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Effects of addition of $Pb(Y_{1/2}Nb_{1/2})O_3$ (PYN) on microstructure and piezoelectric properties of $Pb(Zr_{0.53}Ti_{0.47})O_3$

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Abstract

Pure and $Pb(Y_{1/2}Nb_{1/2})O_3$ (PYN)-doped $Pb(Zr_{0.53}Ti_{0.47})O_3$ have been characterized. The samples were prepared by conventional mixed-oxide ceramic technology. PYN dopant was added to PZT at content levels ranging from 1 to 2.5 mol%. The microstructures of the samples were examined using SEM and TEM. The average grain size was observed to decrease as the dopant content increased. Herringbone-like and wedge-shaped domain patterns were observed in all the samples. The piezoelectric properties of PZT were greatly improved by the addition of PYN. The highest piezoelectric constant d_{31} was nearly twice that of pure PZT.

Keywords: B. Microstructure-final; C. Piezoelectric properties; D. PZT

1. Introduction

Lead zirconate titanate (PZT) solid solutions have achieved wide usage in recent years because of their superior properties [1]. For piezoelectric applications, high relative permittivity values and large piezoelectric effects are necessary. Extraordinary high values are found at the morphotropic phase boundary (MPB) corresponding to the composition $Pb(Zr_{0.53}Ti_{0.47})O_3$ [2]. In addition, dopants are often added to PZT to enhance the piezoelectric properties and to modify the microstructure [3,4].

So far a number of dopants (e.g. Nb^{5+}, La^{3+}, Ta^{5+}, W^{6+}) have been researched to study their effects on the electrical characteristics of PZT [5–8]. Moreover, little work has been initiated to study the combination effect of two or more dopants on the electrical properties of PZT [8–10]. Yoon et al. [8] fabricated a ternary solid solution consisting of $Pb(Zr_{0.53}Ti_{0.47})O_3$ and the complex perovskite type compound $Pb(Y_{2/3}W_{1/3})O_3$, and observed that piezoelectric properties were enhanced for the sample doped with 2 mol% $Pb(Y_{2/3}W_{1/3})O_3$. The $Pb(Y_{1/2}Nb_{1/2})O_3$ (PYN) dopant is therefore an interesting dopant to be studied, since Nb_2O_5 and Y_2O_3 are often used as dopants in PZT to improve electrical properties [5,11]. In this work, PZT doped with PYN in a composition range of 0–2.5 mol% are prepared to study the effects of PYN doping on the piezoelectric properties and microstructures of PZT.

2. Experimental methods

Chemical composition selected for this study was $Pb(Zr_{0.53}Ti_{0.47})O_3$, and various quantities of $Pb(Y_{1/2}Nb_{1/2})O_3$ (1, 1.5, 2, and 2.5 mol%) were added into the composition as dopants. The starting materials were reagent grade PbO, ZrO_2, TiO_2, Y_2O_3, and Nb_2O_5. They were mixed according to the selected compositions and then wet ball-milled for 24 h in ethyl alcohol, followed by drying in oven for about 24 h. The mixed oxide powders were then cold pressed into pellets of 25 mm in diameter. The pellets were pre-sintered at 850 °C for 2 h in air. After calcinations, the pellets were crushed and wet ball-milled for 24 h in ethyl alcohol. After drying, the powders were cold pressed into pellets of approximately 1 cm in diameter and 1 mm thick under 100 MPa pressure with 5 min holding time to ensure good green strength. The pellets were then sealed in Al_2O_3 crucible and sintered at 1200 °C for 1 h to obtain the final specimens.

X-ray diffraction (XRD) analysis of the sintered samples was carried out at room temperature using Cu Kα radiation

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(50 kV) on a Rigaku Dmax 2200 X-ray diffractometer. Scanning electron microscopy (SEM; JEOL JSM 5410LV) was employed to determine the average grain size of PZT samples. SEM specimens were prepared by cutting slices using a slow speed diamond saw. These thin slices were mounted using conducting bakelite, and were mechanically thinned and finally polished to give a 1 μm surface finish using Gatan's precision disc grinder. After polishing, the samples were etched at 100 °C lower than the sintering temperature in air for 1 h. Transmission electron microscopy (TEM; JEOL JEM-2010) was used to study the domain structures in the PZT samples. Thin foils for TEM were prepared by ultrasonically core drilling 3-mm diameter disks from the sintered samples. These disks were then mechanically polished to a thickness of ∼100 μm using Gatan's precision disc grinder. A dimple grinder was then used to produce a ∼20 μm thick region in the center. The specimens were thinned in the precision ion polishing system (PIPS) with argon ions at an accelerating voltage of 5 kV, which were incident at both surfaces at an angle of 5° to yield a reasonably thin specimen.

For electrical measurement, the as-sintered samples were ground and polished on both surfaces to ensure flat and parallel surfaces. Finished samples were about 0.5 mm thick. They were coated with conductive silver paint on both surfaces, and then heat cured at 500 °C for 10 min to ensure the electrodes were completely adhered to the ceramic. The *P–E* hysteresis loops were obtained using a high voltage ferroelectric test system at room temperature (RT600HVS, Radiant Technologies). The piezoelectric constant d_{31} for the PZT samples were determined using an impedance/gain-phase analyzer (HP 4194A).

3. Results and discussion

3.1. XRD results

Fig. 1 shows the XRD patterns of pure and doped PZT samples, in which the PYN is systematically added into PZT. Phase diagram of PZT shows that at room temperature, there are two phases (rhombohedral and tetragonal phase) coexisting in PZT near the MPB [1]. However, in this study, the absence of triplets at 43–46° in the XRD patterns indicates that there is no coexistence of the two phases in our samples. Only the tetragonal phase is detected. Samples containing less than 2 mol% PYN are tetragonal whereas with 2.5 mol% PYN, a pseudocubic phase is observed.

Other researchers have reported the existence of a secondary phase in Nb- or Y-doped PZT using XRD. Klissurska et al. [6] observed a Pb-deficient pyrochlore phase at Nb content of 8 at.% in their Nb-doped PZT samples, while Yoon et al. [8] observed a pyrochlore structured phase appeared at 5 mol% dopant content in their PYW-doped PZT. However, in this study, only the perovskite phase is detected by XRD, no additional secondary phases are detected. This may be due to the low PYN content (≤2.5 mol%) used in this study.

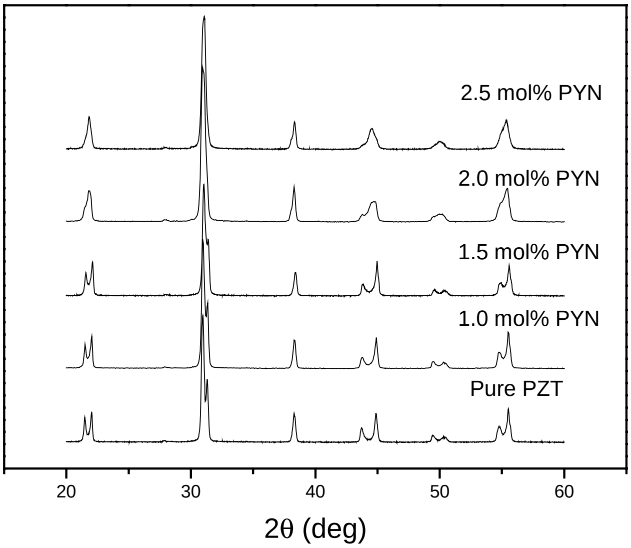

Fig. 1. X-ray diffraction patterns of pure and PYN-doped PZT samples.

3.2. SEM analysis

Low magnification secondary electron images (SEI) revealed the typical microstructure of PZT samples, as shown in Fig. 2. Well-defined grains are observed for all the samples. The average grain size $\bar{G}$ for each sample was determined from these micrographs, and the effect of PYN content on the grain size is graphically shown in Fig. 3. The average grain size decreases with PYN content up to 2 mol%. After which, the decrease in grain size becomes more gradual. At 2.5 mol% dopant content, the average grain size reaches a minimum value of 2.8 μm. Such a trend was also observed by Durruthy et al. [12] in their PZT samples doped with Nb_2O_5.

3.3. TEM analysis

The domain structures were observed using TEM. Domain patterns are either herringbone-like (Fig. 4a) or wedge-shaped (Fig. 4b) and exist in all the samples. Wedge-shaped domains are the most commonly observed configurations. In general, the observed domains are quite mobile and unstable under the influence of the electron beam and typically their sizes range from 100 to 800 nm in width. Moreover, the domain walls observed in this work are mainly the (1 1 0)-type walls. This is not surprising since the surface energy of a twin boundary on a (1 0 0) plane is three times that on a (1 1 0) plane [13]. Hence, (1 1 0)-type walls are more likely to occur compared to (1 0 0)-type walls.

There is clearly a question of whether the domain configurations are related to the observed change in the

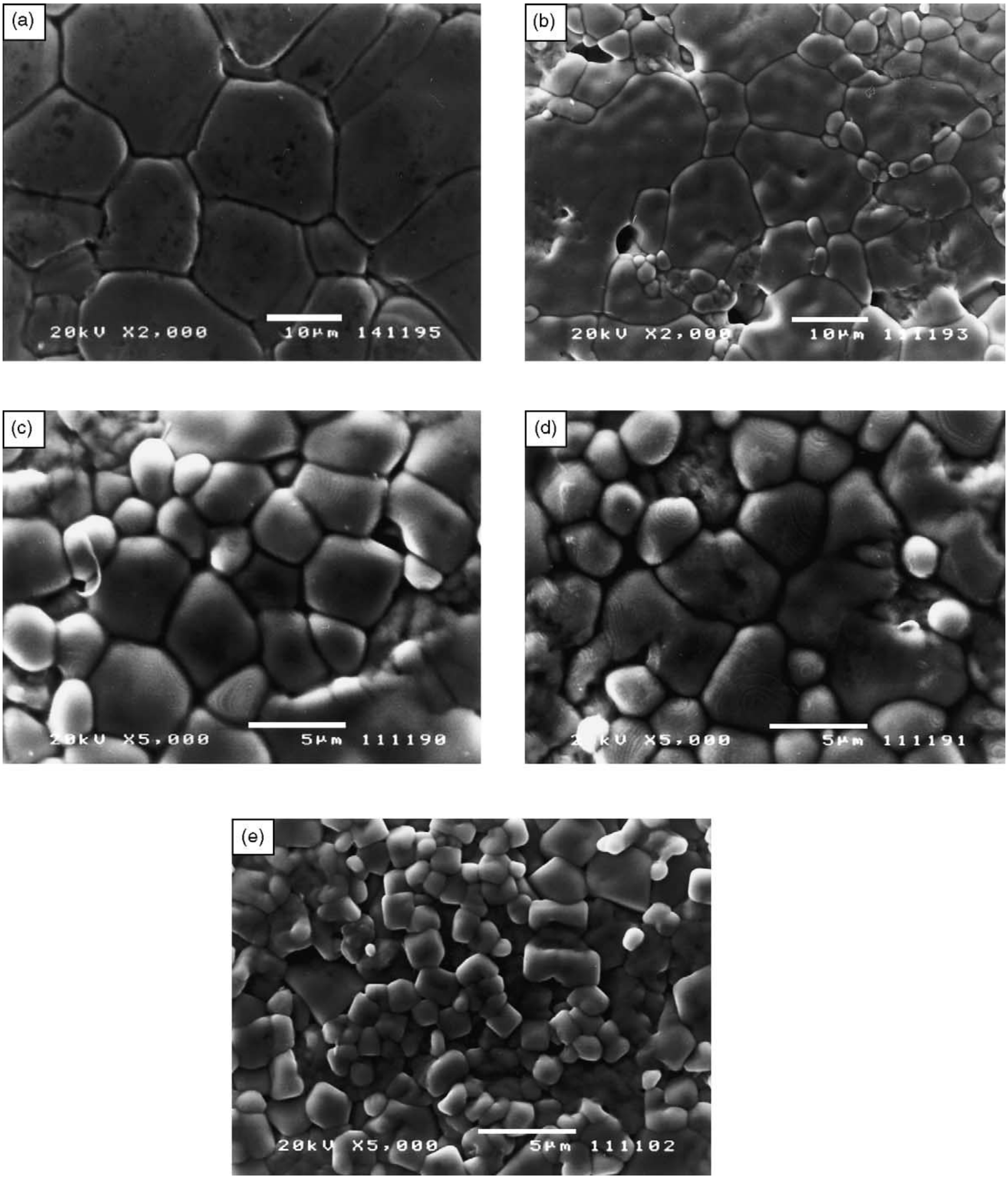

Fig. 2. SEM images (SEI) of pure and PYN-doped PZT specimens: (a) pure PZT; (b) 1.0 mol% PYN; (c) 1.5 mol% PYN; (d) 2.0 mol% PYN; (e) 2.5 mol% PYN.

ferroelectric properties (i.e. the ferroelectric hysteresis loops and the piezoelectric constant). Obviously, the ferroelectric properties originate from the domain structures. However, the observed domain configurations for all the samples exhibit similar characteristic. The only observable difference between the doped and undoped PZT is that the domain configurations were more often observed in the doped PZT specimens. This may be the reason why doped PZT shows much better piezoelectric properties than undoped PZT.

3.4. *Hysteresis loops*

Ferroelectric hysteresis loops of PZT were measured as a function of PYN dopant content (Fig. 5). Remanent polarization (P_r) and saturation polarization (P_{sat}) were

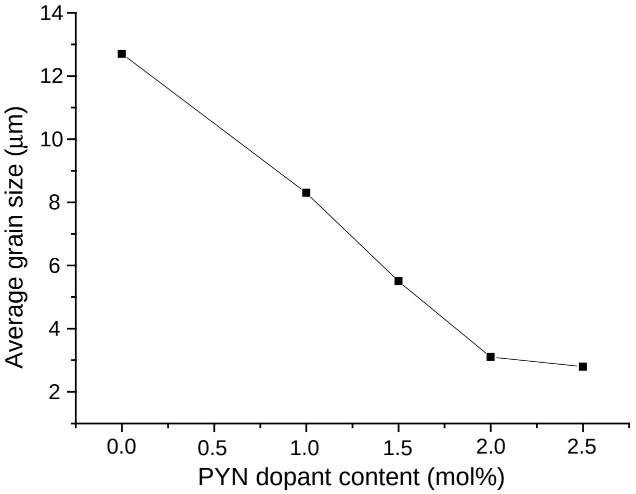

Fig. 3. Effect of PYN dopant content on the average grain sizes of PZT.

determined from these loops, and graphically presented in Fig. 6. P_r and P_{sat} were found to increase with PYN dopant content up to 1.5 mol%. Further increase in PYN content cause a decrease in P_r and P_{sat}. Such observation can be explained by considering the effect of ion substitution. The ionic radii of Pb^{2+}, Zr^{4+}, Ti^{4+}, Nb^{5+}, and Y^{3+} are 1.49, 0.72, 0.61, 0.64, and 0.90 Å, respectively. Hence, only Nb^{5+} ions can substitute for Zr^{4+} or Ti^{4+} ions. The substitution of Zr^{4+} or Ti^{4+} ions by Nb^{5+} ions is accompanied by the formation of Pb-vacancies:

$$2\mathrm{Nb}^{5+}_{\mathrm{Zr}^{4+}} = 2\mathrm{Nb}^{\bullet}{}_{\mathrm{Zr}} + \mathrm{V}''{}_{\mathrm{Pb}}$$

$$2\mathrm{Nb}^{5+}_{\mathrm{Ti}^{4+}} = 2\mathrm{Nb}^{\bullet}{}_{\mathrm{Ti}} + \mathrm{V}''{}_{\mathrm{Pb}}$$

The Pb-vacancies are negatively charged, and these can be paired with Nb^{5+} ions to form the defect dipoles. These defect dipoles can be aligned when there is spontaneous polarization P_s or when there is an applied electric field. This will create a larger polarization, and hence explain why the doped PZT has a larger P_r and P_{sat} than the undoped PZT observed in our samples. The decrease in the P_r and P_{sat} values for samples containing more than 1.5 mol% PYN is due to the tetragonal to pseudocubic phase transition, as indicated in XRD results.

3.5. Piezoelectric constant, d_{31}

The relation of PYN content on d_{31} was graphically presented in Fig. 7. The addition of 1 mol% PYN to pure PZT nearly doubled the d_{31} value. However, further increase in the PYN dopant did not seem to have a positive effect on the d_{31} value. In fact, the d_{31} value decreased as the PYN content is further increased to 1.5 mol%, and remained nearly constant with further addition to 2.5 mol%. The enhancement of d_{31} for doped PZT is attributed to the dopants effect. As described in Section 3.3, adding dopants can produce additional dipoles, and hence increase the piezoelectric properties. Moreover, d_{31} is also affected by grain size. The average grain size monotonically decreases with an increase in dopant content (Fig. 3). With a decrease in grain size, there is an increase in the internal stress due to the difficulty in forming 90° domains. This would result in a "clamping" effect to domain wall and hence decrease the piezoelectric properties. Such an argument is supported by the work of Xu et al. [14] on PZT film. The combined effect of these two factors explains the variation of d_{31} with the dopants content.

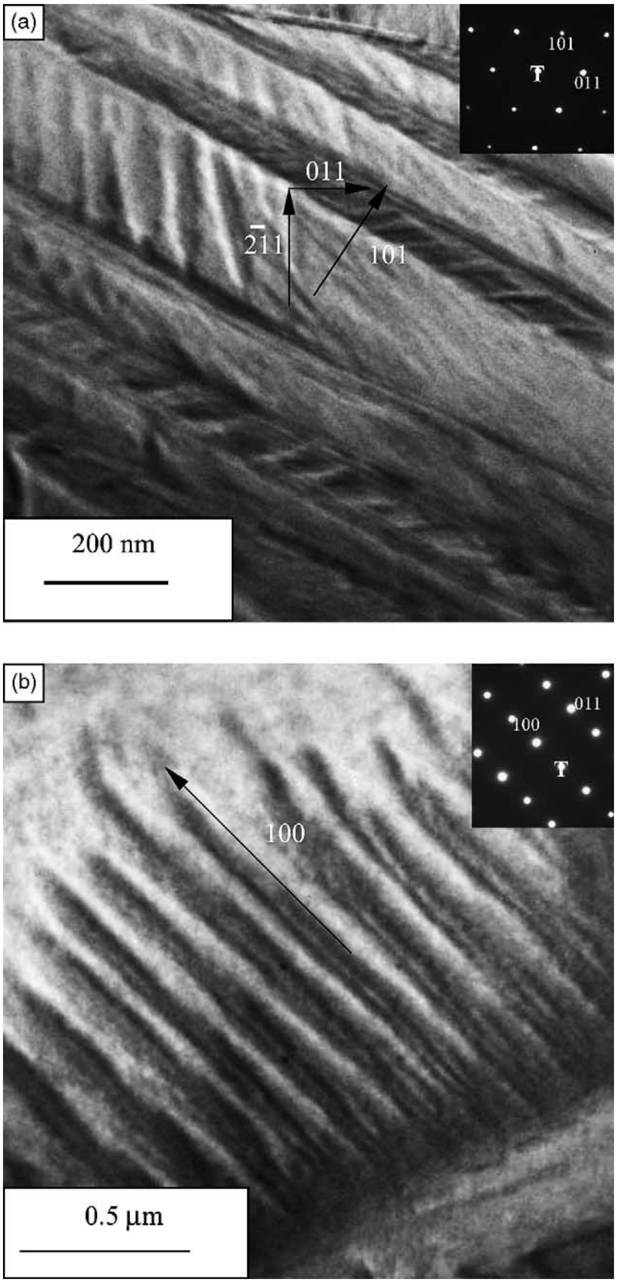

Fig. 4. Typical BF images of PYN-doped PZT ceramics showing (a) a herringbone-like ferroelectric domain configuration, viewed along $(11\bar{1})$; and (b) a wedge-shaped ferroelectric domain configuration, viewed along $(01\bar{1})$.

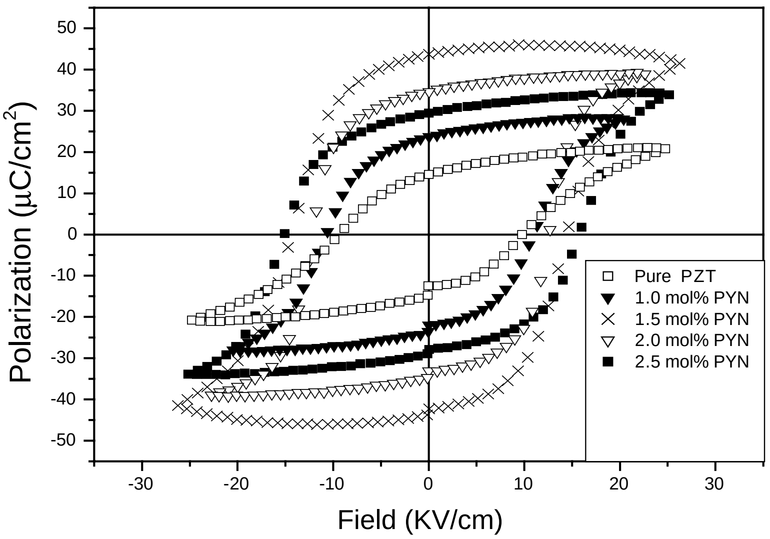

Fig. 5. Hysteresis loops of pure and PYN-doped PZT samples.

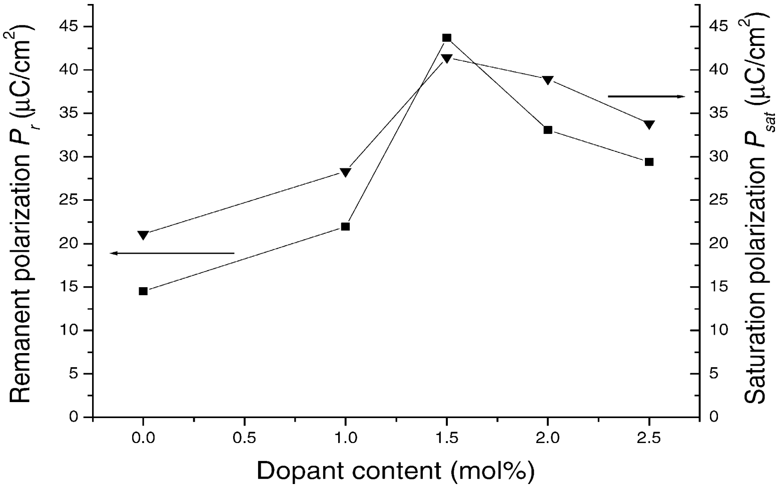

Fig. 6. P_r and P_{sat} values of PYN-doped PZT as a function of PYN content.

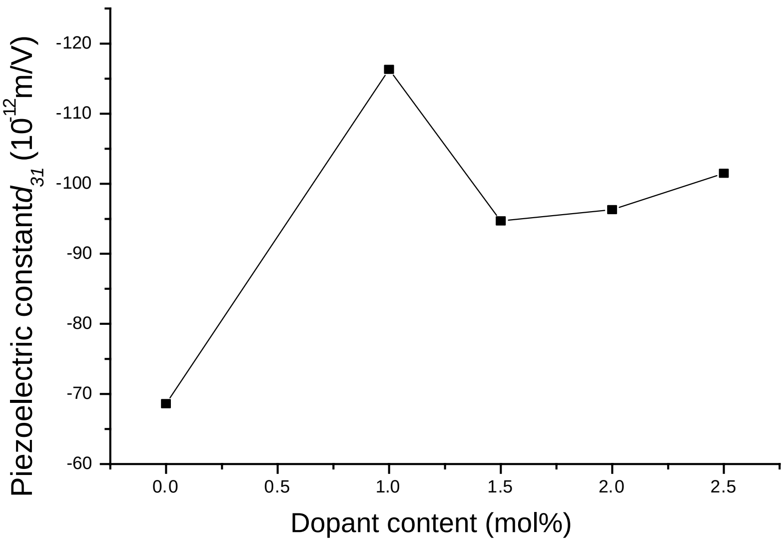

Fig. 7. Variation of piezoelectric constant d_{31} with PYN dopant content.

4. Conclusions

Compared with pure PZT, the addition of PYN dopant can greatly increase the ferroelectric and piezoelectric properties of PZT. P_r and P_{sat} were greatly improved by PYN addition. The piezoelectric constant d_{31} was also improved by the addition of PYN dopant. The maximum value of d_{31} for doped PZT is nearly twice that of pure PZT. The domain structures of pure and doped PZT were analyzed using TEM. The domain configurations for both pure and doped PZT were very similar. The only difference was the occurrence of the domain structures, which were more often observed in doped PZT.

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