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Incipient ferroelectricity and conductivity relaxations in $Dy_2Ti_2O_7$

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$Dy_2Ti_2O_7$ ceramic samples were prepared via the solid-state reaction route. The dielectric properties of the sample were systematically investigated in the temperature range from 4 K to 973 K and the frequency range of 100 Hz to 1 MHz. Both Raman and low-temperature (down to 4 K) dielectric measurements indicate incipient ferroelectricity in the $Dy_2Ti_2O_7$ sample. In addition, two relaxations were observed in the temperature range above 450 K. Our results indicate that the two relaxations are related to conductivity relaxation associated with singly and doubly ionized oxygen vacancies.

1. Introduction

Multiferroic materials, in which magnetic and electric orders coexist, have recently become the focus of much research because of their unusual physics and potential applications [1–4]. Among the presently-known multiferroic materials, a family of rare-earth titanates ($R_2Ti_2O_7$) has attracted a great deal of interest in recent years because of its interesting dielectric, piezoelectric, and ferroelectric properties [5–7]. $R_2Ti_2O_7$ compounds usually crystallize with a cubic pyrochlore type structure [8–11] for ions with smaller radii (e.g., $R^{3+} = Sm^{3+}$–Lu^{3+}) or a monoclinic structure for ions with larger radii (e.g., $R^{3+} = La^{3+}$–Nd^{3+}) [6,12] and some of them are ferroelectrics with very high Curie points [13]. In recent years, $R_2Ti_2O_7$ compounds with a pyrochlore type structure [14–17], especially $Dy_2Ti_2O_7$ (DTO) [18–20], have attracted much attention because of their spin-ice behaviour and large low-temperature paramagnetic magnetic moments.

From the application point of view, dielectric properties are one of the most important properties for multiferroic materials. Unfortunately, the investigation of the dielectric properties of DTO is incomplete. Saito et al. reported the magneto dielectric response of single crystals of $Dy_2Ti_2O_7$ down to 0.26 K [18]. Belov et al. reported the dielectric properties of Ca-doped $Dy_2Ti_2O_7$ ceramics in the low-frequency range (0.5–500 Hz) [21]. The nature of the dielectric properties of DTO has not yet been fully characterized.

We, herein, presented detailed investigations on the dielectric properties of DTO ceramics over wide temperature (4–973 K) and frequency (100 Hz–1 MHz) ranges. Incipient ferroelectricity was confirmed in the sample. Two relaxations were observed, and their mechanisms were discussed.

2. Experimental

Single-phase DTO ceramic samples were prepared by the solid-state reaction method using high-purity (99.99%) starting powders of Dy_2O_3 and TiO_2. First, the powders of Dy_2O_3 were calcined at 900 °C for 10 h in air to dehydrate. Then, stoichiometric powders (1:2) of Dy_2O_3 and TiO_2 were thoroughly mixed using a mortar and calcined at 1300 °C for 10 h in air. After that, the obtained mixture was reground and pressed into pellets with a diameter of 12 mm and thickness of 1–2 mm under a pressure of 20 MPa and finally sintered at 1400 °C for 10 h at a heating rate of 3 °C/min followed by furnace cooling. The phase purity of the sintered pellets was characterized by X-ray diffraction (XRD) performed on a MXP18AHF diffractometer (Mac Science Ltd., Yokohama, Japan) with Cu Kα radiation. The morphology and microstructure of the sintered pellets were studied by a field emission scanning electrical microscope (SEM, Model S-4800, Hitachi Co., Tokyo, Japan). The dielectric properties were measured on a Wayne Kerr 6500B

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precise impedance analyser (Wayne Kerr Electronic Instrument Co., Shenzhen, China) with the sample mounted in a holder placed inside a PST-2000HL dielectric measuring system (Wuhan Pusite Instrument Co., Wuhan, China, presenting a temperature range from room temperature to 973 K) and a Janis SHI-4ST-1 closed-cycle cryostat (Research Co., Inc., USA, presenting a temperature range from 4 K to room temperature). The amplitude of the ac measuring signal was 100 mV. Electrodes were made by printing platinum paste on both sides of disk-type samples.

3. Results and discussion

Fig. 1 plots the XRD pattern of the as-prepared DTO ceramic sample which was analysed using Jade 6.0 software. The fitting result was shown as a solid line. The result indicates that the sample is single-phase with a cubic pyrochlore structure and a space group of Fd-3m. The calculated lattice parameter of $a = 10.0937$ Å is consistent with most of the data in the literature [22,23]. The inset displays the SEM micrograph of the sintered ceramic. It can be observed that the sample exhibits a distinct grain structure, with an average grain size of approximately 1–2 μm.

The temperature (286–973 K) dependence of the dielectric constant $\varepsilon'(T)$ (the real part of the complex permittivityε^*) and dielectric loss tangent tan δ(T) (tan $\delta = \varepsilon''/\varepsilon'$, where ε'' is the imaginary part of the complex permittivity) at various frequencies for the DTO sample are shown in Fig. 2(a) and (b), respectively. At temperatures below ~450 K, $\varepsilon'(T)$ exhibit a frequency-independent decline similar to that found in $SrTiO_3$, $CaTiO_3$, and $KTaO_3$ [24–26]. This behaviour is a common feature for incipient ferroelectrics, which are characterized by increasing dielectric permittivity upon cooling due to the softening of the lowest-frequency polar optical phonon [27]. The dielectric permittivity of an incipient ferroelectric material can be described by the Barrett equation [28].

$$\varepsilon'(T) = C\left(\frac{T_1}{2}\coth\frac{T_1}{2T} - T_0\right)^{-1} + A \tag{1}$$

where C is a constant, T_0 is the hypothetical Curie temperature, T_1 is the onset temperature of quantum fluctuations, and A is the dielectric constant at the high-frequency limit. Fig. 2(c) presents the fitting to the data recorded at 1 kHz by the Barrett equation. Perfect agreement between the experimental data and the fitting curve were obtained. The fitting yields the parameters of $A = 5.6$, $C = 56218$ K, $T_1 = 0.0046$ K, and $T_0 = -1154$ K. These values are comparable with those of the titanate oxides of $Ln_{1/2}Na_{1/2}TiO_3$ (Ln = La, Pr, Nd, Sm, and Eu) [29], indicating the incipient ferroelectric behaviour in the present sample. To further prove this point, we performed dielectric measurements on the DTO pellet in the low-temperature range down to 4 K Fig. 2(d) and (e), present, respectively, the curves of the low-temperature (4–285 K) dielectric constant $\varepsilon'(T)$ and the loss tangent of DTO under different frequencies. No peaks were found in the curves of either $\varepsilon'(T)$ or tan δ(T). The experimental data of the dielectric constant can also be described by the Barrett equation, with the same parameters deduced from the aforementioned fitting. The fitting result of the dielectric constant recorded at 1 kHz was shown as an example in the inset of Fig. 2(c). This finding confirms the incipient ferroelectric nature of the test sample. Very recently, a Raman study on DTO down to 4.5 K also revealed that the modes F_{2g} ~200 cm^{-1} and A_{1g} ~520 cm^{-1} linearly decrease with the decreasing temperature [30]. This result further supports the above point.

When the temperature is higher than 450 K, $\varepsilon'(T)$ increases rapidly with the increasing temperature. Two stepwise increases occurring at ~450 and 700 K can be observed. Correspondingly, two sets of peaks can be identified in the curves of tan δ(T), although the second set of peaks can only be observed in the curves recorded under lower frequencies [Fig. 2(b)]. The positions of the peaks shift to higher temperatures with the increasing frequency, indicating that there are two thermally activated relaxations in DTO. For brevity, they were termed as R1 and R2 in the order of ascending temperature. The low-temperature relaxation R1 (above ~ 450 K) can be well identified intan δ(T), but the high-temperature relaxation R2 (above ~ 700 K) was obscured in the curves measured with higher frequencies due to the pronounced background. In general, the background in both $\varepsilon''(T)$ and tan δ(T) is caused by hopping conductivity [31], which obscures the relaxation information. In this case, we apply the electric modulus M^*, which is defined as $M^* = 1/\varepsilon^*$. It indicates that the higher the values of ε^* caused by the background, the smaller the values of M^* that can be obtained. Therefore, the modulus can greatly lessen the background and become a powerful dielectric function in revealing the background-obscured relaxation [32]. Fig. 2(f) shows the imaginary part of the electric modulus M'' as a function of temperature at several frequencies. We can clearly see that a set of relaxation peaks appears in M'' without remarkable background. Although the low-temperature relaxation can be well identified inM'', the high-temperature relaxation still can only be identified in the lower-frequency curves (e.g., 100 Hz and 1 kHz) in an enlarged view.

Activation energy analysis is favourable for better understanding the relaxation mechanism. Because the peaks of R1 can be well-identified from the curves of$M''(T)$, we first focus on this relaxation. The measuring frequency (f) of R1 was plotted as a function of the reciprocal of the peak temperature (T_P), as shown in Fig. 3. The obtained data for R1 fall perfectly on a straight line in the half-logarithmic presentation, implying that the relaxation follows an Arrhenius law

$$f = f_0 \exp(-E_a/k_B T_P) \tag{2}$$

where f_0 is a pre-exponential factor, E_a is the activation energy, and k_B is the Boltzmann constant. The fitting yields values for E_a and f_0 of 0.92 eV and 6.80 × 10^{11} Hz, respectively.

To calculate the relaxation parameters of R2, we performed detailed dielectric measurements in the frequency domain. Fig. 4 shows the imaginary part of the dielectric modulusM'' as a function of frequency at a series of temperatures. Although the $M''(f)$ curves show two obvious relaxation peaks, the low-frequency peak behaves as a hump superimposed on the high-frequencyM'' peak.

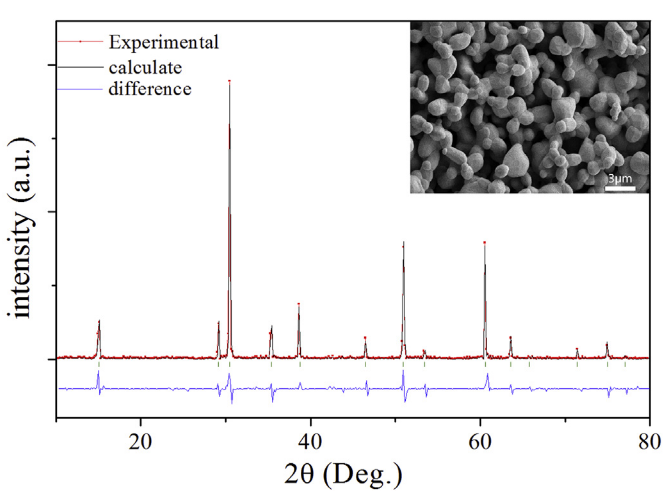

Fig. 1. XRD pattern of the DTO ceramic sample. The inset shows the SEM for an as-prepared pellet of DTO at room temperature.