Colossal permittivity of (Li, Nb) co-doped TiO$_2$ ceramics

Wenlong Li$^{a,b,c}$, Zhifu Liu$^{a,b,*}$, Faqiang Zhang$^a$, Qingbo Sun$^d$, Yun Liu$^d$, Yongxiang Li$^{a,b,c,**}$

$^a$ CAS Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, China
$^b$ Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100034, China
$^c$ School of Physical Science and Technology, ShanghaiTech University, Shanghai, 201210, China
$^d$ Research School of Chemistry, The Australian National University, ACT, 0200, Australia

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ABSTRACT

In this work, (Li, Nb) co-doped TiO$_2$ ceramics (LNTO$_{x}$, $x < 0.1$), were synthesized through a conventional solid state reaction method. As revealed by X-ray diffraction (XRD) spectra, all LNTO ceramics exhibited pure tetragonal rutile structure. The LNTO$_{0.01}$ ceramic showed a colossal permittivity over 7000 and a low dielectric loss ($\tan \delta < 0.06$) in a wide frequency range of $10^2$ Hz to $10^7$ Hz. The dielectric spectra under DC biases were tested at different temperatures. The experimental data could fit the modified Debye equation well. It was found that there are multiple dielectric polarization mechanisms in LNTO ceramics including space charge polarization, relaxor-type relaxation, polaron hopping and dipole polarization related with localized electrons.

1. Introduction

The miniaturization of passive components and the limitation of the traditional MLCC process inspired continuous enthusiasm on the exploration of new dielectric materials with colossal permittivity [1,2]. In recent years, a series of colossal permittivity materials have been reported such as doped BaTiO$_3$ [3], CaCu$_5$Ti$_4$O$_{12}$ [4,5], NiO-based oxide [6,7], La$_{0.5}$Sr$_{0.5}$NiO$_4$ (Ln = La and Nd) [8-10], doped-ZnO [11], CuO [12] etc. However, poor frequency and temperature stability and high dielectric loss have restricted their practical applications. Co-doping strategy has raised much attention since the report of Hu et al. on the (In, Nb) co-doped rutile TiO$_2$ ceramics, which exhibit a temperature and frequency independent colossal permittivity ($\varepsilon_r > 10^6$) as well as a low dielectric loss ($\tan \delta < 0.05$) over a broad temperature and frequency range [13]. They proposed an electron pinned defect-dipoles (EPD) model to explain the excellent dielectric properties, in which donor dopant creates delocalized electrons from the reduction of nearby host transition metal atom while acceptor dopant substitution provides a local oxygen-deficient environment assisting the reduced host cations to hold back the delocalized electrons.

Since Hu's report, co-doping strategy has been widely studied to exploring new colossal permittivity materials and colossal permittivity have been obtained in different co-doping systems like (A$^+$/A$^{2+/3+}$/A$^{4+}$, Nb$^{5+}$/Ta$^{5+}$) co-doped TiO$_2$, where A$^+$ can be Ag$^+$, A$^{2+/3+}$/A$^{4+}$ can be fixed valance elements (e.g. Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$ ... /In$^{3+}$/Al$^{3+}$, Ga$^{3+}$ ...) and A$^{4+}$ can be Zr$^{4+}$ [14-19]. It was reported that the ionic radius of the acceptors and donors ions is an important factor to realize high-performance co-doped TiO$_2$ ceramics. The acceptors with ionic radius larger than that of Ti$^{4+}$ (74.5 Å), like Mg$^{2+}$/Zn$^{2+}$/Sc$^{3+}$/In$^{3+}$/Yb$^{3+}$/Ti$^{4+}$ (ionic radius range from 86 Å to 105 Å), are more likely to realize high-performance [13,14,20-23]. However, too large ions like Ca$^{2+}$/Bi$^{3+}$/La$^{3+}$ (ionic radius beyond 110 Å) are more likely leading to secondary phase aggregation in grain boundary, which may deteriorate dielectric properties [17,24,25]. Therefore, a suitable ionic radius is necessary to realize excellent dielectric properties. Lithium ion has an ionic radius of 90 Å and may be a suitable acceptor for the colossal permittivity (A$^+$, Nb$^{5+}$) co-doped TiO$_2$ ceramics. However, there is not report on the (Li$^+$, Nb$^{5+}$) co-doped TiO$_2$ ceramics and dielectric properties.

On the other hand, enriched phenomena were observed in co-doped TiO$_2$ and diverse mechanisms were proposed from different research groups. Internal barrier layer capacitance (IBLC) model was proposed to explain the origin of colossal permittivity in co-doping TiO$_2$ based on the structures of semiconductor grain and insulator grain boundary [26,27]. The colossal permittivity found in hydrogen-reduced rutile TiO$_2$ crystals could demonstrate that the existence of semiconductor grain and isolator grain boundary might be not a prerequisite for colossal permittivity [28]. Multiply polarization mechanisms were also reported in co-doped TiO$_2$ ceramics such as electrode interfacial effect...
[29], surface layer effect [30,31], and hopping polarization [32]. The relationship between the colossal constant and different polarization mechanisms needs to be further explored.

In this work, the (Li, Nb) co-doped TiO2 ceramics were prepared by a conventional solid-state sintering process and their dielectric properties were investigated. Colossal permittivity and low dielectric loss were obtained in LNTO materials. The dielectric behavior was discussed based on extensive microstructure and electric characterization.

2. Experimental details

Starting materials used in this work were TiO2 (rutile), Nb2O5 and Li2CO3 that all at a high purity of 99.99% from Alfa-Aldrich cooperation. The co-doped ceramics of (Li0.25Nb0.75)xTi1-xO2 (x ranges from 0.25% to 10%, abbreviated as LNT0x) were synthesized according to desired stoichiometric ratio through the conventional solid-state reaction method. Briefly, the raw materials were weighted and mixed by ball milling for 5 h with yttria-stabilized zirconia (YSZ) balls as medium. Then, the mixture was dried, sieved, and calcined at 1100 °C for 2 h in air. The processed powder was milled again. Polyvinyl acetate solution (with 6 wt% PVA) was added as binder. After homogeneously mixed and granulated, the powders were pressed into cylindrical pellets under uniaxial pressure. The pellet samples were de-binder at 650 °C for 2 h and then sintered at 1300 °C–1375 °C for 5 h to obtain dense ceramics. For the dielectric property measurement, silver electrodes were prepared by screen printing the silver paste on both sides of the pellet samples and annealed at 600 °C for 30 min in air. Part of LNT0.01 sample was annealed in oxygen at 1000 °C for 2 h.

The crystal phase of the LNT0 ceramics was identified by an X-ray diffractometer (Bruker D8 Advance XRD, Bruker AXS GmbH, Germany). The microstructure of samples was observed using a scanning electron microscope (SEM, Phenom G5, Phenom World). The dielectric properties dependence on frequency and temperature were measured using an impedance analyzer (Agilent 4990A) and a broadband dielectric spectrometer (Novocontrol Concept 300, Germany).

3. Results and discussion

Although Li–Nb–Ti–O system contains very rich crystal phases, single-phase concentration is higher than 10%. Fig. 1 shows the XRD patterns of (Li, Nb) co-doped TiO2 ceramics, which indicates that a pure tetragonal rutile TiO2 (ICDD card No. 21–1276) can be observed. It was reported that the solid solution limit of Li-doped TiO2 was 2 at%, and Li2TiO3 phase could appear above the limit level [33]. However, no secondary phases can be observed even at the 10% co-doping concentration in this work, which means that the solid solution limit of (Li,Nb) could exceed 10%, and (Li, Nb) co-doping could enhance the solid solution limit of Li ion in rutile TiO2. In addition, the (110) diffraction peak shifts towards a lower diffraction angle 2θ with the increase of (Li, Nb) co-doping contents. This should be caused by the increasing of lattice strain resulting from the substitution of Ti4+ (ionic radius rTi = 74.5 Å) by the larger Nb5+ (ionic radius rNb = 78 Å) and Li3+ (ionic radius rLi = 90 Å) [34].

With the increase of (Li, Nb) co-doping concentration, the optimized sintering temperature decreases slightly. But all the samples can be sintered well at 1300 °C–1375 °C for 5 h. Fig. 2 shows the surface morphologies of the 0.25%, 1%, 2%, 3%, 4%, 5% (Li, Nb) co-doped TiO2 ceramics. All the samples show dense microstructure and uniform grain size. The average grain sizes increase with the increases of (Li, Nb) co-doping concentrations.

Fig. 3 shows the frequency dependence of the permittivity (ε) and dielectric loss (tgδ) of different (Li, Nb) co-doped TiO2 ceramics at room temperature. All co-doped LNT0 ceramics exhibit colossal permittivity in the measuring frequency range of 20–107 Hz. With the increasing of co-doping concentrations, the dielectric loss increases. Particularly, when x > 5%, the dielectric loss increases rapidly. An excellent permittivity and low loss were achieved for the LNT0.01 ceramic with ε ∼7400, tgδ ∼0.016 at 1 kHz. As shown in Fig. 3, there are three dielectric loss peaks at low frequency (< 103 Hz), middle frequency and high frequency (> 106 Hz) ranges, which may correspond to different polarization processes expressed by LDR (low-frequency dielectric response), MDR (middle-frequency dielectric response) and HDR (high-frequency dielectric response), respectively.

3.1. Polarization mechanism of LDR

Usually, the LDR can be attributed to the space-charge polarization happening in low frequency range, which was reported in other co-doped TiO2 ceramics [35,36]. The measurement of dielectric property under DC bias is an effective method to recognize the space-charge polarization. If the space-charge polarization exists, the permittivity and loss at low frequency would alter immediately under different DC bias [35,37,38]. Fig. 4 shows the dielectric permittivity and loss dependence on frequency under an applied DC bias in a range of 0–6 V. Both the dielectric permittivity and loss increase significantly in the low frequency range with the increasing of DC bias, which indicates the existence of the space charge polarization at a low frequency range. However, DC bias has least influence on the dielectric properties in the higher frequency range indicating the different dielectric polarization.
3.2. Polarization mechanism of MDR

The dielectric behavior in middle frequency range mainly relates to the relaxation polarization process in material, which could be discerned by the characteristic activation energy and relaxation time [32,39]. In order to explore the origin of dielectric relaxation in middle frequency range, the frequency dependence of dielectric property of LNTO0.01 sample were measured at different temperature ranging from 163 K to 303 K as shown in Fig. 5. Three dielectric peaks located at different frequency range can be observed (Fig. 5b), namely Peak-1, Peak-2 and Peak-3, implying the existence of three relaxation processes. In order to clarify the origin of dielectric polarization of these peaks, the Cole-Cole equation was used to fit the results [40,41].

\[
\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_1 - \varepsilon_\infty)/(1 + (\omega \tau)^{-\alpha})
\]

where \(\varepsilon_1\) is the static permittivity, \(\omega\) is angular frequency, \(\tau\) is mean relaxation time, and \(\alpha\) is an empirical constant with the value between 0 and 1. The case \(\alpha = 0\) corresponds to the Debye model that has a single relaxation time.

The real part \(\varepsilon'\) and imaginary part \(\varepsilon''\) can be given according to the Cole-Cole function.

Fig. 2. SEM images of as-sintered LNTO\textsubscript{x} ceramics with (a) x = 0.25%, (b) x = 1%, (c) x = 2%, (d) x = 3%, (e) x = 4%, (f) x = 5%.

Fig. 3. Frequency dependence of permittivity and tg\(\delta\) of LNTO\textsubscript{x} ceramics with different co-doping concentrations measured at room-temperature.

Fig. 4. Frequency dependence of permittivity (a) and tg\(\delta\) (b) of LNTO\textsubscript{0.01} ceramic at different DC biases at room-temperature.
\[ \varepsilon'(\omega) = \varepsilon_{\infty} + (\varepsilon_i - \varepsilon_{\infty}) \times \frac{1 + (\omega\tau)^{1-n} \sin \frac{\omega\tau}{2}}{1 + 2(\omega\tau)^{1-n} \sin \frac{\omega\tau}{2} + (\omega\tau)^{2(1-n)}} \]  
\[ \varepsilon''(\omega) = (\varepsilon_i - \varepsilon_{\infty}) \times \frac{(\omega\tau)^{-n} \cos \frac{\omega\tau}{2}}{1 + 2(\omega\tau)^{1-n} \sin \frac{\omega\tau}{2} + (\omega\tau)^{2(1-n)}} \]  

When more than one relaxation peak exists in the polycrystalline ceramics, Eqs. (2) and (3) can be rewritten by

\[ \varepsilon'(\omega) = \sum_{i=1}^{n} \left[ \varepsilon_{\infty} + (\varepsilon_i - \varepsilon_{\infty}) \times \frac{1 + (\omega\tau_i)^{1-n} \sin \frac{\omega\tau_i}{2}}{1 + 2(\omega\tau_i)^{1-n} \sin \frac{\omega\tau_i}{2} + (\omega\tau_i)^{2(1-n)}} \right] \]  
\[ \varepsilon''(\omega) = \sum_{i=1}^{n} k_i (\omega\tau_i)^{-n} \cos \frac{\omega\tau_i}{2} + (\omega\tau_i)^{2(1-n)} \]  

Fig. 5c shows the experimental and fitting results of the dielectric loss \( \varepsilon'' \) of LNTO0.01 as-prepared sample measured at 193 K from Eq. (5) with \( n = 3 \). The excellent agreement between fitting curve and experimental data based on Cole-Cole function was obtained. It indicates that \( \varepsilon'' \) was composed of three Gaussian peaks (Peak-1, Peak-2, and Peak-3). With the increase of measuring temperature, the dielectric loss peaks steadily shifted towards higher frequency indicating a thermal activated dynamic process. Arrhenius relationship was used to fit these dielectric loss peaks at different temperatures:

\[ \tau = 1/2nf = \tau_0 \exp \left( \frac{E_a}{k_B T} \right) \]  

where \( \tau \) is relaxation time, \( k_B \) the Boltzmann constant, \( \tau_0 \) pre-exponential factor, \( f \) the frequency of the relaxation peaks of dielectric loss at different temperatures, \( E_a \) the activation energy. The fitting results are shown in Fig. 5d. The values of activation energy \( E_a \) and \( \tau_0 \) are calculated from the slopes and the intercepts of the fitted straight lines and listed in Table 1. The activation energy \( E_a \) and pre-exponential factor \( \tau_0 \) of Peak-1 and Peak-2 are close for LNTO0.01 sample as prepared, indicating that they could come from the same polarization mechanism. The activation energies of these two peaks are quite large and could relate to dipole polarization of oxygen vacancies [42–44]. The activation energy of Peak-3 is 0.1 eV and \( \tau_0 \sim 2.4 \times 10^{-9} \). This implied that the polarization process could originate from a polaron hopping relaxation of the trapped electrons in a distorted lattice generated from the substitution of Ti4+ by Nb5+[21,36,45].

To further understand the origin of the relaxation mechanism of Peak-1 and Peak-2, the dielectric frequency spectra of the LNTO0.01 sample annealed in O2 atmosphere were measured at a temperature range of 153 K–303 K. Fig. 6 shows the experimental and fitting results according to Eq. (5), and similar relaxation process can be seen. After O2 annealing, the intensity of dielectric loss of Peak-1 obviously increased while that of Peak-2 was almost unchanged, indicating that the relaxation process could not be dominated by dipole polarization related to oxygen vacancy. The calculated results of Arrhenius equation fitting are shown in Table 1. The activation energy changed slightly. The \( \tau_0 \) is about \( 10^{-12} - 10^{-16} \) s and activation energy \( E_a \) is about 0.46–0.54 eV, which are lied in the range of ion hopping (10–4–10–15) and free electron (10–16) time scale. So, the polarization mechanism of Peak-1 and Peak-2 are likely dominated by ionic hopping polarization rather than the polaronic mechanism [32].

Fig. 7 shows the temperature dependence of permittivity of O2 annealed sample at different frequencies. A relaxor-type relaxation behavior with a diffusive permittivity peak that shifted towards a higher temperature with increasing frequency can be observed. Similar relaxor-type relaxation behaviors arising from the off-center movement of doped cations were reported in lightly doped incipient ferroelectric materials [46–48]. The diffuseness of relaxor-type state could be described by a modified empirical quadratic Curie-Weiss law given by
where $\varepsilon_m$ is the maximum permittivity value at $T_m$, $C$ the Curie constant and $\gamma$ the degree of diffuseness of the permittivity peak. The exponent $\gamma$ was obtained by fitting $\varepsilon(T)$ data on the high temperature side of $T_m$ in the range of $(T_m + 25) \sim (T_m + 50)$ K [45]. The $\log(1/\varepsilon - 1/\varepsilon_m)$ was plotted against $\ln(1/T - 1/T_m)$ measured at 100 Hz. A diffuseness $\gamma$ of $\sim 1.5$ was obtained, indicating a relaxor-type behavior caused by cation moving from the center of TiO$_6$ octahedron.

The difference between the relaxation processes of Peak-1 and Peak-2 could come from dielectric polarization responses in different regions of the ceramics. It has been reported that O$_2$ annealed could compensate the oxygen vacancy generated during sintering at a high temperature and formed an insulator layer on the co-doped TiO$_2$ sample surface [30,49]. So, we compared the dielectric polarization responses of O$_2$ annealed LNT0.01 and surface-layer removed ceramic samples. It was found that the Peak-1 disappeared (not shown here). Comparing the permittivity of LNT0.01 as-prepared and O$_2$ annealed ceramics in Figs. 6a and 7a, it is found that permittivity decreases with temperature increasing for as-prepared sample, which was quite different from O$_2$ annealed sample. The similar phenomenon of permittivity decreasing with the temperature increasing was also observed in a semiconductor CuO materials, which is related to the formation of the Schottky barrier.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>Peak-1</th>
<th>Peak-2</th>
<th>Peak-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-prepared $E_a$/eV</td>
<td>0.539 ± 0.02</td>
<td>0.489 ± 0.005</td>
<td>0.101 ± 0.007</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>$5.7 \times 10^{-16}$</td>
<td>$2.3 \times 10^{-16}$</td>
<td>$2.4 \times 10^{-9}$</td>
</tr>
<tr>
<td>O$_2$ annealed $E_a$/eV</td>
<td>0.459 ± 0.003</td>
<td>0.457 ± 0.005</td>
<td>0.105 ± 0.001</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>$7.4 \times 10^{-14}$</td>
<td>$3.1 \times 10^{-16}$</td>
<td>$2.5 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Fig. 6. Frequency dependence of permittivity (a) and dielectric loss (b) of LNT0.01 O$_2$ annealed ceramic measured at different temperatures, (c) the experimental and fitting results of dielectric loss of O$_2$ annealed LNT0.01 ceramic at 193 K, (d) Fitting results of Arrhenius equation.

Fig. 7. Temperature dependence of permittivity (a) and fitting result of a modified empirical quadratic Curie-Weiss law (b) of O$_2$ annealed LNT0.01 ceramic.
layer between the sample and electrode [50]. The decrease of permittivity of as-prepared LNTO0.01 as-prepared could be related to the Schottky barrier layer between the sample and electrode. The Schottky barrier height would decrease with the temperature increasing, resulting in the decrease of permittivity. After O2 annealing, the insulator layer formed on the surface of sample would weaken or even eliminate the influence of electrode on permittivity [29,30].

3.3. Polarization mechanism of HDR

In this work, the colossal permittivity still remains at high frequency range up to 10^6 Hz. So, some other polarization mechanisms must exist.

To further understand the relationship between the different polarization mechanisms and permittivity at high frequencies, Eq. (4) was used to fit dielectric frequency spectra at 193 K. The permittivity dependent on frequency is calculated according to the parameters obtained from Eq. (5) and the results are showed in Fig. 8. Excellent consistency could be obtained between the experimental data and the simulated results. The permittivity is composed of four parts. Part I and II are calculated according to polarization process related to Peak-1 and Peak-2, which originate from relaxor-type relaxation. Part III is calculated according to polarization process related to Peak-3, which is related to polaron hopping. However, these three parts cause the change of permittivity to polarization process related to Peak-3, which is related to polaronic hopping in Al-substituted A5/3Sr1/3NiO4 (A=La, Nd) ceramics, Ceram. Int. 41 (2015) S846–S850.

The above experimental results and discussions indicate that multiple mechanisms including space charge polarization, relaxor-type relaxation, polaron hopping and defect dipoles or hopping related to localized electrons should have contribution to the colossal permittivity of the LNTO ceramics. Considering the remaining high permittivity at high frequency over 10^6 Hz, the defect dipoles or hopping electrons related with localized electrons could be the main origin of the colossal permittivity of the LNTO ceramics. The co-existence of multiple mechanisms should be the reason of the observation of diverse phenomena in the co-doped systems by different research group.

4. Conclusions

(Li, Nb) co-doped TiO2 ceramics (Li0.25Nb0.75)Ti1-xO2, 0.25% < x ≤ 20% were synthesized by the conventional solid-state reaction. All LNTO ceramics exhibited pure tetragonal rutile structure and colossal permittivity in a wide frequency range. Despite multiply polarization mechanisms occurring at different frequencies, polarization correlate with the defect dipoles or hopping electrons in the localized should be the main origin of the colossal permittivity of LNTO ceramics. Good dielectric performance with a colossal permittivity over 7000 and a low dielectric loss (tgδ < 0.06) in a wide frequency range of 100 Hz to 10 MHz were obtained from the LNTO0.01 ceramics.

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