HNUE JOURNAL OF SCIENCEDOI: 10.18173/2354-1059.2022-0024Natural Sciences 2022, Volume 67, Issue 2, pp. 76-85This paper is available online at http://stdb.hnue.edu.vn

STRUCTURAL, FERROELECTRIC AND ELECTRICAL-FIELD-INDUCED PIEZOELECTRIC PROPERTIES OF PbTiO₃-MODIFIED COMPLEX 0.5Ba(Zr0.2Ti0.8)O₃-0.5(Ba0.7Ca0.3)TiO₃ MATERIALS

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Abstract. Complex ferroelectric PbTiO₃-modified 0.5Ba(Zr_{0.2}Ti_{0.8})O₃-0.5(Ba_{0.7}Ca_{0.3})TiO₃ materials were synthesized by a conventional solid-state reaction method. The addition of PbTiO₃ into host 0.5Ba(Zr_{0.2}Ti_{0.8})O₃-0.5(Ba_{0.7}Ca_{0.3})TiO₃ materials are modified the ferroelectric properties of host materials where the maximum polarization slightly increased from 23.09 μ C/cm² to 23.28 μ C/cm² and the remnant polarization is found to increase from 10.07 μ C/cm² to 11.31 μ C/cm². The large piezoelectric dynamic coefficient value of 662 pm/V is obtained for 7 mol. % PbTiO₃ modified 0.5Ba(Zr_{0.2}Ti_{0.8})O₃-0.5(Ba_{0.7}Ca_{0.3})TiO₃ compounds as solid solution. Our work is expected to contribute to the role of *A*-site modification in lead-free ferroelectric BaTiO₃-based materials for advanced function materials for electronic device applications.

Keyworks: Ba(Ti_{0.8}Zr_{0.2})TiO₃, (Ba_{0.7}Ca_{0.3})TiO₃, PbTiO₃, lead-free piezoelectric, lead-based piezoelectric.

1. Introduction

The piezoelectricity effect was first discovered in 1880 by J. Curie and P. Curie [1]. The ferroelectric hysteresis loops were reported by J. Valasek in 1921 while studying the polarization dependence of the electric field of Rochelle Salt-type (KNaC₄H₄O₆.4H₂O) materials and dihydrogen phosphates [2]. The first application of piezoelectric materials was produced from quartz for acoustic transducers in 1917 by Langevin, while Rutherford improved hydrophone's performance using piezoelectricity [3].

Received October 28, 2021. Revised January 14, 2022. Accepted January 21, 2022. Contact Dang Duc Dung, e-mail address: dung.dangduc@hust.edu.vn

However, the piezoelectric and ferroelectric behaviors of Rochelle salt and dihydrogen phosphate materials were small, preventing their application in electronic devices. Since the discovery of large piezoelectric in BaTiO₃ and then Pb(Zr,Ti)O₃ ceramics materials facilitated a step-change in piezoelectric technology from the 1960s until the early 2000s, a wide range of applications was used for sensing and actuating [4-6]. Ferroelectricity was discovered in 1921; however, the origin of ferroelectric ordering in ferroelectric materials is complex and strongly dependent on the crystal structural symmetry, composition materials, nature of bonding, defects chemistry, etc. Grindlay et al. reported that the postulate of a dipolar hydrogen lattice O-H-O bonding leads to qualitative ferroelectric behavior of the isomorphous potassium dihydrogen phosphate (KDP) materials [7]. Cohen et al. predicted that the hybridization between titanium 3d states and oxygen 2p states is essential for ferroelectricity in perovskite oxides [8]. However, the hybridization between lead and oxygen in PbTiO₃ materials leads to a large strain that stabilizes the tetragonal phase. In contrast, the interaction between barium and oxygen is completely ionic, favoring a rhombohedral structure in BaTiO₃ [8]. In addition, Turik et al. point out that in perovskite ABO₃ materials, the A-O bond is possibly connected to an increase in the covalence of the B-O bond [9]. Herein, we needed to note that in the perovskite ferroelectric ABO₃ materials, the B-O bonds have a mixed ionic-covalence nature, whereas the A-O bonds are close to pure ionic ones [10, 11]. Understanding the original ferroelectric ordering in lead-free ferroelectric materials was important to extend the functionality of their materials [12]. Therefore, the observation of ferroelectricity of materials was a very complex source. In other words, understanding the role of bonding in ferroelectric ABO₃ materials is a critical key to archive high-performance ferroelectric and piezoelectric properties for device applications.

Giant piezoelectric coefficient d_{33} of about 620 pC/N was reported in complex binary Ba(Ti_{0.8}Zr_{0.2})TiO₃-(Ba_{0.7}Ca_{0.3})TiO₃ systems fabricated by Liu et al. in 2009, which opened a new direction in researching lead-free ferroelectric materials [13]. of $(1-x)Ba(Ti_{0.8}Zr_{0.2})TiO_3 + x(Ba_{0.7}Ca_{0.3})TiO_3$ Especially, а single-crystal at morphotropic phase boundary with x~0.5 reached giant d_{33} values of 1500 - 2000 pC/N and the dynamic piezoelectric coefficient of 1100 pm/V at 0.5 kV/mm, larger than that of Pb-based system with d_{33} of 300-600 pC/N [13]. Acosta *et al.* suggested that the existence of a triple point or general phase convergence regions did not induce high electromechanical properties observed in complex Ba(Ti_{0.8}Zr_{0.2})TiO₃-(Ba_{0.7}Ca_{0.3})TiO₃ systems, based on the relationship between structural, dynamic piezoelectric, and ferroelectric properties [14]. Instead, Acosta et al. suggested that the achievement of large piezoelectric coefficients occurred at ferroelectric-ferroelectric phase transitions and was rather small at the phase convergence region [14]. Therefore, phase-transition controlling was suggested to be a key factor in enhancing the ferroelectric behaviors of novel advanced ferroelectric materials. At room temperature, crystal symmetry of complex $(1-x)Ba(Ti_{0.8}Zr_{0.2})TiO_3+x(Ba_{0.7}Ca_{0.3})TiO_3$ materials was dependent on the composition where the rhombohedral symmetry was stable for x < 0.5 and tetragonal for x > 0.5 and morphotropic phase existed only in narrow composition x ≈ 0.5 [14, 15]. In addition, the lead-based ferroelectric PbTiO₃ materials exhibited a tetragonal structure at room temperature [8]. Therefore, the idea of this work is to make solid solutions

between the morphotropic phase boundary of $0.5Ba(Ti_{0.8}Zr_{0.2})TiO_3$ - $0.5(Ba_{0.7}Ca_{0.3})TiO_3$ with PbTiO₃ materials and to investigate further the relation of Pb-substitution at complex *A*-sites on the ferroelectric and piezoelectric properties of the (Ba,Ca)(Zr,Ti)O_3 materials.

In this work, PbTiO₃-modified complex [0.5Ba(Ti_{0.8}Zr_{0.2})TiO₃-0.5(Ba_{0.7}Ca_{0.3})TiO₃] materials are synthesized by a solid state reaction method. A large dynamic piezoelectric coefficient of 662 pm/V are obtained for the sample with 7 mol.% PbTO₃. The maximum polarization of [0.5Ba(Ti_{0.8}Zr_{0.2})TiO₃-0.5(Ba_{0.7}Ca_{0.3})TiO₃] compounds is found to increase from 23.09 μ C/cm² to 23.28 μ C/cm² for slight PbTiO₃ addition of 0.5 mol.%. The coefficient electric field values are decreased from 4.16 kV/cm to 3.88 kV/cm.

2. Content

2.1. Experiments

Complex $[0.5Ba(Ti_{0.8}Zr_{0.2})TiO_3-0.5(Ba_{0.7}Ca_{0.3})TiO_3]$ compounds and binary $(1-x)[0.5Ba(Ti_{0.8}Zr_{0.2})TiO_3-0.5(Ba_{0.7}Ca_{0.3})TiO_3]+xPbTiO_3$ (x = 0.5, 1, 3, 5, 7, and 9%) compounds (named as BTO55 and BTO55-xPTO, respectively) are synthesized by a conventional ceramic method. Analytical-grade metal oxides or carbonate powders: BaCO_3, ZrO_2, TiO_2, CaCO_3, and PbO are used as received. Firstly, the raw materials are dried in an oven at 80°C for water to evaporate for one day. Thus, all powders with suitable amounts are mixed by ball milling in alcohol using zirconia balls for 24 hrs. After calcinating at 1100°C for 8 hrs in the air, the samples are ball-milled once again for 24 hrs and then dried. After drying, the mixtures are ground and mixed with 5 wt.% polyvinyl alcohol as a binder, pressed into pellets under 98 - 110 MPa. The resultant pellets are finally sintered at 1350°C for 6 hrs in the air and naturally cooled to room temperature.



Figure 1. The fabrication processes for the BTO55 and BTO55-xPTO compounds

For electrical and electric-induced strain measurements, the disk samples were polished then cleaned with an ultrasonic cleaner under acetone for 10 min. The silver paste is used to cover both sides of each disk. The samples are annealed for 30 min at 800 °C in the air for Ag to diffuse to cover the surface. The fabrication processes are summarized in Figure 1. The phase present in the BTO55 and BTO55-xPTO compounds is studied by X-ray diffraction spectroscopy (XRD, Brucker D8 Advance). The electrical polarization and electrical-field-induced strain measurements (Radiant Precision LC II and Radiant Heated 230°C-HB-PTB) are performed on all samples at room temperature.

2.2. Results and discussions

The crystal structure of the pure BTO55 and PTO-modified BTO55 compounds as a function of PTO concentrations is studied by the X-ray diffraction method. Figure 2(a) shows the X-ray diffraction pattern of the pure BTO55 and PTO-modified BTO55 materials with PTO concentrations from 0.5 to 9 mol.%. The X-ray diffraction peaks of the pure BTO55 are indexed as a single perovskite structure with polycrystalline. In addition, no impurity peak is found in the X-ray diffraction spectrum of the pure BTO55 sample. These results are well consistent with recent reports on the crystal structure of Ca^{2+} and Zr^{4+} co-modified BaTiO₃ lattice as the formation of complex Ba(Ti_{0.8}Zr_{0.2})TiO₃-(Ba_{0.7}Ca_{0.3})TiO₃ stable solid solutions [13-15]. Furthermore, the magnified XRD patterns in the 20 angle of $44.0^{\circ}-46.5^{\circ}$, and $65.0^{\circ}-67.0^{\circ}$ are shown in Figures 2(b) and (c), respectively. The unsymmetric broadening of diffraction peaks is suggested to be originated from the overlapping of a couple of peaks. Each diffraction peak is distinguished by using Lorentzian fitting with an r-square higher than 0.99, as shown in red and blue in Figures 2(b) and (c). Based on the achievement of X-ray diffraction angle peaks and relative intensity, the peaks are indexed as a satellite of couple (002)/(200) and (202)/(220) peaks. The observation in satellite diffraction (002)/(200) peaks around 45.2° and (202)/(220) peaks around 65.9° further confirms the co-existence of tetragonal and rhombohedral structures, respectively. This result is consistent with recent reports on crystal structural symmetry of complex $Ba(Ti_{0.8}Zr_{0.2})TiO_3$ -($Ba_{0.7}Ca_{0.3}$)TiO_3 system [16, 17]. In other words, the X-ray diffraction study of the crystal structure of BTO55 compounds exhibits that the morphotropic phase boundary existed in their composition. The X-ray diffraction spectra of PTO-modified BTO55 materials are shown in Figure 2(a). The number of diffraction peaks of PTO-modified BTO55 materials is similar to diffraction peaks of host BTO55 materials as increasing the PTO concentration up to 9 mol.%. No extra diffraction peak is observed for PTO-modified BTO55 materials with PTO amounts increasing up to 9 mol.%. No trade phase or phase separation could be found in the X-ray diffraction patterns, suggesting that PTO materials were well solid solute into the host BTO55 crystal. The influence of the PTO phase on host BTO55 crystal as a function of PTO concentrations is shown in Figures 2(b) and (c). The results exhibit that the satellite (002)/(200) and (202)/(220) diffraction peaks of host BTO55 materials shifted to higher diffraction angles as increasing the PTO amounts, indicating that the lattice constant of BTO55 materials is compressed. However, the fitting results provided that the complex distortion is obtained for couple (002)/(200) and (202)/(220)

diffraction peaks, as shown in Figures 2(b) and (c). The results are possibly explained by the size difference of Pb^{2+} cations and the host Ba^{2+} and Ca^{2+} cations in the PTO-BTO55 crystal solid solutions. Based on the survey radius size of cations in the chemical compounds by Shannon, the size of Ba^{2+} , Ca^{2+} , and Pb^{2+} cations at coordination of XII were 1.61 Å, 1.34 Å, and 1.49 Å, respectively [18]. Thus, Ba²⁺ larger than Pb^{2+} cations, while Ca^{2+} cations are about 11.2% cations are about 7.4% smaller than Pb²⁺ cations. Therefore, the random incorporation of Pb²⁺ cations for Ba²⁺site results in compression of the lattice parameters, while the contrast of lattice distortion is exhibited for Pb^{2+} cations replaced for Ca^{2+} -sites. As a result, the complex lattice distortion of the BTO55 compound is expected to be obtained as a function of PTO concentrations during the formation of solid solutions. At this moment, the origin of the lattice distortion is needed further investigation. However, the observed shift of diffraction peaks of BTO55 compounds as a function of PTO addition is further evidence for the random distribution of Pb^{2+} cations into the host BTO55 lattice during the formation of solid solutions.



Figure 2. (a) The X-ray diffraction spectra of BTO55 and PTO-modified BTO55 with various PTO concentrations, and the enlarged the X-ray diffraction pattern of diffraction 2θangle from (b) 44.0°- 46.5° and (c) 65.0°- 67.0° for satellite (002)/(200) and (202)/(220), respectively

The influence of PTO amounts on the ferroelectric properties of host BTO55 materials is characterized by electrical-polarization measurements. Figures 3 (a)-(g) showed the polarization versus electric field (P-E) hysteresis loops at room temperature for pure BTO55 materials and PTO-modified BTO55 materials with various PTO concentrations. The inset of each figure showed the enlarged P-E curve at a low applied electric field, showing clear, typical ferroelectric properties for all samples. Pure BTO55 materials have the maxima polarization ($P_{\rm m}$) of 23.09 µC/cm². The observed results are consistent with $P_{\rm m}$ values of 17.0-17.9 µC/cm² reported in the literature [13, 16, 19]. In addition, the remanent polarization ($P_{\rm r}$) and coercive field ($E_{\rm C}$) of pure BTO55 samples are estimated at around 10.07 µC/cm² and 4.16 kV/cm, respectively. The results were 80

also well consistent with recent reports for P_r and E_c values in complex system Ba(Ti_{0.8}Zr_{0.2})TiO₃-(Ba_{0.7}Ca_{0.3})TiO₃ at the morphotropic phase boundary [13, 16, 19]. The addition of PTO with 0.5 mol.% into host BTO55 compounds almost remained the P_m values of 23.28 μ C/cm² while both P_r and E_c are reduced to 9.87 μ C/cm² and 3.88 kV/cm. Both P_m and P_r values of BTO55 materials are reduced as further increasing the PTO amounts up to 5 mol.% with the smallest P_m , and P_r values of about 14.42 μ C/cm² and 4.69 μ C/cm², respectively. Further addition of PTO amounts up to 9 mol.% into host BTO55 compounds resulted in complex observation in both P_m and P_r values. The detail of P_m , P_r and E_c values are listed in Table 1.



Figure 3. The P-E hysteresis loops at room temperature of (a) the pure BTO46 and PTO-modified BTO46 materials with (b) 0.5 mol.%, (c) 1 mol.%, (d) 3 mol.%, (e) 5 mol.%, (f) 7 mol.% and (g) 9 mol.% PTO as solid solutions.

The inset of each figure shows the magnified P-E curves at a low applied electric field

The electrical field-induced strain of BTO55 compounds as a function of PTO concentration is measured at room temperature with the maximum applied electric field strength of 50 kV/cm. Figures 4 (a)-(g) show the unipolar strain of pure BTO55 and PTO-modified BTO55 compounds with 0.5, 1, 3, 5, 7, and 9 mol.% PTO addition, respectively. The maximum strain S_{max} of 0.145% is obtained for the pure BTO55, corresponding to the dynamic piezoelectric coefficient (S_{max}/E_{max}) of 290 pm/V. The addition of PTO into host BTO55 compounds enhances S_{max} value up to 0.331% for 7 mol.% PTO and further decreased to 0.234% as increasing PTO amounts up to 9 mol.%. The maximum S_{max}/E_{max} value is calculated around 662 pm/V in the BTO557 sample with 7-mol.% PTO-addition. The results exhibited a significant enhancement of the dynamic coefficient of BTO55 compounds via PTO modification. The detailed S_{max} and S_{max}/E_{max} values of BTO55 compounds as a function of PTO concentrations are presented in Table 1.

Furthermore, the bipolar strain hysteresis loops of BTO55 and PTO-modified BTO55 compounds are measured at room temperature with a maximum applied electric field of 50 kV/cm. The maximum positive strain (S_{pmax}) and maximum negative strain (S_{nmax}) of pure BTO55 materials are about 0.148% and -0.028%, respectively. The observation of negative strain in bipolar strain further well confirmed the nature

ferroelectric state of BTO50 compounds. The S_{pmax} value of 0.148% in the BTO55 sample deduced from the bipolar strain hysteresis loop is consistent with the estimated S_{max} value of 0.145% from the unipolar strain hysteresis loop, as shown in Figure 4(a). The S_{pmax} values of BTO55 materials were increased from 0.148% to 0.324% for PTO-modified BTO55 compound with 7 mol.% PTO while further addition of PTO amounts up to 9 mol.% resulted in reducing S_{pmax} values to 0.218%.



Figure 4. Unipolar strain hysteresis loops of (a) the pure BTO46 and PTO-modified BTO46 materials with (b) 0.5 mol.%, (c) 1 mol.%, (d) 3 mol.%, (e) 5 mol.%, (f) 7 mol.% and 9 mol.% PTO as solid solutions



Figure 5. Bipolar strain hysteresis loops of (a) pure BTO55 materials and PTOmodified BTO55 materials with (b) 0.5 mol.%, (c) 1 mol.%, (d) 3 mol.%, (e) 5 mol.%, (f) 7 mol.% and 9 mol.% PTO addition as solid solution

The negative strain in all PTO-modified BTO55 materials in the wide range from 0.5 mol.% to 9 mol.% further confirmed the ferroelectric state of PTO-modified BTO55 materials. The dynamic piezoelectric coefficient of 296 pm/V calculated from bipolar strain hysteresis loops (S_{pmax}/E_{max}) is consistent with the observed unipolar strain of 290 pm/V. The S_{pmax}/E_{max} values start to increase up to 648 pm/V for 7 mol.% PTO-modified BTO55 compounds as solid solutions. The S_{pmax}/E_{max} values are further reduced to 436 pm/V for 9-mol.% PTO addition into the host BTO55. The detail of

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 S_{pmax} , S_{nmax} , and $S_{\text{pmax}}/E_{\text{max}}$ values as a function of PTO concentrations are listed in Table 2. The observation in the enhancement of electric-field-induced strain in host lead-free ferroelectric $0.5Ba(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{TiO}_3$ - $0.5(Ba_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ materials is possibly related to the complex distortion of crystal structure during random incorporation of Pb cations into host crystal [20, 21].

No	Sample name	$\frac{P_m}{(\mu C/cm^2)}$	$\frac{P_r}{(\mu C/cm^2)}$	E _c (kV/cm)	S _{max} (%)	S _{max} /E _{max} (pm/V)
1	BTO55	23.09	10.07	4.16	0.145	290
2	BTO55- 0.5PTO	23.28	9.87	3.88	0.148	296
3	BTO55-1PTO	21.43	9.42	4.14	0.196	392
4	BTO55-3PTO	18.91	8.12	4.91	0.226	452
5	BTO55-5PTO	14.42	4.69	4.12	0.286	572
6	BTO55-7PTO	17.76	11.31	7.18	0.331	662
7	BTO55-9PTO	18.12	9.27	6.62	0.234	468

Table 1. The Pm, Pr, EC, Smax, and Smax/Emax values of the BTO46 and PTO-modifiedBTO46 solid solutions with various PTO concentrations

Table 2. The Spmax, Snmax, and Spmax/Emax values of the BTO55 and PTO-modifiedBTO55 as solid solutions with various PTO amounts

No	Sample name	S _{pmax} (%)	S _{nmax} (%)	S _{pmax} /E _{max} (pm/V)
1	BTO55	0.148	-0.028	296
2	BTO55-0.5PTO	0.193	-0.046	386
3	BTO55-1PTO	0.197	-0.043	394
4	BTO55-3PTO	0.221	-0.032	442
5	BTO55-5PTO	0.317	-0.011	634
6	BTO55-7PTO	0.324	-0.047	648
7	BTO55-9PTO	0.218	-0.032	436

3. Conclusions

The PbTiO₃-modified complex ferroelectric $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ - $0.5(Ba_{0.7}Ca_{0.3})TiO_3$ materials are fabricated by the solid-state reaction method. PTO is found to well solid solute into the host $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ - $0.5(Ba_{0.7}Ca_{0.3})TiO_3$, resulting in stable morphotropic phase boundary with both tetragonal and rhombohedral symmetries. The ferroelectricity properties exhibited for PbTiO₃-modified $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ - $0.5(Ba_{0.7}Ca_{0.3})TiO_3$ materials in wide range PbTiO₃ addition from 0.5 mol.% to 9 mol.%. The ferroelectric properties of host $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ - $0.5(Ba_{0.7}Ca_{0.3})TiO_3$ materials

were shown to modify via random incorporation of Pb^{2+} cations into host lattice of $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ - $0.5(Ba_{0.7}Ca_{0.3})TiO_3$ crystal. The PbTiO_3 addition into host $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ - $0.5(Ba_{0.7}Ca_{0.3})TiO_3$ materials was found to increase the piezoelectric dynamic coefficient value up to 662 pm/V for 7 mol. % PbTiO_3 addition as solid solutions. Our work is expected to contribute to the role of A-site modification in lead-free ferroelectric BaTiO_3-based materials for advancing the function materials for electronic device applications.

Acknowledgments. We would like to acknowledge the financial support from the Ministry of Science and Technology, Vietnam, under project number DTDLCN.29/18.

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