Journal of Alloys and Compounds 652 (2015) 1–8

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Dielectric relaxations in multiferroic $La_2Ti_2O_7$ ceramics

N. Zhang [a], Q.J. Li [a, **], S.G. Huang [a], Y. Yu [a], J. Zheng [b], C. Cheng [b], C.C. Wang [a, *]

[a] Laboratory of Dielectric Functional Materials, School of Physics & Material Science, Anhui University, Hefei, 230601, PR China
[b] Center of Modern Experimental Technology, Anhui University, Hefei, 230039, PR China

ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form
19 August 2015
Accepted 20 August 2015
Available online 24 August 2015

Keywords:
Dielectric property
Electric modulus
Cationic vacancies
Conduction progress
Oxygen vacancies

ABSTRACT

$La_2Ti_2O_7$ ceramic samples were prepared via conventional solid-state reaction route. The dielectric properties of $La_2Ti_2O_7$ were investigated as functions of temperature (113–1073 K) and frequency (100 Hz–1 MHz). Our results revealed that $La_2Ti_2O_7$ ceramics exhibit intrinsic dielectric response with a dielectric constant of ~57 in the temperature range below 250 K. Three thermally activated dielectric relaxations were observed when the temperature higher than 250 K. The low-temperature relaxations R1 with the activation energy of 0.38 eV is found to be a polaron relaxation results from hopping holes. The high-temperature relaxations R2 and R3 are related to the conduction progress associated with the singly and doubly ionized oxygen vacancies, respectively.

1. Introduction

The strong interaction between the magnetic and dielectric properties in multiferroic materials is expected to create unprecedented microelectronic and spintronic devices based on the magnetodielectric or magnetocapacitance effects [1–3]. From the application point of view, dielectric properties as one of the most important issues for multiferroic materials have been extensively investigated. Owing to the low magnetic-dielectric coupling temperatures for most of the multiferroic materials, the existing reports on dielectric properties were mainly performed in the low temperature range usually below room temperature [4–7]. Compared with the low-temperature range, dielectric investigation on high-Curie temperature multiferroics like $BiFeO_3$ revealed more dielectric relaxations [8,9]. This is because that both polarisability and conductivity have contribution to dielectric permittivity in the high-temperature range.

Rare-earth titanates with the general formula $Re_2Ti_2O_7$ (Re = rare earth) characterized by the extremely high Curie temperatures$T_C > 1500$ °C [10] have attracted considerable attention recently both in basic science and engineering [11–13]. Among them, $La_2Ti_2O_7$ (LTO) has been studied extensively in the aspects of piezoelectric, electro-optic, and photocatalytic properties [14–17]. LTO is also known as a layered perovskite structure showing monoclinic phase ($P2_1$) at room temperature, with lattice parameter $a = 7.81$ Å, $b = 5.55$ Å, $c = 13.02$ Å, and $\beta = 98.43°$ [18]. At approximately 780 °C, the structure transforms into orthorhombic phase ($Cmc2_1$), and at 1500 °C it transforms into paraelectric phase ($Cmcm$). The layered structure leads to LTO exhibiting high dielectric constant ($\varepsilon_r = 42 \sim 62$) at room temperature together with a low dielectric loss at microwave frequency [19,20]. The excellent temperature stability of the high-dielectric constant and low dielectric loss at microwave frequency make LTO a promising candidate for microwave applications, high temperature transducer material [19], and electro-optic devices [20–22]. It can be conveniently used above 1000 °C for controlling intelligent gas turbine engines. It is also considered as low temperature coefficient of capacitance (TCC) materials [23,24].

However, the low-frequency dielectric properties of LTO were barely reported. In the present work, we performed detailed investigations on the low-frequency (100 Hz–1 MHz) dielectric properties of LTO over a wide temperature range from 113 to 1073 K. We found that LTO exhibits a dielectric plateau resulting from intrinsic dielectric response below 250 K, while above 250 K, LTO shows three relaxations related to oxygen vacancies.

2. Experimental details

Single-phase LTO ceramics were prepared by standard solid state reaction method using high purity (99.99%) starting powders

* Corresponding author.
** Corresponding author.
E-mail addresses: liqj@mail.ustc.edu (Q.J. Li), ccwang@ahu.edu.cn (C.C. Wang).

http://dx.doi.org/10.1016/j.jallcom.2015.08.169
0925-8388/

of La_2O_3 and TiO_2. Stoichiometric amount of powders (1:2) were thoroughly mixed using a mortar and calcined at 1000 °C for 24 h followed by furnace cooling. Then, the mixture was reground and pressed into pellets with size of 12 mm in diameter and about 1 mm in thickness under a pressure of 20 MPa, and finally sintered at 1350 °C for 10 h at a heating rate of 3 °C/min followed by furnace cooling. Phase purity of the sintered pellets was characterized by X-ray diffraction (XRD) performed on a MXP18AHF diffractometer (MARK, Japan) with Cu Kα radiation. The morphology and microstructure of the sample were examined using a field emission scanning electron microscope (SEM, Model S-4800, Hitachi Co., Tokyo, Japan). Element content analysis was measured by X-ray fluorescence (XRF, Model XRF-1800, Shimadzu corporation, Japan) with an Rh anode X-ray tube. The dielectric properties were measured on a Wayne Kerr 6500 B precise impedance analyzer with the sample mounted in a holder placed inside a PST-2000HL dielectric measuring system. The temperature variations were controlled by a Stanford temperature controller. The amplitude of ac measuring signal was 100 mV. Electrodes were made by printing platinum paste on both sides of the disk-type samples. Annealing treatment were performed in flowing (200 ml/min) O_2 and N_2 (both with purity >99.999%) at 800 °C for 2 h.

3. Result and discussion

3.1. Sample characterization

The XRD pattern of the as-prepared LTO ceramic sample at room temperature is shown in Fig. 1. The pattern was analyzed using Jade 5 power diffraction data analysis software. It was found that the pattern can be indexed to a monoclinic structure with the lattice constant $a = 7.7450(2)$ Å, $b = 12.938(7)$ Å, and $c = 5.5539(7)$ Å, which are fairly consistent with those reported in literature [18]. A typical SEM micrograph of LTO ceramic is shown in the inset of Fig. 1, which reveals that the pellet is dense and compact with mean grain size of ~1.8 – 2.5 μm.

3.2. Dielectric properties

Fig. 2(a) and (b) present, respectively, the temperature dependence of dielectric constant $\varepsilon'(T)$(the real part of the complex permittivityε^*) and loss tangent $tan\delta(T)$ ($tan\delta = \varepsilon''/\varepsilon'$, where ε'' is the imaginary part of the complex permittivity) of LTO measured with various frequencies. In the high temperature range (250–1073 K), $\varepsilon'(T)$ shows two stepwise increases occurring around 500 and 750 K. Two sets of humps in the curves of $tan\delta(T)$ can be seen in the temperature range where the two stepwise increases occur. The position of both humps shift to high temperature with increasing frequency, indicating that the two relaxations follow a thermally activated behavior. In the temperature range of 300–500 K, $\varepsilon'(T)$ seems to behave as a dielectric plateau independent of frequency and temperature. However, a careful examination reveals an additional relaxation in this temperature range. The inset of Fig. 2(a) displays the enlarged view of this temperature range, from which an additional stepwise increase can be clearly seen. Correspondingly, a set of thermally activated relaxation peaks can be identified in the curves of $tan\delta(T)$. This finding indicates that there are three relaxations in the sample. To discuss each relaxation clearly, the relaxations are designated as R1, R2, and R3 in the order of ascending temperature as indicated by the arrows in Fig. 2(b).

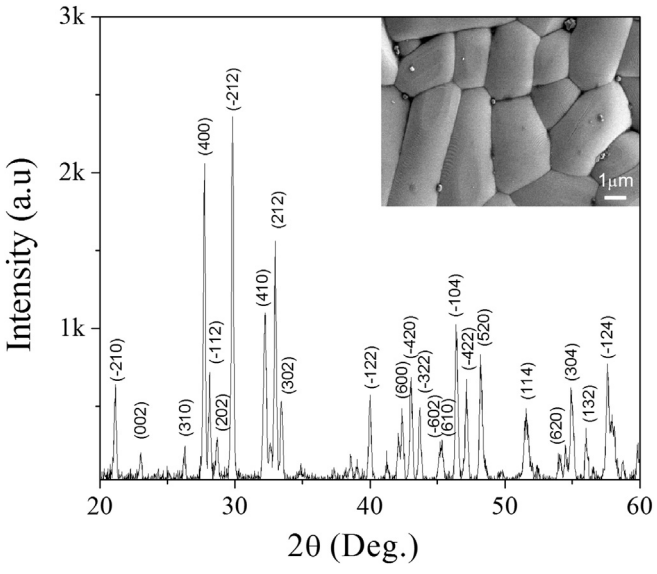

Fig. 1. The XRD pattern and SEM micrograph (inset) obtained at room temperature of the LTO ceramic.

In the inset of Fig. 2(b), it can be seen that ε' for LTO are almost independent of frequency and temperature in the low temperature range from 113 to 250 K. The dielectric constant plateau shows a value of ~57. This behavior indicates that LTO shows intrinsic dielectric response resulting from the electronic and/or ionic polarization in the low temperature range.

From Fig. 2(b) one notes that the high-temperature relaxations (R2 and R3) behave as humps because of the increasing background. The remarkable background in high-temperature is usually caused by conductivity [4]. In this case, we applied the electric modulus, which is a powerful function in revealing the background obscured relaxation [25]. Fig. 3(a) shows the imaginary part of electric modulus as a function of temperature at various frequencies. Thanks to the absence of background, two pronounced relaxations (R2 and R3) are observed. The enlarged view of the low-temperature region is shown in the inset of Fig. 3(a), which clearly shows the low-temperature relaxation R1. The relaxation parameters can be obtained in terms of Arrhenius law

$$f = f_0 \exp(-E_a/k_B T_P), \quad (1)$$

where f_0 is the pre-exponential factor, E_a is the activation energy, k_B is the Boltzmann constant, and T_P is the temperature where the maximum $M''(T)$ occurs. The peak positions of R1 and R2 can be extracted easily. However, the M'' peak of R3 behaves as a hump superimposed on the M'' peak of R2. To extract the peak position of R3 accurately, two Gaussian peaks were used to fit the high-temperature data. As a representative example, Fig. 3(b) displays the fitting result for the experimental data measured at 100 kHz. It is seen that perfect fitting result is achieved. The resultant fitting peaks of R3 at different measuring frequencies were pictured in Fig. 3(c). Fig. 3(d) displays the Arrhenius plots for R1, R2, and R3. It is seen that R1 and R3 follow the Arrhenius law very well. But for R2, a distinct deviation from the Arrhenius relation leading to two linear segments can be clearly seen. The inflection temperature was found to be ~640 K. The relaxation parameters for R1, R2 and R3 of LTO were summarized in Table 1. In the following, we will discuss these relaxations separately.

3.3. The low-temperature dielectric relaxation (R1)

To get further information about R1, the same sample used in Fig. 2 was annealed first in N_2 and then in O_2. After each treatment, dielectric properties were measured as a function of temperature. Fig. 4(a) presents the comparison of the temperature dependence of M'' obtained at 100 kHz. It is clearly seen that R1 disappears after N_2