High dielectric performance and multifarious polarizations in (Lu + Ta) co-doped TiO₂ ceramics

Jiangtao Fan, Zhen Long and Zhanggui Hu

Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, College of Material Science and Engineering, Tianjin University of Technology, Tianjin, China

Abstract
Materials with high dielectric constant have broad application prospects in energy storage elements. In this work, (Lu₀.₅Ta₀.₅)ₓTi₁₋ₓO₂ ceramics (x = 0, 0.01, 0.02 and 0.04) were synthesized by a standard conventional solid-state reaction. Remarkably, (Lu₀.₅Ta₀.₅)₀.₉ₙTi₉ₙ₋₂O₂ ceramic exhibits a high dielectric permittivity (2.55 × 10⁴), low dielectric loss (0.012) and excellent stabilities of frequency and temperature (−150–150°C and 20–5 × 10⁶ Hz). The formation mechanism of excellent dielectric properties was studied based on analysis of the XRD, SEM, XPS, complex impedance and electric modulus. Colossal permittivity (CP) and low tan δ were attributed to the internal barrier layer capacitance (IBLC) effect, electron-pinned defect-dipole (EPDD) effect and electrode effect. This work has important guidance for the further research of giant dielectric materials.

1. Introduction
In recent years, the rapid development of microelectronics technology, which essential the design of miniaturized modules with the integration of electronic components and devices in Multi-layer Ceramic Capacitors (MLCC) [1–3]. Materials with giant dielectric constants have received unprecedented attention. In the last decades, some candidates have been proposed for practical applications including BaTiO₃, CaCu₃Ti₄O₁₂(CCTO), La₂₋ₓSrₓNiO₄ (Pb, La)TiO₃ and NiO [4–10]. However, these types of materials are not applicable directly to electronic devices. Thus, the research and development of materials with CP, low dielectric loss, and good frequency-/temperature stability is an arduous task.

Recently, donor (Nb) and acceptor (In) co-doped TiO₂ ceramics (INTO) with CP (>10⁵), low dielectric loss (<0.05), and weak temperature and frequency dependence have triggered a renaissance research [11]. It is suggested that EPDD effect is responsible for its CP properties. The INTO ceramics has excellent comprehensive dielectric properties and has great prospects in high-density storage devices and miniaturized devices. It is expected to solve the problems of high dielectric loss and poor temperature stability. This research has stimulated interest in the field of co-doped rutile TiO₂ material. Subsequently, a large number of doping modifications were performed on co-doped TiO₂ ceramics [2,11–44]. These efforts have contributed significantly to the theory of CP materials. In addition to EPDD effect, other mechanisms have been proposed, including the IBLC effect [14,25], electrode effect [26], electron hopping [15], surface barrier effect [28], and micro-inhomogeneity and polarization relaxation [29]. Through the study of In+Nb system and other co-doped TiO₂ systems, the origin of giant dielectrics of co-doped TiO₂ ceramics is still controversial [26]. The CP mechanism of co-doped ceramics is related to the ionic sizes, charges and electronegativity of the dopants [28,29]. In particular, Liu et al. found that the Ta+In co-doped TiO₂ ceramics have very low dielectric loss (0.002) at 1 kHz compared to the Nb+In doped system [2,11]. The results show that the very low dielectric loss is due to the fact that the donor ion Ta⁺⁺ has an additional electron shell layer than Nb⁺⁺, which results in a more severe deformation of the replaced Ti sites. Moreover, several studies confirmed the usefulness of EPDD in obtaining low dielectric losses in TiO₂ ceramics, but proposed that the radius of the acceptor ion must be larger than that of the Ti⁺⁺ or Ti⁺⁺⁺ ion [13]. For example, in the (Ta₀.₅Al₀.₅)ₓTi₁₋ₓO₂ ceramic system, large dielectric properties were found even when the radius of the acceptor Al⁺⁺ was smaller than the ionic radius of Ti⁺⁺⁺/Ti⁺⁺⁺, but the investigators believe that the source of the giant dielectric of the Ta +Al system is the IBLC and non-ohmic electrode contact effect, and the defect dipole effect is not formed [27]. Researchers believe that the large ionic radius of the acceptor element leads to a stable defect structure that facilitates the dielectric properties [33]. Therefore, the development of TiO₂-based giant
dielectric constant materials using suitable acceptor-donor co-doping approach is in need of further investigation.

In this work, the large ionic radius Lu$^{3+}$ (0.861 Å) was selected as the acceptor ion and the crystal structural and dielectric property of Lu +Ta co-doped rutile TiO$_2$ ceramics were studied for the first time. The physical causes of the large dielectric constant of LTTO ceramics are also discussed in detail.

2. Experimental

Rutile TiO$_2$ (99.99%), Ta$_2$O$_5$ (99.99%) and Lu$_2$O$_3$ (99.99%) were used as raw materials. Co-doped ceramic composed of (Lu$_{0.5}$Ta$_{0.5}$)$_x$Ti$_{1-x}$O$_2$ were prepared by conventional solid-state reactions, as reference [26]. All co-doped ceramics were sintered at 1400°C for 5 h in air. The (Lu$_{0.5}$Ta$_{0.5}$)$_x$Ti$_{1-x}$O$_2$ ceramics were coated with silver on each side for dielectric characterization.

The phase composition and crystal structure were examined by X-ray diffraction (Smart Lab 9 KW, Rigaku, Japan) and Raman spectroscopy (Renishaw in Via Microscope Raman, UK). The microstructure of co-doped ceramic was observed by scanning electron microscopy (Quanta FEG 250, USA) equipped with EDS. The dielectric behaviors of the frequency and the impedance spectra were studied using a precise impedance analyzer (6500B, Wayne Kerr Electronic Instrument Co., Shenzhen, China) with the sample mounted in a holder inside a dielectric measuring system (HDM5-1000, Partulab, Wuhan, China). The nonlinear I–V characteristics for samples were measured by high-resistance meter (Keithley Model 2400). Chemical states were detected by X-ray photoelectron spectroscopy ((ESCALAB250Xi, THERMO SCIENTIFIC, UK)).

3. Results and discussion

Figure 1(a) shows the XRD pattern of (Lu$_{0.5}$Ta$_{0.5}$)$_x$Ti$_{1-x}$O$_2$ ceramics. All samples show the rutile structure (PDF card: 21–1276). Meanwhile, the impurity phase of Lu$_3$TaO$_7$ (PDF card: 24–0696) was found in Lu+Ta co-doped TiO$_2$ ceramics at the doping quantity of 0.04. Compared with other co-doped TiO$_2$ ceramics, Lu+Ta co-doped TiO$_2$ ceramics has a higher solid solution limit, as shown in Table 1 [18,19,21,30–33]. As shown in Figure 1(b), the diffraction peak shifts to a low angle with the increase of x, indicating the lattice expansion. Figure 1(c) shows Rietveld refinement results for (Lu$_{0.5}$Ta$_{0.5}$)$_{0.01}$Ti$_{0.99}$O$_2$ ceramic with pure rutile structure. The reliability coefficients of the LTTO (x = 0.01) tetragonal crystal structure are $R_p = 6.7$%, $R_{wp} = 8.71$%, $\chi^2 = 2.972$. The ceramics of x = 0.01 is determined as a rutile crystal structure of space group P42/mmm with a = 4.57(1) Å and c = 2.95(5) Å, where Lu$^{3+}$ ions and Ta$^{5+}$ ions substitute for the Ti$^{4+}$ ions site of TiO$_2$. In addition, the lattice parameters (a and c) calculated are summarized

![Figure 1](image-url)

Figure 1. (a) XRD patterns of (Lu$_{0.5}$Ta$_{0.5}$)$_x$Ti$_{1-x}$O$_2$ ceramics. (b) Enlarged (101) plane diffraction. (c) Rietveld refinement results for the sintered ceramic samples (x = 0.01). (d) Cell parameters of (Lu$_{0.5}$Ta$_{0.5}$)$_x$Ti$_{1-x}$O$_2$ as a function of x. (e) Raman spectra of (Lu$_{0.5}$Ta$_{0.5}$)$_x$Ti$_{1-x}$O$_2$ ceramics.
in Figure 1(c). The ionic radius of Ti\(^{4+}\), Lu\(^{3+}\) and Ta\(^{5+}\) are around 0.605 Å, 0.861 Å, and 0.64 Å, respectively. According to the Hum-Rothery rule, a substitution solid solution is more likely to be formed if the mismatch of ionic radii is less than 15% [30]. The mismatch of Lu and Ti ionic radii ([0.861–0.605]/0.605 = 42.0%) is much higher than the infinite solid solution’s upper limit while that of Ta and Ti ionic radii ([0.640–0.605]/0.605 = 5.7%) is far lower than the infinite solid solution’s limit. As a result, when the doping content reaches less than 0.02, the cell parameters increase with the increase of doping, but when x = 0.04, it is difficult to replace the Ti\(^{4+}\) ions in TiO\(^2\)\(_2\) octahedra due to Lu\(^{3+}\) ions, which leads to saturation of the cell parameters. Similar phenomenon has been reported in (Ta + Sm) co-doped TiO\(_2\) ceramic [17].

Due to the occupation of Lu and Ta with large ion radius on the Ti site, the lattice expansion leads to an increase. The lattice parameters of co-doped TiO\(_2\) ceramics increase, further indicating that Lu and Ta have substituted Ti ion. In addition, the structure was analyzed using Raman spectroscopy, and the results are shown in Figure 1(d). The four based B_{1g}, E_g, A_{1g}, and B_{2g} modes of doped TiO\(_2\) ceramics are identical to the standard modes of rutile TiO\(_2\), which proves that the rutile phase of doped ceramics exists [26]. Meanwhile, the peak ~234 cm\(^{-1}\) should be noted that it was multi-phonon peak for second-order effect [26]. The E_g mode slightly shifts to a low wavenumber as x increases, which indicates the presence of oxygen vacancies [26]. In conclusion, the XRD spectra and Raman spectra of all LTTO ceramics showed the rutile phase.

Figure 2(a–c) shows the SEM images of surface for (Lu_{0.25}Ta_{0.75})_{6}Ta_{1-x}O_{2} ceramics. All co-doped TiO\(_2\) ceramics are obtained to have a dense microstructure. The average grain size of co-doped TiO\(_2\) ceramic is about 3.41 μm for the composition with x = 0.01. As x increases to 0.04, the grain size of co-doped ceramics gradually increases to 4.32 μm. This is also found in Sb + Ga, Ta+Zn and Ti+Nb ceramics [15,26,38]. Usually, grain growth is associated with the liquid-phase sintering mechanism, which refers to the diffusive mass transfer of ions or atoms at the grain boundaries. When x = 0.01–0.04, the mean grain size increased from 3.41 μm to 4.32 μm, possibly due to the changes in grain-growth rate related to the replacement of Ti\(^{4+}\) ions with small ion sizes (0.605 Å) by Lu\(^{3+}\) ions with large ion sizes (0.861 Å). To further analyze the distribution of doped elements in ceramics, elemental mapping (Lu, Ta, Ti, and O) was performed for samples with x = 0.01 and 0.04, as shown in Figure 2(e). For the composition of x = 0.01, the doping elements are not aggregated and all elements are uniformly distributed at the grains and grain boundaries. However, small unevenly distributed with high contrast of Lu and Ta have been observed in (Lu_{0.5}Ta_{0.5})_{6}Ta_{0.04}O_{2} ceramic, suggested by impurity phase formed in the sample. This is consistent with the results of XRD analysis.

Figure 3(a,b) show the dielectric-frequency spectrum of (Lu + Ta) co-doped rutile TiO\(_2\) ceramics. All co-doped ceramics exhibit huge dielectric constants
(>10^8) compared to pure TiO_2 ceramics (ε = 800). In addition, both the dielectric constant and dielectric loss increase with increasing x. This is because excessive doping will lead to an increase in defects and interfacial layers in the ceramics, causing significant interfacial effects and deterioration of dielectric loss [26]. Remarkably, (Lu_{0.5}Ta_{0.5})_{0.01}Ti_{0.99}O_2 display excellent dielectric permittivity (ε = 2.55 × 10^8), low dielectric loss (tanδ = 0.012), respectively. In addition, the dielectric constant of (Lu, Ta) co-doped rutile TiO_2 ceramics drops rapidly in the high-frequency region (10^5 ~ 10^6 Hz), and corresponds to a well-developed loss relaxation peak. According to the theory of dielectric polarization, dielectric constant is caused by multiple polarizations (interface polarization and dipolar polarization, etc.) at low and medium frequency (<10^6 Hz), and when the frequency is at high frequency (>10^6 Hz), the interface polarization exits [41]. Since the total polarization decays with frequency, the dielectric constant gradually decreases. To evaluate functional performance of LTTO ceramics more roundly, the dielectric temperature spectrum and the temperature coefficient of ε_τ are presented in Figure 3(c,d). As shown in Figure 3(c), all co-doped LTTO ceramics display CP as well as weak temperature dependence in the temperature range of −150°C−150°C. On the other hand, the sharp increase occurs when the temperature is higher than 180°C. This phenomenon is well explained by the increase in electrical conductivity [26]. The change of temperature coefficient of ε (1 kHz) relative to RT should be less than ±15% for X-R type capacitors [30]. The details of the temperature coefficients of the (Lu + Ta) co-doped TiO_2 ceramics were displayed in Figure 3(d). The temperature coefficient of (Lu_{0.5}Ta_{0.5})_{0.01}Ti_{0.99}O_2 ceramic is lower than ±15% in the temperature range from −150 to 150°C. (Lu_{0.3}Ta_{0.7})_{0.01}Ti_{0.99}O_2 ceramic is suitable for X8R capacitors. Obviously, the (Lu_{0.5}Ta_{0.5})_{0.01}Ti_{0.99}O_2 ceramic exhibits the optimum comprehensive dielectric property.

Complex impedance analysis is an effective method for exploring the electrical conduction information at the grain, grain boundary and electrode interfaces [30]. The impedance spectra of (Lu_{0.3}Ta_{0.7})_{0.01}Ti_{1−x}O_2 ceramics (x = 0.01−0.04) at RT are shown in Figure 4(a). A larger semicircular arc is observed, indicating that the co-doped ceramic has a larger grain boundary resistance. In addition, a nonzero intercept from semiconductive grain was observed, as shown in Figure 4(a) inset. The large difference in resistance between grain boundaries and grains indicates the presence of large electrical inhomogeneities in co-doped ceramics [26]. This phenomenon is similar to (Sb+Ga) [26],[Ta+ Sm] [17] and (Y + Nb) [16] co-doped TiO_2 ceramics, proving that there is an IBLC effect in LTTO ceramics. The low resistance of the grains is associated with the electron

Figure 3. Frequency dependence of (a) dielectric constant and (b) dielectric loss of (Lu + Ta) codoped rutile TiO_2 ceramics at room temperature. (c) Temperature dependence of permittivity of LTTO (x = 0.01, 0.02, 0.04) ceramics at 1 kHz. (d) Δε/ε_{300°C} (−150°C−+200°C) of all LTTO codoped ceramics at 1 kHz.
hopping between Ti$^{3+}$ and Ti$^{4+}$ [26]. In addition, the high resistivity of the grain boundary may be caused by the amorphous structure or relatively complete oxidation of grain boundary compared to the grain [30]. In general, the grain boundary resistance $R_{gb}$ and grain resistance $R_g$ can be determined by a large semicircular arc at low frequencies and a nonzero intercept on the $Z'$ axis at high frequencies from the $Z^*$ plane plots, respectively [30]. Therefore, we can obtain the precise $R_g$ and $R_{gb}$ values by fitting the measured complex impedance data. Considering the weak electrode effect around RT, all data can be fitted by the equivalent circuit $(R_g\text{CPE}_g)(R_{gb}\text{CPE}_{gb})$ by using Zview software as shown in Figure 4(a) [14,34,35,42]. The fitted data are shown in Table 2. In addition, the grain boundary resistance gradually decreases with the increase of co-doping concentration. This is because the introduction of Ta$^{5+}$ induces more electrons. The I–V curve characteristics of LTTO ceramics measured at RT as shown in Figure 4(b). LTTO ceramics show the nonlinear I–V behavior. The nonlinear I–V curves are fitted with the following formula [26]

$$ J = KE^\alpha $$

where $K$ is a constant related to the electrical resistivity of the material, $\alpha$ is the nonlinear coefficient [30]. From the fitting line, the values of $\alpha$ and $E_b$ can be obtained. The $\alpha$ values of LTTO ceramics with $x = 0.01–0.04$ are 5.91, 4.32, and 3.20. The $E_b$ values are 234 V/cm, 128 V/cm, and 74 V/cm. Usually, the height of the potential barrier at the grain boundary decreases as the carrier concentration in the grain boundary increases. As the amount of doping increases, Ta ions release more free electrons, resulting in a decrease in breakdown field strength and nonlinear coefficient. This phenomenon is similar to the Nb+Gd, Sb+Ga and Ta+Zn systems [26,30,38].

Figure 4(c) shows the impedance spectrum for LTTO ceramics ($x = 0.01$) at high temperature. The impedance data of LTTO ($x = 0.01$) ceramics can be fitted by three parallel R-CPE elements by using ZVIEW software (inset of Figure 4(c)). With the increase of temperature, the decreasing grain boundary resistance indicates that the activation process is thermally activated [30]. This conductivity ($\sigma$) can follow Arrhenius’s law [26].

| x   | $R_{gb} \times 10^3$ (Ω) | $R_g$ (Ω) | $E_b$ (eV) |
|-----|--------------------------|-----------|------------|
| 0.01| 22.2                     | 2.2       | 0.79       |
| 0.02| 1.59                     | 1.8       | 0.76       |
| 0.04| 1.31                     | 0.5       | 0.71       |
\[
\sigma = \sigma_0 \exp\left(\frac{E_a}{k_B T}\right)
\]  
(2)

Where \(\sigma_0\) refers to the pre-factor, \(E_a\) is the activation energy, \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature [26]. The activation energy of LTTO (\(x = 0.01–0.04\)) ceramics were 0.79, 0.76 and 0.71 eV as shown in Figure 4(d). The \(E_{ab}\) value decreased with increasing co-dopant concentration. Usually, the higher the height of the potential barrier the stronger the hindrance to the movement of free electrons, leading to high activation and low dielectric loss [26]. As the amount of doping increases, more free electrons are induced, resulting in a decrease in activation energy. The decrease in grain boundary activation energy explains to some extent the enhanced interfacial polarization [37]. This indicates that the accumulation of space charge leads to enhanced interfacial polarization, which results in deterioration of the dielectric properties. Therefore, suppression of excess space charge-induced interfacial polarization is the key to obtaining excellent dielectric properties. This is quite similar to the behavior for Gd+Nb co-doped rutile TiO\(_2\) [30].

In order to effectively study the dielectric relaxation mechanism and conductive behavior of co-doped TiO\(_2\) ceramics, a combination of complex electric modulus and complex impedance spectroscopy is usually used [42,43]. The frequency-dependent permittivity of LTTO ceramics (\(x = 0.01\)) is shown in Figure 5(a,b). The dielectric constant \((f < 10^4 \text{ Hz})\) increases sharply with increasing temperature, which is evidence of the presence of interfacial polarization [26]. Three relaxation peaks can be observed in different frequency ranges (Figure 5), noted as Peak-1, Peak-2 and Peak-3, indicating the presence of three relaxation processes. It can be concluded that the dielectric response of LTTO ceramics is contributed by grain response, grain boundary response and electrode response. Similar phenomena can also be observed in the Nb+Al, Nb+La, Nb+In, Nb+Li and Sb+Ga systems [2,26,42–44]. As the temperature increases, the peak shifts to higher frequencies, the activation energy were simulated by formulas (3):

\[
f_p = f_0 \exp\left(-\frac{U}{k_B T}\right)
\]  
(3)

where \(f_p\) is the frequency of imaginary modulus peak at certain temperature (relaxation frequency), \(f_0\) is the frequency constant, \(U\) the activation energy for the dielectric relaxation, \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature [26]. Table 3 summarizes the \(U_{a1}, U_{a2}\) of co-doped ceramics\((x = 0.01–0.04)\). Since \(U_{a3}\) has fewer temperature points, this

![Figure 5](image-url)  
**Figure 5.** (a–b) The frequency dependence of dielectric permittivity and the electric modulus \(M^{*}\) at different temperatures. (c) The fitting activation energies for polarizations at \(-150^\circ\text{C}\) to \(240^\circ\text{C}\) for LTTO ceramic\((x = 0.01)\). (d) The conductivity of \(x = 0.01\) ceramics at different temperatures.
value is not presented. The $U_{a1}$ of co-doped ceramics ($x = 0.01–0.04$) are determined to be 0.076, 0.069 and 0.069 eV, which is very close to the activation energy (0.063–0.074 eV) of EPDD polarization in Nb+La co-doped TiO$_2$ [18]. Meanwhile, $U_{a1}$ remains nearly constant as the amount of co-doping increases, which indicates that the electron fixation process is well synchronized with the enhanced electrons as the amount of co-doping increases [18]. The immobile numerical values of $U_{a1}$ further demonstrate the EPDD polarization. Similarly, the $U_{a2}$ of co-doped ceramics ($x = 0.01–0.04$) related with grain boundary effect (0.87, 0.77 and 0.72 eV) is comparable with (0.60 eV) from IBLC effect in Sb+Ga co-doped TiO$_2$ ceramic [26]. In addition, as the doping amount increases, $U_{a2}$ gradually decreases. Because the donor ion (Ta$^{3+}$) introduces more electrons lead to the weakened block effect of the long-range motion of electron [30]. High potential barrier height leads to the higher activation energy, which makes electrons more difficult to transfer [26]. In the (In$_{0.5}$Nb$_{0.5}$)$_{0.005}$(Ti$_{1-x}$Zr$_x$)$_{0.995}$O$_2$ ceramics, the activation energy from EPDD polarization was continuously enhanced by increasing x. This is because the increase in the electrons hopping distance leads to an increase in the height potential of the EPDD polarization [40]. In the TENO-$x$wt% B$_2$O$_3$ ceramic, the addition of B$_2$O$_3$ causes the activation energy to increase from 0.504 eV to 0.795 eV. The existence of B$_2$O$_3$ leads to an increase in grain boundary potential, which hinders the long-distance movement of electrons [41]. Hence, to achieve excellent dielectric properties, the potential barrier height of different polarizations should be increased.

The microstructure of TiO$_2$ ceramic is composed of semi conductive grains, insulating grain boundaries and metallic electrode, which can be analyzed by the ac conductivity measurements [45]. Figure 5(d) shows the frequency dependences of ac conductivities of the (Lu$_{0.5}$Ta$_{0.5}$)$_{0.01}$TiO$_{2.99}$O$_2$ ceramic at different temperatures. Two plateaus can be clearly observed. The conductivity maintains the same value at high frequencies ($\sim 10^5$ Hz), which represents the grain effect. In addition, the conductivity gradually tends to a constant value with increasing temperature at low frequencies ($\sim 10^2$ Hz), which indicates that the electrode effect gradually enhances with increasing temperature [31,45]. To investigate the structure of EPDD defects formed by oxygen vacancies and Ti$^{3+}$, XPS analysis results for LTTO ceramic ($x = 0.01$) are shown in Figure 6. Lu 4d 5/2 and 3/2 peaks with binding energies of 191.17 eV and 206.41 eV reveal the existence of Lu$^{3+}$ (Figure 6(a)) [39]. The Lu$^{3+}$ substitution for Ti$^{4+}$ leads to oxygen vacancy:

$$\text{Lu}_2\text{O}_3 \rightarrow 2\text{Lu}_2\text{O}_2 + V_O + 3\text{O}_2$$

The O 1s profile in Figure 6(b) in co-doped TiO$_2$ contains of three components, including 529.88 eV for bulk Ti-O, 531.08 eV associated with oxygen vacancies and surface hydroxyl (OH), and 532.08 eV for adsorbed surface H$_2$O. As shown in Figure 6(c), XPS peaks at 26.29 eV and 28.30 eV correspond to Ta 4 f 7/2 and 5/2. It further confirms the oxidation state of Ta is +5 [38]. The formation of Ti$^{3+}$ can be explained by the following equations [38]:

$$\text{Ta}_2\text{O}_5 + 2\text{TiO}_2 \rightarrow 2\text{Ti}^{3+} + 2\text{Ta}^{4+} + 8\text{O}_2 + 1/2\text{O}_2$$

The Ti2p3/2 in Figure 6(d), the strong-binding peak at 458.81 eV is Ti$^{4+}$, indicating that the co-doped ceramic has a large amount of Ti$^{4+}$. In addition, the small peak with lower binding energy (458.31 eV) indicates the existence of Ti$^{3+}$. A conclusion could be drawn that defect structures such as $[(\text{Lu}^{3+})_{n} \rightarrow V_O \leftrightarrow (\text{Lu}^{3+})_{n} \rightarrow V_O \rightarrow (\text{Ti}^{4+})_{n}]$, $[(\text{Ti}^{4+})_{n} \rightarrow V_O \rightarrow (\text{Ti}^{3+})_{n} \rightarrow (\text{Ta}^{4+})_{n} \rightarrow (\text{Ta}^{5+})_{n}]$ and $[(\text{Ta}^{5+})_{n} \rightarrow (\text{Ti}^{3+})_{n}]$ promote free electronic localization and EPDD polarization from XPS data analysis.

Figure 7(a) shows the frequency dependences of $M''$ and $Z''/Z''_{\text{max}}$ as a function of frequency of $x = 0.01$ ceramic sample at 30°C and 240°C. When the carriers are long-range transitions, the positions of $Z''$peak and $M''$peak should be in the same frequency range [41]. Otherwise, the short-range motion of electrons dominates [41]. In Figure 7(a), the $Z''$-peak and $M''$-peak appear in different frequency ranges at 30°C and 240°C. This demonstrates that oxygen vacancies and electrons as well as defective dipole clusters are localized in a finite lattice. The short range hopping of electron around defect clusters (EPDD effect), resulting in a large dielectric constant and low dielectric loss. Figure 7(b) shows the dielectric properties of several modified TiO$_2$ ceramic systems. Compared with other systems, the Ta+Lu system has a large dielectric constant and a low dielectric loss. Figure 8 shows a multi-scale mechanism for CP behavior in LTTO ceramic. The motion of the weakly bonded electron has been localized by these defect dipole clusters, the effectively pinned progress makes the electrons with short-range local motion, which behaves by the EPDD polarization [37]. Furthermore, the free electron cannot be completely fixed in the dipole clusters [30]. Enrichment of free electrons around grain boundaries interface and ceramic-metal interface under applied AC electric field lead to IBLC polarization and electrode
polarization [30]. To obtain excellent dielectric properties, the long-distance movement of electrons should be suppressed. Increasing the height of the potential barrier of different polarizations is the best strategy to achieve excellent dielectric properties.

4. Conclusions

(Lu + Ta) co-doped TiO$_2$ ceramics were successfully prepared using a conventional solid-state method. XRD analysis showed that the (Lu$_{0.5}$Ta$_{0.5}$)$_x$Ti$_{1-x}$O$_2$ ceramic phase structure is rutile. All of the ceramics possess a dense microstructure. XPS revealed the formation of oxygen vacancies and Ti$^{3+}$, which form the highly stable defect clusters. Notably, a large permittivity ($2.55 \times 10^4$), low dielectric loss (0.012) and superior temperature and frequency stability ($-150$–$150^\circ$C and $20$–$5 \times 10^6$ Hz) were observed for (Lu$_{0.5}$Ta$_{0.5}$)$_{0.01}$Ti$_{0.99}$O$_2$ ceramic. The excellent dielectric properties of LTTO ceramics come from multiple polarizations, including electrode polarization, IBLC polarization and EPDD polarization.

Figure 6. XPS results of (Lu+ Ta) co-doped TiO$_2$ with $x = 0.01$ (a)Lu 4d, (b) O1s, (c) Ta4f, (d) Ti 2p.

Figure 7. (a) Frequency dependences of Z“/Z“max and M” for LTTO ceramic ($x = 0.01$) at 30°C and 240°C. (b) The dielectric constant and loss of several co-doped TiO$_2$ ceramics at 1 kHz.
Figure 8. Schematic images for multiple origins for CP behavior of LTTO ceramics.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This study was supported by the Program for National Key R&D Program of China [Grant No.2016YFB0402103], Tianjin Science and technology plan Program [Grant No. 19ZYSJC00070].

References

[1] Wang Y, Jie W, Yang C, et al. Colossal permittivity materials as superior dielectrics for diverse applications. Adv Funct Mater. 2019;5:1808118.
[2] Li W, Liu Z, Zhang F, et al. Colossal permittivity of (Li, Nb) co-doped TiO<sub>2</sub> ceramics. Ceram. Int. 2019;45 (9):11920–11926.
[3] Peng H, Liang P, Zhou X, et al. Good thermal stability, giant permittivity, and low dielectric loss for X9R-type (Ag<sub>1/2</sub>Li<sub>1/2</sub>)<sub>0.005</sub>Ti<sub>0.95</sub>Sb<sub>0.005</sub>O<sub>2</sub> ceramics. J Am Ceram Soc. 2019;102:970–975.
[4] Guillemet-Fritsch S, Valdez-Nava Z, Tenailleau C, et al. Colossal permittivity in ultrafine grain size BaTiO<sub>3</sub> and Ba,<sub>9.95</sub>Li<sub>0.05</sub>TiO<sub>3</sub> materials. Adv Mater. 2008;20 (3):551–555.
[5] Buscaglia MT, Viviani M, Buscaglia V, et al. High dielectric constant and frozen macroscopic polarization in dense nanocrystalline BaTiO<sub>3</sub> ceramics. Phys Rev B. 2006;73(6):064114.
[6] Han H, Voisin C, Guillemet-Fritsch S, et al. Origin of colossal permittivity in BaTiO<sub>3</sub> via broadband dielectric spectroscopy. J Appl Phys. 2013;113(2):024102.
[7] Fang TT, Liu CP. Evidence of the internal domains for inducing the anomalously high dielectric constant of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>. Chem Mater. 2005;17(20):5167–5171.
[8] Krohns S, Lunkenheimer P, Pronin AV, et al. Colossal dielectric constant up to gigahertz at room temperature. Appl Phys Lett. 2009;94(12):122903.
[9] Wu J, Nan CW, Lin YH, et al. Giant dielectric permittivity observed in Li and Ti Doped NiO. Phys Rev Lett. 2002;89(21):217601.
[10] Kim BG, Cho SM, Kim TY, et al. Giant dielectric permittivity observed in Pb-based perovskite ferroelectrics. Phys Rev Lett. 2001;86(15):3404.
[11] Hu W, Liu Y, Withers RL, et al. Electron-pinned defect-dipoles for high-performance colossal permittivity materials. Nat Mater. 2013;12(9):821–826.
[12] Hu W, Lau K, Liu Y, et al. Colossal dielectric permittivity in (Nb+Al) codoped rutile TiO<sub>2</sub> Ceramics: compositional gradient and local structure. Chem Mater. 2015;27(14):4934–4942.
[13] Dong W, Hu W, Berlie A, et al. Colossal dielectric behavior of Ga+Nb co-doped rutile TiO<sub>2</sub>. ACS Appl Mater Interfaces, 2015;7(45):25321–25325.
[14] Li J, Li F, Zhuang Y, et al. Microstructure and dielectric properties of (Nb + In) co-doped rutile TiO<sub>2</sub> ceramics. J Appl Phys. 2014;116(7):074105.
[15] Guo B, Liu P, Cui X, et al. Colossal permittivity and dielectric relaxations in Ti+ Nb codoped TiO<sub>2</sub> ceramics. Ceram Int. 2018;44:12137–12143.
[16] Wang X, Zhang B, Xu L, et al. Dielectric properties of Y and Nb co-doped TiO<sub>2</sub> ceramics. Sci Rep. 2017;7(1):8517.
[17] Wang X, Zhang B, Shen G, et al. Colossal permittivity and impedance analysis of tantalum and samarium co-doped TiO<sub>2</sub> ceramics. Ceram Int. 2017;43 (16):13349–13355.
[18] Li L, Lu T, Zhang N, et al. The effect of segregation structure on the colossal permittivity properties of (La<sub>0.5</sub>Nb<sub>2.5</sub>)<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> ceramics. J Mater Chem C. 2018;6 (9):2283–2294.
[19] Zhao C, Wu J. Effects of secondary phases on the high-performance colossal permittivity in titanium dioxide ceramics. ACS Appl Mater Interfaces. 2018;10 (4):3680–3688.
[20] Tse MY, Wei X, Hao J, et al. High-performance colossal permittivity materials of (Nb + Er) co-doped TiO<sub>2</sub> for large capacitors and high-energy-density storage devices. Phys Chem Chem Phys. 2016;18 (35):24270–24277.
[21] Wang Z, Chen H, Wang T, et al. Enhanced relative permittivity in niobium and europium co-doped TiO<sub>2</sub> ceramics. J Eur Ceram Soc. 2018;38 (11):3847–3852.
[22] Thongyong N, Tuichai W, Chanlek N, et al. Effect of Zn<sup>2+</sup> and Nb<sup>5+</sup> co-doping ions on giant dielectric properties of rutile-TiO<sub>2</sub> ceramics. Ceram Int. 2017;43 (17):15466–15471.
[23] Yang C, Tse YM, Wei X, et al. Colossal permittivity of (Mg + Nb) co-doped TiO<sub>2</sub> ceramics with low dielectric loss. J Mater Chem C. 2017;5(21):5170–5175.
[24] Li Z, Luo X, Wu W, et al. Niobium and divalent-modified titanium dioxide ceramics: colossal permittivity and composition design. J Am Ceram Soc. 2017;100(7):3004–3012.
[25] Tuichai W, Danwittayakul S, Chanlek N, et al. Effects of sintering temperature on microstructure and giant dielectric properties of (V + Ta) co-doped TiO<sub>2</sub> ceramics. J Alloy Compd. 2017;725:310–317.
[26] Fan J, Leng S, Cao Z, et al. Colossal permittivity of Sb and Ga co-doped rutile TiO<sub>2</sub> ceramics. Ceram Int. 2019;45(1):1001–1010.
[27] Zhao XG, Liu P, Song YC, et al. Origin of colossal permittivity in (In<sub>x</sub>Nb<sub>2</sub>)TiO<sub>3</sub> via broadband dielectric spectroscopy. Phys Chem Chem Phys. 2015;18 (35):23132.
[28] Nachaithong T, Kidkhunthod P, Thongbai P, et al. Surface barrier layer effect in (In + Nb) co-doped TiO<sub>2</sub> ceramics: an alternative route to design low dielectric loss. J Am Ceram Soc. 2017;100 (4):1452–1459.
[29] Mandal S, Pal S, Kundu AK. Direct view at colossal permittivity in donor-acceptor (Nb, In) co-doped rutile TiO₂. Appl Phys Lett. 2016;109(9):092906.

[30] Cao Z, Zhao J, Fan J, et al. Colossal permittivity of (Gd + Nb) co-doped TiO₂ ceramics induced by interface effects and defect cluster. Ceram Int. 2021;47(5):6711–6719.

[31] Wang W, Li L, Lu T, et al. Multifarious polarizations in high-performance colossal permittivity titanium dioxide ceramics. J Alloy Compd. 2019;806:89–98.

[32] Wang M, Li L, Zhang K, et al. Colossal permittivity Ti₁ₓ(Eu₀.₅Ta₀.₅)O₂ ceramics with excellent thermal stability. ACS Appl Electron Mater. 2020;2:1700–1708.

[33] Yu Y, Li WL, Zhao Y, et al. Large-size-mismatch co-dopants for colossal permittivity rutile TiO₂ ceramics with temperature stability. J Eur Ceram Soc. 2018;38:1576–1582.

[34] Song Y, Wang X, Zhang X, et al. The contribution of doped-Al to the colossal permittivity properties of AlₓNd₀.₀₅Ti₀.₉₇₋ₓO₂ rutile ceramics. J Mater Chem C. 2016;4:6798–6805.

[35] Song Y, Wang X, Sui Y, et al. Origin of colossal dielectric permittivity of rutile Ti₀.₉₈Nd₀.₀₂O₂ single crystal and polycrystalline. Sci Rep. 2016;6(1):1–8.

[36] Zhao X, Liu P. Dielectric and electric relaxations induced by the complex defect clusters in (Yb+ Nb) co-doped rutile TiO₂ ceramics. J Am Ceram Soc. 2017;100:3503–3513.

[37] Xu Z, Li L, Wang W, et al. Colossal permittivity and ultralow dielectric loss in (Nd₀.₅Ta₀.₅)ₓTi₁₋ₓO₂ ceramics. Ceram Int. 2019;45:17318–17324.

[38] Fan J, Yang TT, Cao Z. Colossal permittivity and multiple effects in (Zn + Ta) co-doped TiO₂ ceramics. J Asian Ceram Soc. 2020;8:4.

[39] Hu B, Sun K, Wang J, et al. High dielectric performance of (Nb⁵⁺, Lu³⁺) co-doped TiO₂ ceramics in a broad temperature range. Mater Lett. 2020;271:127838.

[40] Guo B, Liu P, Cui X, et al. Influence of Zr dopant on polarization in rutile (In₀.₃Nb₂₀.₀₂5(Ti₁₋ₓZrₓ)₀.₉₉₅O₂ ceramics. J Am Ceram Soc. 2020;103:1854–1863.

[41] Guo X, Pu Y, Wang W, et al. Colossal permittivity and low dielectric loss in niobium and europium co-doped TiO₂ ceramics by adding B₂O₅. J Alloy Compd. 2019;797:58–64.

[42] Han HS, Dufour P, Mhin S, et al. Quasi-intrinsic colossal permittivity in Nb and In co-doped rutile TiO₂ nanoceramics synthesized through a xolate chemical-solution route combined with spark plasma sintering. Phys Chem Chem Phys. 2015;17:6864.

[43] Wang XW, Zheng YP, Liang BK, et al. Preparation and properties of La and Nb co-doped TiO₂ colossal dielectric ceramic materials. J Mater Sci-Mater El. 2020;31(18):16044–16052.

[44] Liu G, Fan H, Xu J, et al. Colossal permittivity and impedance analysis of niobium and aluminum co-doped TiO₂ ceramics. RSC Adv. 2016;6:48708–48714.

[45] Wang ZJ, Cao MH, Zhang Q, et al. Dielectric relaxation in Zr-doped SrTiO₃ ceramics sintered in N₂ with giant permittivity and low dielectric loss. J Am Ceram Soc. 2015;98:476–482.