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Short communication

Polaronic relaxation in Ca_2TiMnO_6 at low temperatures

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ABSTRACT

Dielectric properties of Ca_2TiMnO_6 (CTM) were systematically investigated. Our results revealed that (1) the observed relaxation does not feature one clear Arrhenius behavior, (2) the peak intensity of the imaginary part of the complex permittivity can be well expressed by a relation similar to the Fermi–Dirac distribution function, and (3) the colossal dielectric behavior of the sample can be well understood based on the framework of universal dielectric response. These features indicate that the dielectric properties of CTM are related to polaron relaxation.

1. Introduction

As electronic components miniaturized, colossal dielectric materials are going to play an important role, which warrants both fundamental and more applied research in this field. With the colossal dielectric constant (CDC) effect found in $CaCu_3Ti_4O_{12}$ (CCTO), the study of this kind of materials was pushed to a climax [1–3]. More and more research activities have been performed in an effort to understand the physics behind the CDC effect [4–6] and to search for new types of CDC materials with low dielectric loss [7,8]. So far, a large number of materials have been reported to show colossal and flat dielectric constants in a broad temperature range around room temperature. Complex perovskite oxides are the promising type among these materials and being the focus of researchers in recent years [9–14].

A new type of complex perovskite Ca_2TiMnO_6 (CTM), which is a single ABO_3 perovskite with Ti^{4+} and Mn^{4+} occupying the B site randomly, had been synthesized recently via solid-state reaction technique [15]. Dielectric measurements revealed that CTM exhibits very strange dielectric properties that behave as dispersive dielectric plateaus depending on measuring frequencies at low temperatures, followed by an asymmetric peak over 10,000 around room temperature. The peak position was found to be independent of frequency but its intensity notably decreases with increasing frequency. At temperatures above ~320 K, the peak rapidly drops to a nearly frequency-independent dielectric plateau with almost the same level as the low-temperature ones [15]. These disparate features are alien from the CDC behavior that shows a low- and high-plateau in the low- and high-temperature range respectively with a step-like decrease connecting them. The exact mechanism of the colossal dielectric behavior of CTM is unclear. Hence, the aim of this work is to investigate, in details, the dielectric properties in the temperature range from −180 to 60 °C.

2. Experimental details

Polycrystalline samples of CTM were prepared by the conventional solid-state reaction method. Stoichiometric amounts of high-purity (99.99%) $CaCO_3$, TiO_2, and MnO_2 were thoroughly mixed. The mixture was calcined at 1000 °C for 10 h, then reground and recalcined at 1200 °C for 10 h. Finally, the resultant product was ground, pelletized and sintered at 1350 °C in air for 10 h followed by furnace cooling to room temperature. The crystal structure was characterized by X-ray diffraction (XRD) using XD-3 diffractometry with Cu Kα radiation. The morphology and microstructure of the sintered samples were characterized by a field emission scanning electron microscopy (SEM) (Model S-4800, Hitachi Co., Tokyo, Japan). The temperature-dependent dielectric properties were measured using a Wayne Kerr 6500B precise impedance analyzer with the sample mounted in a holder placed inside a PST-2000HL dielectric measuring system. The system can provide a temperature range from −180 to 60 °C. The temperature variations were automatically controlled using a Stanford temperature controller with a heating rate of 2 °C/min. The amplitude of ac measuring signal was 100 mV rms. Electrodes were made by printing silver paste on both sides of the disk-type samples and then fired at 600 °C for 1 h in order to remove the polymeric component.

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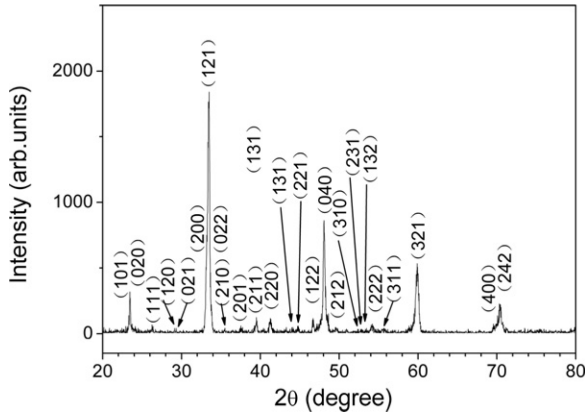

Fig. 1. XRD pattern of CTM polycrystalline powders.

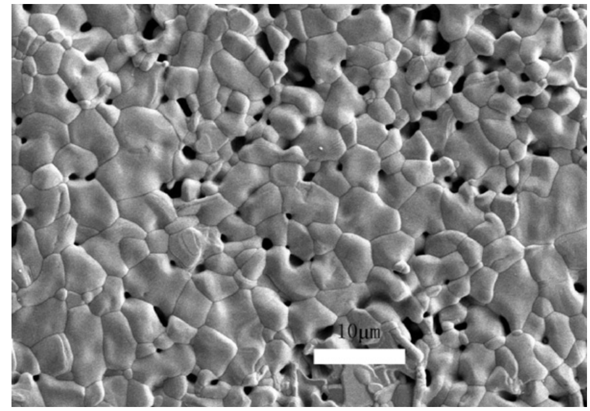

Fig. 2. SEM image of the as-sintered CTM pellet.

3. Results and discussion

XRD pattern shown in Fig. 1 indicates that the as-sintered disks are of single phase with orthorhombic structure. The calculated lattice parameters of $a = 0.53560(9)$ nm, $b = 0.75378(6)$ nm, $c = 0.53476(8)$ nm, are fairly consistent with those reported ($a = 0.53586(7)$ nm, $b = 0.75508(4)$ nm, $c = 0.53285(8)$ nm) by Shi et al. [15].

A typical SEM micrograph of CTM is shown in Fig. 2. The microstructure reveals a porous nature with the grain size about 5–10 μm. The density was found to be 3.66 g/cm^3, which is about 71% of the theoretical value (5.13 g/cm^3).

Fig. 3 shows the typical results of the variation in dielectric constant (ε') and dielectric loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$, where ε'' is the imaginary part of the complex permittivity) with temperature (T) for CTM. It is seen that $\varepsilon'(T)$ shows weak temperature-dependent high values at high temperatures. As the temperature decreases, $\varepsilon'(T)$ step-like decreases to a flat plateau that moves out of the measuring temperature window. The step-like decrease in $\varepsilon'(T)$ is accompanied by a peak in corresponding loss tangent (shown in Fig. 3(b)). These features agree well with those of CDC effect but quite different from those reported by Shi et al. [15]. Our results indicate that there exists a typical Debye-type dielectric relaxation. To better understand the mechanism of the dielectric relaxation in CTM, we try to deduce the relaxation parameters in terms of Arrhenius relation. The insert of Fig. 3(b) presents the Arrhenius plot of $\log_{10} f$ (f is the experimental frequency) vs $1/T_p$ (T_p is the peak temperature of loss tangent for CTM). We note that the data at the low temperatures distinctly deviate from the linear line leading to two Arrhenius segments (open circles). The relaxation time τ_0 and activation energy E were deduced, to be 6.79×10^{-9} s, 0.10 eV and 4.35×10^{-10} s, 0.14 eV for the low- and high-temperature segments, respectively. Preethi Meher et al. pointed out that such low activation energy indicates the polaron relaxation due to free carriers hopping motions [16,17]. The relaxation was argued to be related to the dynamic slowing down of the dipolar fluctuations [17]. In this case, the dielectric and conductive behaviors are infinitely related. A tentative explanation to this deviation suggested by Zhang and Tang [18] is that the Mott's variable range hopping (VRH) relation might fit the data better:

$$f = f_0 \exp\left[-\left(\frac{T_0}{T_p}\right)^{1/4}\right] \quad (1)$$

where f_0 is the eigenfrequency and T_0 is a constant related to the activation energy. The VRH relation truly produces quite good linear behavior shown also in the same inset (closed circles). This fact implies that the present dielectric behavior might be related to the polaronic relaxation. The deduced parameters are $f_0 = 1.0652 \times 10^{19}$ Hz and $T_0 = 2.16412 \times 10^8$ K. But such a high value of f_0 is unrealistic for polarons their eigenfrequency is typical of the order of 10^{14} Hz [18]. The VRH relation, therefore, does not suitably describe the relaxation behavior. The failure of this attempt can be ascribed to the fact that the motion of polaron actually determined by a thermally activated mechanism at high

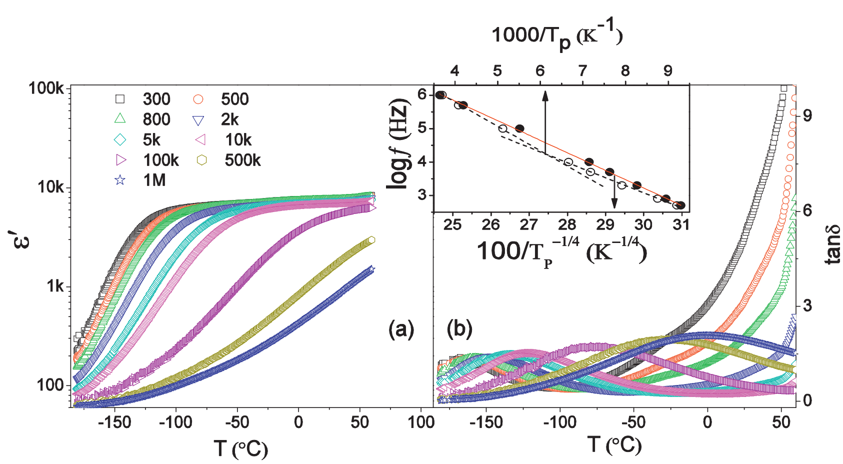

Fig. 3. Temperature dependence of (a) the real part of the complex permittivity and (b) dielectric loss tangent for a CTM pellet measured at different frequencies. The inset shows the Arrhenius and VRH plots. The dotted lines illustrate two Arrhenius segments. The solid line is the result of linear fit.