

# Complex structure change of Pb-site doping $\text{PbMTiNb}_2\text{O}_8$ (M=Ba, Ca, Zn, Co, Ni) piezoelectric ceramics for energy harvester

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**Abstract.**  $\text{PbTiNb}_2\text{O}_8$  is a new piezoelectric ceramic that satisfy applications of energy harvesters. Complex structure change and dipole relaxation of Pb-site doping  $\text{PbTiNb}_2\text{O}_8$  piezoelectric ceramics were investigated. The synchrotron radiation study results show that with 5mol% divalent cation substitution to Pb-site brings the various structure changes. Zn and Ni doping bring the centrosymmetry secondary phase, and affect the performance greatly. The dielectric spectroscopy of polarized and unpolarized samples in the frequency range of 50Hz~100MHz were studied. The dipole relaxation of  $\text{Pb}_{0.95}\text{M}_{0.05}\text{TiNb}_2\text{O}_8$  ceramics occurred at around 107Hz, and the dipole resonant frequency (the first highest peak of spectroscopy) of polarized sample is lower than the unpolarized sample.

## Introduction

Energy harvesting has experienced significant growth over the past few years due to the ever-increasing desire to produce portable and wireless electronics with extended lifespans. The energy scavenging devices are designed to capture the ambient energy surrounding the electronics and convert it into usable electrical energy. A number of sources of harvestable ambient energy exist, including waste heat, vibration, electromagnetic waves, wind, flowing water, and solar energy. Piezoelectric ceramics can be configured in many different ways that prove useful in power harvesting application.  $\text{PbTiNb}_2\text{O}_8$  were reported as low dielectric constant and low dielectric loss ceramic material [1]. The  $\text{PbTiNb}_2\text{O}_8$  composited by  $\text{PbTiO}_3$  and  $\text{PbNb}_2\text{O}_6$  shows space group of  $\text{Am} \bar{2}$  with large lattice and large number of atoms per unit cell (Z). The complex crystal structure with highly ordered cation has highly structure change possibility. Study the crystal structure and crystal structure change of  $\text{PbTiNb}_2\text{O}_8$  is important to its mechanism root of electrical property research and also important to mechanism root of electrical property research for Perovskite and Tungsten Bronze. The piezoelectric effect [2] is closely related to the occurrence of dipole moments. Dielectric spectroscopy [3,4] measures the dielectric properties as a function of frequency which based on the interaction of external field with the dipole moment, often expressed by permittivity. The study of dipole relaxation which occurred around 104~ 108 Hz via dielectric spectroscopy is important to the further research on the nature of piezoelectric effect in  $\text{PbTiNb}_2\text{O}_8$  systems. In this paper, we plan to study the contribution of Pb-site to crystal structure or electrical properties of  $\text{PbTiNb}_2\text{O}_8$  piezoelectric ceramic, and pick five of different ionic radius divalent cations to substitute the Pb ion. Crystal structure change, dipole relaxation, piezoelectric properties, and dielectric properties were investigated.

## Experimental section

The research samples with formula of  $\text{Pb}_{0.95}\text{M}_{0.05}\text{TiNb}_2\text{O}_8$  (M=Ba, Ca, Zn, Co, Ni) were prepared by conventional solid-state reaction techniques using high purity (better than 99.9%)  $\text{Pb}_3\text{O}_4$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{BaCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{ZnO}$ ,  $\text{CoO}$ ,  $\text{NiO}$  as the starting materials. They were mixed follow the formula of  $\text{Pb}_{0.95}\text{M}_{0.05}\text{TiNb}_2\text{O}_8$  (M=Ba, Ca, Zn, Co, Ni) and ball-milled using de-ionized water and

zirconia balls for 10h. The dried powders were calcined at 850°C for 2.5h, and then pressed into pellets with 12mm in diameter and 1mm in thickness with addition of appropriate amount PVA (5%). The green bodies were sintered at 1120°C for 3.5h. The powder X-ray diffraction analysis was carried out at the 4B9A beamline at the Beijing synchrotron radiation facility (BSRF) with an X-ray wave length of 0.15406nm. The crystal symmetry and lattice parameters of all samples were determined by ab initio and Rietveld refinement [5]. The ceramic pellets for electrical characterization were polished and coated with Ag electrodes, and then were poled at ~ 120 °C for 20 min under an electric field of ~ 4 kV/mm in a silicone oil bath. The piezoelectric properties were measured after 24 h aging at room temperature. The planar electromechanical coupling factor  $k_p$  and  $Q_m$  were derived by the resonance and anti-resonance method. The piezoelectric constant  $d_{33}$  was measured by a quasistatic piezoelectric ZJ-3D  $d_{33}$  meter produced by Institute of Acoustics, Chinese Academy of Sciences. The dielectric spectroscopy and dielectric properties were measured by Agilent 4294A impedance analyzer.

### Results and Discussions

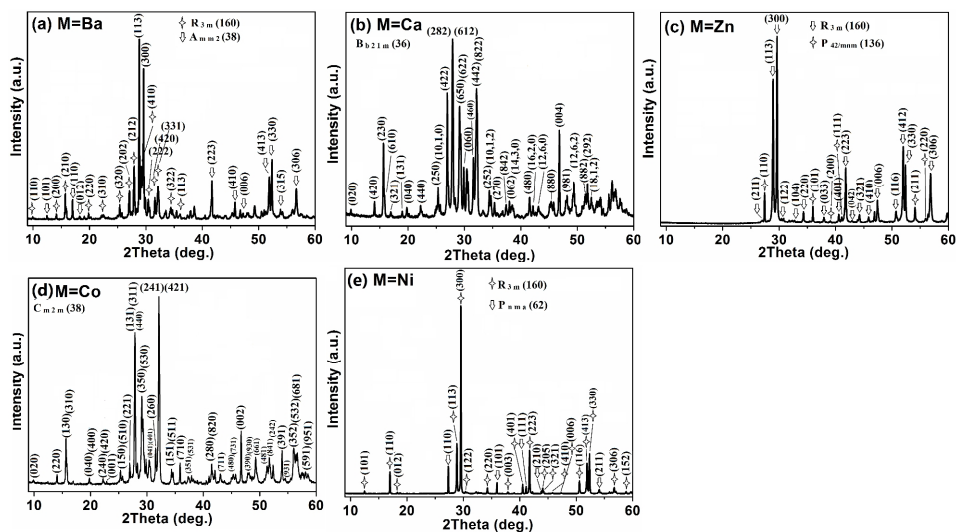


Fig. 1 The synchrotron radiation X-Ray Powder Diffraction patterns of  $Pb_{0.95}M_{0.05}TiNb_2O_8$  ceramics

$\triangle$ $\square$	$R_{Pb} - R_M$	Main Phase	Secondary Phase
M=Ba $R_{ion}=1.75 \text{ \AA}$	0.12	$A_{mm}2 (38)$ $e=7.7711 \text{ \AA}$ $a=b=12.6368 \text{ \AA}$	$R_{3m} (160)$ $e=11.582 \text{ \AA}$ $a=b=10.4700 \text{ \AA}$
M=Ca $R_{ion}=1.48 \text{ \AA}$	0.15	$B_{b21m} (36)$ $e=7.7518 \text{ \AA}$ $a=35.3007 \text{ \AA}$ $b=17.9229 \text{ \AA}$	
M=Zn $R_{ion}=104 \text{ \AA}$	0.59	$R_{3m} (160)$ $e=11.5961 \text{ \AA}$ $a=b=10.4547 \text{ \AA}$	$P_{42/mmm} (136)$ $e=2.9675 \text{ \AA}$ $a=b=4.6116 \text{ \AA}$
M=Co $R_{ion}=104 \text{ \AA}$	0.59	$C_{m2m} (38)$ $e=3.8845 \text{ \AA}$ $a=17.6869 \text{ \AA}$ $b=17.9519 \text{ \AA}$	
M=Ni $R_{ion}=83 \text{ \AA}$	0.80	$R_{3m} (160)$ $e=11.5218 \text{ \AA}$ $a=b=10.4727 \text{ \AA}$	$P_{nma} (62)$ $e=5.379 \text{ \AA}$ $a=5.4772 \text{ \AA}$ $b=7.6349 \text{ \AA}$

Fig. 2 The ionic radius, difference between substitution ion and Pb ion, and phase constitutions of each  $Pb_{0.95}M_{0.05}TiNb_2O_8$  system. The lattice parameters of each phase also were shown.

Fig. 1 shows the synchrotron radiation X-Ray Powder Diffraction patterns of  $Pb_{0.95}M_{0.05}TiNb_2O_8$  (a: M=Ba, b: M=Ca, c: M=Zn, d: M=Co, e: M=Ni) ceramics. The phase constitution and phase symmetry of each sample were shown. The main crystal faces of each phase were marked. It can be seen from Fig. 1 that with 5mol% divalent cation substitution to Pb-site, the crystal structure shows various transition. Fig. 2 summarizes the ionic radius, difference between substitution ion and Pb ion,

and phase constitutions of each system. The lattice parameters of each phase also were shown in Fig. 2. The difference between substitution ion and Pb ion  $\Delta$  were defined as follows:  $\Delta=|R_{Pb}-R_M|$ . The  $\Delta$  of  $Pb_{0.95}Ba_{0.05}TiNb_2O_8$ ,  $Pb_{0.95}Ca_{0.05}TiNb_2O_8$ ,  $Pb_{0.95}Zn_{0.05}TiNb_2O_8$ ,  $Pb_{0.95}Co_{0.05}TiNb_2O_8$ ,  $Pb_{0.95}Ni_{0.05}TiNb_2O_8$  was 0.12, 0.15, 0.59, 0.59, 0.80, respectively. The main phase of  $Pb_{0.95}Ba_{0.05}TiNb_2O_8$  shows phase symmetry of  $A_m m 2$  (38), and has the lattice constant of  $a=b=12.6368\text{\AA}$ ,  $c=7.7711\text{\AA}$ . With the substitution of Ba, the part of crystal structure transform to  $R_3 m$  (160) which has the lattice constant of  $a=b=10.4700\text{\AA}$ ,  $c=11.5382\text{\AA}$ .  $Pb_{0.95}Ca_{0.05}TiNb_2O_8$  has the single phase with phase symmetry of  $B_b 2 1 m$  (36) which has the lattice constant of  $a=35.3007\text{\AA}$ ,  $b=17.9229\text{\AA}$ , and  $c=7.7518\text{\AA}$ . It indicated that with substitution of Ca, the phase of  $PbTiNb_2O_8$  transform from  $A_m m 2$  to  $B_b 2 1 m$ . In other words, the crystal structure is more ordered than pure  $PbTiNb_2O_8$ . The main phase of  $Pb_{0.95}Zn_{0.05}TiNb_2O_8$  shows phase symmetry of  $R_3 m$  (160) with lattice constant of  $a=b=10.4547\text{\AA}$ ,  $c=11.5961\text{\AA}$ . It can be noticed that there is a part of crystal structure transform to Rutile  $P_{42/mmm}$  (136) which indicated that a part of crystal structure became disordered.  $Pb_{0.95}Co_{0.05}TiNb_2O_8$  shows the single phase with phase symmetry of  $Cm 2 m$  (38) which has the lattice constant of  $a=17.686\text{\AA}$ ,  $b=17.9519\text{\AA}$ , and  $c=3.8845\text{\AA}$ . It indicated that with substitution of Co, the phase of  $PbTiNb_2O_8$  transform from  $A_m m 2$  to  $Cm 2 m$ . The main phase of  $Pb_{0.95}Ni_{0.05}TiNb_2O_8$  shows phase symmetry of  $R_3 m$  (160) with lattice constant of  $a=b=10.4727\text{\AA}$ ,  $c=11.5218\text{\AA}$ . It can be seen that with substitution of Ni, the main phase transform to  $R_3 m$  (160), and there is also another part of phase transform to disordered  $P_{nm a}$  (62) with lattice constant of  $a=5.4772\text{\AA}$ ,  $b=7.6349\text{\AA}$ , and  $c=5.3793\text{\AA}$ .

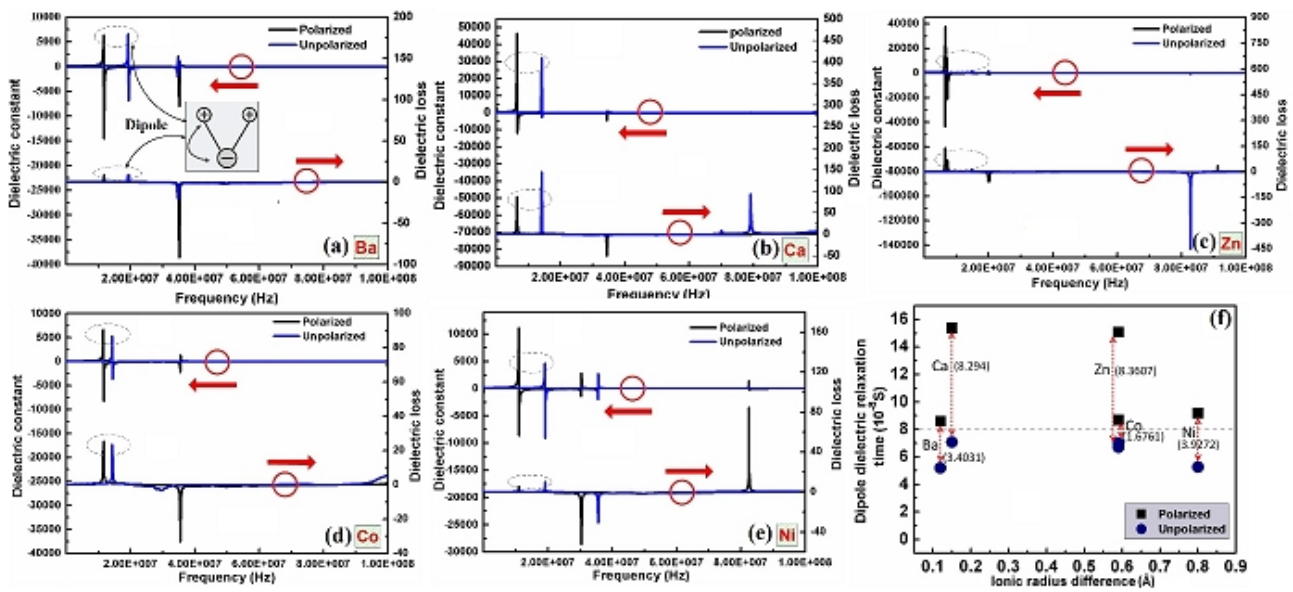


Fig. 3 (a)~(e) The dielectric spectroscopy of the  $Pb_{0.95}M_{0.05}TiNb_2O_8$  ceramics with frequency range of 50Hz~100MHz. (f): The dipole dielectric relaxation time of polarized/unpolarized  $Pb_{0.95}M_{0.05}TiNb_2O_8$  ceramics.

Fig. 3 shows the dielectric spectroscopy and dipole relaxation time of  $Pb_{0.95}M_{0.05}TiNb_2O_8$  (a:  $M=Ba$ , b:  $M=Ca$ , c:  $M=Zn$ , d:  $M=Co$ , e:  $M=Ni$ ) ceramics which frequency range of 50Hz~100MHz. In order to study the influence of polarization on the dipole relaxation, the polarized and unpolarized samples were measured at the same time. It can be seen that the dipole relaxation of  $Pb_{0.95}M_{0.05}TiNb_2O_8$  ceramics occurred at around 107Hz, and the dipole resonant frequency (the first highest peak of spectroscopy) of polarized sample is lower than the unpolarized sample. In some area near the resonance, the value of dielectric property shows negative. It maybe because that the high-variability of impedance near resonance frequency lead to the value which measured by equipment shows negative. The dipole relaxation time was calculated from the first highest peak of spectroscopy and shown in Fig. 3 (f), and the difference value between polarized and unpolarized sample was also shown in the figure. The difference between polarized and unpolarized sample should be correlated to the piezoelectric constant mainly contributed by polarized pole. But it is not shown clearly in this paper, and further research need to focus on this in the future.

Table 1 shows the piezoelectric and dielectric properties of  $\text{Pb}_{0.95}\text{M}_{0.05}\text{TiNb}_2\text{O}_8$  (M=Ba, Ca, Zn, Co, Ni) ceramics at sintering temperature of 1120°C. The  $\text{Pb}_{0.95}\text{Ba}_{0.05}\text{TiNb}_2\text{O}_8$  ceramic has the  $d_{33}$  of 13 pC/N,  $k_p$  of 0.15,  $Q_m$  of 52.2. The  $\text{Pb}_{0.95}\text{Ca}_{0.05}\text{TiNb}_2\text{O}_8$  ceramic has the  $d_{33}$  of 14 pC/N,  $k_p$  of 0.15,  $Q_m$  of 54.7. The  $\text{Pb}_{0.95}\text{Zn}_{0.05}\text{TiNb}_2\text{O}_8$  ceramic has the  $d_{33}$  of 22 pC/N,  $k_p$  of 0.12,  $Q_m$  of 85.7. The

**Table 1** The piezoelectric and dielectric properties of  $\text{Pb}_{0.95}\text{M}_{0.05}\text{TiNb}_2\text{O}_8$  (M=Ba, Ca, Zn, Co, Ni) ceramics

M	$d_{33}$ [pC/N]	$K_p$	$Q_m$	$K_{33}$ *	$\tan\delta$ * [ $10^{-2}$ ]
Ba	13	0.15	52.2	271.8	0.48
Ca	14	0.15	54.7	292.8	0.20
Zn	22	0.12	85.7	220.5	0.14
Co	15	0.17	47.5	299.0	0.33
Ni	23	0.13	80.7	191.7	0.10

\* Poled, measured at 1[kHz]

$\text{Pb}_{0.95}\text{Co}_{0.05}\text{TiNb}_2\text{O}_8$  ceramic has the  $d_{33}$  of 15 pC/N,  $k_p$  of 0.17,  $Q_m$  of 47.5. The  $\text{Pb}_{0.95}\text{Ni}_{0.05}\text{TiNb}_2\text{O}_8$  ceramic has the  $d_{33}$  of 23 pC/N,  $k_p$  of 0.13,  $Q_m$  of 80.7. It can be seen that the ordered non-centrosymmetry crystal structure phase samples have the relatively lower  $d_{33}$ ,  $Q_m$ , and relatively higher  $k_p$  than the samples which has the secondary phase of centrosymmetry phase. The  $K_{33}$  (poled and measured at 1kHz) of  $\text{Pb}_{0.95}\text{M}_{0.05}\text{TiNb}_2\text{O}_8$ , where M=Ba, Ca, Zn, Co, and Ni are 271.8, 292.8, 220.5, 299.0, and 191.7, respectively. The  $\tan\delta$  (poled and measured at 1kHz) of  $\text{Pb}_{0.95}\text{M}_{0.05}\text{TiNb}_2\text{O}_8$ , where M=Ba, Ca, Zn, Co, and Ni are 0.48, 0.20, 0.14, 0.33, and  $0.10 \times 10^{-2}$ , respectively. It indicated that the existence of centrosymmetry phase will lower the  $K_{33}$  and  $\tan\delta$ .

## Conclusions

In summary, crystal structure change and dipole relaxation of  $\text{PbMTiNb}_2\text{O}_8$  (M=Ba, Ca, Zn, Co, Ni) ceramics which for the application of energy harvesting were studied. The synchrotron radiation study results show with 5mol% divalent cation substitution to Pb-site brings the various structure changes. The main phase of  $\text{Pb}_{0.95}\text{Ba}_{0.05}\text{TiNb}_2\text{O}_8$  shows phase symmetry of  $A_{m m 2}$  (38) and the part of crystal structure transform to  $R_{3 m}$  (160). With substitution of Ca, the phase of  $\text{PbTiNb}_2\text{O}_8$  transformed from  $A_{m m 2}$  to  $B_{b 2 1 m}$ . Zn and Ni doping bring the centrosymmetry secondary phase Rutile  $P_{42/mnm}$  (136) and disordered  $P_{n m a}$  (62), respectively. The main phase of both  $\text{Pb}_{0.95}\text{Zn}_{0.05}\text{TiNb}_2\text{O}_8$  and  $\text{Pb}_{0.95}\text{Ni}_{0.05}\text{TiNb}_2\text{O}_8$  are  $R_{3 m}$  (160). With substitution of Co, the phase of  $\text{PbTiNb}_2\text{O}_8$  transformed from  $A_{m m 2}$  to  $C_{m 2 m}$ . The dipole relaxation of  $\text{Pb}_{0.95}\text{M}_{0.05}\text{TiNb}_2\text{O}_8$  ceramics occurred at around 107Hz, and the dipole resonant frequency (the first highest peak of spectroscopy) of polarized sample is lower than the unpolarized sample.

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