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# Structural and electrical properties of Nd ion modified lead zirconate titanate nanopowders and ceramics*

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A modified sol-gel method is used for synthesizing Nd ion doped lead zirconate titanate nanopowders $Pb_{1-3x/2}Nd_xZr_{0.52}Ti_{0.48}O_3$ (PNZT) in an ethylene glycol system with zirconium nitrate as zirconium source. The results show that it is critical to add lead acetate after the reaction of zirconium nitrate with tetrabutyl titanate in the ethylene glycol system for preparing PNZT with an exact fraction of titanium content. It has been observed that the dopant of excess Nd ions can effectively improve the sintered densification and activity of the PNZT ceramics. Piezoelectric, dielectric and ferroelectric properties of the PNZT ceramics are remarkably enhanced as compared with those of monolithic lead zirconate titanate (PZT). Especially, the supreme values of piezoelectric constant ($d_{33}$) and dielectric constant ($\varepsilon$) for the PNZT are both about two times that of the monolithic PZT and moreover, the remnant polarization ($P_r$) also increases by 30%. According to the analysis of the structures and properties, we attribute the improvement in electrical properties to the lead vacancies caused by the doping of Nd ions.

**Keywords:** PNZT, ferroelectric properties, piezoelectric properties, sol-gel method
**PACC:** 7700, 7760, 7780

## 1. Introduction

Lead zirconate titanate (PZT) is one of the most widely used piezoelectric and ferroelectric ceramics due to its excellent piezoelectric properties.[1−7] PZT-based materials have been found to have different applications such as ultrasonic transducers, hydrophones, speakers, fish finders, sensors, actuators, electrical resonators, and wave filters.[8−16] As is well known, the microstructures and physical properties of PZT can be modified by fabricating the material through an improved synthesis process and appropriate substitutions at A and/or B-sites.[17−22] Therefore, the synthesis of the PZT powders plays an important role in achieving the properties of the PZT based materials. Traditional PZT powders are obtained through the solid phase reaction of PbO, $ZrO_2$ and $TiO_2$ each with a certain fraction. However, there exist some defects, such as component heterogeneity, low chemical purity and powder particle diameter distribution breadth, in the solid phase reaction. Consequently, wet chemical synthetic methods developed successively, e.g. the sol-gel method,[23] coprecipitation,[24] the metal oxide decomposition method,[25] the hydrothermal method,[26] and so on. The sol-gel method is extensively used for preparing PZT powders due to its low reaction temperature, uniform reactant mixing, exactly controllable components, high product purity and easy doping modification. A lot of sol-gel systems are used to synthesize PZT with lead acetate, zirconium alkoxides and titanium alkoxides as common reactants and methoxyethanol or acetic acid as common solvents.[27−31] In these systems, the hydrolysis reactions and condensation reactions are sensitive to water and humidity in the air; as a result, it is necessary to add a stabilizing agent, such as acetylacetone, to control the reaction process. On all accounts, in the polyalcohol system, the stable sol is easily obtained as long as the sensitivity of the sol-gel reaction to water

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and humidity is reduced. On the other hand, a wide variety of substitutions have been made at different atomic sites of PZT to enhance the electric properties. It has been reported that the doping of some modifiers such as Nb, Sb, Mn, La, Sm, Eu, and Nd could largely improve the properties of PZT.[32−35] Ahamad *et al*[34] investigated the effect of Nd doping on structural, dielectric and thermodynamic properties of PZT (65/35) ceramic. Shannigrahi *et al*[35] reported on the structural and dielectric properties of Nd modified $Pb(Zr_{0.60}Ti_{0.40})O_3$ ceramics. Interesting results were obtained from the referred studies, and the doping of Nd ions was reported to be a fine approach to enhancing the properties of PZT. Whereas, to our knowledge, there has been no work dealing with Nd ion doped PZT nanopowders prepared through a modified glycol-based sol-gel route in an ethylene glycol system and the piezoelectric, dielectric and ferroelectric properties of Nd ion doped nano-PZT ferroelectric ceramics have been limitedly investigated.

In the present paper, Nd ion-doped lead zirconate titanate $Pb_{1-3x/2}Nd_xZr_{0.52}Ti_{0.48}O_3$ (PNZT) nanopowders are synthesized by using a modified sol-gel method and PNZT ceramics are prepared through a normal sintering process in air. Based on our previous research,[36] the microstructures and the characteristics of the PNZT nanopowders are studied. The effects of the fraction of Nd ion content on the morphology, piezoelectric, dielectric and ferroelectric properties of the PNZT ceramics are investigated, and the possible mechanism of the PNZT is also discussed.

## 2. Experiment

Nd ion-doped lead zirconate titanate PNZT nanopowders were synthesized by using the modified sol-gel method[36] using analytical grade reagents lead acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$), zirconium nitrate pentahydrate ($Zr(NO_3)_4{\cdot}5H_2O$), tetrabutyl titanate ($Ti(OC_4H_9)_4$) and neodymium nitrate hexahydrate ($Nd(NO_3)_3{\cdot}6H_2O$) as raw materials, and ethylene glycol ($CH_3CH_2OH$) as solvent. Neodymium nitrate hexahydrate ($Nd(NO_3)_3{\cdot}6H_2O$) was dropped into the mixture together with lead acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$). The modified process was used to prepare stable sol, and then the sol was dried at 90 °C until xerogel formed. PNZT nanopowders were obtained after thermal treatment of the xerogel at 650 °C for 2 h. The PNZT nanopowders were pressed into pellets (16 mm in diameter and 1.2 mm in thickness) and the pellets were sintered at 1100 °C for 2 h. Finally, poling treatment was carried out in silicon oil at 110 °C for 30 min with an electric field of 3–4 kV/mm. In addition, monolithic PZT ceramics were also prepared for comparison.

The crystalline phase structures of the nanopowders were examined by using a Japan Science D/max2 ⅡBX2 X-ray diffractometer (XRD) with Ni-filtered Cu Ka radiation. The morphologies of the nanopowders and the sintered ceramics were studied by a JSM-6301F scanning electron microscope (SEM) and a JEM-2010 transmission electron microscope (TEM). The piezoelectric constants of the polarized specimens were measured by using a quasistate piezoelectric tester (ZJ-3A), and the dielectric characteristics (dielectric constant) were calculated with a Model HP 4194 Impedance analyzer. The hysteresis curves and ferroelectric properties (the remnant polarization and coercive electric field) were detected by using a ferroelectric hysteresis loop tester (ZT-1).

## 3. Results and discussion

### 3.1. Process modification of sol preparation

In the methoxyethanol-based sol-gel route, the sol is prepared by drop-wise adding titanate solution into the reaction system of lead acetate and zirconate water solution. In the reaction, water catalyses hydrolysis and condensation of the reactants in the system, but it is adverse to the sol stability. Therefore, the control of water content increases the difficulty of the whole reaction process. The modified process of preparing the sol is simple in the sense that inorganic zirconate (zirconium nitrate) is used as a zirconium source, ethylene glycol serves as the solvent, and the process is free from stabilizing agent. The modified sol process is confirmed to be useful by comparing PNZT powders prepared by the following processes A and B.

**Process A** After the reaction of zirconium nitrate water solution with lead acetate ethylene glycol solution at 60 °C for 0.5 h, tetrabutyl titanate ethylene glycol solution is added into the reaction system. After 2 h, the sol is obtained.

**Process B** After the reaction of zirconium nitrate water solution with tetrabutyl titanate ethylene glycol solution at 60 °C for 0.5 h, lead acetate ethy-

lene glycol solution is added into the reaction system. After 2 h, the sol is obtained.

Figure 1 shows the X-ray diffraction patterns of the PNZT nanopowders prepared by drying the sol at 90 °C and sintering at 650 °C for 2 h through process A (Fig.1(a)) and B (Fig.1(b)) separately. Figure 1(b) indicates that the pure perovskite phases are formed but no other diffraction peak is found. However, in Fig.1(a), the diffractive peaks cannot be distinguished and the perovskite phases are not formed. As a result, process B is an evidently simple manipulation with a short reaction time and an exact control of reactant components.

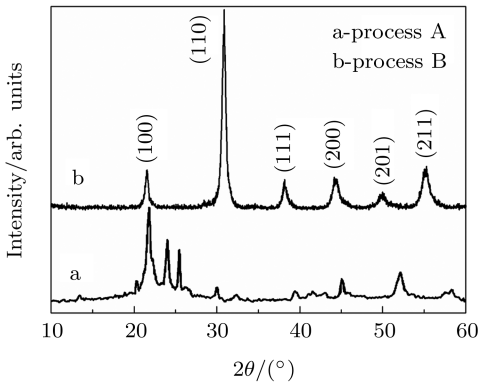



**Fig.1.** XRD patterns of the PZT nanopowders prepared through processes A and B separately.

The reaction mechanisms of the sol synthesis, preparation of xerogel and agglutinating process were discussed in our previous paper[36] by using Fourier transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, thermogravimetric Fourier transform infrared (TG-FTIR) spectroscopy, and gas chromatography-mass spectrometry (GC-MS). Our research results showed that the formation of sol in the ethylene glycol system was due to the chain or network of large molecules that resulted from the complexation of ethylene glycol and bulk Ti and minor Pd, Zr. For process B, the formation of the network polymer gel was caused by complexation of ethylene glycol, all Ti, and minor Pd and Zr in the xerogel, and in the sintering of the xerogel, the chief vapour decomposition resultants were oxycompounds, aldehyde-ketone compounds and carbon dioxide, besides volatility of ethylene glycol. Accordingly, process B is proved to be suitable to prepare stable lead zirconate titanate precursor sol, in which ethylene glycol is used as solvent, zirconium nitrate is used as zirconium source, but stabilizing agent is not used.

The XRD patterns of the PNZT nanopowders prepared through process B at different temperatures for a treatment time of 2 h, and at 650 °C for different treatment times are separately shown in Fig.2. It is observed from Fig.2 that as the temperature or the time of the thermal treatment increases, the characteristic peaks gradually strengthen, cystalline degrees intensify, and the particle sizes gradually increase. Perovskite structure forms capitally at 600 °C and completely converts into the pure perovskite PZT after thermal treatment at 650 °C for 2 h. When the thermal treatment temperature is too high, for example, as high as 700 °C (Fig.2(a)) or the thermal treatment time extends to 3 h (Fig.2(b)), the XRD patterns of the PNZT powder obtained is rough as shown in Fig.2.

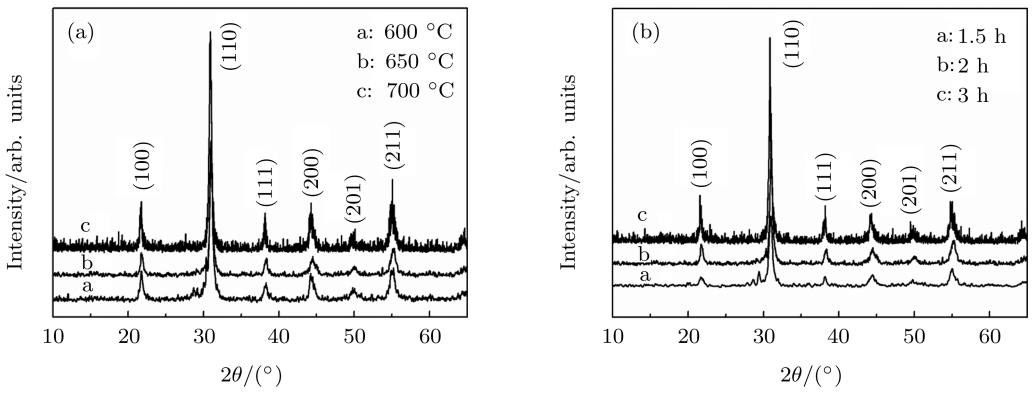



**Fig.2.** XRD patterns of the PZT nanopowders sintered (a) at different temperatures for 2 h (b) at 650 °C for different treatment times.

Figure 3 shows SEM and TEM images of the PNZT nanopowders with a fraction of 6 mol% Nd ion content, calcined at 650 °C for 2 h. It is observed that particles of the PNZT nanopowders synthesized through process B are more or less spherical and homogeneous and dispersed uniformly as seen from the SEM image in Fig.3(a). The average particle size calculated from the TEM image in Fig.3(b) is in a range of about 50–100 nm. The corresponding selected-area electron diffraction shows distinct rings, which are indicative of a diffraction pattern obtained from an assembly of a nano-polycrystalline phase as shown in the inset of Fig.3(b).

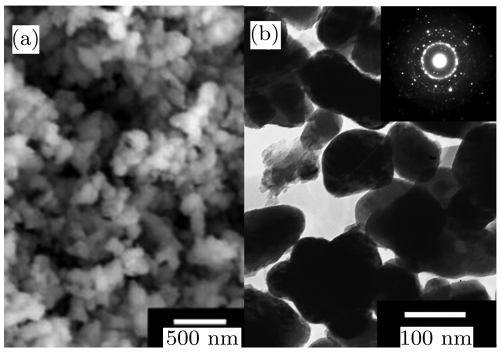



**Fig.3.** (a) SEM and (b) TEM images of the PNZT nanopowders obtained at 650 °C for 2 h.

Consequently, it is important to prepare the stable sol with an exact fraction of titanium content added into the lead acetate after the reaction of zirconium nitrate with tetrabutyl titanate. Moreover, 650 °C and 2 h are the best conditions for preparing the PNZT nanopowders.

## 3.2. Microstructures and characteristics of PNZT

Figure 4 shows the XRD patterns of the PNZT nanopowders with adding different fractions of Nd ion content. It is clearly observed that when the fraction of Nd ion addition is below 9 mol%, the pure perovskite phases are formed after the heat treatment at 650 °C for 2 h. However, pyrochlore phases (Py) are present when the fraction of Nd ion addition is higher than 9 mol%.

Figure 5 shows the SEM images of fractured surfaces of the PZT and PNZT ceramics. The grain sizes of the PNZT are found to be about 400–600 nm. The PNZT ceramics have a grain boundary more distinct and a structure more compact than the monolithic PZT. Furthermore, the grain size of PNZT ceramics is markedly larger than that of the monolithic PZT and so the dense sintered PNZT ceramics are obtained. Hence, Nd ion doping can effectively improve the sintering activity of ceramics and is beneficial to the densification of sintered ceramics.

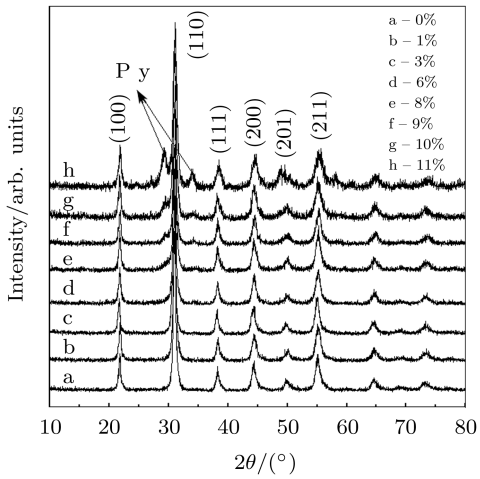



**Fig.4.** XRD patterns of PNZT nanopowders doped with different fractions of Nd ion content.

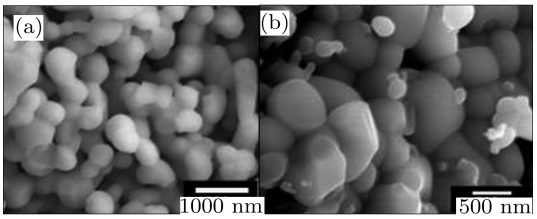



**Fig.5.** SEM images of fractured surfaces of (a) PZT and (b) PNZT ceramics.

## 3.3. Piezoelectric behaviour of PNZT ceramics

Figure 6 shows the variation of piezoelectric properties of PNZT ceramics as a function of fraction of Nd ion content. Obviously, it is found that the values of the piezoelectric constant ($d_{33}$) of PNZT are higher than those of the monolithic PZT. The value of $d_{33}$ obviously increases initially with the fraction of Nd ion content increasing, reaching a maximum value when the fraction of Nd ion content is 1 mol%, and then it decreases with further increases of the fraction of Nd ion content. At 1 mol% Nd ion doping, the PNZT ceramics exhibit the optimal value of $d_{33}$, which is about two times that of the monolithic PZT.

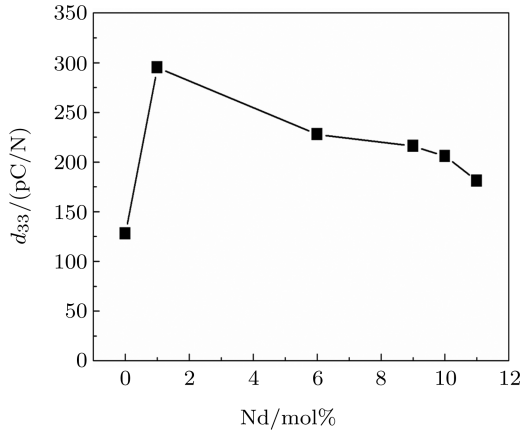



**Fig.6.** Effect of Nd ion dopant on the value of the piezoelectric constant ($d_{33}$) of the PNZT ceramics.

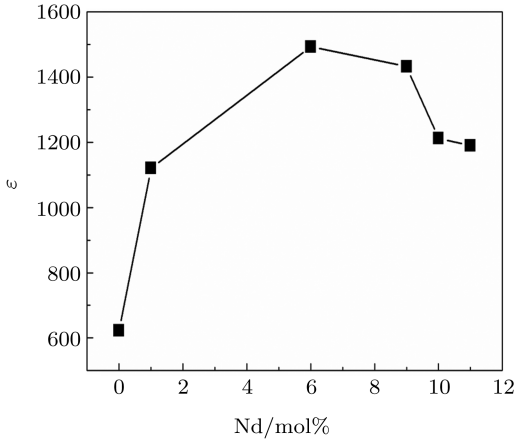



**Fig.7.** Effect of Nd ion dopant on the value of the dielectric constant ($\varepsilon$) of the PNZT ceramics.

The great increase in $d_{33}$ of the PNZT ceramics can be attributed to the Pb ion vacancies produced by the Nd ions, which will increase the mobility of the ferroelectric domain wall as a consequence of the drop in stress of the lattice. Replacement of Pb ions with Nd ions creates Pb ion vacancies in the system according to the following reaction:

$$\mathrm{Nd}^{3+} \xrightarrow{\mathrm{Pb}^{2+}} \mathrm{Nb}^{\cdot}_{\mathrm{Pb}} + \frac{1}{2}V''_{\mathrm{Pb}}. \qquad (1)$$

Nd is one of the donor dopants that could promote the movement of the ferroelectric domain walls and the polarization of the PNZT ceramics. Hence, there is a significant increase in the value of $d_{33}$ when the fraction of Nd ion content is low. Nevertheless, for the higher doping, Nd ions would accumulate in the crystal boundary and so inhibit the growth of the grains. This tendency makes it hard for the ferroelectric domain to switch over in the process of polarization, leading the piezoelectric activity and the values of $d_{33}$ to reduce.

## 3.4. Dielectric behaviour of PNZT ceramics

Figure 7 shows the effect of Nd ion dopant on the dielectric constant ($\varepsilon$) of the PNZT ceramics. Compared with the dielectric constant of monolithic PZT, the value of $\varepsilon$ of PNZT ceramics substantially increases with increasing fraction of Nd ion content, and it reaches a maximum value, which is about two times that of the monolithic PZT, when the fraction of Nd ion content is 6 mol%. However, the value of $\varepsilon$ decreases after the maximum value as the fraction of Nd ion content increases.

Nd ions act as donor dopants which are substituted for Pb ions, thereby producing Pb ion vacancies and reducing the oxygen vacancy concentration simultaneously according to reactions (1) and (2)

$$\mathrm{Nd}^{3+} + \frac{1}{2}V^{\cdot\cdot}_{\mathrm{O}} \xrightarrow{\mathrm{Pb}^{2+}} \mathrm{Nd}^{\cdot}_{\mathrm{Pb}}. \qquad (2)$$

Whereas, the high value of $\varepsilon$ may be caused by the movement of the ferroelectric domain wall. Reduction in oxygen vacancies makes domain realignment easy, thus increasing the value of the dielectric constant. The reason for the value of $\varepsilon$ reducing after reaching its peak is the same as that for the dropping of the $d_{33}$ value, i.e. these phenomena may be ascribed to the accumulation of Nd ions in the crystal boundaries.

## 3.5. Ferroelectric behaviour of PNZT ceramics

Figure 8 shows the effect of Nd ion dopant on the hysteresis loop of the PNZT ceramics. The variations of the ferroelectric properties (remnant polarization $P_{\mathrm{r}}$ and the coercive electric field $E_{\mathrm{c}}$) of the PNZT with fraction of Nd ion doping content can be seen from Fig.9. It is observed that the samples exhibit well-saturated hysteresis curves. The ferroelectric properties of bodies with Nd ion addition are superior to those without Nd ion addition. It is clearly indicated that the value of $P_{\mathrm{r}}$ of the PNZT ceramics is relatively higher than that of the monolithic PZT, rising from 35 $\mu c/\mathrm{cm}^2$ (PZT) to 45 $\mu c/\mathrm{cm}^2$ (PNZT). However, after reaching its peak, the value of $P_{\mathrm{r}}$ decreases with increasing fraction of Nd ion content. On the contrary, the value of $E_{\mathrm{c}}$ of the PNZT descends primarily and

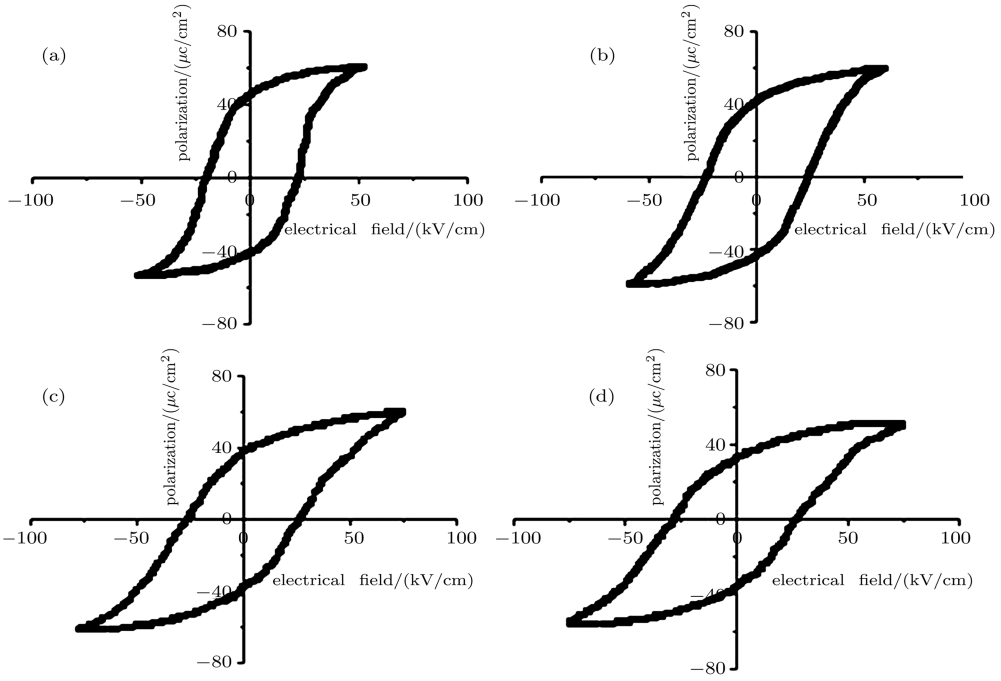



**Fig.8.** Hysteresis loops of PNZT ceramics doped with different fractions of Nd ion content.

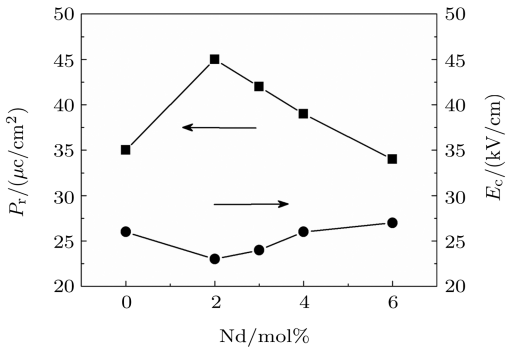



**Fig.9.** Effects of Nd ion dopant on the ferroelectric properties ($P_r$ and $E_c$) of the PNZT ceramics.

then rises with increasing fraction of Nd ion content. The lowest value of $E_c$ is about 23 kV/cm.

Substitution of Nd ions for Pb ions leads to the augmentation of Pb ion vacancies and the decrease of oxygen vacancies, which makes the movement of the ferroelectric domain wall easier. That is to say, with smaller polarization electric field or mechanical stress, the domain wall can move. Consequently, the value of $P_r$ of the PNZT is higher than that of the monolithic PZT after polarization. Similarly, the value of $E_c$ of the PNZT is lower than that of the monolithic PZT due to the Nd ion doping. However, with increasing fraction of Nd ion doping content, Nd ions would assemble in the crystal boundary and so prevent the ferroelectric domain from switching over in the process of polarization, thereby causing the value of $P_r$ to reduce and the value of $E_c$ to augment.

## 3.6. The mechanism of PNZT ceramics

PZT compositions, doped with foreign ions, show some significant merits. The changes of dielectric, piezoelectric and ferroelectric properties depend on the sites occupied by the foreign ions in the $ABO_3$ perovskite structure. The mechanism for the PNZT ceramics is schematically shown in Fig.10. Substitution of Nd ions for Pb ions leads to the augmentation of Pb ion vacancies and the decrease of oxygen vacancies (just as indicated in reactions (1) and (2)). This result shows that the incorporation of Nd ions into the perovskite structure produces lead vacancies (A site) and may likely intensify the effect on the domain movement because of the elongation of the unit cell in the direction of the polarization. The augmentation of Nd ion concentration increases the A-site vacancy concentration and strengthens a higher ferroelectric domain motion. Consequently, the dielectric, piezoelectric and ferroelectric properties of PNZT are enhanced with increasing doping of Nd ions.

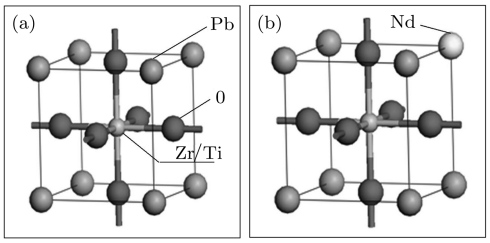



**Fig.10.** Schematic illustration of the mechanism for the PNZT.

# 4. Conclusions

Nd ion-doped PZT (PNZT) nanopowders are synthesized successfully by using a modified sol-gel method. Our research results indicate that it is important to prepare the stable sol with an exact fraction of titanium content added into lead acetate after the reaction of zirconium nitrate with tetrabutyl titanate. For the PNZT, a pure perovskite phase of the PNZT nanopowders is obtained, with a fraction of less than 9 mol% Nd ion content added. The addition of the Nd ion dopant could effectively improve the sintering densification and activity of ceramics probably due to the substitution of Nd ions for Pb ions. Reinforced piezoelectric, dielectric and ferroelectric properties of the PNZT are observed. Excess Nd ion doping possibly produces lead vacancies and reduces the oxygen vacancy concentration. Consequently, the values of $d_{33}$, $\varepsilon$ and $P_{\rm r}$ are enhanced by doping Nd ions into the PZT. Adding an appropriate quantity of Nd ions into PZT ceramics is a good approach to improving the electrical properties of the ceramics. PNZT with good electrical properties are promising for further applications.

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