Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 38S (2012) S33–S36

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The dielectric properties of $BaTiO_3$ based ceramics co-doped with Bi/Mn

Ding Shihua [a,*], Song Tianxiu [a], Yang Xiaojing [b], Liu Xiaobing [b], Liu Guobiao [a]

[a] School of Materials Science and Engineering, Xihua University, Chengdu 610039, China
[b] School of Energy and Environment, Xihua University, Chengdu 610039, China

Abstract

$BaTiO_3$ based ceramics (with some additives such as ZrO_2, SnO_2, etc.) were prepared by solid state reaction. Mn^{2+} or Mn^{3+} as an acceptor substituting for Ti^{4+} in B site and Bi^{3+} as a donor substituting for Ba^{2+} in A site were co-doped in $BaTiO_3$ based ceramics. The dielectric properties of $BaTiO_3$ based ceramics co-doped with Bi/Mn were investigated. The results show that the dielectric properties of $BaTiO_3$ based ceramics co-doped with Bi/Mn are affected by the mole ratio of donor and acceptor (Bi/Mn). When the mole ratio of donor and acceptor is high, dielectric dispersion behavior was observed and the dielectric constant decrease and remnant polarization, coercive field and piezoelectric constant will varied. When Bi varied from 1.0% to 2.0 mol% (Mn = 0.8 mol%), remnant polarization from 10.35 to 2.25 $\mu C/cm^2$, coercive field from 4 to 2.75 kV/cm, and piezoelectric constant d_{33} from 137 to 36 pC/N respectively.

Keywords: C. Diffuse phase transition; C. Dielectric properties; Piezoelectric constant; Random field

1. Introduction

The dielectric constant of barium titanate ($BaTiO_3$) ceramics depends on temperature, and show a dramatic change and a maximum at Curie temperature. The dielectric properties are very dependent on the substitution of minor amounts of other ions for Ba or Ti. Some applications for Y5V, X7R, etc. requires the broad or flat dielectric constant-temperature peaks. The flatter characteristics could be obtained with the forming of a core–shell structure by proper additives or a diffuse phase transition (DFT) in $BaTiO_3$-based ceramics.

The core–shell grain consists of the core region, a ferroelectric tetragonal structure, surrounded by the shell which contains some additive elements and is a paraelectric. The most important in forming a core–shell structure is the selection of proper additives which leads to the reaction with dielectric grains [1–4]. The core–shell grain was proposed by Okazaki et al., who found a flat temperature dependency of dielectric constant in $BaTiO_3$ based ceramics with Bi as additive [1]. The temperature of forming of $Bi_2(TiO_3)_3$, $Bi_2(SnO_3)_3$, $Bi_2(ZrO_3)_3$ is lower than $BaTiO_3$ based ceramics which consists of the core with ferroelectric phase, some $Bi_2(TiO_3)_3$, $Bi_2(SnO_3)_3$, $Bi_2(ZrO_3)_3$ will form the shell grain during cooling from sintering temperature.

The relaxor ferroelectrics with diffuse phase transition (DFT) have a broad maximum for temperature dependence of dielectric constant as well as frequency dispersion. Several theories have been proposed to understand the behavior of the relaxor ferroelectrics [5–8]. The concept of polar microregions in relaxors was first introduced by Smolenskii within chemical inhomogeneity theory and was later confirmed experimentally [5]. Polar regions of varying composition and Curie temperature led to the DFT. The disordered distribution of different ions on B site is the essential structure characteristic of relaxor in complex perovskite compounds [6–8]. Westphal et al. proposed that the diffuseness of the ferroelectric phase transition is due to random electric field originating from charged compositional fluctuations [8]. The substitutional disorder, shift of ions from their equilibrium positions in ideal lattice, and excess charge compensation can be considered to be the sources of the random field. These additional fields should be rather large to destroy the long-range ferroelectric order.

In this paper, Bi and Mn ions were selected as a donor and acceptor substituting for A site and B site of $BaTiO_3$-based ceramics respectively. The influence of Bi and Mn on the diffuse phase transition and dielectric properties was investigated.

---

* Corresponding author. Tel.: +86 28 87720869; fax: +86 28 87720514.
E-mail address: dshihua@263.net (D. Shihua).

0272-8842/$36.00 © 2011 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2011.04.043

2. Experimental procedures

All ceramics were prepared by means of a mixed powder method starting with the pure (>99.8%) powders of $BaCO_3$, TiO_2, SnO_2, ZrO_2 as basic compositions (provided by Songde Electronic Co.), Bi_2O_3 and $Mn(CO_3)_2$ as additives. The amount of Bi/Mn is 1%/0.8%, 1.3%/0.8%, 2%/0.8%, 2.3%/0.8%, 3%/0.8% and 2%/1.6%, (mol) respectively. Because of small $Bi_2(TiO_3)_3$, $Bi_2(SnO_3)_3$ and $Bi_2(ZrO_3)_3$ segregating in the shell grain [1], the amount of Bi has an excess. The weighed batches were wet mixed in distilled water for 8 h. After drying, the powders were calcined at 1250 °C for 150 min. The calcined powders were mixed again, dried, and the disks were pressed uniaxially at 300 MPa with 5 wt% PVA solution added as binder. The pellets were sintered at 1350 °C for 150 min.

Disk densities were evaluated using Archimedes principle and found to be ~97% of their theoretical density. The dielectric constant and loss of the ceramics were measured using an Agilent4284A. Ferroelectric hysteretic loops were measured using ZT-I polarization hysteresis loops tester. Piezoelectric constant d_{33} and conductivity of poling ceramics were measured using ZJ-4AN d_{33} tester and Kethely 6517A respectively.

3. Results and discussion

Dielectric constants as a function of temperature for the different mol ratios of Bi/Mn are given in Fig. 1. It can be seen that the transition becomes more diffuse and the peak values of the dielectric constant decrease and more flatter when the ratio of Bi/Mn is increased. The temperature (T_m) at which the dielectric constant is at maximum shifts to low temperature.

Fig. 2(a)–(d) illustrates the temperature dependency of dielectric constants for the different amounts of Bi/Mn, Mn is fixed at 0.8% (mol) and Bi at 1%, 2.0%, 2.3% (mol) respectively. When the mol ratio of Bi/Mn is smaller than 2, the characteristics of dielectric constant-temperature appeared a normal ferroelectric. As the ratio of Bi/Mn is larger than 2, it showed a broadened dielectric constant peak (diffuse phase transitions) with a frequency dispersion. It can be seen that the frequency dispersion becomes strong as the mol ratio of Bi/Mn increase. For the specimens with Bi/Mn of 1.0%/0.8% and/or 2.0%/1.6%, however the transition becomes weaker diffuse without frequency dispersion, given in Fig. 2(d).

The remanent polarization P_r, coercive field E_c and piezoelectric constant d_{33} of $BaTiO_3$ based ceramics are given in Table 1. When the mole ratio of donor and acceptor changed, the remanent polarization, coercive field and piezoelectric constant varied. When Bi varied from 1.0% to 2.0 mol% (Mn = 0.8 mol%, T_m is above room temperature), the remnant polarization from 10.35 to 2.25 μC/cm^2, coercive field from 4 to 2.75 kV/cm, and piezoelectric constant d_{33} from 137 to 36 pC/N respectively. All of these decrease when the amount of Bi increases. The conductivity of $BaTiO_3$ base ceramics doped with Bi/Mn is given in Table 2. It can be seen that an increase of the mole ratio of Bi/Mn leads to a decrease of the conductivity.

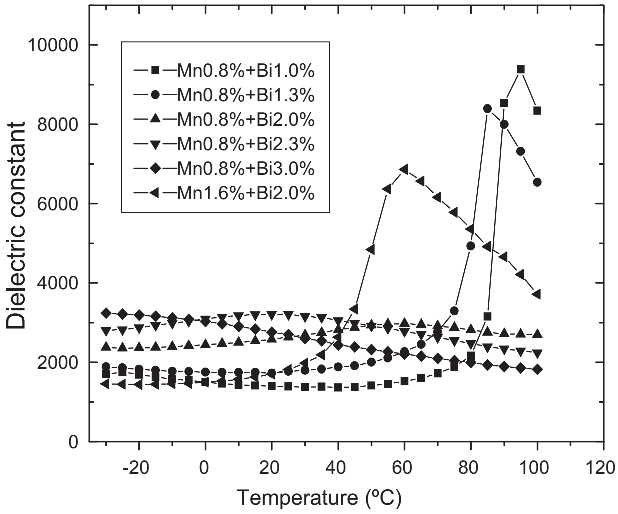

Fig. 1. Influence of Bi/Mn on dielectric constant-temperature characteristics (at 1 kHz).

The shift of ions from their equilibrium positions in ideal lattice, and excess charge compensation can be considered to be the sources of the random field which result in the transition from normal ferroelectrics to relaxor ferroelectrics [5–8]. Bi^{3+} substitutes for A site as a donor and Mn^{2+} or Mn^{3+} substitutes for B site as a acceptor for $BaTiO_3$ based ceramics co-doped with Bi/Mn. In the case of Bi^{3+} substituting for Ba^{2+} in A site, a positive charged ionic defect can be formed. Similarly a negative charged ionic defect can be formed as Mn^{2+} or Mn^{3+} substituting for Ti^{4+} in B site. First when the Bi/Mn increases, the positive ionic charged defects could not compensate the negative ionic charged defects and there are some net positive ionic charged defects. They would associate with other ionic defects such as metal vacancies and lead to associate defects or defect dipoles resulting in a localized random field. Second the increase of doping ions will lead to the distortion of lattice that result in localized random field. As the Bi/Mn increases, the localized random electric field will be stronger and phase transition more diffusive, as can be seen in Fig. 2(a)–(c). There is no diffuse phase transition (DFT) behavior, showed a sharp transition, for the Bi/Mn about 1. When the Bi/Mn is lager than 2, $BaTiO_3$ based ceramics show the more pronounced DFT behavior and frequency dispersion. The diffuseness of the transition and the frequency dispersion increases with increasing the Bi/Mn. And when Bi varied from 1.0% to 2.0 mol% (in this case, T_m is above room temperature), the remnant polarization decreases from 10.35 to 2.25 μC/cm^2, coercive field from 4 to 2.75 kV/cm. The localized random electric field will affect the motion of domain wall and the piezoelectric constant d_{33} decreases from 137 to 36 pC/N, given in Table 1 [9].

As $BaTiO_3$ based ceramics doped with some additives will form a core–shell grain [1,2]. Some Bi and Mn will segregate in the shell which is pseudocubic paraelectrics. The segregation of Bi and Mn increases when the amount of Bi and Mn simultaneously increases, e.g. Bi/Mn of 2.0%/1.6%. The shell

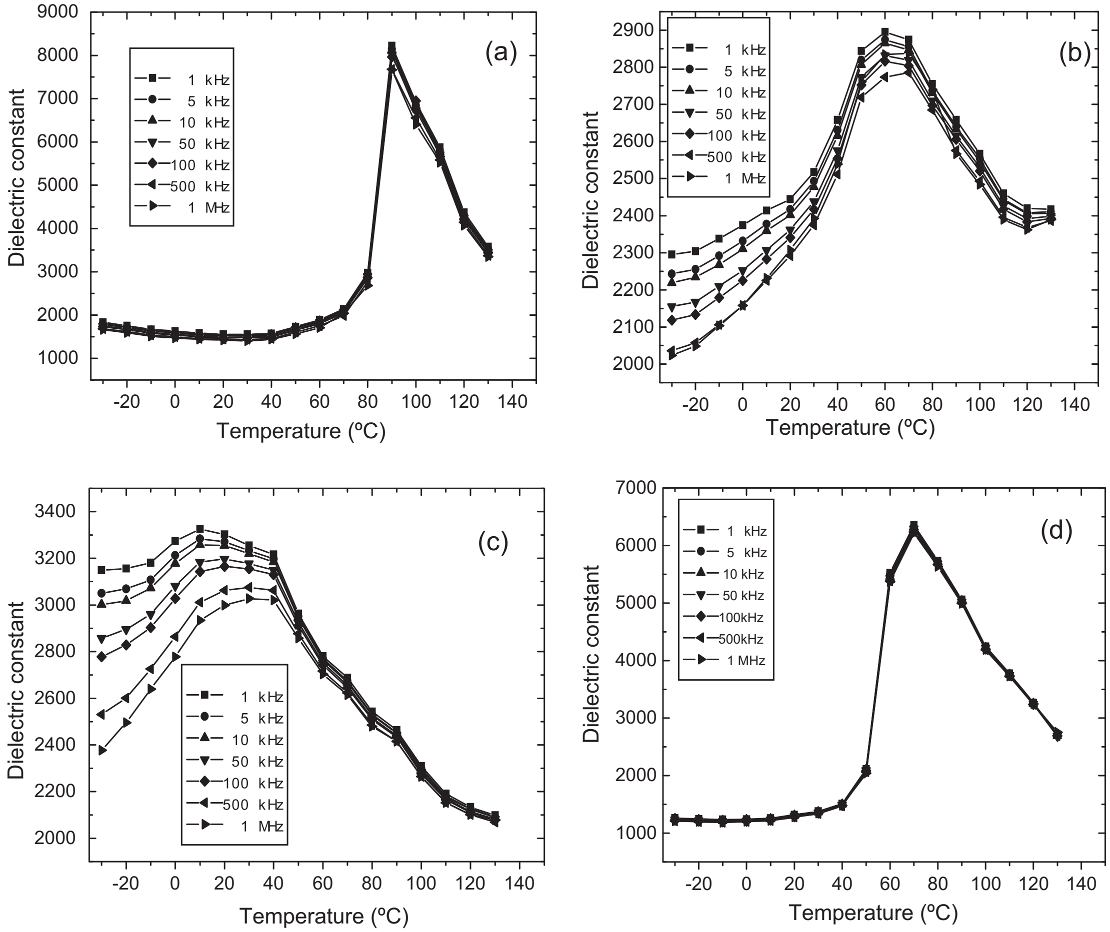

Fig. 2. Dielectric constants as a function of temperature for different mol ratios of Bi/Mn. (a) 1%/0.8%; (b) 2%/0.8%; (c) 2.3%/0.8%; and (d) 2%/1.6%.

grain becomes thicker and the increase of nonferroelectric phase leads to the broad peak and the decrease of the dielectric constant compared with Bi/Mn of 1%/0.8%. However the dielectric constant is independent of frequency because of the charge balance of donors and acceptors. No frequency dispersion appeared in Fig. 2(d).

It is well known that Mn ions in $BaTiO_3$ lattice act as acceptors on B sites. It seems to be certain that Mn ions exist in the state of Mn^{2+} or Mn^{3+}, Mn^{4+} depending on the oxygen partial pressure. The valence of Mn can be considered to be coexisted +3 and +2 sintering in air [10]. When the Bi/Mn is small, the positive charged defects as a result of Bi^{3+} substituting for Ba^{2+} in A site could not compensate the negative charged defects originating from Mn^{3+} or Mn^{2+} substituting for Ti^{4+} in B site. $Mn^{3+} + e = Mn^{2+}$, an electron conductivity exist in the ceramics. When the Bi/Mn increases, the charged defects from Mn substituting for B site could completely be compensated by the donors and the conductivity of $BaTiO_3$ based ceramics decreases with the increase of the mole ratio of Bi/Mn (see Table 2).

Table 1
Remnant polarization, coercive field and piezoelectric constant of $BaTiO_3$ based ceramics doped with Bi/Mn.

Mn mol% + Bi mol%	0.8 + 1.0	0.8 + 1.3	0.8 + 2.0	0.8 + 3.0	1.6 + 2.0
P_r (μC/cm^2)	10.35	8.21	2.25	1.49	5.99
E_c (kV/cm)	4.0	4.0	2.75	2.0	3.7
d_{33} (pC/N)	137	110	36	13	100

Table 2
Conductivity of $BaTiO_3$ base ceramics doped with Bi/Mn.

Mn mol% + Bi mol%	0.8 + 1.0	0.8 + 1.3	0.8 + 2.0	0.8 + 3.0	0.8 + 4.0
Conductivity (10^{-8} S/m)	12.1	4.5	1.3	1.0	1.5

4. Conclusions

Dielectric constants as a function of temperature becomes more diffuse and the peak value of the dielectric constant decrease and more flat when the ratio of Bi/Mn is increased in $BaTiO_3$-based ceramics doped with Bi and Mn. The remanent polarization P_r, coercive field E_c and piezoelectric constant d_{33} of $BaTiO_3$ based ceramics decrease when the amount of Bi increases. The associated defects and the distortion of lattice resulting from doping ions which result in localized random electric field leads to the diffuseness of the transition and the frequency dispersion. The conductivity of $BaTiO_3$ base ceramics doped with Bi/Mn is related with the charged defects from Mn substituting for B site which result in electronic conductivity. As acceptors are completely compensated by the donors, the conductivity would decrease when the mole ratio of Bi/Mn increases.

Acknowledgments

The work was supported by National Natural Science Foundation of China under Grant No. 11074203, Key Disciplinary of Materials Science and Fluid Machine of Sichuan Province under Grant Nos. XZD0814-09-1, SZD0412-08 and the Talents Foundation of Xihua University under Grant No. R0620109.

References

[1] K. Okazaki, S. Kashiwabara, Microstructure and dielectric properties of high permittivity ceramics, Journal of Japanese Ceramic Society 73 (1965) 60–66.

[2] Song xiangyun, Chen daren, Ma litai, Wen shulin, Yin zhiwen, Grain core–grain shell structure and domain based on $BaTiO_3$, Journal of Chinese Ceramic Society 20 (1992) 256–261.

[3] Chang-Hoon Kim, Kum-Jin Park, Yeo-Joo Yoon, et al., Role of yttrium and magnesium in the formation of core–shell structure of $BaTiO_3$ grains in MLCC, Journal of European Ceramic Society 28 (2008) 1213–1219.

[4] D. Hennings, G. Rosenstein, Temperature-stable dielectrics based on chemically inhomogeneous $BaTiO_3$, Journal of American Ceramic Society 67 (1984) 249–254.

[5] G.A. Smolenskii, Physical phenomena in ferroelectrics with diffuse phase transition, Journal of Physical Society of Japan 28 (Supp1.) (1970) 26–37.

[6] N. Setter, L.E. Cross, The role of B-site cation disorder in diffuse phase transition behavior of perovskite ferroelectrics, Journal Applied Physics 51 (1980) 4356–4360.

[7] G. Burns, F.H. Dacol, Ferroelectrics with a glassy polarization phase, Ferroelectrics 104 (1980) 25–35.

[8] V. Westphal, W. Kleemann, M.D. Glinchuk, Diffuse phase transitions and random-field-induced domain states of the 'relaxor' ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$, Physical Review Letters 68 (1992) 847–850.

[9] G. Arlt, N.A. Pertsev, Force constant and effective mass of 90° domain walls in ferroelectric ceramics, Journal of Applied Physics 70 (1991) 2283–2289.

[10] D.K. Lee, H.I. Yoo, K.D. Becker, Nonstoichiometry and defect structure of Mn-doped $BaTiO_{3-\delta}$, Solid State Ionics 154-155 (2002) 189–193.