Unusual Impurity Effects on the Dielectric Properties of $CaCu_{3-x}Mn_xTi_4O_{12}$

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Abstract

$CaCu_3Ti_4O_{12}$ 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 ε 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 ε of the order of 2%. Thus the present substitution effect suggests that dipole moments interact (probably frustrate) in $CaCu_3Ti_4O_{12}$, which is broken by a small amount of impurities.

Key words: dielectric constant; impurity

1. Introduction

The giant dielectric material $CaCu_3Ti_4O_{12}$ 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 ~100-600 K. The third is that the dielectric constant drops rapidly to 100 below about 100 K.

Comparing $CaCu_3Ti_4O_{12}$ with other Ti oxides, $BaTiO_3$ 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 $CaCu_3Ti_4O_{12}$. Recently there is a discussion whether the mysterious dielectric properties of $CaCu_3Ti_4O_{12}$ are intrinsic or extrinsic[4]. In $CaCu_3Ti_4O_{12}$ 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 $CaCu_3Ti_4O_{12}$, and suggest a possible mechanism for the large dielectric constant.

2. Experimental

Polycrystalline samples of $CaCu_{3-x}Mn_xTi_4O_{12}$ (x = 0, 0.03, 0.06, and 0.6) and $Ca_{1+y}Cu_{3-y}Ti_4O_{12}$ (y = -0.1, -0.05, 0, 0.05, and 0.1) were prepared by a solid-state reacton. Stoichiometric amounts of $CaCO_3$, CuO, Mn_3O_4, and 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 a parallel-plate capacitor arrangement using an AC four-probe method with an LCR meter (Agilent-4284A) from 10^2 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 patern of the polycrystalline samples are fully indexed on the structure reported in [8]. The crystal structure of $CaCu_3Ti_4O_{12}$ 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(ε) of $CaCu_{3-x}Mn_xTi_4O_{12}$ (x = 0, 0.06). The value of ε of $x = 0$ at 1 MHz at 300 K is ~10000, which is roughly equal to the value reported in [2]. We should emphasize that only 2% Mn substitution dramatically suppresses ε 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 ε of the order of 2%. Thus the present substitution effect suggests that dipole moments interact (probably frustrate) in $CaCu_3Ti_4O_{12}$, which is broken by a small amount of impurities.

Figure 2 shows the dielectric constant(ε) of $Ca_{1+y}Cu_{3-y}Ti_4O_{12}$ (y = -0.1, -0.05, 0, 0.05, and 0.1) at 1 MHz at 300 K. For $y < 0$, ε is severely suppressed with y , while it is insensive to y for $y > 0$. Note that Ca ions form bcc structure in $CaCu_3Ti_4O_{12}$, 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 ε.

Ikeda *et al.*[9] reported the anomalous dielectric response of $LuFe_2O_4$, which is surprisingly similar to those of $CaCu_3Ti_4O_{12}$. 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 $CaCu_3Ti_4O_{12}$, though the origin of domains is not clear at present. Then the rapid decrease in ε is attributed to pinning or breaking the domain wall.

4. Summary

In conclusion, we present the anomalous substitution effects on $CaCu_3Ti_4O_{12}$, and propose that an origin of the large dielectric constant is a domain-wall motion, similarly to the large ε for $LuFe_2O_4$.

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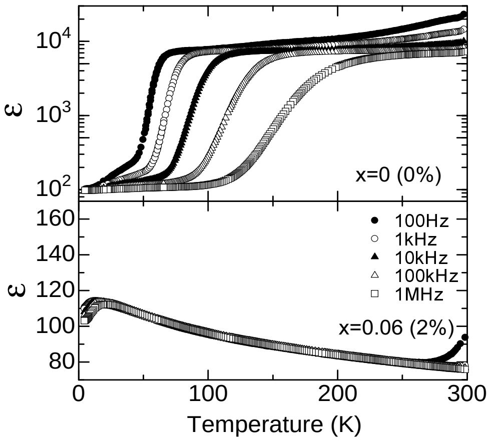

Fig. 1. The dielectric constant of $CaCu_{3-x}Mn_xTi_4O_{12}$ (x = 0, 0.06)

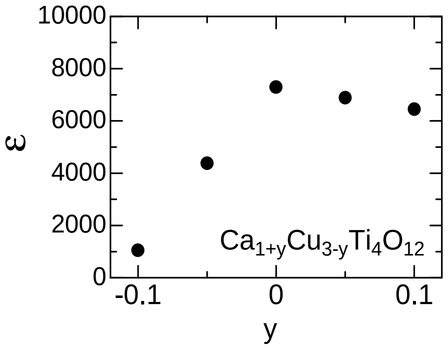

Fig. 2. The dielectric constant of $Ca_{1+y}Cu_{3-y}Ti_4O_{12}$ (y = -0.1, -0.05, 0, 0.05, 0.1) at 1MHz at 300K

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