below $\sim$ 100 K. (b) The temperature dependence of the dielectric loss tangent $\tan\delta = \epsilon_2/\epsilon_1$ of the dielectric response for the same frequencies. The solid lines are drawn as guides to the eye.

II. DISCUSSION

A. *$CaCu_3Ti_4O_{12}$*

A single crystal of $CaCu_3Ti_4O_{12}$ was grown using a traveling-solvent floating-zone method in an image furnace; details of the synthesis are discussed in reference [6]. Below room temperature the material is insulating and the dc conductivity is described by variable range hopping [13]. At low temperature, antiferromagnetic order is observed below $T_{\rm N} \simeq 24$ K [14]. The temperature dependence of the dielectric permittivity ($\epsilon_{\rm r}$) and the dielectric loss tangent ($\tan\delta$) are shown in Figs. 2(a) and 2(b), respectively. For low frequencies, $\epsilon_{\rm r} \geq 10^4$ over a broad temperature range; however, at high frequencies or at low temperature, the permittivity decreases dramatically until $\epsilon_{\rm r} \simeq 100$. In general, the accompanying dielectric loss function shown in Fig. 2(b) is rather large. The dramatic behavior of the permittivity prompted an optical investigation of this material where the temperature dependence of the reflectivity was measured at a near-normal angle of incidence over a wide frequency range [15], allowing the complex dielectric function, $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, to be determined from a Kramers-Kronig analysis of the reflectivity [16]. Interestingly, in the THz region, $\epsilon_1 \simeq 100$ [6], which is the value attributed to the contribution of the dipole active lattice modes to $\epsilon_1(\omega)$ [17]. In the absence of other excitations, it would be the case that $\epsilon_{\rm r} \equiv \epsilon_1(\omega \to 0)$; however, $\epsilon_{\rm r} \gg \epsilon_1({\rm THz})$, indicating the presence of a low-frequency process. The permittivity data in Fig. 2(a) can be recast as a function of frequency, as shown in Fig. 3. In this form, the permittivity clearly has the character of an overdamped oscillator whose frequency is steadily decreasing with temperature. The fact that the permittivity is dominated by relaxation processes suggests that that the Debye model for the relaxation time of a dipole is appropriate,

$$P(t) = P_0 e^{t/\tau}, \tag{2}$$

where P_0 is the dipole moment, and τ is the relaxation time. The corresponding complex dielectric function is

$$\tilde{\epsilon}(\omega) = \epsilon_\infty + \frac{P_0\tau(1+i\omega\tau)}{1+(\omega\tau)^2}, \tag{3}$$

where ϵ_∞ is the high-frequency contribution to the real part of the dielectric function, and $P_0\tau = \epsilon_{\rm r} - \epsilon_\infty$. This expression describes the data in Fig. 3 (shown as the solid lines) quite well, and reveals that the $\tau \simeq 500$ ns at 250 K, but the relaxation time is of the order of seconds at 10 K, indicating that the dipole processes are frozen out at low temperature. Early explanations of the large permittivity focused on the microstructure; the observation of twin boundaries at very small length scales [18] suggested an equivalent circuit of parallel capacitors, similar to a boundary-layer dielectric [19]. This proposal was validated by an impedance spectroscopy study on a ceramic sample that revealed two different types of dielectric response: one associated with semiconducting

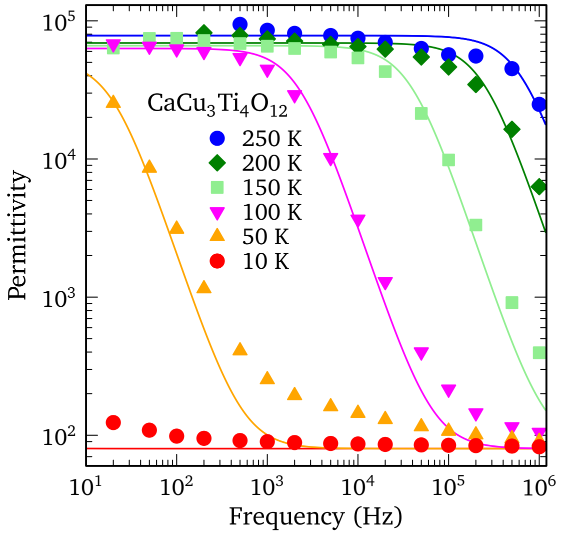

Fig. 3. The frequency dependence of the dielectric permittivity of $CaCu_3Ti_4O_{12}$ shown for several different temperatures. The solid lines represent the calculated values using the Debye model in (3) with $\epsilon_\infty = 80$; at at 150 K, the model parameters are $\tau \simeq 8.2\,\mu$s and $P_0\tau = 8 \times 10^4$. The relaxation times are quite short at high temperature and increase dramatically as the temperature is reduced.

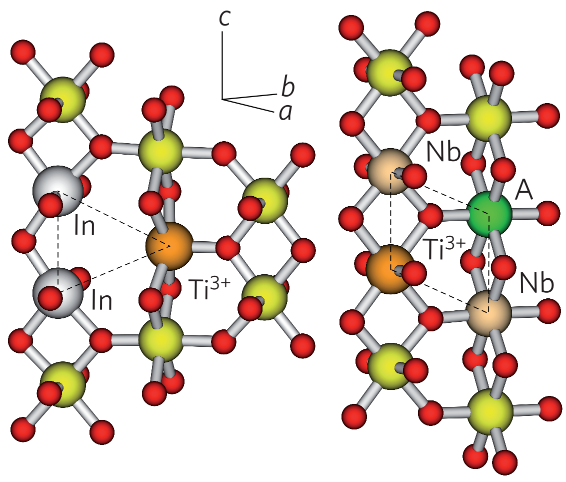

Fig. 4. Ambipolar co-doping in a rutile TiO_2 structure where electron donors (Nb^{5+}) create diamond-like complexes; the oxygen vacancies associated with the acceptors (In^{3+}) result in triangular complexes. The close proximity (or overlap) of these structures create defect-dipoles that give rise to colossal permittivity and low dielectric losses. Depending on the precise configuration of these two entities, A (green) could be Ti^{3+}, Ti^{4+}, or In^{3+}. The unlabeled atoms in the figures are the Ti^{4+} (yellow) and O (red). Reproduced from reference [23].

grains; the other with insulating boundaries [10], effectively forming an internal barrier layer capacitor. At high temperatures, the network of parallel capacitors leads to an enhanced ϵ_r, while at low temperature the increasingly resistive nature of the semiconducting grains destroys this effect, resulting in a continuous medium where the value for ϵ_r reverts back to the contribution from the lattice modes. While this is a reasonable explanation for the large permittivity in $CaCu_3Ti_4O_{12}$, it is not the only one; other mechanisms, such as structurally-frustrated relaxor ferroelectrics [20], nanoscale disorder [21], and Mott variable-range hopping [13], [22], have been suggested, and none have been fully accepted as the origin for the high permittivity. Regardless of the true underlying mechanism, the issue of high dielectric loss remains a significant obstacle to the incorporation into electronic or power devices. Indeed, the Kramers-Kronig relation, which describes the relation between the real and imaginary parts of dielectric function, requires that in any linear, homogeneous material, a large ϵ_r will always be accompanied by a high dielectric loss [16]. A solution to this problem is to deliberately engineer defect dipoles to create an inhomogeneous material.

B. Defect Dipoles

An approach to avoid the difficulties imposed by the Kramers-Kronig relation is to employ localized lattice defect states. Co-doping (doping with equal amounts of donors and acceptors) is a way of introducing defect dipoles within a metal oxide so that the pinned electron is localized to a length scale of the order of nm, allowing for significant displacements. The resulting defect dipoles are large and behave like lattice-defect dipoles rather than free-electron hopping. In this way, the material can display both a high permittivity and a low dielectric loss. The feasibility of this approach was demonstrated by Hu *el al.* [12], where Nb+In co-doping into a TiO_2 parent material was able to achieve a colossal permittivity of $\epsilon_r > 10^4$ with a low dielectric loss ($\tan\delta < 0.1$, which is more than an order of magnitude lower that what is observed in other high permittivity materials) over a wide temperature interval (80 – 250 K) in the radio-frequency range. This result has since been reproduced by several other groups [24]–[27]. The co-doping arrangement of the In and Nb defects is shown in Fig. 4. The In doping creates a triangular complex with a double oxygen vacancy, while the Nb doping creates a diamond-like complex. The defect sites, if they existed independently of one and other, would result in a large permittivity, but also a high dielectric loss. However, when the complexes cluster together, the electrons are tightly bound to these complexes, yielding a large permittivity, but with a small dielectric loss [12]. However, other studies on co-doping in TiO_2 have reproduced the same large value for $\epsilon_r \gtrsim 10^4$, they have also reported a high dielectric loss [28]. It has been suggested that, as in the case of $CaCu_3Ti_4O_{12}$, the large permittivity is the result of both surface and internal barrier capacitance effects [29]. The initial investigation by Hu *it al.* examined the temperature dependence down to 80 K. More recently, a study of Nb+In co-doping in a single crystal of TiO_2 extended the measurements of the dielectric properties down to 2 K; at high temperatures a colossal permittivity of $\epsilon_r \simeq 10^5$ was observed [30], [31]; below about 20 K the permittivity decreases rapidly to about $\epsilon_r \simeq 10^3$, which is still well above the expected value of $\epsilon_r \simeq 100$ associated with the lattice contribution. This suggests that the large values for ϵ_r observed in co-doping studies at high temperature likely originate from either surface or internal barrier capacitance effects; these effects are suppressed at low temperature, and thus the large residual value of $\epsilon_\mathrm{r} \simeq 10^3$ observed at low temperature is attributed to the defect dipoles.

While engineered defect dipoles are a promising avenue of research into high permittivity materials, it is clear that further studies are needed to isolate the microscopic mechanism responsible for the high values of ϵ_r in this class of materials.

III. SUMMARY

There has been a sustained effort over many years to develop high permittivity materials for electronic and energy storage applications. The field was reinvigorated by the discovery of colossal permittivity ($\epsilon_\mathrm{r} \gtrsim 10^4$) in the $\mathrm{CaCu_3Ti_4O_{12}}$ material. While not completely settled, it is generally agreed that the high value for ϵ_r in this material is an extrinsic effect due to either surface or internal barrier capacitance effects (or a combination of the two) that arise from nanodomains in crystals or intergrain effects in ceramics. The issue of high loss in this class of materials has limited their application in real-world devices. The ability to engineer defect-dipoles in transition-metal oxides to yield colossal permittivity wqith low dielectric loss may result in the removal of what has been a persistent barrier to the large-scale implementation of this class of materials.

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