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Colossal permittivity in titanium dioxide ceramics modified by tantalum and trivalent elements

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ABSTRACT

Colossal permittivity (CP) materials continue to attract significant interest for their applications in high-performance capacitors and scaling advances in electronic devices. However, the unbalanced developments of their dielectric constants, dielectric losses, and stabilities still hinder practical applications. In this study, we attained a colossal permittivity ($\varepsilon_r = 10^4$~10^5, 1 kHz) in a series of new titanium dioxide (i.e., $(A_{0.5}Ta_{0.5})_xTi_{1-x}O_2$, where A = Al, Sm, Bi, Fe, In, Dy, Ga, Gd, Yb, or Sc) ceramics containing Ta and trivalent elements that is comparable or superior to the previously reported results in In and Nb co-doped ceramics. In addition, a low dielectric loss (tan δ~5.4%, 1 kHz) was achieved in the ceramics by tailoring the types of trivalent elements used; such a ceramic also shows relatively good dielectric properties with regard to frequency (10^2~10^6 Hz) and temperature (−150–200 °C) stabilities. The formation of defect-dipole clusters (e.g., $Al^{3+}V_O^{\bullet\bullet}Ti^{3+}$ and $Ta^{5+}Ti^{3+}A_{Ti}$ ($A = Ti^{3+}/Al^{3+}/Ti^{4+}$)) induced by Ta and trivalent elements should be responsible for the observed enhancements in dielectric properties. We believe that TiO_2-based ceramics are one of the most promising candidates in the field of electronic and energy-storage devices.

1. Introduction

Research in colossal permittivity (CP) materials has been given significant attention because these materials have many potential applications [1–23] in modern microelectronics and high-density energy storage. However, the developments of materials with specific dielectric constants (ε_r), dielectric losses (tan δ), and corresponding stabilities have seriously hindered the practical applications of CP materials [1–23]. If a CP material exhibits a large ε_r and a large tan δ, the material will be of limited interest if energy cannot be stored [23]. In addition, these materials also require dielectric properties (e.g., ε_r and tan δ) with good temperature stabilities; otherwise, their practical applications will not be realized due to fluctuations in these properties [23]. However, it is difficult to simultaneously achieve all three of these criteria (e.g., a large ε_r, a low tan δ, and a good stability) in the same CP material [1–23].

In prior decades, several types of CP materials have been developed [1–32], including $BaTiO_3$ [13,17,20,29], $CaCu_3Ti_4O_{12}$ [6–11], NiO [4,14,31], $SrTiO_3$ [16], $(Pb,La)TiO_3$ [12,30] as well as their substitutions or other materials that use acceptor and donor dopants [21–32]. One limitation is that a CP material exhibits a large ε_r, which typically yields a larger tan δ [4,6–11,14]. Fig. 1 shows the summarized dielectric properties of CP materials known to date [1–23]. Although a large ε_r can be attained in a CP material, a high tan δ is then typically present [4,14]. Both a large ε_r and a low tan δ are achievable, but a strong temperature or frequency dependence of their dielectric properties is often found [6–13,16,17,20]. Based on the developments of CP materials, few CP materials are shown to simultaneously meet the three requirements mentioned above [24]. As a result, it is necessary to continue the search for a new type of CP material that has better comprehensive performance. Recently, titanium-dioxide ceramics with ion substitutions have been found to exhibit both a large permittivity and a low dielectric loss [24]. In this study, the colossal-permittivity results based on the addition of both In and Nb, where the Nb not In causes an increased permittivity due to the different oxidation states of the dopant elements (e.g., In^{3+} (electron acceptor) and Nb^{5+} (electron donor)) [24–27]. Based on the developments of CP materials,

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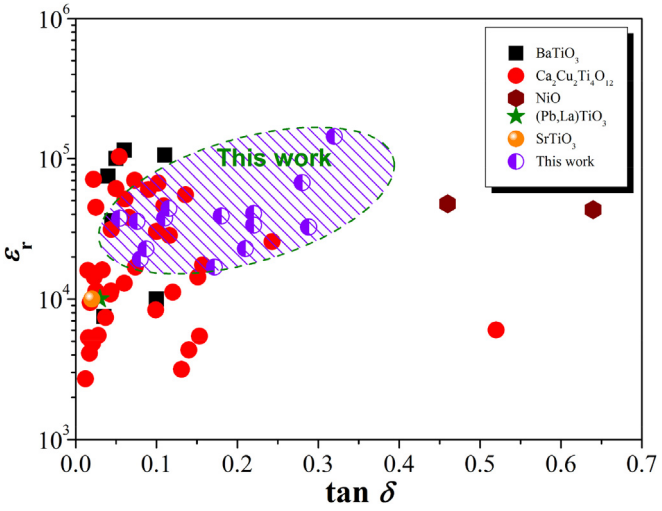

Fig. 1. ε_r and tan δ of CP materials [1–31].

further breakthroughs or improvements in dielectric properties should be achieved before practical applications will be feasible. For example, ε_r should be increased compared to the reported results in a CP material [4,6–11,14]. In addition, the effects of different A and B element types on dielectric properties and their stabilities have not been systematically investigated by many studies, although a colossal permittivity can be attained in ceramics with compositions such as $(In_{0.5},Nb_{0.5})_xTi_{1-x}O_2$. As a result, it has been considered whether other pentavalent and trivalent elements could induce a colossal permittivity in TiO_2 ceramics in a manner similar to that of In and Nb [24–27].

To further investigate the dielectric properties of $(A^{3+}_{0.5}, B^{5+}_{0.5})_xTi_{1-x}O_2$ ceramics with different A and B elements, we developed a series of new CP materials with a composition of $(A^{3+}_{0.5}, B^{5+}_{0.5})_xTi_{1-x}O_2$ in this study, where A^{3+} (i.e., A = Al, Sm, Bi, Fe, Dy, Ga, Gd, Yb, or Sc) and B^{5+} (i.e., B=Ta or Sb) were used to replace the Ti site of TiO_2. As shown in Tables 1 and 2, both Ta and trivalent elements can significantly promote ε_r (e.g., 19,000–143,000) of TiO_2 while maintaining a tan δ of 5.4%~32%; however, most of the results shown were poor when Sb and other trivalent elements were introduced except for Sb and Bi (ε_r~50,000 and tan δ~41.3%). In this study, we present a specific example of a (Al, Ta) co-doped TiO_2 $\{(Al_{0.5}Ta_{0.5})_xTi_{1-x}O_2\}$ rutile that exhibits a colossal permittivity that is nearly independent of temperature and frequency and exhibits a low dielectric loss (~5.4%). The evolutions of the dielectric properties in $(Al_{0.5}Ta_{0.5})_xTi_{1-x}O_2$ ceramics are studied in detail, and the effects of $Al_{0.5}Ta_{0.5}$ content on the electrical properties of the ceramic were investigated. In addition, related physical mechanisms were also considered. Three objectives have thus been achieved by the proposed composition design: (1) colossal permittivity; (2) low dielectric loss; and (3) a relative stability. As a result, the proposed material may be another choice to attain one type of new CP ceramic material using new pentavalent and trivalent elements.

Table 2
Dielectric properties of $(A_{0.5}Sb_{0.5})_{0.10}Ti_{0.90}O_2$ ceramics.

A^{3+}	Al	Ga	Sc	Fe	Bi
ε_r (1 kHz)	75	88	92	121	50,000
tan δ (1 kHz)	0.023	0.033	0.061	0.260	0.413

2. Experimental procedure

Ceramics with a composition of $(A^{3+}_{0.5}B^{5+}_{0.5})_xTi_{1-x}O_2$, where {A = Al, Sm, Bi, Fe, Dy, Ga, Gd, Yb, or Sc, and B=Ta, Sb, were prepared using the conventional solid-state reaction method. The raw materials used in this study included rutile TiO_2 (99.5%), Ta_2O_5 (99.99%), Sb_2O_3 (99.99%), Al_2O_3 (99.99%), Fe_2O_3 (99.99%), Ga_2O_3 (99.99%), Sc_2O_3 (99.999%), Bi_2O_3 (99.99%), Sm_2O_3 (99.99%), Dy_2O_3 (99.99%), Gd_2O_3 (99.99%), and Yb_2O_3 (99.99%). The weighed powders were mixed with the ZrO_2 balls for 24 h in isopropanol; then, calcinations were conducted at 1100 °C for a dwell time of 4 h. Finally, the dried mixtures were added to 8-wt% polyvinyl alcohol (PVA) as a binder for granulation and were then pressed into disks of ~10 mm in diameter and ~1.0 mm in thickness under a pressure of 10 MPa. All green pellets were sintered at 1200–1500 °C in air for 3 h after removing PVA. For comparison, Al^{3+} or Ta^{5+}-doped TiO_2 and pure TiO_2 were also prepared via the same method. An Ag electrode was created onto both parallel surfaces to characterize their electrical properties, where the thickness and diameter of the sintered samples were ~0.9 mm and 0.95 cm, respectively.

The phase purity and crystal structure of the sintered samples were analyzed using an X-ray diffraction (XRD) machine with a PANalytical X'Pert PRO X-ray diffractometer with a CuK_α radiation (λ = 1.54187 Å) operating at 40 kV and 40 mA, and using Raman spectroscopy (HORIBA JOBIN YVON, France) experiments. The surface morphologies, the energy-dispersive spectrometry (EDS), backscattering, and element mapping of the sintered samples were measured using a field emission-scanning electron microscopy (FE-SEM, JSM-7500, Japan). The relative molar ratios of the elements in the samples were determined using X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD, Japan). The dielectric constant and dielectric loss of the samples were measured using an *LCR* meter (HP 4980, Agilent, U.S.A.). The temperature dependencies of the dielectric properties of the unpoled samples were investigated by heating the samples from −150 to 200 °C at 1 °C/min (Tonghui 2816A, P. R. China) at a frequency of 1 kHz. The dielectric properties related to frequencies were measured using an impedance analyzer (Agilent 4294A) over the range of 100 Hz–1 MHz.

3. Results and discussion

Fig. 2 shows the XRD patterns of the $(Al_{0.5}Ta_{0.5})_xTi_{1-x}O_2$ ceramics created in this study at room temperature. A pure rutile phase was observed in all of the ceramics, showing that both Al^{3+} and Ta^{5+} had been well substituted into TiO_2. In addition, we also measured the XRD patterns of Al- or Ta-doped TiO_2 ceramics. It was found in Fig. 2 that a pure rutile phase could still be shown in Ta^{5+}-doped ceramics, while some secondary phases were observed in the Al^{3+}-doped ceramics; these results were confirmed by XRD

Table 1
Dielectric properties of $(A_{0.5}Ta_{0.5})_{0.10}Ti_{0.90}O_2$ ceramics.

A^{3+}	Ga	Gd	Yb	Bi	Dy	Fe	Sc	Sm	Al
ε_r (1 kHz)	19,000	38,000	39,000	23,000	40,000	34,000	67,000	1,43,000	33,000
tan δ (1 kHz)	0.08	0.11	0.18	0.21	0.22	0.22	0.28	0.32	0.29