Colossal permittivity and multiple effects in (Zn + Ta) co-doped TiO₂ ceramics

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Abstract

The search for giant dielectric constant materials is imperative because of their potential for important applications for the areas of device miniaturization and energy storage. In this work, we report a (Zn + Ta) co-doped TiO₂ (ZTTO) ceramics that manifests high dielectric permittivity (>10⁴) and low dielectric loss. This dielectric property shows a high stability in wide temperature range (25-200°C) and frequency range (20-10⁶ Hz). The crystalline structure, microstructure and dielectric properties of ZTTO ceramics were systematically investigated. XPS, Impedance spectroscopy and frequency dependent dielectric constant under DC bias results reveal that the colossal dielectric properties of (Zn²⁺₁/₃Ta⁵⁺²/₃)ₓTi₁₋ₓO₂ ceramics were mainly caused by electron-pinned defect-dipoles (EPDD) model, internal barrier layer capacitance (IBLC) effect and electrode effect. This work would provide a guidance to further researching the colossal permittivity CP materials.

Key words: Rutile-TiO₂ ceramic ; Colossal permittivity ; XPS analysis ; Impedance spectroscopy ;

1. Introduction

With the continued development of microelectronics information technology, the colossal permittivity (CP) materials have received unprecedented attention[1-3]. In the past decades, a series of emerging CP materials have been prepared and then further modified to achieve high CP for practical applications including BaTiO₃, CaCu₅Ti₄O₁₂ (CCTO), La₂₋ₓSrₓNiO₄, NiO, and (Pb, La)TiO₃ [4-10]. Although the discovery of these new materials has greatly promoted the experimental research and related theoretical development of giant dielectric materials, the comprehensive dielectric properties of these systems cannot meet the requirements of practical applications.
Exploring for the material with high dielectric permittivity but acceptable dielectric loss and weak frequency/temperature dependence remains as a challenge.

Recently, it has been found that (In, Nb) co-doped rutile TiO$_2$ material has high dielectric constant ($>10^4$) and low dielectric loss(<0.05) over a very broad temperature range from 80 K to 450 K[11]. Substitution of Nb$^{5+}$ into Ti$^{4+}$ sites produces free electrons, while doping with In$^{3+}$ causes formation of oxygen vacancies. It is suggested that large defect dipole clusters containing highly localized electrons are responsible for its CP properties. Subsequently, a lot of doping modification of TiO$_2$ based ceramics is carried out and the mechanism of its colossal dielectric effect is discussed[12-26]. In addition to EPDD, other mechanisms have been proposed, including the IBLC effect, electrode effect[14,26], electron hopping[27], surface barrier effect[28], and micro-inhomogeneity and polarization relaxation [29]. Hence, the mechanism is still controversial. Further exploration of new co-doped elements is significance on colossal permittivity material and the origin of the CP.

To our knowledge, there is no report on the dielectric properties of Zn$^{2+}$ Ta co-doped TiO$_2$ system. In this work, we prepared Zn$^{2+}$ Ta co-doped TiO$_2$ (ZTTO) ceramics by traditional solid-phase method. The crystal structure, micromorphology and dielectric properties of ZTTO ceramics were systematically studied. The origin of the dielectric response behavior is discussed in detail.

2. Experimental

Ceramics with a composition of (Zn$^{2+}$)$^{1/3}$Ta$^{5+}$$(2/3)$xTi$_{1-x}$O$_2$ were prepared using conventional solid-state reactions. Rutile TiO$_2$ (99.9%), Ta$_2$O$_5$ (99.9%) and ZnO (99.9%) were used as raw materials. These powders were weighted according to their stoichiometric composition and then fully grinded by ball-milling with zirconia balls for 5 h in ethanol. All of the mixed powders were calcined at 1100 °C for 4 h in air. The dried mixtures were added with 5wt.% polyvinyl alcohol (PVA) as a binder for granulation and then pressed into disks of 12 mm in diameter and 2 mm in thickness under a pressure of 100 MPa. These pellets were sintered at 1400 °C for 5 h in air. All ceramic pellets were coated with silver on each side and then fired at 580 °C for 20 min to ensure good electrical contact.

X-ray diffraction (Smart Lab 9KW, Rigaku, Japan) and Raman spectroscopy (Renishaw inVia Microscope Raman, UK) were used to examine the phase composition and crystal structure. The microstructure of sintered pellets was observed on the fresh cross section of ceramic fragment after
ultrasonic cleaning by scanning electron microscopy (S-3400, JEOL, Japan) equipped with EDS. The temperature-dependent dielectric properties were measured 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 (HDMS-1000, Partulab, Wuhan, China). The elemental composition on the sample surface was examined using X-ray photoelectron spectroscopy (250XI, Thermo Fisher Scientific Escala, USA).

3. Results and discussion

XRD patterns of (Zn$_{2+}$Ti$_{1-x}$O$_2$ ceramics are shown in Fig. 1. Pure rutile-TiO$_2$ (JCPDS 21-1276) is observed in all samples with no impurity phase. In addition, the ionic radius of Ti$^{4+}$, Zn$^{2+}$, and Ta$^{5+}$ are around 0.605 Å, 0.74 Å, and 0.64 Å, respectively. The small mismatch of ionic radius between Ta$^{5+}$, Zn$^{2+}$ and Ti$^{4+}$ indicates impurity phase is hard to formed, which is different from rare earth co-doped TiO$_2$ ceramics[16,17,20,32]. The Fig 1b clearly shows that the (110) diffraction peak slightly shifts toward a lower angle, which indicates that Ta and Zn on the Ti site leads to a larger cell volume due to lattice expansion. The lattice parameters (a and c) calculated from the Rietveld refinement are summarized in Fig 1c. The lattice parameters of co-doped TiO$_2$ ceramics increase. This phenomenon indicates that Zn and Ta replaces Ti ions in the crystal lattice, just like Nb+ Ti and Nb+Zn system[15,22].

In order to better describe the grain size of (Zn$_{2+}$Ti$_{1-x}$O$_2$ ceramics with the change of doping concentration, we polished and hot-etched the surface of ceramic samples to obtain SEM images of ceramic samples. Fig.2 shows the SEM images of polished surface for (Zn$_{2+}$Ti$_{1-x}$O$_2$ ceramics after thermally etching. All ceramics possess a dense microstructure. When the co-doping amount is 0.01, the average grain size of the ceramic is about 10.83μm. Moreover, the grain size increases slightly with the increase of doping amount. This is also found in Sb+Ga ceramics[26]. The elemental composition and distribution of the ZTTO ceramics element maps was presented in Fig. 3. Zn, Ta, Ti, and O distribute homogeneously in the microstructure, indicating that the Ta$^{5+}$ and Zn$^{2+}$ have diffused into the Ti lattice of the rutile phase.

To further investigate the element composition and its chemical state of the samples, X-ray photoelectron spectroscopy (XPS) analysis were performed and results were shown in Fig. 4. Zn
2p3/2 and 1/2 peaks with binding energies of 1044.63 eV and 1021.68 eV reveal the existence of Zn$^{2+}$ (Fig. 4a). The Zn$^{2+}$ substitution for Ti$^{4+}$ leads to oxygen vacancy[22].

$$\text{ZnO} \xrightarrow{\text{Ti}^{4+}} \text{Zn}^{2+} + V_{O}^{+} + O_{2}$$  \hspace{1cm} (1)

In order to confirm the existence of oxygen vacancies, the XPS spectrum of the fitted O1s curve is shown in Fig. 4(b). The O1s curves of ZTTO ceramics with composition x = 0.02 shows three peaks at 529.98, 531.03 and 532.03 eV, which correspond to the Ti-O bond vibration of the constituents, oxygen vacancies and H$_2$O adsorbed on the surface. As seen from Fig. 4c, XPS peaks at 27.78 eV and 25.87 eV correspond to Ta 4f 5/2 and 4f 7/2, which further confirms the Ta$^{5+}$ in the ZTTO ceramics[30]. Generally, Ta$^{5+}$ can act as a donor to provide electrons to reduce Ti$^{4+}$[30]

$$\text{Ta}_2\text{O}_5 + 2\text{TiO}_2 \xrightarrow{4\text{Ti}^{4+}} 2\text{Ti}^{3+} + 2\text{Ta}^{5+} + 8\text{O}_2 + 1/2 \text{O}_2 \uparrow$$  \hspace{1cm} (2)

$$\text{Ti}^{4+} + e \rightarrow \text{Ti}^{3+}$$  \hspace{1cm} (3)

For XPS spectrum of Ti 2p in Fig. 4d, the main peak of Ti 2p 3/2 locates at 458.68 eV, indicating the presence of Ti$^{4+}$. The small peak with relatively lower binding energy (457.78 eV) indicates the existence of Ti$^{3+}$ in the ZTTO (x = 0.02) ceramic.

Fig 5 shows the dielectric frequency spectrum and dielectric temperature spectrum of (Zn + Ta) co-doped TiO$_2$ ceramics. Fig. 5a shows the frequency dependence of the dielectric constant and loss of (Zn + Ta) co-doped rutile TiO$_2$ ceramics. Compared with pure TiO$_2$ ceramics, co-doped ceramics have larger dielectric constant and lower dielectric loss. For the composition with x = 0.02, the permittivity increased to 6.34×10$^4$ while the dielectric loss remained lower than 0.053. Further increase of co-doping level to 0.08 leads to systematic improvement of dielectric constant. But compared with the ceramic sample of x = 0.02, the dielectric loss increased significantly. Similar phenomenon has been reported in (Y + Nb), (Sm + Ta) and (Zn + Nb) co-doped ceramics[16,17,22]. The concentration of free electrons is generally proportional to the Nb5+ dopant concentration[22]. More free electrons lead to a decrease in the insulating properties of the sample and an increase in dielectric loss for the composition is x=0.04 and 0.08. Obviously, the (Zn + Ta) co-doped ceramics with x = 0.02 exhibit the optimum comprehensive dielectric property (ε=6.34×10$^4$ and tanδ=0.053 at 1 kHz). Fig 5(b) shows the dielectric temperature spectrum of ZTTO ceramic at 1kHz. All co-doped
ceramics (x=0.02-0.08) have excellent temperature stability in the temperature range of 25-200℃. Therefore, (Zn+ Ta) co-doped rutile TiO₂ ceramics with x=0.02 have achieved comprehensive dielectric properties of low dielectric loss, high dielectric constant and excellent temperature stability.

Complex impedance spectroscopy is commonly used to study the physical origin of giant dielectric properties in co-doped TiO₂ ceramics [26]. The microstructure of TiO₂ ceramics consists of grains and grain boundaries[11]. Fig 6 (a) shows the impedance spectrum of all of the ZTTO ceramics at room temperature. Considering the electrode effect around room temperature, all impedance data can be well fitted by three parallel RC elements connected in series. The simulated results have been summarized in Table 1. We observed a large semi-circular arc, indicating its large grain boundary resistance [26]. The decrease of radius of arcs indicates that grain boundary resistance (R_gb) of the ZTTO ceramics decreases with increasing co-dopant concentration, which can be attributed to the free electrons introduced by the pentavalent ion dopant (such as Nb, Sb and Ta)[26]. In addition, the non-zero intercept observed in the impedance plots in Fig 6(b) indicates the semiconducting nature of grain[22]. Therefore, the semiconductive grains are separated by the insulative grain boundary, which indicates that internal barrier layer capacitance (IBLC) should be responsive for the colossal dielectric constant of (Zn + Ta) co-doped TiO₂. This phenomenon is similar to the impedance diagram of (Y + Nb) and (Sb + Ga) co-doped TiO₂ ceramics[16,26], proving that there is IBLC responses in ZTTO ceramics. Fig. 6c shows the impedance complex plot of the composition with x = 0.02 at various temperatures. Considering the weak grain effect around high temperature (Fig.6c), the impedance data of ZTTO (0.02) ceramics at high temperature are fitted (solidus line) using equivalent circuit (R_eCPE_e)(R_gbCPE_gb). These results have been summarized in Table 2. Moreover, the resistance of the grain boundary decreases with increasing temperature, indicating that the activation process is thermally activated, and its conductivity can follow Arrhenius's law

\[
\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_BT}\right)
\]

(4)

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, and the unit is K[26]. As shown in Fig 6d, the activation energy of ZTTO ceramic was 1.03, 1.19 and 1.21 eV, which is very close to the activation energy of oxygen vacancies
(0.7-1.2eV) at the grain boundaries of TiO$_2$ system and other oxides [5,22,26]. The $E_{gb}$ value increased with increasing co-dopant concentration, which indicates that other factor such as space charge might affect the observed dielectric behavior[26]. Similar phenomenon has been observed in the Sb+Ga and Nb + La co-doped TiO$_2$ ceramics[18, 26].

To further verify the IBLC and electrode responses mechanism, frequency dependence of dielectric properties under different DC bias for the ZTTO ceramic is shown in Figure 7a. After DC bias has been applied, notable enhancement of dielectric constant and loss has been observed indicating that the existence of interface polarization[26]. Increasing DC bias induced the occurrence of additional step-like dielectric constant at low frequency range ($\leq 10^2$ Hz). Obviously, the additional dielectric constant plateau at low frequency is related to the electrode effect[31]. In Fig. 7a, three dielectric plateaus with increasing frequency correspond to the electrode, grain boundary and grain effects. After applied DC bias, more electrons could pass through the barrier and increase the dielectric constant at low frequency. In the middle frequency range (around $10^5$ Hz), a fully developed loss peak corresponding to grain boundary effect has been observed. Usually, the electrostatic potential barriers, i.e., double Schottky barriers, can be created at interfaces between n-type grains caused by trapping at acceptor states, leading to the bending of the conduction band across the grain boundary[26]. Under a DC bias, the barrier becomes asymmetric such that the barrier height in the reverse direction increases whereas the barrier in the forward direction decreases. This may result in an slight increase in DC conductivity and loss around $10^5$ Hz[26,32]. Therefore, the IBLC effect and electrode response is mainly responsible for the high permittivity in Zn + Ta co-doped TiO$_2$ ceramics in middle frequency range. Fig. 7b shows the dielectric constant for Zn + Ta co-doped rutile TiO$_2$ (x = 0.02) with different electrodes (Au and Ag). The results show that dielectric constant is seriously dependent on electrode, which is similar to the previous work[26]. This result further confirms that the giant dielectric performance should be mainly attributed to the IBLC and electrode response effect at low frequency. By contrast, the giant dielectric constant around $10^6$ Hz (in Fig.7a) does not affected by the DC bias. In the EPDD model, the permittivity remains nearly unchanged under DC biases[33]. The outstanding high permittivity ($>10^4$) in the high frequency range can not be understood by the interfacial polarization occurring in the low and middle frequency range[26,32]. It is suggested that the defect or defect clusters...
\[
\begin{align*}
(Zn^{2+})_{n} & \rightarrow V_{O}^{\#} \leftrightarrow (Zn^{2+})_{n}, \quad (Zn^{2+})_{n} \rightarrow V_{O}^{\#} \leftrightarrow (Ti^{3+})_{n}, \quad (Ti^{3+})_{n} \rightarrow V_{O}^{\#} \leftrightarrow (Ti^{3+})_{n}, \quad (Zn^{2+})_{n} \rightarrow (Ta^{5+})_{n}, \quad (Ta^{5+})_{n} \rightarrow (Ti^{3+})_{n}
\end{align*}
\]

in grain is responsible for the abnormal high and DC voltage independent dielectric response in high frequency range (around \(10^6\) Hz). This is consistent with the literature Sb+Ga, Nb+Lu and Nb+La system[18,26,32].

Fig. 8a shows the frequency dependent permittivity of the composition with \(x = 0.02\) at selected temperatures. The permittivity increases rapidly with increasing temperature at low frequencies. This also confirms the interfacial polarization, which is consistent with Zr co-doped \((Ga_{0.5}Nb_{0.5})_{0.03}Ti_{0.97}O_2\) ceramics [34]. Fig.8b shows the imaginary part of the complex modulus for GNTO sample with \(x = 0.01\). Complex modulus \(M^*\) can be written as

\[
M^* = M'^* + M''^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' + i\varepsilon''} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + \frac{i\varepsilon''}{\varepsilon'^2 + \varepsilon''^2},
\]

where \(\varepsilon^*, \varepsilon', \varepsilon'', M'^*\) and \(M''^*\) complex permittivity, real and imaginary part of complex permittivity, the real and the imaginary part of the complex modulus, respectively. Two different relaxations following the thermally activated Arrhenius model from electrode and grain boundary effects are clearly observed in low and middle frequency regions [26]. In addition, these two \(M''\) peaks show a notable frequency dependence. The peak shifts to higher frequency with increasing temperature, suggesting an increase in dipole density and a faster polarization process:

\[
\ f_\rho = f_0 \exp\left[\frac{-U}{K_BT}\right]
\]

where \(f_\rho\) 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, \(K\) is the Boltzmann constant, and \(T\) is the absolute temperature. As seen from the fitting results in Fig. 8c, the activation \(U\) are determined to be \(0.65\) eV and \(0.91\) eV, respectively. The value of \(0.65\) eV is very close to the activation energy of oxygen vacancy at grain boundary with the Maxwell-Wagner-type polarization in other co-doped TiO\(_2\) ceramic [15-17, 26]. Similarly, the activation energy of \(0.91\) eV is comparable with that \((0.88\) eV\) from electrode effect in Sb+Ga co-doped TiO\(_2\) ceramic [26]. These results clearly demonstrate electrode effect and grain boundary effect contribute to the low and middle frequency giant dielectric constant.

Based on the above discussion, the excellent dielectric performances come from multiple
mechanisms including EPDD effect, IBLC effect and electrode effect. Some reports have shown that more than one polarization can contributed to CP properties in co-doped TiO$_2$ ceramics[26,15]. Different polarizations can contribute to permittivity in different temperature/frequency ranges[15]. For EPDD effect, this short range motion of elections can fully follow up the fluctuation of applied electric field and lead to the low dielectric loss and excellent frequency stability. By contrast, the long range motion of electron is more likely to be blocked by the grain boundary and ceramic-metal interface, which lead to high dielectric loss and low insulation. Hence, to achieve the excellent dielectric properties above room temperature, the effects from the IBLC effect and electrode effect should be suppressed and effect from the lattice structural defect (EPDD effect) should be enhanced.

4. Conclusions

(Zn + Ta) co-doped TiO$_2$ ceramics were prepared by a standard solid-state method. The crystalline structure, microstructure, electrical and dielectric properties of GNTO ceramics were systematically investigated. XPS analysis indicated that oxygen vacancies, Ti$^{3+}$ and defect dipoles were present in the ceramic samples. Especially, an excellent dielectric loss of 0.053 and a high dielectric permittivity of $6.34 \times 10^4$ at 1 kHz are obtained for the composition with $x = 0.02$. In addition, co-doped ceramics have excellent temperature and frequency stability at 25-200°C and 20-10$^6$Hz. Combined with Impedance analysis, DC bias voltages and XPS results, the giant dielectric response should contain all contributions from EPDD, IBLC and electrode effects.

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References

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Figures and captions

**Fig. 1.** (a) XRD patterns of ZTTO ceramics (b) Magnified graph of (101) diffraction and (c) cell
parameters of \((\text{Zn}^{2+}_{1/3}\text{Ta}^{5+}_{2/3})_x\text{Ti}_{1-x}\text{O}_2\) as a function of \(x\).

**Fig. 2.** SEM results of polished surface for \((\text{Zn}^{2+}_{1/3}\text{Ta}^{5+}_{2/3})_x\text{Ti}_{1-x}\text{O}_2\) ceramics (a) \(x = 0.02\) (b) \(x = 0.04\) (c) \(x = 0.08\)

**Fig. 3.** Element mapping of \((\text{Zn}^{2+}_{1/3}\text{Ta}^{5+}_{2/3})_x\text{Ti}_{1-x}\text{O}_2\) ceramic with \(x = 0.02\).

**Fig. 4.** XPS results of \((\text{Zn} + \text{Ta})\) co-doped TiO2 with \(x = 0.02\) (a) Zn 2p, (b) O 1s, (c) Ta4f, (d) Ti 2p

**Fig. 5.** (a) Frequency dependence of dielectric constant and dielectric loss, (b) Temperature dependence of dielectric constant and loss for the ZTTO ceramics at 1 kHz

**Fig. 6.** (a) Complex impedance spectroscopy for ZTTO ceramics (b) enlarged view of high frequency region for ZTTO ceramics (c) Complex impedance spectroscopy for ZTTO ceramic \((x = 0.02)\) at selected temperature (d) Arrhenius plot of the conductivity of grain boundary.

**Fig. 7.** (a) Frequency-dependent dielectric properties of ZTTO ceramics \((0.02)\) measured under different DC bias voltages. (b) Dielectric constant of ZTTO ceramic \((x = 0.02)\) with Ag and Au electrodes.

**Fig. 8.** (a) Dielectric constant and the imaginary part of the electric modulus of ZTTO ceramic \((x = 0.02)\) (b) temperature dependence of the relaxation peak frequency

**Table 1** Fitting results of electrode, grain boundary, grain resistance and activation energy of grain boundary for ZTTO ceramics

**Table 2** Fitting resistances of grain, grain boundary and electrode effects for ZTTO ceramics at different temperature