巨介电常数材料 CCTO 的可变程跳跃电导研究

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摘 要 文章研究了巨介电常数材料 $CaCu_3Ti_4O_{12}$(CCTO) 在宽温区(－120℃～ 300℃) 及宽频域 (1 Hz ～ 10 MHz) 的交流电导及介电性能。在低温区和高温区，CCTO 表现出两种不同的导电过程，均可以由 Mott 提出的可变程跳跃电导机制 (Variable-Range-Hopping，VRH) 来描述。研究发现高温 VRH 过程与氧空位的二次离子化相关，而低温过程符合普适介电响应方程，其介电弛豫行为起源于极化子的弛豫。

关键词 CCTO；巨介电常数；可变程跳跃电导；极化子弛豫
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Variable-Range-Hopping Conduction of CCTO over Broad Temperature Range

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Abstract The ac conductivity and dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics were investigated in a temperature range of －120℃ to 300℃ and a frequency range of 1 Hz to 10 MHz. Two different conduction processes, which can be well described by Mott's variable-range-hopping (VRH) mechanism, were observed in different temperature regions. The high temperature VRH conduction is related to the second ionization of oxygen vacancy. The low temperature dielectric properties of CCTO could be described by the so-called universal dielectric response (UDR) when a polaron relaxation is considered.

Keywords CCTO; colossal dielectric constants; variable-range-hopping; polaron relaxation

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1 Introduction

$CaCu_3Ti_4O_{12}$ (CCTO) has been reported to have a perovskite structure and a colossal dielectric constant (CDC) in the order of 105, which is almost independent of temperature from 400 K to 100 K but drops dramatically to less than 102 below 100 K[1]. Since then a huge amount of work[1-5] has been accomplished in an attempt to understand the origin of these remarkable dielectric properties. Similar dielectric behavior has been observed in charge-density-wave (CDW) systems[6]. CDW materials are generally metals in low dimensions with a critical temperature, below which an insulating state could be observed. CCTO is unlikely a CDW material, because it is cubic and does not display any metallicity[2]. An internal barrier layer capacitance (IBLC) mechanism has been widely used to explain the colossal dielectric constants[5]. In the IBLC picture, the insulating grain boundary layers between semiconducting grains act as barrier layers which block the current flow.

However, Ramirez et al. argued that the Maxwell-Wagner (MW) type mechanism could not be solely responsible for the anomalous relaxation near 100 K in CCTO[2]. The CDC behavior has also been reported on a number of materials, such as A_2FeBO_6 (A＝Ba, Sr, and Ca; B＝Nb, and Ta, etc.)[7], $La_{1-x}S_{rx}MnO_3$[8], $Pr_{0.7}Ca_{0.3}MnO_3$[9], $TbMnO_3$[10], and Li/Ti doped NiO[11]. It indicates that this phenomenon may be governed by a unified mechanism of relaxational excitations. The anomalous low temperature relaxation in manganites has been attributed to localized hopping of polarons between lattice sites within a characteristic timescale[8,9]. Zhang and Tang[12] also found that the state of mixed valences of Ti ions in CCTO induces a bulk polaron conduction by variable range hopping (VRH) at low temperatures.

The complex frequency-dependent ac conductivity characterizes in depth of the charge transport behavior by hopping of localized charge carriers (such as polarons)[13,14]. In the present letter, we report measurements of the complex ac conductivity of CCTO over a temperature range from －130℃ to 300℃. Besides the low temperature polaronic conduction[12], a high temperature polaronic conduction behavior was also detected with a higher hopping energy. The low temperature dielectric properties of CCTO could be described by the so-called universal dielectric response when a polaron relaxation is considered.

2 Experimental

Single phase CCTO ceramics were prepared through a conventional mixed oxide route and the detailed processing parameters can be found elsewhere[4]. The single phase was confirmed by X-ray diffraction (XRD). Silver paint was coated on both surfaces of the sintered disks and fired at 650℃ for 20 minutes. The sample pellets are 12 mm in diameter and about 1 mm in thickness. The dielectric properties and ac conductivity were measured by using a frequency-response analyzer (Novocontrol Alpha-analyzer) over a broad frequency range (1 Hz—10 MHz) at different temperatures from －130℃ to 300℃.

3 Results and Discussions

Fig. 1 shows the frequency dependence of the conductivity σ' at various temperatures. For the

conductivity σ' shown in Fig. 1(a), similar to an earlier report[12], there is a rapid increase at low frequencies and a slow increase at high frequencies. The σ' in the high frequency range can be described by the "universal dielectric response" (UDR)[15]

$$\sigma'(f)=\sigma_{dc}+\sigma_0 f^s \qquad (1)$$

where σ_{dc} is the dc bulk conductivity, f is the frequency and $0<s<1$. Equation (1) is typical of thermally assisted tunneling between localized states. In CCTO, it has been attributed to the localized charge carriers[12]. It should be mentioned that σ_{dc} used here is not the measured dc conductivity of CCTO, but the extrapolated value at low frequency.

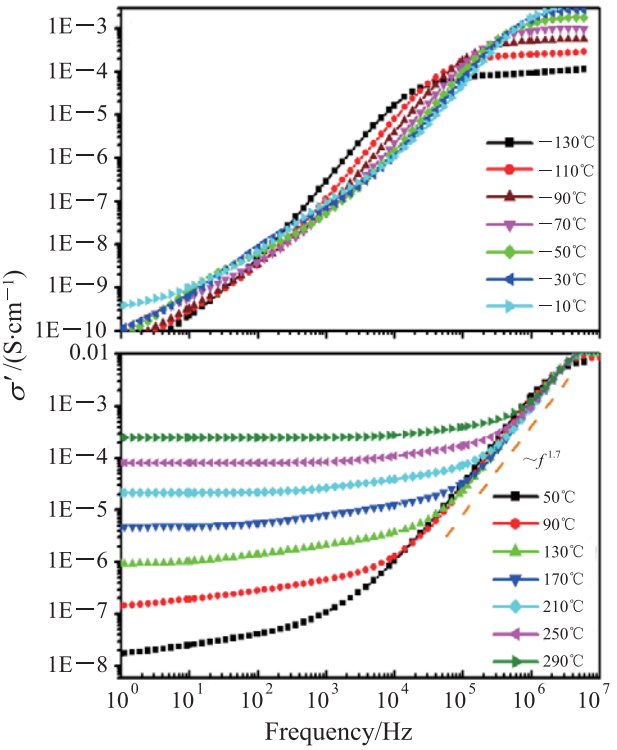

Fig. 1. Frequency dependence of conductivity σ' of CCTO in two temperature ranges: (a) −130℃ to 10℃; (b) 50℃ to 290℃

The steplike increase in Fig. 1(a) shifts to higher frequencies with increasing temperature. The localized charge carriers contribute to the conductivity by a hopping process. The frequency dependence of the conductivity in the hopping regime for only one hopping center has been given by Pollak[16],

$$\sigma'(f)=\sigma_{dc}+\frac{Nef^2\tau^2}{E\tau(1+f^2\tau^2)} \qquad (2)$$

Where N is the number of charge carriers, E is the magnitude of the applied electric field, τ is the relaxation time related to the critical frequency. Equation (2) clearly predicts a steplike increase of $\sigma'(f)$ in Fig. 1(a). Such a steplike increase in $\sigma'(f)$ is accompanied by a loss peak in the imaginary part of the permittivity ε'' through the Kramors-Kronig relationship and is also related to the steplike increase in the real part of the dielectric permittivity $\varepsilon'(T)$.

The frequency dependence of the conductivity σ' from 50℃ to 290℃ is shown in Fig. 1(b). The log-log curves are flat in the low frequency region as the conductivity values approach those of σ_{dc}. As the frequency increases, the curves become dispersive and can be parameterized using the UDR power law with exponential $s<1$. With further increase in frequency, the conductivity could be fitted by using a superlinear power law (SLPL)[17], a law which is universal for all classes of disordered condensed matters. Usually the exponential is less than 2. Our results show that CCTO can be regarded as a disorder system (oxygen vacancy doped semiconductor) with localized charge carriers that satisfy the superlinear power law. The exponential in the SLPL calculated is $s\approx1.7$ for CCTO (Fig. 1(b)), which sits within the range of less than 2.

In the hopping conduction of charge carriers, the nearest-neighbor hopping obeys the Arrhenius law and the VRH obeys the Mott's VRH equation[18],

$$\sigma_{dc}=\sigma_1\exp[-(T_0/T)^\gamma] \qquad (3)$$

where σ_1 is a constant, the exponential γ can be 2,

3 or 4, which depends on the detailed conduction mechanism. T_0 is the parameter related to the density of localized states at the Fermi level and the decay length of the localized wave function. Fig. 2 shows the dc conductivity versus the inverse quarter power of temperature in low and high temperature regions, respectively. The solid lines are the best fitted curves of the experimental data according to Equation (3) with an exponential $\gamma=4$. It can be seen that the inverse quarter power law predicted by the VRH mechanism describes the bulk conductivity of CCTO perfectly well. It is also noted that the Arrhenius plot of the dc conductivity of CCTO does not lead to a straight line over significant temperature range and therefore the nearest-neighbor hopping mechanism can be excluded.

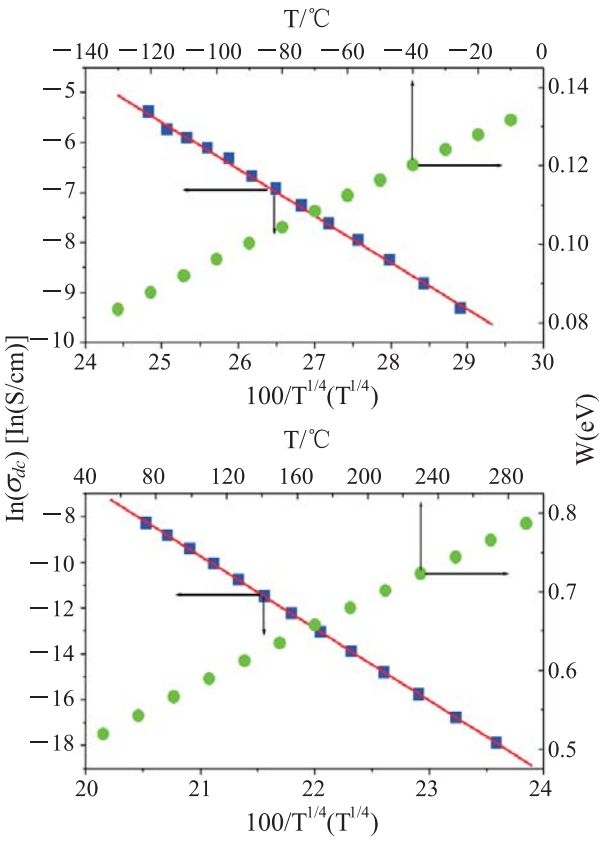

Fig. 2. Temperature dependence of dc conductivity σ_{dc} (solid squares, bottom and left axes) and the hopping energies W (solid circles, top and right axes) for CCTO ceramics in (a) low temperature range and (b) high temperature range

The solid lines are the best fitted lines according to Equation (3).

It is worth noting that the VRH equation with the exponential $\gamma=2$ could also be used to fit the bulk conductivity of CCTO in the high temperature range but not in the low temperature one (The figure was not shown here.). In the VRH model[18], $\gamma=4$ is predicted for isotropic charge transport, while $\gamma=2$ and 3 arise from the VRH conduction in two-dimension and one-dimension, respectively. As pointed out by Efros and Shklovskii[19], an alternative explanation for $\gamma=2$ can also be given when the Coulomb interaction between the charge carriers is taken into account in the three-dimensional Mott's model. It should be noted that in the framework of Mott's model, when samples are close to the Anderson transition, a transition of the exponential γ from 2 to 4 could occur[18].

From Mott's VRH model[18], we can also obtain the hopping energy,

$$W=0.25k_B T_0^{1/4} T^{3/4} \tag{4}$$

The temperature dependence of the hopping W is also plotted in Fig. 2. The hopping energy W is from 0.08 to 0.13 eV in the low temperature range and from 0.52 to 0.8 eV in the high temperature range. The large difference of W between the low temperature and high temperature ranges implies that there are two different VRH processes in CCTO or two different types of polarons. Usually the VRH mechanism is valid below room temperature in crystals with defects, where the thermal energy is insufficient to excite the charge carrier across the Coulomb gap[18]. The conduction is then taken place by hopping of small region ($\sim k_B T$) in the vicinity of Fermi level. In Bidault's work[20], it has

been shown that the activation energy of the polaron relaxation is nearly the same (≈0.075 eV) for all the investigated perovskites. This is consistent with the low temperature behavior of CCTO. Zhang and Tang suggested that the low temperature polaron should be induced by the mixed valences of Ti ions associated with oxygen vacancies[12]. The high temperature VRH of CCTO has not been reported before. We argue that it should also be associated with oxygen vacancies in CCTO. It is well known that in perovskite materials including titanate, the ionization of the oxygen vacancy will donate electrons and can be written as $V_O \Leftrightarrow V_O^{\bullet}+e'$ for the first ionization and $V_O^{\bullet} \Leftrightarrow V_O^{\bullet\bullet}+e'$ for the second ionization, where $V_O^{\bullet}$ and $V_O^{\bullet\bullet}$ represents the oxygen vacancy carrying one and two excess positive charges, respectively. The activation energy for the first ionization of oxygen vacancy is 0.1 eV in perovskite oxides while it is 0.7 eV for the second ionization of oxygen vacancy. The observed hopping energy at low temperature is close to 0.1 eV, which indicates that the charge carriers are electrons from the first ionization of oxygen vacancies. The high temperature VRH hopping energy in CCTO is close to the second ionization energy of oxygen vacancy 0.7 eV. Although such a high temperature hopping could be different in detail from that happened at low temperature, it may takes place throughout the crystal, similar to the long range hopping process observed in NiO at room temperature[21]. In a typical perovskite material, n-type doped $BaTiO_3$, it is found that nonadiabatic small polarons are the major charge carriers up to a temperature of 400 K[22]. It is also predicted that the polaron conduction dominates even up to a temperature of 1000 K since the electron transfer integral between neighboring Ti ions is still below the "classic limit"[22]. Therefore the observed high temperature polaron conduction in CCTO is not an experiment artifact although the detailed physics picture is still unclear.

It is well known that in semiconductors, the hopping of localized charge carriers between spatially fluctuating lattice potentials not only produce conductivity but also give rise to dipolar effects. As a result, the dielectric properties are closely related to the polaron conduction. As mentioned above, the anomalous dielectric relaxation near 100 K in CCTO is directly related to the hopping regime. The imaginary part of the permittivity can be described by UDR through the relation $\sigma'=2\pi f\varepsilon''\varepsilon_0$. From the UDR model[15], ε' can be expressed as

$$\varepsilon'=\tan(s\pi/2)\sigma_0 f^{s-1}/\ \varepsilon_0 \qquad (6)$$

where f is the measuring frequency, σ_0 and s are the temperature-dependent constants. Equation (6) can be rewritten as

$$f\varepsilon'=[\tan(s\pi/2)\sigma_0/\ \varepsilon_0]f^s \qquad (7)$$

Therefore, at a given temperature, a straight line with a slop of s should be obtained in the log-log plot of $f\varepsilon'$ *vs*. f as is shown in Fig. 3. It can be seen that when the relaxation takes place, $f\varepsilon'$ starts to deviate from the straight line. It is interesting to note that the linear relation holds again when the frequency is further increased. The two straight lines are parallel and there is a crossover from a higher conductivity σ_0 to a lower one when $f\varepsilon'$ switches from one straight line to another. The relaxation shifts to lower frequency with decreasing temperature. Similar results have also been found by Wang and Zhang[10]. Moreover, as is shown in Fig. 3, the local maximum of $f\varepsilon'$ corresponds to the position of a peak in $\varepsilon''(f)$.

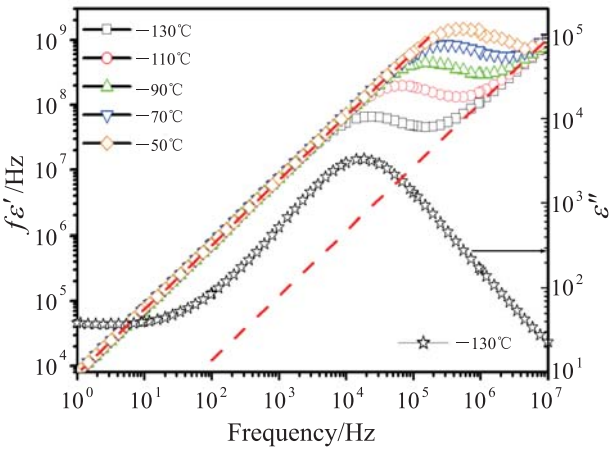

Fig. 3.　Plot of $f\varepsilon'$ against f for CCTO at a number of temperatures（left and bottom axes）and frequency dependence of the imaginary dielectric permittivity at −130℃（right and bottom axes）

4　Conclusions

In summary, the ac conductivity of CCTO ceramics has been measured over a broad temperature range. The temperature dependence of the bulk ac conductivity can be well described by the VRH mechanism. The high temperature VRH conduction is related to the second ionization of oxygen vacancy. The low temperature dielectric relaxation in CCTO can be well understood by the UDR relation considering a polaron relaxation process.

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