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Ferroelectric characteristics of ytterbium-doped barium zirconium titanate ceramics

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Abstract

Ferroelectric characteristics of ytterbium-doped barium zirconium titanate (BZT in brief) ceramics have been investigated. It is found that ytterbium dopant greatly influences the dielectric properties of BZT ceramics. With the increase of ytterbium content, the Curie temperature is lowered by three apparent stages identified by the falling "rate", and the relative permittivity maximum is enhanced and broadened enormously. The diffuseness of the ferroelectric phase transition for BZT is increased monotonously as well. The A/B ratio in perovskite structure plays another important role on the ferroelectric phase transition characteristics for ytterbium doped BZT. The alternation of the substitution preference of ytterbium ions for the host cations in perovskite lattice seems to account for these effects. Thanks to the modifications of ytterbium on BZT, we developed a novel Y5V dielectric material with the room temperature dielectric constant over 23,000, and the dielectric strength higher than 4.0 kV/mm under AC field, which can be used in manufacturing high voltage ceramic capacitors.

Keywords: Barium zirconium titanate; Ytterbium; Diffusive phase transition; Substitution reaction

1. Introduction

Ceramics based on barium titanate ($BaTiO_3$) are frequently used to manufacture multilayer ceramic capacitors (MLCCs) and thermistors owing to their high dielectric constant. Much effort has been expended to improve the dielectric properties by way of controlling grain growth and designing microstructure inhomogeneity. Substitution of both isovalent and aliovalent cations for the host ones in perovskite lattice plays a very important role in these modification mechanisms.

The substitution of isovalent cations, Zr^{4+}, Sn^{4+} for Ti^{4+} and/or Mg^{2+}, Sr^{2+} for Ba^{2+} can give birth to such materials as $BaZrO_3$, $BaSnO_3$, $MgTiO_3$, and $SrTiO_3$. These form solid solutions with $BaTiO_3$ and alter the lattice constant, leading to the shift of phase transition temperature and bringing about high and broad dielectric constant maximum. Barium zirconium titanate ceramics ($BaZr_xTi_{1-x}O_3$, BZT in brief), based on the solid solution of $BaZrO_3$ and $BaTiO_3$, have been widely studied owing to the very high and broad relative permittivity maximum at the ferroelectric Curie point [1,2]. According to Hennings and his colleagues, the ferroelectric and paraelectric phases coexist in a wide temperature region for higher (Zr) containing barium zirconium titanate ceramics [2]. The phase transition remains first order when the Zr content is less than 16%, above which the phase transition turns to second order. The diffuse character is promoted by the small energy differences between the ferroelectric and paraelectric phases appearing at higher Zr concentration.

The experiment data of the relative dielectric constant for most ferroelectric materials with diffusive phase transition can be successfully fitted by a semiempirical equation of the form [3]

$$1/\varepsilon = 1/\varepsilon_{\max} + (T - T_a)^{\gamma}/A \quad (1)$$

where $\varepsilon_{\max}$ is the maximum dielectric constant value at the apparent transition temperature T_a. A is a constant, and γ an exponent that varies between 1 and 2 (γ is also known as the diffuseness). The exponent γ is 1 when the phase transition is of the Curie–Wess type, and the exponent is 2 when the transition is a completely diffusive one.

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Eq. (1) can be rewritten more conveniently in a new form [4]:

$$(\varepsilon_{max} - \varepsilon)/\varepsilon = (T_a/\sigma)(T/T_a - 1)^{\gamma} \quad (2)$$

where σ is defined as a constant that shows the degree of thermal diffuseness or it is defined as a Curie–Wess constant at $\gamma = 1$. Together γ and σ can indicate the degree of deviation from the ideal Curie–Wess law. The exponent γ can be determined from the slope of the log-log plot of Eq. (2); σ can be determined from the y-axis intercept of the same plot.

Aliovalent cations incorporated in perovskite lattice serve as donors or acceptors, which can affect the electrical characteristics greatly even though the solubility remains in a trace level [5]. Trivalent rare earth cations have been widely used in the modification of barium titanate ceramics owing to their special electronic structure and their moderate ionic radii, which allow them being incorporated in both A-sites and B-sites in the ABO_3 lattice [6,7,8]. Ohsato has reported that there were three stages of substitution of rare earth element in $BaTiO_3$. In the first stage, Ti ions located on the B site were mainly replaced by rare earth elements and in the second stage Ba ions on the A site were also mainly replaced by rare earth elements. The third stage was over the limit of substitution and a secondary phase appeared [9]. The influence of rare earth dopant on the dielectric properties of barium titanate has been widely researched as well. The doping of ytterbium into BZT ceramics, however, is rarely found in literature. In this paper the dielectric characteristics of ytterbium doped barium zirconium titanate ceramic have been investigated and the possible mechanism has been discussed.

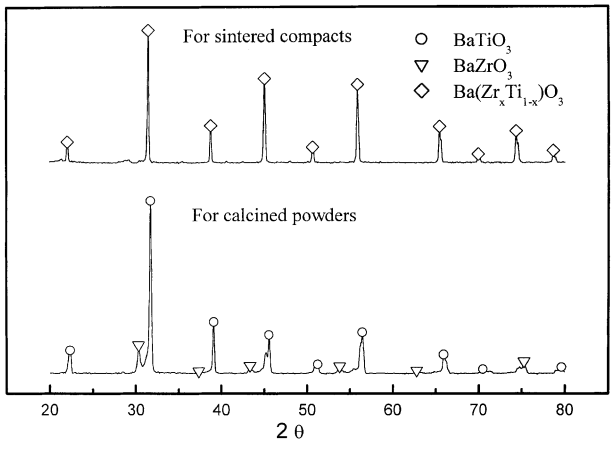


Fig. 1. X-ray diffraction patterns of calcined BZT powders and sintered compacts.

2. Experimental

The crystalline powder of $BaZr_xTi_{1-x}O_3$ ($x = 0.15$) was prepared from reagent-grade $BaCO_3$, ZrO_2 and TiO_2 using a traditional mixed oxide technique. The weighed raw materials were mixed and ground by ball milling for 24 h. After being dried, the powder was calcined at 1150 °C for 4 h in an alumina crucible using a heating rate of 200 °C/h. The calcined powder was ball milled again for 4 h and dried. Powder X-ray diffraction analysis was then conducted with Cu-K_α to determine the phase composition of the acquired powder. An acquisition of pure perovskite phase had been attempted, but the coexistent diffraction peaks of $BaTiO_3$ and $BaZrO_3$ indicate that the powder is rather a mixture than solid solution of $BaTiO_3$ and $BaZrO_3$ (see Fig. 1).

The ytterbium element was then added to $BaZr_xTi_{1-x}O_3$ (BZT in brief) by means of titrating Yb^{3+} aqueous solution into the water soaked powder. The content of dopant was designed from 0–1.0 at %. The doped powder was then pressed into pellets of the size of ϕ10 mm × 1.5 mm and sintered at 1250, 1280 and 1300 °C, respectively. The heating rate was controlled at 200 °C/h and the soaking time was 4 h. The X-ray diffraction results indicated that as-fired compacts consisted of single phase with cubic or pseudocubic perovskite structure (see Fig. 1). Trace amount of $BaCO_3$ or TiO_2 was added into BZT powders to control the A/B ratio from 0.995–1.010. Silver electrodes were deposited onto both main sides of the compacts to conduct dielectric measurement.

An automatic temperature controller and a HP4192A LF impedance analyzer were utilized to measure the temperature or frequency dependence of the dielectric constant and dielectric loss of BZT samples. The density of the sintered compacts was measured by Archimedes' method, with water as the liquid medium. The microstructure of samples was observed by SEM experiments.

3. Results

The temperature dependence of the relative permittivity for ytterbium doped BZT ceramics sintered at 1300 °C is illustrated in Fig. 2. With the increase of ytterbium content, the Curie point temperature is lowered greatly from 56 °C for none (ytterbium) doped sample to −55 °C for 0.75 at % ytterbium doped one, accompanied by large enhancement of the corresponding dielectric maximum. The lower phase transition temperature, which could be identified clearly on the permittivity versus temperature curve for 0.025 at %-ytterbium doped BZT, is shifted to a higher level. As a result, the two corresponding ϵ_r maxima move closer to each other and finally coalesce into a single broad peak with the maximal value over 20,000. At higher ytterbium

concentration, the obvious phase transition point shifts to lower temperature and the dielectric constant maximum is depressed and broadened at the same time.

Fig. 3 shows the ytterbium concentration dependence of the Curie point temperature and the corresponding dielectric constant maximum for samples sintered at three different temperatures. The phase transition temperature shifts to lower temperature by three stages. In the first stage the Curie temperature falls steeply by 32 °C with the ytterbium concentration less than 0.05 at.%. The corresponding dielectric maximum leaps rapidly from 9,800 to more than 20,000 with the increase of dopant content. The ferroelectric phase transition temperature in the second stage, however, is flattened to a steady level of 21 °C, within the dopant content range of from 0.05 to 0.1 at.%. In the third stage, the Curie temperature is lowered again by 76 °C and the corresponding dielectric maximum is depressed and broadened as well. The three stages can be identified by the different ratio of the Curie temperature vs ytterbium content: −640 °C per 1 at.% for the first stage, about 0 °C per 1 at.% for the next stage, and about −110 °C per 1 at.% for the third stage, as marked in Fig. 3.

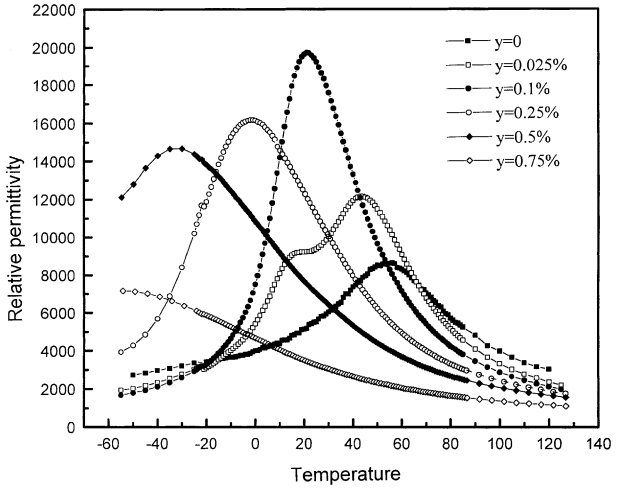


Fig. 2. Temperature dependence of relative permittivity for BZT ceramics with different ytterbium content y (at.%). The compacts are sintered at 1300 °C for 4 h.

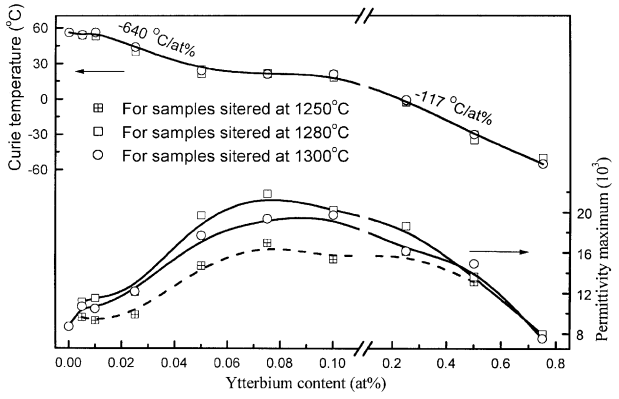


Fig. 3. Dopant content dependence of the Curie temperature and the corresponding relative permittivity maximum for BZT ceramics, sintered at 1250 °C, 1280 °C, and 1300 °C, respectively.

The sintering temperature has little effect on the Curie temperature for certain amount of ytterbium doped BZT ceramics, while it can influence the dielectric constant maximum to a considerable extent. It appears that the 1280 °C sintered samples have the highest dielectric constant and the 1250 °C sintered ones have the lowest dielectric constant in the mass.

The diffuse characteristics indicated by σ are illustrated in Fig. 4. The σ value increases monotonously with ytterbium content, indicating that the more the ytterbium element is added, the stronger diffusive characteristics the phase transition shows in the mass, which is consistent with the results illustrated in Fig. 2.

Diffusive phase transition characterized by a broad dielectric constant maximum, for typical ferroelectric relaxors such as PMN ($PbNb_{2/3}Mg_{1/3}O_3$), is usually companied by frequency dispersion at temperatures lower than Curie point. The ytterbium doped BZT ceramics with broadened dielectric constant maximum exhibits obvious frequency dispersion behavior as well. Fig. 5 shows the dielectric constant and loss tangent as a function of temperature and frequency for 0.25 at.% ytterbium doped BZT ceramic samples, with the sintering temperature of 1300 °C. The dielectric constant and loss tangent exhibit strong frequency dependence below Curie temperature.

The Curie point temperature, the corresponding relative permittivity maximum and σ value as functions of A/B ratio are shown in Fig. 6. For the present samples the ytterbium concentration is set as 0.25 at.% and the sintering temperature is 1280 °C. It is obvious that with the increase of A/B ratio from 0.995–1.010, the Curie temperature is monotonously lowered from 15 to −15 °C, and the permittivity maximum falls from

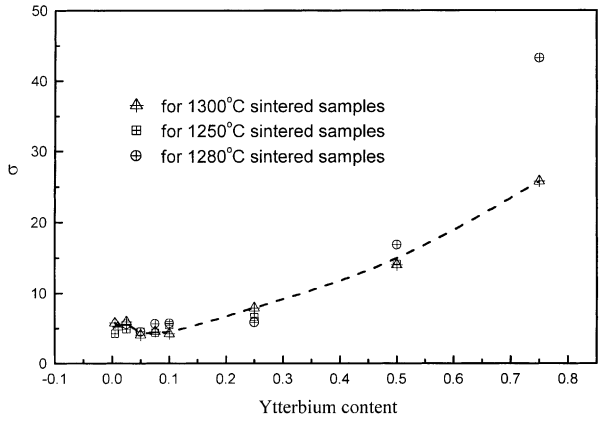


Fig. 4. Diffusive characteristics for samples doped with ytterbium.

23,970 to 9238 at the same time. The σ value, however, increases greatly with the increase of A/B ratio.

4. Discussion

The dielectric characteristics for BZT ceramics can be greatly affected by ytterbium dopant as well as A/B ratio. The influences are most probably caused by the replacing reaction of ytterbium ions for the host cations in perovskite lattice. The ionic radii of Ba^{2+} in 12 coordinates and Ti^{4+} or Zr^{4+} in 6 coordinates are 0.161 and 0.0605 nm or 0.072 nm, respectively. And the ionic radii of Yb^{3+} in 12 coordinates and it in 6 coordinates are 0.107 and 0.086 nm, respectively. Therefore Yb^{3+} can occupy either A-sites or B-sites in the BZT solid solution in term of size.

According to Ohsato's results, there is a transition from B-site preference to A-site preference for the rare earth element occupation in perovskite lattice [9]. The three apparent stages in the dopant content dependence of Curie temperature for ytterbium doped BZT ceramics seem to be in close relation to the substitution preferences and the transition process. In the first stage, Yb^{3+} tends to occupy the ferroelectric sensitive B-site and serves as acceptor-dopant. Because of the larger radius, the occupation of Yb^{3+} of B-sites may depress the oriented displacement of Ti^{4+} or Zr^{4+} in the oxygen octahedrons, which are responsible for the spontaneous polarization. The depression effect finally results in the enormously falling of Curie point temperature. The substitution reaction of this stage could be formulated as following:

$$Yb_2O_3 \rightarrow 2Yb'_B + 3O^x_O + V_{\ddot{O}} \quad (3)$$

Whereafter with the increase of dopant content, Yb^{3+} tends to occupy A-sites rather than B-sites. The transition can compensate both the lattice stress and the charge imbalance generated in the former stage. As a result the concentration of oxygen vacancies is decreased, as is formulated in Eq. (4).

$$V_{\ddot{O}} + Yb_2O_3 \rightarrow 2Yb_{Ba} + 3O^x_O \quad (4)$$

The lattice distortion is moderated and the spontaneous polarization is partially recovered as well. The Curie temperature exhibits a constant value at about 21 °C independent of the ytterbium content between 0.05–0.1 at.%, which might correspond to the coexistence of the two substitution modes.

At higher concentration, Yb^{3+} is incorporated into A-site principally, resulting in the generating of ferroelectric sensitive titanium vacancies and the drop of the Curie temperature

$$2Yb_2O_3 \rightarrow 4Yb_{Ba} + 6O^x_O + V''''_{Ti} \quad (5)$$

Ohsato proposed that a secondary phase appeared in the third stage, which corresponds to the ytterbium content more than 3 at.% in $BaTiO_3$ according to Molokhia [10]. Therefore all the concentrations in question are within the range of solution limit, and none secondary phase has been found via X-ray diffraction.

The substitution preference could be modified by the A/B ratio. According to Takada and his colleagues, an excess of BaO would cause the substitution preference shift toward the B-site and vice versa [11]. With the increase of A/B ratio, more Yb^{3+} would be incorporated into B-sites, resulting in the descending of Curie temperature even for samples with same ytterbium content, as is illustrated in Fig. 6. This is consistent with Takada's results.

The dielectric constant maximum is changed greatly by ytterbium dopant and A/B ratio. This effect could be attributed to the coalescence of the two dielectric constant maxima and the well-developed grains during

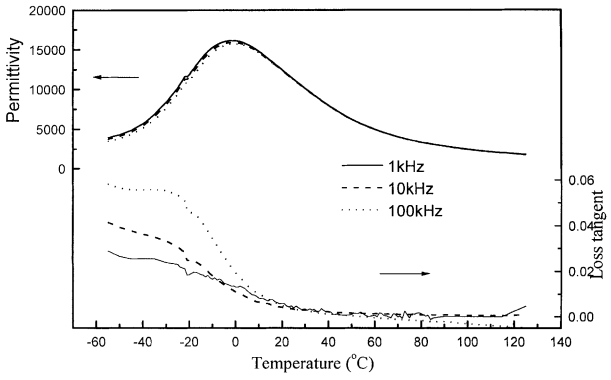


Fig. 5. Dielectric constant in 0.25 at.% ytterbium doped BZT ceramics as a function of temperature and frequency, with the sintering temperature of 1300 °C.

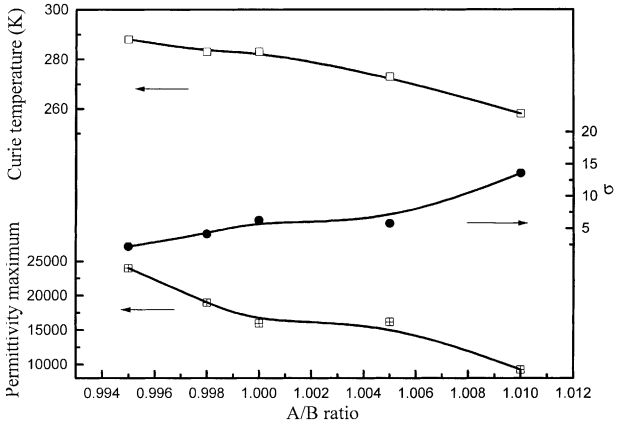
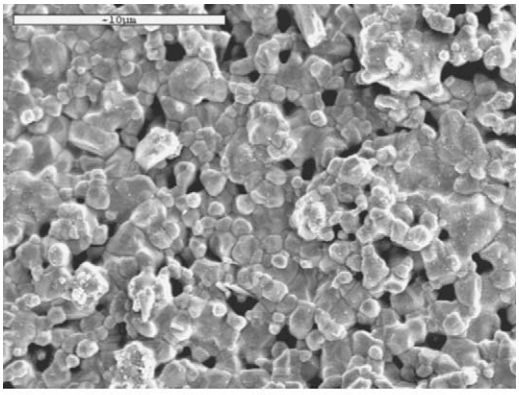
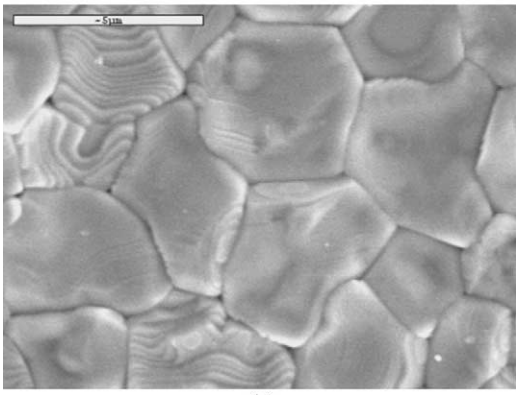


Fig. 6. A/B ratio dependence of T_C, σ value and permittivity maximum for samples doped with 0.25 at.% ytterbium, the sintering temperature is 1280 °C.



(a)



(b)

Fig. 7. Microstructure of none and 0.1 at.% ytterbium doped BZT ceramics, sintered at 1280 °C. (a) None ytterbium doped BZT; (b) 0.1 at.% ytterbium doped BZT.

sintering. Fig. 7(a) and (b) shows the micrographs of non-ytterbium and 0.1 at.% ytterbium doped BZT, revealing the sintering promotion effects of trace amount of ytterbium. The diffusive characteristics and the frequency dispersion of BZT ceramics might be associated with the chemical inhomogeneity and the uniform fine grains (see Fig. 7b) like those typical ferroelectric relaxors.

Thanks to the particular influences of ytterbium on the dielectric properties for BZT ceramics, we developed a novel dielectric materials satisfying EIA Y5V specification (with the temperature coefficient of capacitance within +22 to −82% from −30 °C to 85 °C). At room temperature this dielectric material is characterized by very high dielectric constant over 23,000 and low dielectric loss below 0.01. Another advantage is that the voltage this material can withstand (more than 4 kV/mm under AC field) is higher than that those lead-based Y5V materials do. This favors the ytterbium doped BZT to be used in manufacturing high voltage ceramic capacitors.

5. Conclusions

The dielectric and ferroelectric characteristics of ytterbium doped barium zirconium titanate ceramics have been investigated. The ferroelectric phase transition temperature is shifted to lower temperature by three stages, identified by the value of the ratio of the Curie temperature vs ytterbium content. The dielectric constant maximum is enhanced and broadened enormously by ytterbium dopant. A/B ratio can alter the ferroelectric characteristics for certain amounts of ytterbium doped BZT ceramics. Sintering temperature has a little effect on the phase transition temperature, but proper sintering temperature can bring about higher dielectric constant and lower dielectric loss. The substitution preference of Yb^{3+} changes from B- to A-site cations seems to account for these influences of ytterbium content and A/B ratio. Thanks to the modification behaviors of ytterbium in BZT, we developed a novel Y5V dielectric material with the room temperature dielectric constant over 23,000, and the dielectric strength higher than 4.0 kV/mm under AC field, which can be used in manufacturing high voltage ceramic capacitors.

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