Transactions of the Materials Research Society of Japan 28 [1] 137-139 (2003)

Low temperature heat capacity and dielectric relaxation in $CaCu_3Ti_4O_{12}$ ceramics

Yosuke Moriya, Hitoshi Kawaji, Takeo Tojo, and Tooru Atake
Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8503 Japan
Fax: 81-45-924-5339, e-mail: y.moriya@msl.titech.ac.jp

Heat capacity and dielectric constant of $CaCu_3Ti_4O_{12}$ (CCT) ceramics were measured below about 420 K. A lambda-shaped heat capacity anomaly due to an antiferromagnetic transition was observed at 25 K, while no heat capacity anomaly was observed around 100 K, where the dielectric constant shows a large anomaly. The temperature and frequency dependence of the dielectric constant were reproduced from the calculation of dielectric constant on the basis of "barrier layer capacitor model". The results suggest that the dielectric relaxation phenomenon in CCT is not caused by orientational relaxation of ferroelectric nanoregions (FNR), but by thermal excitation of conduction electrons in the microstructure composed of semiconductive bulks and insulating thin layers.
Key words: $CaCu_3Ti_4O_{12}$, relaxor, dielectric constant, heat capacity

1. INTRODUCTION

Recently, very high value of dielectric constant has been found for a perovskite-related compound, $CaCu_3Ti_4O_{12}$ (CCT), above 100 K [1]. CCT shows a characteristic dielectric relaxation phenomenon similar to so-called relaxors, and the dielectric constant drops down drastically around 100 K on cooling [2]. In the typical relaxors such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT), it has been proposed that ferroelectric nanoregions (FNR) are formed in the paraelectric matrix with decreasing temperature, and the dielectric relaxation phenomenon is caused by the orientational relaxation of FNR [3]. We have been investigating thermodynamic properties of PMN and PMT and found a very broad heat capacity anomaly, that is the first observation concerning the thermal response of the formation of FNR in the relaxors (Fig.1). On the analogy of the $Pb(B'B'')O_3$-type relaxors, FNR might be formed in CCT, and it is expected to observe a similar heat capacity anomaly. Although the possibility of the formation of FNR in CCT has been investigated [2,4], no evidence of FNR has been given. In order to detect a heat capacity anomaly caused by FNR, highly precise heat capacity measurements are needed over a wide temperature range because the anomaly might broaden out as in PMN and PMT (Fig.1). In the present study, we performed precise heat capacity measurements and dielectric measurements on CCT ceramic sample from liquid helium temperature up to 420 K to clarify the origin of the dielectric relaxation phenomenon in CCT.

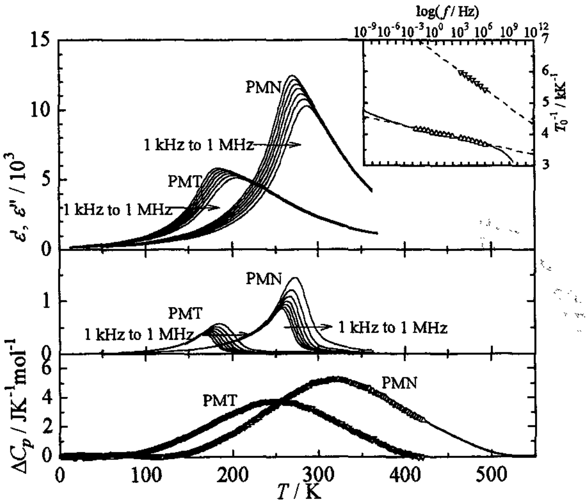

Fig.1. Dielectric constant and excess heat capacity of PMN and PMT. The inset shows $1/T_{max}$ vs. $\log f$ plot, where T_{max} is the maximum temperature of dielectric loss and f is the measurement frequency.

2. EXPERIMENTAL

The ceramic sample of CCT was prepared by conventional solid phase reaction method. Powder materials of $CaCO_3$, CuO, and TiO_2 (Rare Metallic Co., Ltd. 99.99 %) were mixed and then calcined at 1000 °C for 12h. The resultant was reground and then pressed into disks with 10 mm diameter and ~1 mm thickness. The disks were sintered at 1100 °C for 24 h. The powder X-ray diffraction pattern of the sample is shown in Fig. 2, where a single-phase sample without any impurities is confirmed and the crystal structure is identified as a cubic perovskite-related structure (*Im*3). The dielectric constant was measured between 15 and 300 K using HP4284A Precision LCR Meter, and between 300 and 420 K using HP4192A Impedance Analyzer in different cryostats with frequencies of 1, 3, 10, 30, 100, 300, and 1000 kHz. The measurements were carried out in both cooling and heating directions with the rate of 1 K/min, and no hysteresis was observed in both runs. The heat capacity was measured between 13 and 420 K using a homemade adiabatic calorimeter, and between 2 and 60 K using PPMS (Quantum Design, Inc.). The amounts of the sample used for the measurements were 3.4523 g and 23.370 mg, respectively.

3. RESULTS AND DISCUSSION

The temperature and frequency dependence of the dielectric constant of CCT is shown in Fig. 3. The dielectric constant drops down on cooling, and the dielectric relaxation phenomenon similar to typical relaxors is clearly seen. The absolute values are smaller than the previous report (~10^4) [2], which should be caused by low density of sintered sample and/or Cu deficiency [1]. The measured heat capacity is shown in Fig. 4; C_pT^{-1} vs. T plot is also given in an enlarged scale together with the data of Koitzsch et al. [4]. A lambda-shaped heat capacity anomaly due to an antiferromagnetic transition is clearly observed at 25 K. On the other hand, no remarkable heat capacity anomaly is observed above 50 K, even in the temperature region where the dielectric relaxation phenomenon was detected. To analyze the heat capacity data, we converted the measured heat capacity to the corresponding Debye characteristic temperature, Θ_D, which is more sensitive to a small and/or broad anomaly. The result is shown in Fig. 5 with those of PMN and PMT. In the curves of PMN and PMT, there is a deep minimum in the lowest temperature region, which is commonly observed in a variety of compounds. This is mainly caused by low frequency optical phonons, which is strongly affected by the mass of ions; the frequency decreases with increasing the mass. In the higher temperature region, an extra minimum is observed around 300 K, which clearly demonstrates the existence of the broad heat capacity anomaly in PMN and PMT. In the curve of CCT, there is also a deep minimum in the lowest temperature region, which is caused by the low frequency optical phonons and the heat capacity anomaly due to the antiferromagnetic phase transition; the low frequency optical phonon contribution is not clear because of the large contribution from the antiferromagnetic phase transition. Except for the anomaly, only a very small hollow around 50 K as indicated by an arrow in Fig. 5 appears to exist, which might correspond to an additional anomaly. However, this might be caused by low frequency optical phonons because the contribution of the optical phonons shifts to higher temperature from those in PMN and PMT by the mass effect. To investigate the origin of the hollow around 50 K, the Debye temperature of CCT was compared

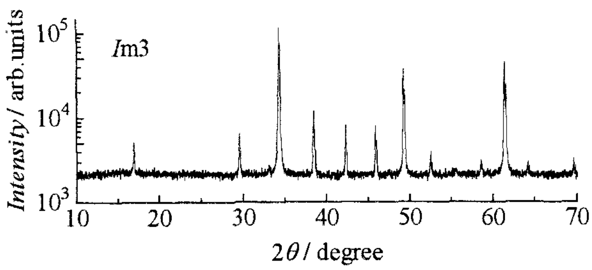

Fig.2. Powder X-ray diffraction pattern of CCT ceramic sample.

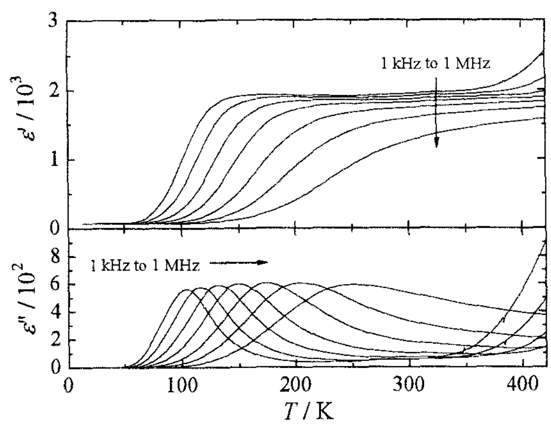

Fig.3. Dielectric constant of CCT ceramic sample.

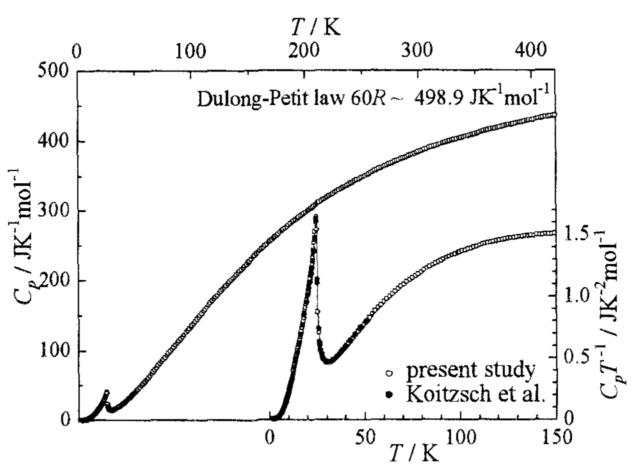

Fig.4. Heat capacity of CCT ceramic sample (open circles). C_pT^{-1} vs. T plot below 150 K is also shown in an enlarged scale, where the data reported by Koizsch et al. [4] below 50 K are also plotted (closed circles).

with that of $CaTiO_3$ which has the similar mass ions in the formula. As shown in the inset of Fig. 4, the minimum in the curve of $CaTiO_3$ just corresponds to the hollow in the curve of CCT. Therefore, the small hollow is caused by the low frequency optical phonons. This implies that no heat capacity anomaly related to the dielectric relaxation phenomenon exists and thus the relaxation phenomenon should not be caused by the FNR.

Another possible model should be considered, that is "barrier layer capacitor model", which is composed of semiconductive grains separated by insulating grain boundaries [5]. Assuming that CCT can be represented by an equivalent series circuit of a resistance as semiconductive bulk and a capacitor as insulating thin films, we calculated the temperature and frequency dependence of the dielectric constant. The calculated dielectric constant is shown in Fig. 6, which is in good agreement with the experimental data. In this model, the temperature dependence of the electric conductivity is considered as a thermal activation type. The excitation of only a few electrons can lead to a drastic change in the value of the resistance and thus result in the apparent dielectric constant, which should contribute a negligibly small electronic heat capacity. Consequently, no remarkable heat capacity anomaly can be detected in this model. In addition, the glasslike dielectric relaxation phenomenon in CCT obeys the Arrhenius law, which suggests a simple thermal activation process, while PMN and PMT obeys modified Arrhenius law with a temperature-dependent activation energy implying the growth of FNR.

The barrier layer capacitor model was originally proposed to represent the characteristics of ceramics. However, such a relaxation phenomenon was also reported in a single crystal sample of CCT [6]. This implies that CCT contains by nature two different characters, i.e., semiconductive and insulating, in the crystal. On the other hand, single crystal X-ray diffraction studies revealed that the sample is twinned with microdomains, and twin boundaries may be insulating [1]. However, it is a little bit strange, because CCT is of cubic symmetry with $Im3$. From the present study, the origin of the dielectric relaxation phenomenon seems to be explained by barrier layer capacitor model. However, further studies are highly desired for complete understanding.

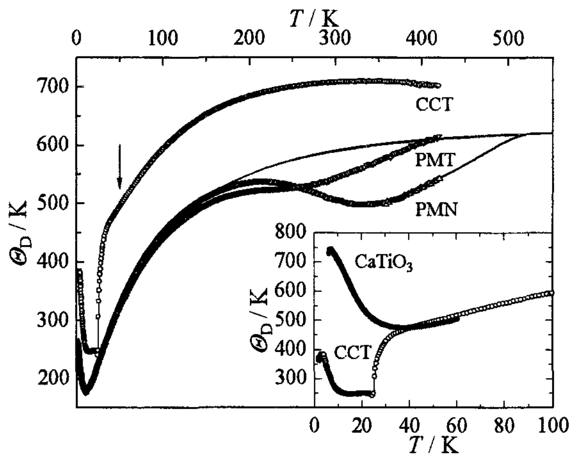

Fig.5. Debye characteristic temperature Θ_D calculated from the measured heat capacity of CCT, PMN and PMT assuming 15 N_A degrees of freedom. Solid lines denote the estimated lattice contribution of PMN and PMT. The inset shows Θ_D of CCT and $CaTiO_3$ in the low temperature region.

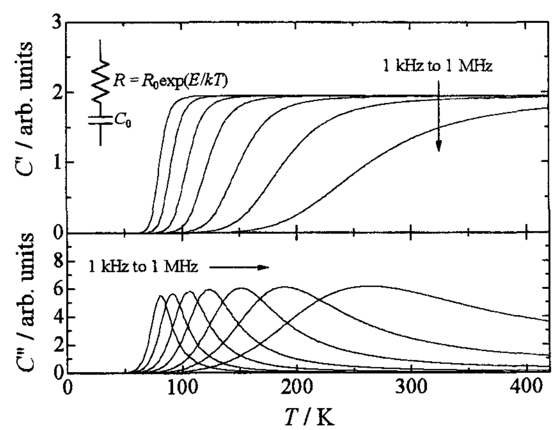

Fig.6. Calculated dielectric constant using a series equivalent circuit according to the "barrier layer capacitor model".

[1] M.A. Subramanian, D.Li,N. Duan, B.A. Reisner, and A.W. Sleight, *J. Solid State Chem.*, **151** (2000) 323.

[2] A.P. Ramirez, M.A. Subramanian, M. Gardel, G. Blumberg, D.Li,T. Vogt, and S.M. Shapiro, *Solid State Commun.*, **115** (2000) 217.

[3] Z.-G. Ye, *Ferroelectrics*, **184** (1996) 193.

[4] A. Koitzsch, G. Blumberg, A. Gozar, B. Dennis, A.P. Ramirez, S. Trebst, and S. Wakimoto, *Phys. Rev.* **B65** (2002) 52406.

[5] C.-F. Yang, *Jpn. J. Appl. Phys.*, **36** (1997) 188.

[6] C.C. Homes, T. Vogt, S.M. Shapiro, S. Wakimoto, and A.P. Ramirez, *Science*, **293** (2001) 673.

(Received December 21, 2002; Accepted January 31, 2003)