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# Dielectric and ferroelectric characteristics of doped BZT-BCT ceramics sintered at low temperature

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The paper presents relaxor properties of lead-free nanostructured ZnO doped BZT-BCT ceramics sintered at low temperature. Curie-Weiss, Quadratic, Vogel-Fulcher laws were applied to study dielectric properties. The fitting experimental data to the mentioned laws showed the typical diffuseness characteristic of the materials as a result of the substitution of  $Zn^{2+}$  ions into BZT-BCT substrate. Also, received ferroelectric loops were well saturated and fairly slim for all samples that assert again diffuse ferroelectric nature in the investigated ceramics. The characterized values of remnant polarization,  $P_{p}$  and coercive field,  $E_{c}$ , depended on ZnO nanoparticles concentration. According to that, when varying doping content in the region of 0.00-0.25% wt,  $P_{r}$  improved and reached a maximum value of 6.19  $\mu$ C/cm<sup>2</sup> at 0.15% wt, then decreased monotonously. Meanwhile  $E_{c}$  continuously intensified in the range of 1.36-2.72 kV/cm. In other words, nanosized ZnO particles made the ceramics harder.

Key words: BZT-BCT, Ferroelectric, ZnO nanoparticles, sintering.

## Introduction

Perovskite  $ABO_3$ -type compounds with high flexibility in symmetry play an important role in materials science. Typical materials such as PZT based on family and BaTiO<sub>3</sub> have received a lot of attention due to their outstanding dielectric, ferroelectric and piezoelectric performance.

In 2009, based on alternating with A or/and B sites in perovskite BaTiO<sub>3</sub>, Liu and Ren established a new lead-free pseudo binary ferroelectric system Ba( $Zr_{0.2}Ti_{0.8}$ )O<sub>3</sub>- $x(Ba_{0.7}Ca_{0.3})TiO_3$  (abbreviated as BZT-BCT) that possesses excellent piezoelectricity (d<sub>33</sub> = 620 pC/N at x = 50 composition). Since then, the BZT-BCT materials have been widely studied [2-5]. It is noted that based BaTiO<sub>3</sub> ceramics have been usually sintered at a very high temperature to obtain the desired properties [6-8], which causes many difficulties in the preparation and application of these materials. It is well-known that there are some methods for reducing the sintering temperature such as the usage of nanostructured raw materials and sintering aids [9-10].

In our previous work, we successfully synthesized ZnO nanoparticles doped BZT-BCT ceramics at a low sintering temperature of 1350 °C. According to that,

nanosized ZnO particles have enhanced some dielectric and piezoelectric properties. This article presents the effect of ZnO nanoparticles on dielectric and ferroelectric properties in detail.

## **Experimental Procedure**

Lead-free ceramics ZnO nanoparticles doped  $0.48BaZr_{0.2}Ti_{0.8}O_3-0.52Ba_{0.7}Ca_{0.3}TiO_3$  sintered at a low temperature of 1350 °C (noted BCZT-y, y is the concentration of nanostructured ZnO in wt%, y = 0.00, 0.05, 0.10, 0.15, 0.20, and 0.25) were prepared as in a previous report. The silver electrodes were made on both sides of these sintered bulks for electrical measurements. The dielectric properties of the materials were determined using HIOKI3532 equipment. The ferroelectricity was studied using Sawyer-Tower circuit method.

### Discussions

As discussed in our previous report, all BCZT-y samples possessed pure perovskite structure with a tetragonal symmetry (belonging to space group P4mm) characterized by splitting (002)/(200) diffraction peaks at around of 44 °-46 °. We have demonstrated that  $Zn^{2+}$ entered into B-site to replace  $Ti^{4+}/Zr^{4+}$  within ABO<sub>3</sub> structure because of the similarity in ionic radius. In that case,  $Zn^{2+}$  acts as an acceptor dopant to accrue oxygen vacancy for compensation, and the solid

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**Fig. 1.** Inverse permittivity,  $1/\varepsilon$ , as a function of temperature of BCZT-0.15 sample measured at the frequency of 1 kHz.

solution BCZT-y can be formed as follows

$$ZnO \xrightarrow{BCZT-y} Zn''_{Ti/Zr} + V^{**}_{o}$$
(1)

Such oxygen vacancies V o could influence on

Table 1. Values of  $T_o$ , C,  $T_B$ ,  $T_m$ , C as changing ZnO nanoparticles content.

y(%)	$C \times 10^4$ (°C)	<i>T</i> <sub>o</sub> (°C)	$T_m$ (°C)	$T_B$ (°C)	$\Delta T(^{\circ}C)$
0.00	6.9	89.5	70.2	106.7	36.5
0.05	7.2	87.8	69.4	106.8	37.4
0.10	7.3	86.4	68.5	106.9	38.4
0.15	7.5	84.6	67.2	106.7	39.5
0.20	7.1	83.5	66.2	104.5	38.3
0.25	6.8	81.6	65.4	102.2	36.8

some electric properties of the ceramics.

It is well-known that temperature dependence of permittivity of a normal ferroelectric above the ferroelectric-paraelectric transition point obeys the Curie-Weiss law

$$\frac{1}{\varepsilon} = \frac{T + T_0}{C}, \qquad T > T_C$$
(2)

where  $T_o$  is the Curie-Weiss temperature, and C is the Curie-Weiss constant reflecting the character of ferroelectric phase transition.

Fig. 1 illustrates the plot of the inverse permittivity



Fig. 2. Temperature dependence of permittivity of BCZT-y ceramics fitted with quadratic law.  $\ln(1/\varepsilon - 1/\varepsilon_m)$  versus  $\ln(T-T_m)$  in inset.



**Fig. 3.**  $\delta$  and  $\gamma$  as a function of y.

versus temperature for the BCZT-0.15 composition at 1 kHz complying with the Curie-Weiss law.

As shown from Fig. 1, the  $\varepsilon(T)$  relationship does not comply with the Curie-Weiss law within the region of  $(T_m / T_B)$ . It is noted that  $T_m$  is the temperature corresponding to maximal permittivity, and  $T_B$  is called the Burn temperature from which  $\varepsilon$  begins to follow the Curie-Weiss relationship. The similar results were also achieved for other compounds. The fitting and related parameters are listed in Table 1. The difference DT of  $T_B-T_m$  varies for each composition used to represent the degree of the deviation from the Curie-Weiss law (Table 1).

It can be seen from Table 1 that the C values of about  $10^4$  °C are obtained for all samples, implying that the high temperature paraelectric state is controlled by a displacive transition . Also, the obtained temperatures are together lessened as y increases. Especially, the reduction of  $T_m$  also reflects  $Zn^{2+}$  incorporation in BCZT substrate . Besides, DT varies and reaches the highest value of 39.5 °C at y = 0.15. This composition is expected to have the highest diffuseness degree. The outcome is well conformable with the ZnO nanoparticles content dependence of diffuseness,  $\gamma$ .

The above  $T_m$  side of  $\epsilon(T)$  can be described by a quadratic law as follows

$$\frac{\varepsilon_a}{\varepsilon} = 1 + \frac{(T - T_a)^2}{2\delta_a^2}$$
(3)

where  $T_a$  (<  $T_m$ ) is the parameter defining the



Fig. 4. Permittivity-temperature relationships of BCZT-y samples recorded at various frequencies.

y (%)	$T_f(^{\circ}\mathrm{C})$	E <sub>a</sub> (eV)	$f_o (10^{12} \text{ Hz})$
0.00	63.1	0.0321	8.2
0.05	62.3	0.0321	5.3
0.10	61.7	0.0316	3.2
0.15	60.4	0.0315	2.2
0.20	59.6	0.0314	1.8
0.25	58.4	0.0312	1.3

Table 2. Vogel-Fulcher fitting parameters for BCZT-y ceramics.



**Fig. 5.** presents P-E relationships for BCZT-y ceramics measured at room temperature.

temperature and position of the peak and  $\varepsilon_{\alpha}$  is the extrapolated value of  $\varepsilon$  at T<sub>a</sub>. The parameter  $\delta$  describes the shape of quadratic curve. Experimental data for BCZT-y compounds was fitted to the quadratic law based on a least squares method, and the received results were demonstrated in Fig. 2.

As shown from Fig. 2, a good fit occurred at the region over  $T_m$ , while the deviation took place at low temperature. The fitting parameters were obtained and presented in each picture corresponding to each sample. Among them,  $\delta_{\alpha}$  is used to measure the width of the quadratic peak. Meanwhile,  $\gamma$  presents the diffuseness of the experimental permittivity, the values of which were calculated in our previous work and illustrated in the inset of each picture. In addition, ZnO nanoparticles content dependences of  $\gamma$  and  $\delta_{\alpha}$  are similar in manner (Fig. 3)

In other to show more clearly the relaxor nature of BZCT-y system, the permittivity versus temperature measured at various frequencies was studied (Fig. 4). Drastic frequency dispersions below the temperature  $T_m$  are identified with the increase of  $T_m$  and the decrease of  $\varepsilon_m$  as rising measured frequency. These are typical characteristics of relaxor materials. Received results are attributed to the freezing of the polar nano regions.

In order to analyze the frequency dependence of  $T_m$ , the Vogel – Fulcher formula is applied as follows



**Fig. 6.** Values of  $E_C$ ,  $P_r$ ,  $G_S$  as a function of y.

$$f = f_{o} exp\left[\frac{-E_{a}}{k_{B}(T_{m} - T_{f})}\right]$$
(4)

where,  $T_f$  is the freezing temperature,  $E_a$  is the activation energy for polarization fluctuation of a nano polar region,  $f_o$  is a characteristic frequency or Debye frequency, and  $T_m$  is the peak temperature corresponding to the applied frequency. The fitted results are presented in Table 2. We can see that the freezing temperature and Debye frequency decrease, whereas the change in the activation energy is negligible as the concentration of ZnO nanoparticles increases.

Received ferroelectric loops were well saturated and fairly slim for all samples that assert again diffuse ferroelectric nature in BCZT-y ceramics. The characterized values of remnant polarization,  $P_{\rm r}$ , and coercive field,  $E_{\rm c}$ , depended on ZnO nanoparticles concentration as illustrated in Fig. 6. As shown, when varying y in the region of 0.00-0.25, Pr improved and reached a maximum value of  $6.19 \,\mu\text{C/cm}^2$  at y = 0.15, then decreased monotonously. This result could be explained based on an amelioration in microstructure . According to that, poor ferroelectricity was received at grain boundary. Thus, polarization of grain boundary may be very small or zero. Alternatively, space charges eliminate polarization charge from grain surface that depletion layer can be established. That caused polarization interruption on particle surface to form depolarization field which lowers polarization. The reduced number of grain boundary is due to increasing grain size that could be the reason for raising remnant polarization and vice versa. In our work, the grain size,  $G_{\rm S}$ , of these ceramics was controlled by varying doping concentration of nanosized ZnO particles as shown in Fig. 6(c) 11. The dependence of coercive field on ZnO nanoparticles content shows that the parameter continuously intensified in the range of 1.36-2.72 kV/cm as raising y. In other words, ZnO nanoparticles made the ceramics

harder. The enhancement of  $E_c$  value could be due to the increase of charged oxygen vacancies as doping that pinned to the movement of ferroelectric domain walls. The obtained values of  $E_c$  demonstrated that the BCZT-y materials are typically soft compared to electric properties.

## Conclusions

In this research, the dielectric and ferroelectric properties of lead-free nanostructured ZnO doped BZT-BCT ceramic sintered at low temperature were studied. The addition of nanostructuted ZnO particles influenced the relaxor behavior of the materials. As a result, BCZT-0.15 composition possessed the highest diffuseness characteristic. Also, remnant polarization was improved and reached a maximum value of 6.19  $\mu$ C/cm<sup>2</sup> at y = 0.15 whereas coercive field went up continuously under increasing doping concentration.

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