Effect of Cd Dopant on Dielectric Properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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The doping effect of Cd ions on the giant dielectric response in $\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics with $x=0, 0.01, 0.03, 0.05$ and 0.1 was studied in the frequency range of $10\text{ kHz} - 1\text{ MHz}$ over the temperature range of $300 - 850\text{ K}$. It is found that the chemical substitution of Cd ions at the Ca sites results in decrease in dielectric constant by $9\% - 55\%$ for Cd-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, at room temperature. Although the decrease in the dielectric constant was observed by Cd doping, no drastic suppression of dielectric response could be observed by Cd-doping. The dielectric anomaly was found at T_1 (727 K for $x=0.05$), which suggests a phase transition. This T_1 decreases linearly with increasing x . $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is still a member of high-dielectric materials.

Key words: CCTO, dopant, high dielectric constant, oxide

1. INTRODUCTION

Giant dielectric response was discovered in the perovskite-related oxide $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (abbreviated as CCTO) over a wide temperature range of $100 - 600\text{ K}$ by Subramanian and coworkers.[1] This compound exhibits dielectric constants as high as 10^4 at room temperature, although no ferroelectric phase transition has been reported until now. In the low temperature region, the dielectric constant decreases down to 10^2 around 100 K , accompanying with large dielectric dispersion.[2] Furthermore an antiferromagnetic phase transition was observed at 25 K by magnetic susceptibility and specific heat measurements.[3] Compared with typical perovskite-type ferroelectrics such as BaTiO_3 and PbTiO_3 , the nature of this perovskite-related compound is very peculiar in exhibiting high dielectric constants over the wide range of temperature. The giant dielectric behavior seems to originate from an extrinsic origin. The extrinsic effects, such as the interfacial polarization effect [4], the internal boundary layer capacitance effect, and the grain boundary effect [5-10] have also been. Many experimental results suggest that an internal barrier layer capacitor (IBLC) model is responsible.[8, 11-13] However, the occurrence of the dielectric relaxations in both single crystals and ceramic samples indicates that the simple IBLC model is not the only possible explanation.[14] Zhu et al.[15] found recently that some Cu ions occupy the Ca sites, which may split the degeneracy and result in a metal-like behavior and enhance the dielectric responses.

The crystal structure of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is cubic ($\text{Im}\bar{3}$, $a = 7.3781\text{ \AA}$) at room temperature, where the unit cell is $2 \times 2 \times 2$ times the size of typical perovskite ABO_3 . [16] The Ca^{2+} ions occupy a body centered position in a doubled perovskite-type cubic cell, whereas the Cu^{2+} ions

are located on the face and edge centers of the unit cell, as shown in Fig. 1. The $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ ($A = \text{Cd, Bi, Sr, Na, rare-earth elements, or vacancy}$) series of compound were reported to have dielectric constants less than 4000 . [17-19] Another series of isomorphous $\text{ACu}_3\text{M}_4\text{O}_{12}$ ($M = \text{Mn, Ru, Ge, Cr, Ga, Nb, Fe, Sb, Ta}$) offers dielectric constants below 1000 . [11, 17, 20] Recent first-principles calculations reveal that CCTO provides dielectric constants only in the range $40 - 50$. [21] Many researchers considered that the large dielectric response is not intrinsic, and should be extrinsic and related to the special microstructure. [22]

Figure 1 Crystal structure of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ oxide: Ca (large circle) at the corner and body centered position, Cu on the face and edge centers of the unit cell. Octahedra are TiO_6 perovskite units. Solid lines indicate the unit cell of typical perovskite ABO_3 structure and square CuO_2 plane.

Due to its unusual perovskite-related structure, the dielectric properties of CCTO have attracted considerable attention in recent years. Recently a

new dielectric anomaly was found at 732 K (T_1). [23,24]. Although extensive works have been done to understand the anomalous dielectric behavior, the origin of the novel high dielectric response is still unclear. In this paper, we prepared Cd-doped CCTO and studied the role of Cd ions in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ structure, since the dielectric constant of isomorphous $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ is only 409 at 100 kHz and room temperature. [1]

2. EXPERIMENTAL

$\text{CaCd}_x\text{Cu}_{3-x}\text{Ti}_4\text{O}_{12}$ ($x=0, 0.01, 0.03, 0.05, \text{ and } 0.1$) ceramics were synthesized via the conventional solid-state reaction method using stoichiometric amounts of high-purity CaCO_3 , CuO , TiO_2 , and CdO . The mixed powders were calcined in air at 1273 K for 12 h and at 1373 K for 24 h with an intermediate grinding. The calcined samples were milled and pressed into pellets of 20 mm in diameter and about 1 mm in thickness. Then the pellets were sintered in air at 1373 K for 12 h. X-ray powder diffraction data were recorded on an X-ray diffractometer with $\text{MoK}\alpha$ radiation and a diffracted-beam graphite monochromator operated at 50 kV and 100 mA. To measure the dielectric properties, silver electrodes were painted on the samples' surfaces. Dielectric constant and $\tan\delta$ data were collected by using HP-4274A and HP-4275A LCR meters in the temperature range of 300–850 K.

3. DOPING EFFECT ON DIELECTRIC CONSTANT

$\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ has been reported to have a relative low dielectric constant, although it is isomorphous with CCTO : the room temperature dielectric constant of $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ was reported to be 409 (100 kHz), which is only 4% of that of CCTO [1]. The doping effect of Cd ions on the giant dielectric constant was studied in mixed $\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics. Figures 2 and 3 show the temperature dependence of dielectric constant of $\text{Ca}_{0.95}\text{Cd}_{0.05}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ from room temperature to 850 K at the frequencies of 10 kHz, 100 kHz and 1 MHz.

Figure 2. Temperature dependence of Cd-doped CCTO with $x=0.05$ at 10 kHz, 100 kHz and 1 MHz.

Figure 3. Expanded figures of dielectric constant of Cd-doped CCTO.

The value of dielectric constant is 4×10^4 at 350 K, which is almost the same as those observed in pure CCTO. With increasing temperature, the dielectric constant increases monotonously and reaches to 6.6×10^5 at 600 K. Above 600 K, the dielectric constant increases rather rapidly, and exhibits a shoulder-like round anomaly around 630 K at 10 kHz. A new dielectric anomaly was found at 728 K (T_1), of which peak values are 1.8×10^6 at 10 kHz, 1.7×10^5 at 100 kHz and 3.8×10^4 at 1 MHz. The dielectric evidence shows that Cd-doped CCTO undergoes a phase transition at T_1 , as observed in pure CCTO. [24] The shoulder-like anomaly shifts from 630 K to 650 K with increasing frequency (1 MHz). This shoulder-like behavior is coincident well with pure CCTO. [23] This dispersion has been observed in CCTO by Zhang et al. [25], Patterson et al. [26], and Choudhary et al. [27]. The molar ratio (x) dependence of dielectric constant is shown in Fig. 4. The overall values decrease once with increasing x , and then turn to increase for the samples over $x=0.03$. The dielectric constant at 350 K is 8.3×10^4 for pure compound at 1 MHz, and shows a minimum ($\epsilon \sim 3 \times 10^3$) for $x = 0.03$. However, it increases for the sample with $x = 0.05$ ($\epsilon \sim 1.1 \times 10^4$).

The Cd-doped samples have also high dielectric constant and a dielectric anomaly at T_1 . The transition temperature T_1 shifts linearly from 732 K ($x=0$) to 727 K ($x = 0.05$) with increasing x (Fig. 5). However, no drastic dielectric suppression could be observed by Cd-doping as shown in Fig. 6. This conclusion is consistent with a previous dielectric measurement of pure $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ ($\epsilon \sim 9 \times 10^3$ at room temperature (100 kHz)) by Zuo et al. [28], in contrast to the first report, $\epsilon=409$, for pure $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ [1].

Figure 4. (a) Dielectric constant of Cd-doped ceramics, $\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ with $x = 0, 0.01, 0.03$ and 0.05 at 1 MHz. The inset is an expanded figure around T_1 for $x = 0.03$. (b) Dielectric loss of $\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ with $x = 0.05$ at 1 MHz.

This evidence means that $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ is also a member of high-dielectric materials.

Figure 5. Molar ratio (x) dependence of the transition temperature (T_1) in $\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics.

4. DISCUSSION

The chemical formula $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ can be expressed as $4(\text{Ca}_{1/4}\text{Cu}_{3/4})\text{TiO}_3$ in the ideal perovskite ABO_3 structure. The unit cell contains eight TiO_6 octahedra. Owing to the presence of Ca and Cu, the TiO_6 octahedra are highly distorted in the framework of O-Ca-O and

Figure 6. Dependence of dielectric constant at 350 K and T_1 on molar ratio (x) in $\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ at 1 MHz.

O-Cu-O.[29, 30] In typical perovskite ferroelectrics, the dipole moment induced by the distortion of TiO_6 octahedron from its regular configuration plays an important role for the appearance of ferroelectricity. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ exhibits the enormously high dielectric constant of the order of 10^4 in both forms of single crystals, ceramics and thin films at room temperature. Cohen et al. [31] interpreted the giant dielectric constant of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ arising from spatial inhomogeneity of local dielectric response. Present study indicates that $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ undergoes a phase transition at about 730 K (T_1). As the precise crystal structure of constituting atoms in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ above T_1 has not been clear at present, it may be probable that X-ray diffuse scattering behavior at high temperatures suggests an order-disorder motion between Ca and Cu. Such motions of Ca and Cu are closely related to the large fluctuation of TiO_6 octahedra, which allows the strong dipolar correlation as Jahn-Teller interaction. Whangbo and Subramanian explained the high dielectric property may arise from local dipole moments associated with off-center displacement of Ti ions, but the transition to a ferroelectric state is frustrated by the TiO_6 octahedral tilt which is required to accommodate the CuO_2 square planar coordination.[32] It may be probable that the present work is associated with such structural behavior at high temperatures.

Dielectric measurements of Cd-doped CCTO ceramics were studied. A new dielectric anomaly was found at a high temperature (T_1), just as in pure CCTO. No drastic suppression of dielectric response could be observed by Cd-doping. $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ is still a member of high-dielectric materials. Further studies of precise crystal structure below and above T_1 will be necessary to clarify the new phase transition in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$.

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(Received December 25, 2009; Accepted January 31, 2010)