



# Colossal permittivity and dielectric relaxations in $(\text{La}_{0.5}\text{Nb}_{0.5})_x\text{Ti}_{1-x}\text{O}_2$ ceramics

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## ABSTRACT

A series of La+Nb co-doped TiO<sub>2</sub>  $(\text{La}_{0.5}\text{Nb}_{0.5})_x\text{Ti}_{1-x}\text{O}_2$  ( $0.25\% \leq x \leq 5\%$ ) ceramics were prepared using a solid-state reaction method. Colossal permittivity (CP) ( $\epsilon' > 10^4$ ) and low dielectric loss ( $\tan\delta < 0.05$ ) were obtained when the ceramics were sintered at 1673 K in an N<sub>2</sub> atmosphere and annealed at 1073–1173 K in air. A pure rutile phase was achieved when  $x = 0.25\%$  and secondary phase La<sub>2</sub>TiO<sub>5</sub> was detected when  $x \geq 0.5\%$ . The optimum dielectric performance of  $\epsilon' > 10^4$  and  $\tan\delta < 0.05$  within 1 Hz–2 MHz and 25–350 K was obtained for  $x = 0.5\%$ . Three types of dielectric relaxations were observed through the dielectric-temperature spectrum: electron-pinned defect-dipoles (EPDD) polarization, electron hopping, and Maxwell–Wagner polarization. The CP ( $> 25$  K at 1 kHz) was primarily related to EPDD polarization. The high activation energy of the grain boundary ( $E_{gb} = 1.98$  eV) is one of the reasons for the low  $\tan\delta$  in this study.

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## 1. Introduction

The colossal permittivity (CP) of dielectric materials has been extensively investigated in recent years because of the increasingly high-performance requirements for capacitive devices used in high-energy density storage and microelectronics applications. Many dielectric materials that exhibit unusually high dielectric permittivities above  $10^3$  without any detectable ferroelectric phase transitions, such as doped NiO [1], CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO) [2] and AFe<sub>1/2</sub>B<sub>1/2</sub>O<sub>3</sub> (A = Ba, Sr and Ca; B = Nb, Ta and Sb) [3] have been studied. However several severe problems have still not been resolved, thereby preventing the wide application of these materials and hindering further advances in device performance. These problems include the high dielectric loss ( $\tan\delta$ ) and strong dependence of dielectric properties on temperature and frequency [4,5]. A new CP material of co-doped TiO<sub>2</sub> has been extensively investigated in recent years owing to its excellent electrical properties: the (Nb, In) co-doped TiO<sub>2</sub> ceramics are characterized by  $\epsilon_r > 10^4$  and  $\tan\delta \leq 0.05$  within of frequency range of 20 Hz–2 MHz at 80 K–450 K [6,7]. The novel co-doped TiO<sub>2</sub> system provides insights for studying a CP material with low  $\tan\delta$ .

CP co-doped TiO<sub>2</sub> ceramics, such as the TiO<sub>2</sub> co-doped with

different trivalent element (In, Y, Yb, Er, Ga or Al) with pentavalent Nb/Ta or divalent element (Mg, Ca, or Zn) with Nb/Ta or even Zr+Nb, have been extensively studied [8–20]. These studies indicated that the co-doped TiO<sub>2</sub> with CP is easy to obtain, but the low  $\tan\delta < 0.05$  in the frequency range of 20 Hz–2 MHz is difficult to achieve [6,8,15,18,21,22]. Generally, in  $(\text{A}^{3+}\text{B}^{5+})_x\text{Ti}^{4+}_{1-x}\text{O}_2$  type ceramics, the electrons can be introduced by Nb<sup>5+</sup>. By doping the A<sup>3+</sup> ion, the electrons were confined within complex defect clusters ( $\text{A}_2^{3+}\text{V}_\text{o}^{2-}\text{Ti}^{3+}$  or  $\text{B}_2^{5+}\text{Ti}^{3+}\text{CTi}^{4+}$  (C = A<sup>3+</sup>, Ti<sup>3+</sup>, or Ti<sup>4+</sup>)) into TiO<sub>2</sub> lattice, so co-doped TiO<sub>2</sub> ceramic/film/single crystal with CP and low  $\tan\delta$  properties were obtained due the presence of electron-pinned defect-dipoles (EPDD) polarization [6,12,22,23]. However, further studies indicated that many additional factors such as electron hopping or internal barrier layer capacitor (IBLC) polarization contribute to the dielectric response in those co-doped TiO<sub>2</sub> ceramics over a broad frequency and temperature ranges in addition to EPPD polarization [8,24–27]. As a typical oxide of co-doped TiO<sub>2</sub>, oxygen vacancies are easily produced during the sintering process, so the oxygen vacancy hopping effect on dielectric properties cannot be ignored [28].

The conventional method is to choose elements with similar ionic radii to form a solid-solution. For the  $(\text{In}_{0.5}\text{Nb}_{0.5})_x\text{Ti}_{1-x}\text{O}_2$  ceramics, The radius of In<sup>3+</sup> ( $R_{\text{In}^{3+}} = 0.094$  nm, CN = 6) is considerably larger than Ti<sup>4+</sup> ( $R_{\text{Ti}^{4+}} = 0.0745$  nm, CN = 6) [29], yet the pure solid-solution rutile was achieved at doping level  $x = 0.1$  due to the combination effect of Nb and In, while the solid solubility limit was

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only  $x = 0.01$  for  $\text{In}_x\text{Ti}_{1-x}\text{O}_2$  ceramics [6]. This phenomenon enlightens us to use much bigger ion to dope into  $\text{TiO}_2$  with Nb. Some studies have indicated that the CP mechanisms in co-doped  $\text{TiO}_2$  are closely related to the size of doped trivalent ion [12,30–33]. The dielectric properties of the ion Bi ( $R_{\text{Bi}^{3+}} = 0.117$  nm, CN = 6) with Nb co-doped  $\text{TiO}_2$  have been researched and the low  $\tan\delta$  is obtained due to Bi ions which are doped into the  $\text{TiO}_2$  lattice and the formation of the  $\text{Bi}_{1.74}\text{Ti}_2\text{O}_{6.624}$  phase [34]. Good dielectric performance in  $(\text{La}_{0.5}\text{Nb}_{0.5})_{0.3}\text{Ti}_{0.7}\text{O}_2$  ceramics was thought to be caused by the formation of a segregation structure [33]. The much bigger trivalent element radius compared to that of  $\text{Ti}^{4+}$  often leads to lattice mismatch, causing the second phase to establish the dense grain-boundary structure. In this study, we chose the very big and stable  $\text{La}^{3+}$  ( $R_{\text{La}^{3+}} = 0.1172$  nm, CN = 6) as the acceptor and  $\text{Nb}^{5+}$  as the donor co-doped into  $\text{TiO}_2$ . The  $(\text{La}_{0.5}\text{Nb}_{0.5})_x\text{Ti}_{1-x}\text{O}_2$  ( $x = 0.25\%–5\%$ ) ceramics were investigated. By adjusting the sintering and annealing processes, excellent dielectric properties ( $\epsilon' > 10^4$  and  $\tan\delta \leq 0.05$  within 1 Hz–2 MHz) were obtained. The structures, elements distribution, dielectric relaxations in the temperature range of 15 K–425 K, and impedance characteristics were investigated in detail.

## 2. Experimental

The  $(\text{La}_{0.5}\text{Nb}_{0.5})_x\text{Ti}_{1-x}\text{O}_2$  ceramics samples were prepared by a solid-state reaction method. The starting materials used in this work were high-purity  $\text{TiO}_2$  (rutile, 99.99%),  $\text{Nb}_2\text{O}_5$  (99.99%), and  $\text{La}_2\text{O}_3$  (99.99%). Those powders were accurately weighed according to the compositions  $(\text{La}_{0.5}\text{Nb}_{0.5})_x\text{Ti}_{1-x}\text{O}_2$  ( $x = 0.25\%, 0.5\%, 1.5\%, 2.5\%, 3.5\%$ , and  $5.0\%$ ),  $\text{La}_{0.5}\text{Ti}_{99.5\%}\text{O}_2$  ( $\text{TiO}_2\text{-La}$ ),  $\text{Nb}_{0.5}\text{Ti}_{99.5\%}\text{O}_2$  ( $\text{TiO}_2\text{-Nb}$ ) and then ball-mixed for 12 h with ethanol as the medium. After the ball-milling, the powders, incorporating a 5 wt% polyvinyl alcohol (PVA) binder solution, were pressed into disks with a diameter of 10 mm and thickness of 1.2–1.5 mm at a uniaxial pressure of 200 MPa. Then, the disks were put in the tube furnace. The closed tube furnace is connected to the flow gas controller (MKS 247D, Four Channel Power Supply/Readout, USA), which is used to control the pressures of mixed gas. The mixed gases are  $\text{O}_2$  (gas purity:

99.999%) and  $\text{N}_2$  (gas purity: 99.999%), respectively. The samples were debound for 2 h at 773 K and sintered at 1623–1723 K for 10 h in the different atmosphere at a flow rate of 160 ml/min; finally, all sintered samples were polished to 0.6 mm in thickness and annealed at 923–1473 K for different times in air. The heating rate was set at 3 K/min and the cooling rate was 3 K/min until the temperature decreased to 773 K, then the samples cooled inside the furnace to room temperature (RT). The parallel surfaces of the samples were coated using silver at 923 K for 30 min for the characterization of their electrical properties.

X-ray diffraction (XRD) was performed on a Rigaku D/Max 2250 diffraction-meter (Japan) with  $\text{Cu } \alpha$  radiation (40 kV and 100 mA). The data were measured using the continuously-scan mode at a speed of  $8^\circ/\text{min}$ , and the data for refining measured with a slow scanning speed of  $0.01^\circ/\text{second}$ . Surface, cross-section morphologies and elements distribution information were collected using field emission scanning electron microscopy (FEI Nova Nano-SEM 450).

Dielectric dispersion was studied by the combination of an impedance analyzer Agilent 4991A in the frequency range of 2 MHz–3 GHz, Agilent E4980A with the frequency range of 20 Hz–2 MHz and alpha-A high-performance frequency analyzer in the frequency range of  $10^{-3}$  Hz–1 MHz, respectively. The dielectric properties as a function of temperature were measured using an Agilent E4980A with a temperature controller vibration sample magnetometer (VSM, CFM-8T, Cryogenic Ltd, England) ranging from 15 to 250 K. A Novocontrol broadband dielectric spectrometer was used with an alpha-A high-performance frequency analyzer (BDS40, Germany) over the temperature range of 123 K–425 K. The margin of error for the permittivity (20 Hz–2 MHz) at RT between two different temperature-variation measurement-systems was below 5%.

## 3. Results and discussion

The dielectric properties of La+Nb co-doped rutile  $\text{TiO}_2$  ceramics with respect to the sintering and annealing conditions are summarized in Table 1. For  $x = 0.5\%$ , the ceramics with  $\epsilon'$  over  $10^4$

**Table 1**  
The dielectric properties for La+Nb co-doped rutile  $\text{TiO}_2$  ceramics with respect to the sintering and annealing conditions.

component	Prepared process				Dielectric properties		
	Sintering atmosphere	Sintering temperature(K)	Annealed temperature(K)	Annealed times(hours)	$\epsilon'$ (@1 kHz)	$\tan\delta$ (@1 kHz)	Frequency range ( $\epsilon' > 8000$ & $\tan\delta < 0.05$ )
$x = 0.5\%$	$\text{N}_2$	1673	No	0	24450	0.13	×
$x = 0.5\%$	flow air	1673	No	0	1060	0.14	×
$x = 0.5\%$	0.10 <sup>a</sup>	1673	No	0	260	0.11	×
$x = 0.5\%$	0.25 <sup>a</sup>	1673	No	0	130	0.075	×
$x = 0.5\%$	0.50 <sup>a</sup>	1673	No	0	110	0.097	×
$x = 0.5\%$	$\text{N}_2$	1623	No	0	33340	0.13	×
$x = 0.5\%$	$\text{N}_2$	1723	No	0	21560	1.0	×
$x = 0.5\%$	$\text{N}_2$	1673	923	2	11360	1.5	×
$x = 0.5\%$	$\text{N}_2$	1673	1073	2	17430	0.007	573 Hz- 273 kHz
$x = 0.5\%$	$\text{N}_2$	1673	1123	2	12010	0.018	1 Hz- 2 MHz
$x = 0.5\%$	$\text{N}_2$	1673	1173	2	13960	0.049	1 Hz-2 MHz
$x = 0.5\%$	$\text{N}_2$	1673	1273	2	2087	0.14	×
$x = 0.5\%$	$\text{N}_2$	1673	1473	2	1590	0.25	×
$x = 0.5\%$	$\text{N}_2$	1673	1123	0.5	24920	0.10	75 kHz-467 kHz
$x = 0.5\%$	$\text{N}_2$	1673	1123	1	23570	0.047	659 Hz- 1 MHz
$x = 0.5\%$	$\text{N}_2$	1673	1123	10	11000	0.019	1 Hz –2 MHz
$\text{La}_{0.5}\text{Ti}_{99.5\%}\text{O}_2$	$\text{N}_2$	1673	1123	2	300	0.019	×
$\text{Nb}_{0.5}\text{Ti}_{99.5\%}\text{O}_2$	$\text{N}_2$	1673	1123	2	21000	0.74	×
$x = 0.25\%$	$\text{N}_2$	1673	1123	2	650	0.038	×
$x = 1.5\%$	$\text{N}_2$	1673	1123	2	9150	0.013	1 Hz-30 kHz
$x = 2.5\%$	$\text{N}_2$	1673	1123	2	11010	0.021	1 Hz-187 kHz
$x = 3.5\%$	$\text{N}_2$	1673	1123	2	10860	0.025	1 Hz-62 kHz
$x = 5.0\%$	$\text{N}_2$	1673	1123	2	26780	0.017	42 Hz-324 kHz

<sup>a</sup> The mix gases were  $\text{O}_2$  and  $\text{N}_2$ , controlled oxygen partial pressure at 0.1, 0.25, and 0.50.

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