Unusual Impurity Effects on the Dielectric Properties of \( \text{CaCu}_3-x\text{Mn}_x\text{Ti}_4\text{O}_{12} \)

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Abstract

\( \text{CaCu}_3\text{Ti}_4\text{O}_{12} \) has a large dielectric constant (\( \varepsilon \sim 10^4 \) at 300 K), which is almost constant above 100 K, followed by a 100-fold reduction below 100 K. The physical mechanism of this anomalous behavior has been extensively investigated. We found that only 2\% substitution of Mn for Cu dramatically quenches the huge \( \varepsilon \) of \( 10^4 \) down to \( 100 \) over the measured temperature range from 4.2 to 300 K. In usual substitution effects, 2\% impurity induces a tiny change in \( \varepsilon \) of the order of 2\%. Thus the present substitution effect suggests that dipole moments interact (probably frustrate) in \( \text{CaCu}_3\text{Ti}_4\text{O}_{12} \), which is broken by a small amount of impurities.

1. Introduction

The giant dielectric material \( \text{CaCu}_3\text{Ti}_4\text{O}_{12} \) has three mysterious dielectric properties\(^1-3\). The first is that the dielectric constant is very large values (10000 for ceramics and 80000 for single crystals). The second is that the dielectric constant is nearly constant over a wide temperature range \( \sim 100-600 \) K. The third is that the dielectric constant drops rapidly to 100 below about 100 K.

Comparing \( \text{CaCu}_3\text{Ti}_4\text{O}_{12} \) with other Ti oxides, \( \text{BaTiO}_3 \) has a large dielectric constant near the ferroelectric phase transition temperature. However, the dielectric constant strongly depends on temperature, which makes a remarkable contrast with that of \( \text{CaCu}_3\text{Ti}_4\text{O}_{12} \). Recently there is a discussion whether the mysterious dielectric properties of \( \text{CaCu}_3\text{Ti}_4\text{O}_{12} \) are intrinsic or extrinsic\(^4\). In \( \text{CaCu}_3\text{Ti}_4\text{O}_{12} \) any structural phase transition does not occur, and it is difficult to explain these properties by intrinsic mechanism. Thus recent researches tend to support the extrinsic mechanism\(^5,6\), where the semiconducting-insulating grain boundary due to the oxide/planar defect makes the dielectric constant very large through surface and internal barrier layer capacitors mechanism\(^7\).

At present impurity substitution effect has not been reported. In this paper, we present Mn substitution effects on \( \text{CaCu}_3\text{Ti}_4\text{O}_{12} \), and suggest a possible mechanism for the large dielectric constant.

2. Experimental

Polycrystalline samples of \( \text{CaCu}_{3-x}\text{Mn}_x\text{Ti}_4\text{O}_{12} \) \( (x = 0, 0.03, 0.06, \text{and} 0.6) \) and \( \text{Ca}_{1+y}\text{Cu}_{3-y}\text{Ti}_4\text{O}_{12} \) \( (y = -0.1, -0.05, 0, 0.05, \text{and} 0.1) \) were prepared by a solid-state reacton. Stoichiometric amounts of \( \text{CaCO}_3 \), \( \text{CuO} \), \( \text{Mn}_3\text{O}_4 \), and \( \text{TiO}_2 \) were mixed, and the mixture was calcined at 1000°C for 12 h in air. The product was finely ground, pressed into a pellet, and sintered at 1090°C for 24 h in air. Dielectric constants and loss tangent of the samples were measured with an AC four-probe method with an LCR meter (Agilent-4284A) from \( 10^4 \) to \( 10^6 \) Hz. The temperature was varied between 4.2 and 300 K in a liquid He cryostat.

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3. Results and Discussion

X-ray diffraction pattern of the polycrystalline samples are fully indexed on the structure reported in [8]. The crystal structure of CaCu$_3$Ti$_4$O$_{12}$ is the perovskite structure with Cu located at the A site. Since Cu is small ion, TiO$_6$-octahedron is highly canted.

Figure 1 shows the dielectric constant ($\varepsilon$) of CaCu$_{3-x}$Mn$_x$Ti$_4$O$_{12}$ ($x = 0, 0.06$). The value of $\varepsilon$ of $x = 0$ at 1 MHz at 300 K is $\sim 10000$, which is roughly equal to the value reported in [2]. We should emphasize that only 2% Mn substitution dramatically suppresses $\varepsilon$ over the measured temperature range from 4.2 to 300 K. The loss tangent data of $x = 0$ has a peak around 100 K as reported in [2], but the data of $x = 0.06$ has no peak from 4.2 to 300 K. In usual substitution effects, 2% impurity induces a tiny change in $\varepsilon$ of the order of 2%. Thus the present substitution effect suggests that dipole moments interact (probably frustrate) in CaCu$_3$Ti$_4$O$_{12}$, which is broken by a small amount of impurities.

Figure 2 shows the dielectric constant ($\varepsilon$) of Ca$_{1+y}$Cu$_{3-y}$Ti$_4$O$_{12}$ ($y = -0.1, -0.05, 0, 0.05, 0.1$) at 1 MHz at 300 K. For $y < 0$, $\varepsilon$ is severely suppressed with $y$, while it is insensitive to $y$ for $y > 0$. Note that Ca ions form bcc structure in CaCu$_3$Ti$_4$O$_{12}$, which remains unchanged for $y > 0$, and is disordered for $y < 0$. Therefore we think the Ca bcc structure plays an important role for the large $\varepsilon$.

Ikeda et al.[9] reported the anomalous dielectric response of LuFe$_2$O$_4$, which is surprisingly similar to those of CaCu$_3$Ti$_4$O$_{12}$. This is explained in terms of the motion of the polar domains with the charge ordering of Fe$^{2+}$ and Fe$^{3+}$. Thus we think that a similar scenario will be applicable to CaCu$_3$Ti$_4$O$_{12}$, though the origin of domains is not clear at present. Then the rapid decrease in $\varepsilon$ is attributed to pinning or breaking the domain wall.

4. Summary

In conclusion, we present the anomalous substitution effects on CaCu$_3$Ti$_4$O$_{12}$, and propose that an origin of the large dielectric constant is a domain-wall motion, similarly to the large $\varepsilon$ for LuFe$_2$O$_4$.

Acknowledgements

We would like to thank K. Kohn for valuable discussions, and also thank Y. Yoshino for technical support.