Dielectric anomalies in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ at high temperatures

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We reported the dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ in the temperature range from room temperature to 800°C and the frequency range from 20 Hz to 10 MHz. Apart from the widely reported dielectric anomaly occurring around 200°C, three additional dielectric anomalies were found. The new anomalies are very sensitive to electrode sintering conditions and annealing atmospheres, indicating that they are dependent not only on the electrode-sample contact but also on oxygen vacancies.

ceramics, dielectrics, grain boundaries

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Since the perovskite-related $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has been reported to have colossal and flat dielectric constants in the order of 10^3 – 10^5 in a wide temperature range around room temperature, which presents promising potential applications for kinds of devices, researchers have carried out a great deal of investigations on this material [1–3]. In addition to the stunning colossal dielectric behavior with its main features appearing in the temperature range below room temperature, a relaxor-like dielectric anomaly occurring in the temperature range from 400 to 600 K was considered as another surprising feature in CCTO [4–6]. Although this feature is still an open question and ascribed to various causes, such as ferroelectric relaxor [4], electronic ferroelectrics [5], artificial phenomenon due to negative capacitance, and pseudo-relaxor caused by Maxwell-Wagner (MW) relaxation [6], it reveals the rich dielectric phenomena in CCTO at high temperatures. These phenomena have not been illustrated thoroughly until now. In this work, we measured samples of CCTO in the high temperature range from room temperature to 800°C. The results showed that apart from the above-mentioned dielectric anomaly, three additional anomalies related to oxygen vacancy and electrode-sample contact were found.

1 Experimental

CCTO pellets used for dielectric measurements were prepared by solid-state reaction method. High-purity (99.99%) powders of CaCO_3 , TiO_2 and CuO were mixed according to molar ratios and well ground in a mortar. The mixture were fired in air at 1000°C for 12 h and then reground, followed by a sintering process at 1100°C for 29 h. Finally, the mixture was pressed into pellets and sintered in air at 1100°C for 10 h. The purity of the resultant compound was examined by powder X-ray diffraction (XRD) on an XD3 diffractometer with $\text{Cu K}\alpha$ radiation. After polishing both sides of the samples, platinum or silver paint were coated on them and fired at high temperature for different time to remove the polymeric components. Details about the sintering temperature and time were listed in Table 1. A Wayne Kerr 6500B precise impedance analyzer with a heating ramp of 3 K/min controlled by a Stanford temperature controller was used to collect data for temperature dependent dielectric properties. The dielectric measurements were performed in ambient air. Annealing treatments were performed in flowing (200 mL/min) O_2 and N_2 (both with purity >99.999%) at 1000°C for 2 h. The heating and cooling rates in sample preparation and annealing processes were controlled to be 5 K/min. The ac measuring signal was 100 mV rms.

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Table 1 Electrode preparation for samples A, B, C and D

Sample	Electrode preparation
A	Sintered at 600°C for 0.5 h
B	Sintered at 600°C for 1 h
C	Sintered at 800°C for 1 h
D	Sintered at 800°C for 2 h

2 Results and discussion

The XRD patterns of CCTO ceramics measured at several temperatures are presented in Figure 1. The patterns were analysed using Jade 5 power diffraction data analysis software. It revealed that the as-sintered samples are single phase with a cubic perovskite structure. The room temperature lattice parameter calculated to be $a=0.7356$ nm is fairly consistent with that reported (0.7393 nm) by Subramanian et al. [1]. Besides the fact that all the reflections moves to lower two theta values with increasing temperature due to thermal expansion, no alien reflections were detected. This indicates that there are not any structure phase transitions at least up to the highest measuring temperature of 900°C.

The main results of the high-temperature dielectric properties of CCTO pallets coated with Pt paste electrode are summarized in Figure 2. Details of the preparation of the electrodes are tabulated in Table 1. From Figure 2 we can

Figure 1 XRD patterns of CCTO sample at several temperatures from room temperature to 900°C.

see a relaxor-like dielectric anomaly appears around 200°C, whose position hardly changes, whereas its intensity varies notably with the electrode fabrication. This is because that the relaxor-like behavior was revealed to be associated with the surface-layer-related Maxwell-Wagner relaxation due to oxygen vacancy inhomogeneous distribution. Details of this investigation will appear elsewhere. In spite of the relaxor-like anomaly, three additional dielectric anomalies were observed in the temperature range 300–800°C. For brevity, these anomalies were designated as A1, A2 and A3 in the

Figure 2 Temperature dependence of dielectric constant for CCTO samples coated with Pt paste electrode but prepared with different conditions as listed in Table 1.

order of ascending temperature as indicated in the figures. Compared with the relaxor-like anomaly, three main features of the newly appeared anomalies can be extracted: (1) both the position and the intensity of A1 to A3 depend strongly on the electrode fabrication, indicating that they are related to sample-electrode contact. (2) The positions of anomalies A1 to A3 hardly vary, but their intensities remarkably decrease with increasing measuring frequency. This feature implies that these anomalies might be associated with phase transition. High-temperature XRD measurements revealed that CCTO undergoes a structural phase transition at 732 K (459°C) [7]. Unfortunately, none of the anomalies occurs at the temperature of the transition, indicating a mechanism other than structural phase transition underlies these anomalies. (3) It is clearly seen that higher sintering temperature or longer sintering time of the electrode can greatly destroy A3 but notably enhance A1 and A2. This fact implies that A3 can be ascribed to the Maxwell-Wagner relaxation due to the dielectric mismatch between the sample and electrode. When the electrode was sintered at higher temperature or with longer sintering time, Pt diffusion into the sample becomes more pronounced, which in turn, weakens the dielectric mismatch thereby destroying A3.

Relaxor-like anomaly was widely reported in various materials [8]. There is a wide consensus that the anomaly appearing in the temperature range of 400–900°C in oxide materials, especially for those containing titanium, is related to oxygen vacancies [9]. This suggests that the high-temperature anomaly in CCTO may be related to oxygen vacancy. In order to confirm this inference, sample D was further annealed firstly in N₂ and then in O₂ atmospheres. After each annealing treatment, dielectric properties were measured as a function of temperature. Figure 3 compares the results of $\varepsilon'(T)$ after O₂- and N₂-annealing treatments. One can clearly see that the N₂-annealing treatment greatly enhances A1 and A2 (the two anomalies are almost overlapped), but the O₂-annealing treatment destroys these anomalies. It therefore follows that the oxygen vacancy is truly responsible for A1 and A2. A more careful examination of Figure 3 reveals that only A2 exists after O₂-annealing treatment. In this case, the dielectric loss tangent ($\tan\delta$) shown in Figure 4 presents distinct information about A2 due to the absence of other anomalies. It was found that A2 was accompanied by a set of loss tangent peaks as indicated by an arrow in Figure 4. The peak position moves to higher temperatures as the measuring frequency increases, implying that A2 might be a relaxational process. The inset of Figure 4 displays the measuring frequency, f , versus the reciprocal of the peak temperature, T_p . The data fall perfectly on a straight line in the half-logarithmic presentation, indicating that the relaxation follows the Arrhenius law:

$$\tau = \tau_0 \exp(E_a/k_B T_p), \quad (1)$$

where τ is the relaxation time, τ_0 is the pre-exponential fac-

tor, E_a is the activation energy, and k_B is the Boltzmann constant. The plot yields values of τ_0 and E_a to be 3.07×10^{-19} s and 1.96 eV, respectively. The anomaly A2 appears at temperatures where oxygen vacancies can move due to thermal activation [10]. The oxygen-vacancy movement also can be accompanied by a dipole relaxation; this process is considered to be a competitive phenomenon between the dielectric relaxation and the electric conduction [11]. The relaxation parameters E_a and τ_0 associated with oxygen-vacancy movement were widely reported to be around 1.0 eV and 10^{-11} – 10^{-16} s, respectively [12,13]. The present parameters are far away from these values indicating they have no physical meaning. This fact prompts us to suggest that A2 is associated with a process of phase transition instead of a relaxational process. This phase transition, if it ever exists, is neither symmetry breaking nor endothermic/exothermic, and therefore cannot be detected by XRD and thermal measurements. This should be the so-called phase transition from the static disordered state to the dynamic disordered state of oxygen vacancy distribution [13,14]. As aforementioned that the A2 is related to delocalized oxygen vacancies, the delocalization process is actually

Figure 3 Temperature dependence of dielectric constant for sample D in the cases after being annealed in N₂ and O₂ atmospheres.

Figure 4 Temperature dependence of $\tan\delta$ for sample D after being annealed in N₂.

a thermally activated diffusion-related process depending exponentially on temperature. At high enough temperatures, oxygen vacancies diffuse randomly and form a disordered state. This state is the so-called dynamic disordered state, which will be “frozen in” and change to a static disordered state when temperature decreases sufficient low. Although the transition from dynamic to static disordered states cannot be evidenced by XRD and thermal measurements, it can be easily detected by electrically and mechanically dynamic methods, since the oxygen vacancies produce not only electric dipoles but also elastic dipoles [13]. On the other hand, this kind of phase transition depends strongly not only on the concentration of oxygen vacancy but also on doping level. A small amount of doping level can notably enhance this transition [13]. It is, therefore, reasonable that higher sintering temperature or longer sintering time makes Pt more easily diffuse into the inner part of the sample, which acts as doping particles and favors the phase transition. Hence, A2 can be ascribed to be related to the phase transition. Since A1 has similar features to A2, it might have the same origin as A2 but be associated with different relaxing species such as singly or doubly ionized oxygen vacancies. Definite conclusion about A1 still awaits further investigation.

3 Conclusions

Three oxygen-vacancy-related dielectric anomalies were found in the temperature range of 300–800°C. The highest temperature one (A3) was ascribed to Maxwell-Wagner relaxation due to electrode-sample contact. The medium temperature one (A2) was suggested to be related to phase transition from the static disordered state to the dynamic disordered state of oxygen vacancy distribution. Although the lowest temperature one (A1) has same features as those of A2, further investigations are required to identify its origin.

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