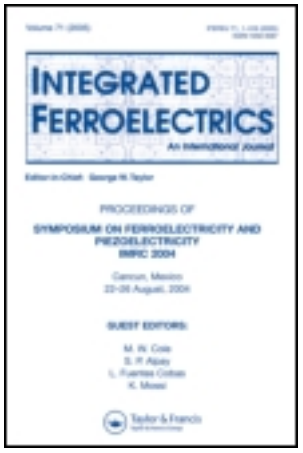

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Piewpan Parjansri [a], Uraiwan Intatha [b], Sukum Eitssayeam [a], Kamonpan Pengpat [a c], Gobwute Rujijanagul [a c] & Tawee Tunkasiri [a c]

[a] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand

[b] School of Science, Mae Fah Luang University, Chiang Rai, 57100, Thailand

[c] Materials Science Research Center, Faculty of Science, Chiang Mai University, 50200, Thailand

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Effects of Mn and Sr Doping on the Electrical Properties of Lead-Free 0.92BCZT-0.08BZT Ceramics

PIEWPAN PARJANSRI,[1] URAIWAN INTATHA,[2] SUKUM EITSSAYEAM,[1,*] KAMONPAN PENGPAT,[1,3] GOBWUTE RUJIJANAGUL,[1,3] AND TAWEE TUNKASIRI[1,3]

[1]Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[2]School of Science, Mae Fah Luang University, Chiang Rai 57100, Thailand
[3]Materials Science Research Center, Faculty of Science, Chiang Mai University, 50200, Thailand

The effects of Mn and Sr doping on the electrical properties of lead-free 0.92[($Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}$)$O_3$]-0.08[($BiZn_{0.5}Ti_{0.5}$)$O_3$] ceramics have been studied. A-site and B-site doping with 0.00–0.05 mol% of $SrCO_3$ and 0–0.25 mol% of MnO_2 was performed. The ceramics were prepared using the solid state reaction technique. The powder was ball-milled for 24 h, then calcined at 1,000°C for 4 h and sintering at 1,300°C for 2 h. Phase formation and microstructure of ceramics were examined using an x-ray diffractometer (XRD) and scanning electron microscopy (SEM). All samples have a single phase of perovskite structure. Grain size and density value were in the range of 3.43–4.07μm and 5.78–5.83 g/cm^3, respectively. The electrical properties of the ceramics were investigated as a function of Mn and Sr doping. It was found that the dielectric constant, activation energy and ac conductivity change with the dopant. Moreover, Mn and Sr doping lead to a decrease of dielectric loss, lower than 0.003 for all samples (at 1 kHz).

Keywords Lead Free Ceramics; Phase Formations; Solid State Reaction; Dielectric Properties; Perovskite Structure

1. Introduction

For many years, $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) was reported to exhibit exceptionally high dielectric and piezoelectric properties. These ceramics are very important for many electronic applications, including multilayer capacitors, sensors, transducers and actuators [1–3]. However, PZT ceramics are not environment friendly because of the toxicity of lead oxide and especially its high vapor during the sintering process at high temperature. Therefore, non-lead base ferroelectric ceramics such as modified $BaTiO_3$ have been widely investigated due to the phase transition temperature of $BaTiO_3$ which can be altered by doping the A-site or B-site [4]. The substitution of Ba^{2+} with Ca^{2+} does not strongly affect the Curie temperature

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*Corresponding author. E-mail: sukum99@yahoo.com

[4, 5]. In the case of doping of $BaTiO_3$ ceramics such as $(Ba_{(1-x)}\text{-}Ca_x)(Ti_{0.9}Zr_{0.1})O_3$, these show excellent dielectric constant and piezoelectric properties [6, 7]. Highest piezoelectric value was observed for a composition of $x \sim 0.15$ [6, 7]. Moreover, lead-free BCZT doped with Ho, CeO_2 or Pr_2O_3 improved the electrical properties [8–10].

The development of new lead free bismuth ferroelectric materials, e.g., $Bi(Zn^{2+}, Ti^{4+})O_3$ have been widely investigated experimentally [11, 12]. Because of the relative small size of Bi^{3+}, $Bi(M)O_3$ (where M is: Fe^{3+}, Sc^{3+}, $Ni_{1/2}Ti_{1/2}$, $Zn_{1/2}Ti_{1/2}$, etc.) compounds are not stable in the perovskite form. However, the smaller tolerance factor and the highly polarizable Bi^{+3} ion can enhance the transition temperature in BZT-containing solid solutions with $PbTiO_3$, $BaTiO_3$ or $Bi_{1/2}K_{1/2}TiO_3$ and show clearly relaxor ferroelectric behavior with increasing BZT content [11, 12]. However, doping of ABO_3-BZT ceramics has not been investigated. Previously, we studied the (1-x)BCZT-xBZT ceramic systems and found that 0.92BCZT-0.08BZT exhibits the highest density value. Moreover, the doping with MnO_2 has been reported to improve the densification of ceramics [13] and the substitution of $SrCO_3$ in $BaCO_3$ ionic site can improve the dielectric constant of BZT ceramics [14]. In the present work, the effect of $SrCO_3$ and MnO_2 doping on the electrical properties of (1-x)BCZT-xBZT ceramics for the composition of $x = 0.08$ was studied.

2. Experimental

2.1 Materials and Ceramics Preparation

The 0.92BCZT-0.08BZT ceramics doped with x mol% of $SrCO_3$ at the BCZT site and MnO_2 at the BZT site were prepared by using the solid state reaction method with composition of ceramic systems as shown in Table 1. Oxide powders were weighed according to stoichiometric formulae and mixed in ethanol for 24 h using zirconia grinding media. Then the slurry was dried on a hotplate and calcined in crucibles at 1000°C for 4 h. After that, the dried powders were mixed with organic binder (6 wt% PVA). The powders were pressed into cylindrical pellets 10 mm in diameter and 1 mm in thickness isostatically at 1 ton. The pellets were then sintered at 1300°C for 2 h with a heating/cooling rate of 5°C/min after the PVA binder was burned out at 500°C for 1 h.

2.2 Characterization

Phase formation and microstructure of the samples were studied by an X-ray diffraction (XRD) technique and scanning electron microscopy (SEM), respectively. The density of

Table 1
The compositions of BCZT-0.08BZT dope with $SrCO_3$ and MnO_2.

Sample	$SrCO_3$ (%mol)	MnO_2 (mol%)
M1	0.00	0.00
M2	0.01	0.05
M3	0.02	0.10
M4	0.03	0.15
M5	0.04	0.20
M6	0.05	0.25

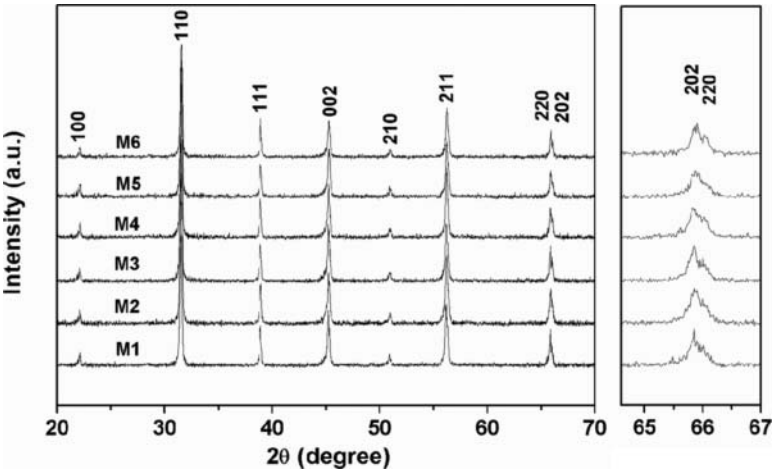

Figure 1. XRD diffraction patterns of the sintered ceramics.

sintered samples was determined by Archimedes method with distilled water as the fluid medium. For electrical properties characterization, the sintered samples were ground to obtain parallel faces, and the faces then coated with silver as electrodes. The dielectric properties of the sintered ceramics were measured as a function of frequency and temperature with an automated dielectric measurement system.

3. Result and Discussions

3.1 XRD, SEM and Density Analysis

The X-ray diffraction patterns of the ceramics as a function of mol% Mn and Sr for BCZT-BZT ceramics are illustrated in Fig. 1. It can be seen that the samples exhibited pure perovskite phase for all concentrations. At room temperature, all samples exhibited the rhombohedral phase, observed by single (200) peak at 2θ of 45° and splitting of the (220)/(202) peaks at 2θ of 65-66° [6, 15]. Figure 2 illustrates SEM micrographs of the sintered ceramics. The grain size and density values of the ceramics increased with increasing dopant content for M1–M3 samples, then decreased with dopant content (Table 2). The highest density value and grain size were found for the M3 sample (5.83 g/cm^3

Table 2
The grain size and density of Mn and Sr doping for BCZT-BZT ceramics.

Sample	Grain size (μm)	Density (g/cm^3)
M1	3.43	5.82
M2	3.75	5.80
M3	4.07	5.83
M4	3.84	5.81
M5	3.95	5.80
M6	3.91	5.78

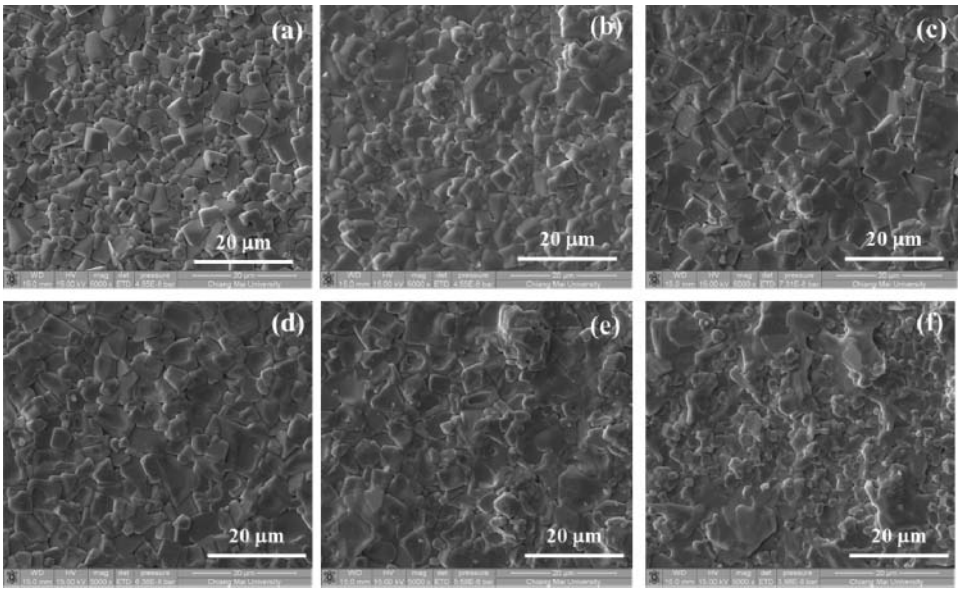

Figure 2. SEM micrograph of surface 0.92BCZT-0.08BZT ceramics: a (M1), b (M2), c (M3), d (M4), e (M5) and f (M6).

and 4.07 μm, respectively). It result suggests that the addition with 0.02 mol% Sr and 0.10 mol% Mn enhanced the density and grain growth of BCZT-BZT ceramics.

3.2 Dielectric Properties Analysis

Figure 3 shows the dielectric constant and dielectric loss of the ceramics as a function of frequency. The dielectric constants decreased with increasing x mol% of MnO_2 and $SrCO_3$ and decreased with increasing frequency for all samples. The dielectric loss for ceramics in frequency range of 1–100 kHz showed the lowest value less than 0.02.

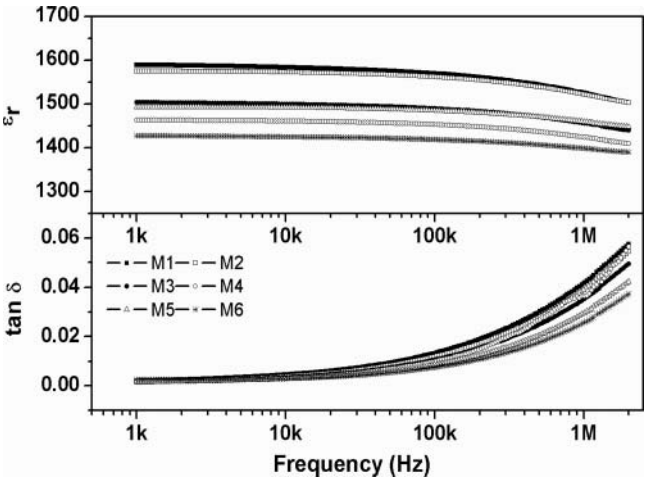

Figure 3. Dielectric constant and dielectric loss as function of frequency at room temperature.

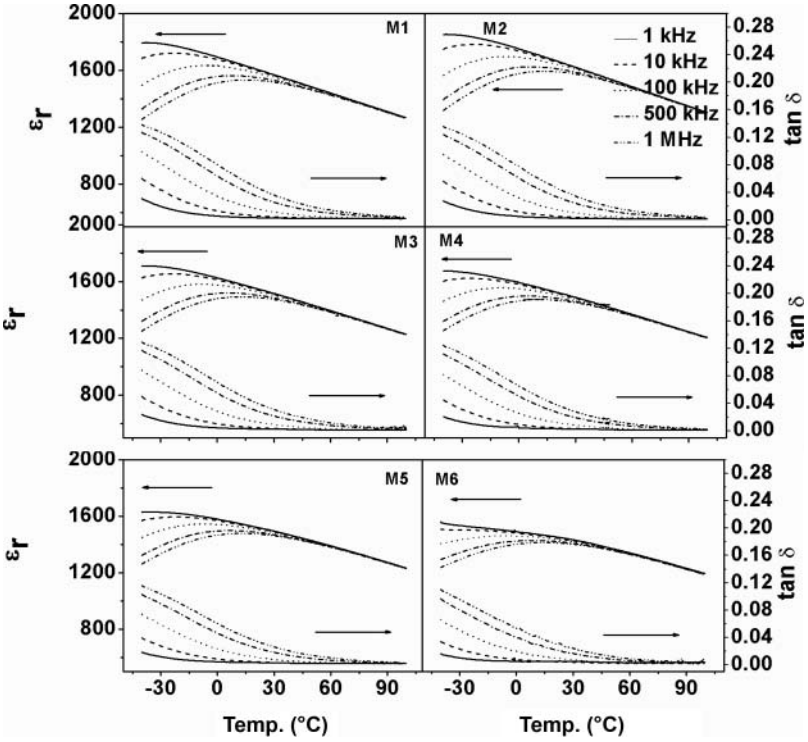

Figure 4. Dielectric constant and dielectric loss as functions of temperature for Mn and Sr dope content for BCZT-BZT ceramics.

Dielectric properties as a function of temperature for mol% Mn and Sr doped for BCZT-BZT ceramics are shown in Fig. 4. It can be seen that the dielectric constant and dielectric loss dependend on the frequency when the temperature is below T_{max} (Curie maximum temperature). These observations suggest a transition from a normal ferroelectric to a relaxor ferroelectric for all conditions of the ceramics. The clear signature of relaxor behavior is observed by a broading in the diffuse phase transition for the Curie maximum temperature (T_{max}) and strong dispersion of the dielectric constant and dielectric loss with frequency [16]. It appears that the dielectric constant at T_{max} tends to decrease with increasing mol% Mn and Sr dopant for BCZT-BZT ceramics. The dielectric loss values gradually decreased with increasing temperature and doping content, with the loss values lower than 0.02 for all samples. It can be noted that Mn and Sr doping decreased the dielectric loss values for BCZT-BZT ceramics. This result may be consistent with a decrease of defects in the structure of ceramics and is considered to be an important factor to change the balance of long range and short range forces which deseribe the relaxor state. Figure 5 illustrates the plot of ln ω ($\omega = 2\pi$f) as a function of $1000/T_m$ of the samples. These values were calculated by the following expression was used to calculate activation energies;

$$f = f_o exp\left(\frac{-E_a}{kT_m}\right) \tag{1}$$

where f_0 is the pre-exponential factor, E_a is the activation energy for the relaxation, k is Boltzmann's constant, f is the applied frequency and T_m is the temperature where the

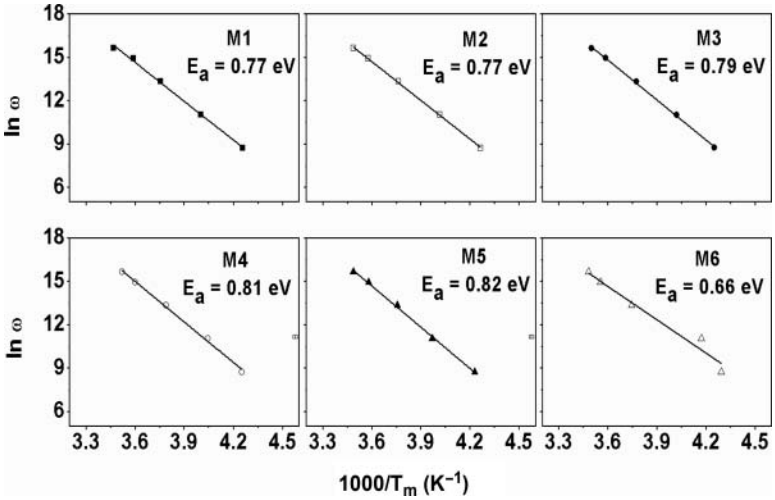

Figure 5. Plot of ln (ω) as a function of $1000/T_m$ for the sample of BCZT-BZT ceramic dope with mol% Mn and Sr (symbols: experimental data; solid line: Eq. 1 fits).

dielectric constant is the maximum. The activation energy can be considered to be typical of a hopping process of localized charge carriers [17, 18]. From Fig. 5 it can be observed that the activation energy increases with increasing mol% Mn and Sr doped BCZT-BZT samples for compositions of M1-M5 samples ($E_a = 0.77$–0.82 eV). Thus, it should be noted that the charge carrier hopping between ions in the structure of BCZT-BZT ceramics increases with increasing ion substitution. Further, the increase in E_a with dopant concentration is similar to work done by Wu et al. [19]. Moreover, these activation energies help support the description of relaxor behavior of dielectric materials.

The ac conductivity (σ_{ac}) of BCZT-BZT doped with mol% Mn and Sr was measured at room temperature and is shown in Fig. 6. The ac conductivity (σ_{ac}) can be defined as

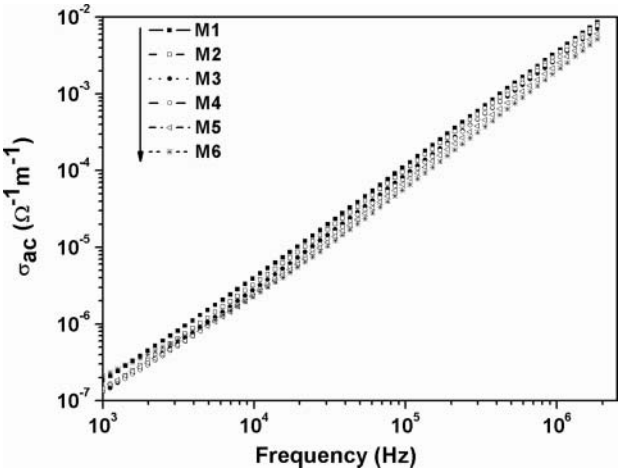

Figure 6. The plot of log ac conductivity with log frequency of mol% Mn and Sr dope for BCZT-BZT ceramics.

following equation:

$$\sigma_{ac} = \omega \varepsilon_r \varepsilon_o \tan \delta \quad (2)$$

where ω is angular frequency ($\omega = 2\pi f$), f is frequency, ε_o and ε_r are the permittivity of vacuum and dielectric constant and tan δ is dielectric loss, respectively. The ac conductivity shows great frequency dependence as observed from the sloped line of σ_{ac} with increasing frequency. The σ_{ac} values tend to increase with increasing frequency. Note that increasing σ_{ac} values correspond to decreasing resistance. The dependence of ac conductivity with frequency is a mechanism for the low temperature region which results from charge carriers, space-charge polarization in structure or with extrinsic dipoles of impurities [20, 21]. Moreover, the σ_{ac} decreased with increasing dopant content. This might be caused from the presence of defects or impurities in the ceramics.

3. Conclusions

In the present work, we report the effects of Mn and Sr doping on the electrical properties of lead-free (1-x)BCZT-xBZT ceramics. The ceramics were prepared via a solid state reaction method. XRD patterns showed pure perovskite phase for all conditions. Highest density was obtained for the M3 (0.02 mol% Sr and 0.10 mol% Mn) sample with a value of 5.83 g/cm^3. BCZT-BZT doped with Mn and Sr lead to a decrease of dielectric loss, lower than 0.003 for all samples (at 1 kHz). The dielectric constant, dielectric loss, activation energy and ac conductivity change with the dopant concentrations.

Acknowledgments

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