

Microstructures, Dielectric and Photovoltaic Properties of Barium Zirconate Titanate

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Abstract: The microstructures, dielectric and photovoltaic properties of barium zirconate titanate (short for BZT) powders, ceramics and films were investigated. The average particle size of BZT powders prepared by sol-gel method is about 20 nm and increases with the increasing of the holding time and aging temperature. The BZT ceramics with smaller grain size prepared by sol-gel method have the lower Curie temperature and dielectric constant, the higher dielectric loss and the stronger diffuse phase transition than that of the ceramics with larger grain size prepared by solid state reaction method. In $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics domains with herri-bone, lamellar and “water-mark” characters are observed and 90° -domain has not been observed in large grain size sample. The dielectric constant and tunability of the $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films using inorganic zirconate are 113 and 10.2%, respectively. There are obvious photovoltaic characteristics in $\text{BaZr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ films and the short-circuit current is about 0.3 μA .

Keywords: barium zirconate titanate; ferroelectric; photovoltaic; domain

1. Introduction

Barium titanate (BaTiO_3) is the most common ferroelectric oxide in the perovskite ABO_3 structure, which is used as various electronic devices such as capacitors, thermistors, transducers and non volatile memories in semiconductor industries because of its dielectric and ferroelectric properties. The electric and dielectric properties of BaTiO_3 can be modified by doping with various isovalent cations on both A (Ba) and B (Ti) sites [1-4]. The isovalent A site dopants such as Sr are effective in displacing or shifting the Curie temperature but don't have a dramatic effect on dielectric maximum [1, 2]. However, the introduction of isovalent cations on the B site such as Zr has significant effect on dielectric maximum [3, 4].

In this work, the microstructures, dielectric and photovoltaic properties of barium zirconate titanate ($\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$, short for BZT) powder, ceramics and film are investigated.

2. Experimental Procedure

$\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ powders were prepared by sol-gel method [5]. BZT ceramics were prepared by sol-gel method and solid state reaction method, respectively [6]. BZT films were prepared by sol-gel method [7].

Thermal analyses of the gels were performed based on a thermoanalyzer in the temperature range from 0 $^\circ\text{C}$ to 1000 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$. X-ray diffraction (XRD) with Cu $K\alpha$ radiation ($\lambda=0.1541$ nm) was

performed to examine the phase constitution of the specimens at room temperature. Transmission electron microscopy (TEM) was applied to observe the powder surface morphology and estimate the particle size. Scanning electron microscopy (SEM) was used to investigate the morphology of ceramics and films.

The dielectric properties of specimens were measured by fabricating metal-insulator-metal (MIM) structures. The capacitance and loss tangent ($\tan\delta$) were measured with an Agilent-4284A Precision LCR Meter by applying an ac voltage of 0.1 V at 1 kHz frequency. The dielectric constant was calculated from the capacitance by the following equation:

$$\varepsilon = Cd/\varepsilon_0 A \quad (1)$$

where C is the capacitance (farads), ε_0 the free space dielectric constant value (8.854×10^{-12} F/m), A the capacitor area (m^2) and d the thickness (m). The dielectric constant-DC bias field tunabilities of the materials were studied. The tunability of the material is determined by the formula:

$$\% \text{ tunability} = \frac{\varepsilon(0) - \varepsilon(V_{\text{app}})}{\varepsilon(0)} \quad (2)$$

where $\varepsilon(0)$ is the dielectric constant without DC bias field applied, and $\varepsilon(V_{\text{app}})$ is the dielectric constant with maximum DC bias field applied. The polarization-electric voltage (P - V) hysteresis was performed out using a Radiant Precision LC material analyzer. All these properties were measured at room temperature.

3. Results and Discussion

3.1. BZT Nanopowders

The BZT powders aged at different temperature were calcined at 900°C for 4 h. Fig. 1 shows XRD patterns of the BZT powders prepared at different aging temperatures. Firstly, it is found that the BZT powders aged at room temperature and 105°C are both single perovskite phase. Secondly, the height of the diffraction peaks of the BZT powders aged at room temperature is higher than that of the BZT powders aged at 105°C. It indicates that the crystallinity of the BZT powder aged at room temperature is higher than that of the BZT powder aged at 105°C. Thirdly, by the Scherrer formula, the particle size of the BZT powders aged at room temperature and at 105°C is calculated to be about 14.5 nm and 19.5 nm, respectively.

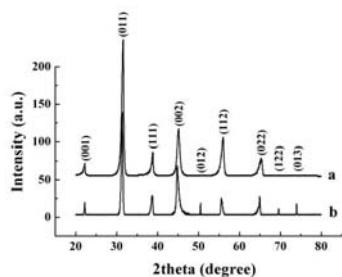


Figure. 1 XRD patterns of BZT powders prepared at different aging temperature: (a) aging at room temperature, (b) aging at 105°C.

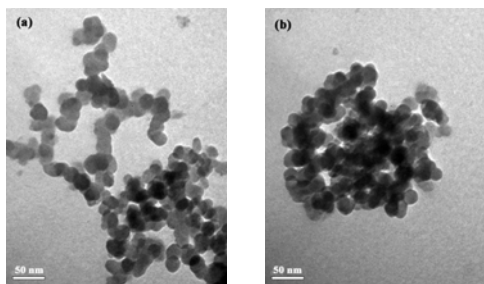


Figure. 2 TEM micrographs of BZT powders prepared at different aging temperature: room temperature, (b) 105°C.

Fig. 2 shows the TEM micrographs of the BZT powders prepared at different aging temperature. It can be seen that the average particle size of the BZT powders aged at room temperature and 105°C is 16 nm and 23 nm, respectively. The results of the particle size of powders determined by XRD and TEM are similar. That is to say, the average size of powders increases as aging temperature increases. At the same time, the agglomeration of powders aged at 105°C is more severe than that of powders aged at room temperature. It is suggested that the low aging temperature can reduce the agglomeration of the BZT nanopowders.

3.2. BZT Ceramics

3.2.1. Preparing Method

The grain size of the BZT ceramics was determined by SEM micrographs. Firstly, it can be seen that the sintered ceramics are both dense, and the average grain size of the ceramics by sol-gel method is much smaller than that of the ceramics by solid state reaction method. Secondly, the shape of grain of the ceramics by sol-gel method almost is spherical, while the shape of grain of the ceramics by solid state reaction method is irregularly polygonal. Thirdly, for the BZT ceramics prepared by solid state reaction method, the largest grain is about 80 μm, while the smallest grain is about 7 μm. The grain of the BZT ceramics by sol-gel method becomes much more homogeneous than that of the ceramics by solid state reaction method. These results indicate that the sol-gel method is superior to solid state reaction method for preparing the BZT ceramics with small, spherical and homogeneous grains.

Fig. 3 shows the temperature dependences of dielectric constant and dielectric loss of the BZT ceramics prepared by different preparation methods at 1 kHz. Firstly, it can be found that the Curie temperature (T_C), corresponding to the maximum relative permittivity, of the BZT ceramics prepared by sol-gel and solid state reaction method is 25°C and 50°C, respectively. As mentioned above, the grain size of the ceramics prepared by sol-gel method is much smaller than that of the ceramics prepared by solid state reaction method. That is to say, the Curie temperature of BZT ceramics falls with the decreasing of the grain size. The result is in agreement with Tang's result [8]. Secondly, it can be seen that the dielectric constant of the BZT ceramics prepared by sol-gel method is much lower than that of the ceramics prepared by solid state reaction method when temperature is above 20°C. It is due to effect of grain size on dielectric constant. It is well known that the grain boundary is a low-permittivity region. The grain size of the BZT ceramics is larger, and then the grain boundary becomes less so that the dielectric constant becomes higher. Thirdly, Fig. 3(b) shows that the dielectric loss of the ceramics prepared by sol-gel method is higher than that of the ceramics by solid state reaction method when temperature is above -25°C. Furthermore, the dielectric peaks of the ceramics prepared by two methods are broad and the dielectric peak of the ceramics prepared by sol-gel method is broader than that of the ceramics prepared by solid state reaction method. The result indicates that there is diffuse phase transition in the BZT ceramics prepared by two methods.

The hysteresis loops at room temperature and 1 kHz indicated that the BZT ceramics prepared by two methods have obvious ferroelectric character. The coercive electric field (E_C) of the BZT ceramics prepared by sol-gel method is much more than that of the BZT ceramics

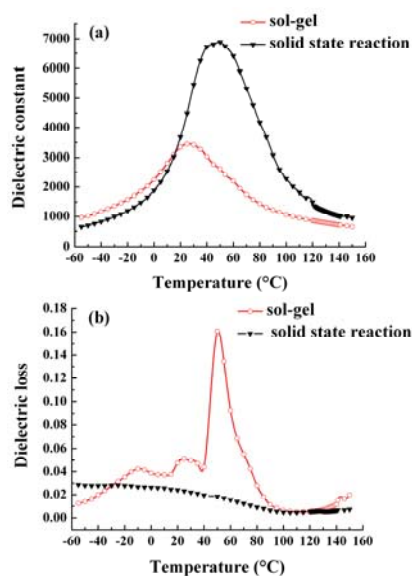


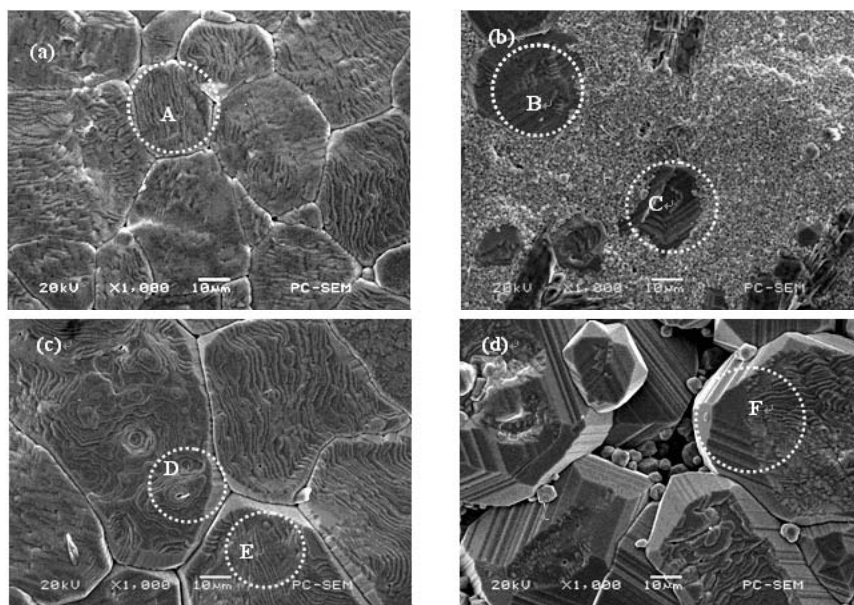
Figure. 3 Temperature dependences of dielectric constant and dielectric loss of the BZT ceramics prepared by two method at 1 kHz: (a) $\epsilon = f(T)$ and (b) $\tan\delta = f(T)$.

prepared by solid state reaction method. The result could be attributed to grain size of the BZT ceramics. Energy barrier for switching ferroelectric domain must be broken through and energy barrier increases as grain size decreases. So reversal polarization process of a ferroelectric domain is more difficult inside a small grain than in a large grain [9]. As mentioned above, the grain size of the BZT ceramics prepared by sol-gel method is much smaller than that of the BZT ceramics prepared by solid state reaction method. Thus, E_C of the BZT ceramics

prepared by sol-gel method is much more than that of the BZT ceramics prepared by solid state reaction method. Moreover, it is also found that the remanent polarization (P_r) of the BZT ceramics prepared by sol-gel method is less than that of the BZT ceramics prepared by solid state reaction method. It could be attributed to grain boundary. Grain boundary is a low permittivity region. That means the grain boundary has poor ferroelectricity. Polarization of grain boundary may be little. Space charges in grain boundary exclude polarization charge on grain surface, and depletion layer on grain surface can be formed. It results in polarization discontinuity on grain surface to form depolarization field, and polarization decreases. As mentioned above, the number of grain boundary of the BZT ceramics prepared by sol-gel method is much more than that of the BZT ceramics prepared by solid state reaction method. Thus, P_r of the BZT ceramics prepared by sol-gel method is less than that of the BZT ceramics prepared by solid state reaction method.

3.2.2. Domain Structure

By using SEM and Image Pro Plus software, the grain sizes of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramic samples had been determined. There was amorphous phase in BZT ceramics sintered for 0.5h. It was too short for sintering time to crystallize. BZT ceramics sintered for 2h, had a dense microstructure and uniform grain. The average grain sizes of the BZT ceramics were $\sim 25\text{ }\mu\text{m}$, $\sim 40\text{ }\mu\text{m}$, $\sim 45\text{ }\mu\text{m}$ and $\sim 80\text{ }\mu\text{m}$, respectively. BZT ceramics sintered for 8h had some large grains. That is to say, the grain sizes of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics increased as the sintering time increased.



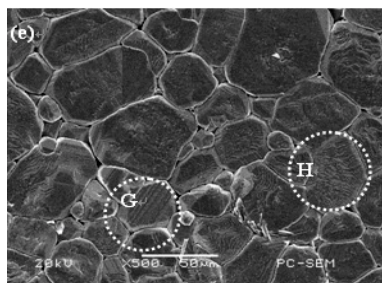


Figure. 4 Domain structures of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics with various average grain sizes: (a, b) 25 μm , (c) 40 μm , (d) 45 μm , (e) 80 μm

The domain structures of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics with various grain sizes can be clearly seen from Fig. 4. 180° -domains are observed in $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics samples with 25 μm , 40 μm , 45 μm and 80 μm , as indicated with circles B, E, G and I in Fig. 4(b), (c), (d) and (e). But 90° -domains only can be observed in samples with 25 μm , as indicated with circle C in Fig. 4(b).

This means that the BZT ceramics with the large grain have no 90° -ferroelectric domains. This is because that the strain energy on the grain boundary is higher than the grain. The strain energy of the BZT ceramics with small grain is more than that of the BZT ceramics with large grain. The depolarization energy of the BZT ceramics with large grain is primary. Therefore, the strain energy and the depolarization energy of the BZT ceramics with small grain can be reduced by forming 90° -domains and 180° -domains. However, the BZT ceramics with large grain can reduce energy by forming 180° -domains.

Domain shapes of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics include herribone, lamellar and “water-mark”. Domains with herribone character are observed in $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics sintered for 0.5h, as indicated with circle C in Fig. 4 (b). Domains with “water mark” character appear in $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics samples, as shown in circles A, E, F and H. Domains with the lamellar feature are only observed in $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics samples sintered for 2h, as indicated with circle D in Fig.4 (c). It is found that sintering time (or say grain size) influence types of domain of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics, the BZT ceramics with large grain size have no 90° -domains.

3.3. BZT Films

3.3.1. Ferroelectric Properties

It is found that well-behaved hysteresis loops of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films at a frequency of 1 kHz can be observed. This suggests that at room temperature the crystal structures are in the ferroelectric phase, which is consistent with the XRD patterns. The remanent polarization ($2P_r$) and the coercive field ($2E_c$) of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films obtained from the P - V hysteresis loop are 0.1669 $\mu\text{C}/\text{cm}^2$ and 21.53 kV/cm, respectively. The lower value

of remanent polarization could be attributed to the smaller grain size.

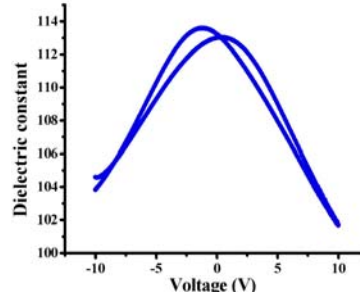


Figure. 5 ϵ - V characteristics of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films at 1 kHz and room temperature.

The non-linear dielectric (ferroelectric) properties of BZT thin films were performed using a HP4284A impedance analyzer. Fig. 5 showed the influence of dielectric constant (ϵ) on electric voltage (V) of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films at 1 kHz and room temperature by applying a small signal of 100 mV. The voltage was applied from -10 V to +10 V and back again. Butterfly-shaped ϵ - V curves indicate the ferroelectric property of the BZT thin films. The $\epsilon(0)$ and tunability of the $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films are 113 and 10.2% at 62.5 kV/cm, respectively. The lower values of dielectric constant and tunability could be attributed to the smaller grain size.

3.3.2 Photovoltaic Properties

The photovoltaic properties of $\text{BaZr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ thin films were performed using an IV Test Station 2000. Fig. 6 showed that there are obvious photovoltaic characteristics in $\text{BaZr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ thin films. It is determined that the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) are 0.28 μA and 0.247 V, respectively.

4. Conclusions

BZT nano-powders, ceramics and films were prepared. The particle size of the BZT powders is in nanometer scale, and increases as the increasing of the holding time and aging temperature. Compared with the ceramics sintered at the same temperature prepared by solid state method, the grain of the BZT ceramics prepared by sol-gel method is much smaller and more homogeneous, and

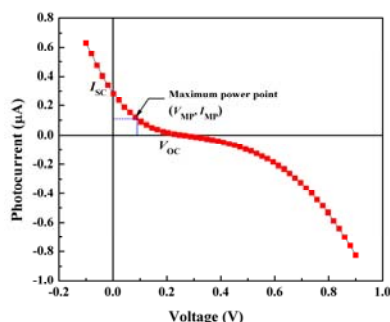


Figure. 6 Photovoltaic characteristics of BaZr_{0.1}Ti_{0.9}O₃ thin films.

the shape of grain tends to be spherical. It is found that sintering time (or say grain size) influence types of domain of BZT ceramics, i. e. no 90°-domains have been observed in those ceramics with large grain sizes. Domains with herribone, lamellar and “water-mark” characters are observed.

The obvious polarization versus electric voltage hysteresis loop and butterfly-shaped ϵ - V curves were observed in BaZr_{0.2}Ti_{0.8}O₃ thin films. The remanent polarization and the coercive field of BaZr_{0.2}Ti_{0.8}O₃ films obtained from the P - V hysteresis loop are 0.1669 $\mu\text{C}/\text{cm}^2$ and 21.53 kV/cm, respectively. The $\epsilon(0)$ and tunability of the BaZr_{0.2}Ti_{0.8}O₃ films are 113 and 10.2% at 62.5 kV/cm, respectively. The lower values of remanent polarization, dielectric constant and tunability could be attributed to the smaller grain size. The short circuit current and open circuit voltage of BaZr_{0.1}Ti_{0.9}O₃ thin films are 0.28 μA and 0.247 V, respectively.

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