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Microstructure and dielectric properties of $Pb_{0.94}La_{0.06}Nb_2O_6$ ceramics

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Abstract

$Pb_{0.94}La_{0.06}Nb_2O_6$ ceramics were prepared by solid state reaction of high energy ball milled precursor powders. Calcination temperature of the milled precursor was lowered to 850 °C. Single orthorhombic phase was obtained after the ceramics were sintered at 1205 °C and 1230 °C. Lattice parameters, porosity and grain size were all affected by sintering temperature. A normal ferroelectric–paraelectric phase transition was observed at Curie temperature. The ceramic sintered at 1230 °C showed Curie temperature of 525 °C, piezoelectric constant of 62.3 pC/N, electromechanical coupling factor of 0.3342 and mechanical quality factor of 11.64, making it a potential candidate as high-temperature piezoelectric transducers.
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1. Introduction

Lead metaniobate ($PbNb_2O_6$, PN) is a ferroelectric material with tungsten–bronze structure and high Curie temperature of 570 °C, which is desirable to construct transducers for high temperature applications [1]. PN possesses three crystal phases. The stable low temperature form is rhombohedral phase. The stable high temperature form is tetragonal phase, which transforms to metastable orthorhombic phase at Curie temperature during cooling [2]. Only the orthorhombic phase shows piezoelectric property. It is inevitable to experience the phase transition from the low- to high-temperature forms in order to obtain the orthorhombic phase. This phase transition is always accompanied by extensive grain growth [3]. A major problem of preparing PN ceramics is the difficulty in obtaining high density ceramics with single orthorhombic phase. Quenching method was used to obtain PN ceramics with orthorhombic phase [4].

Various elements have been used to PN ceramics to improve densification and electrical properties. The addition of Ca and excessive Ti into PN ceramics increased density and Curie temperature, but slightly decreased piezoelectric property [5]. The addition of Mn and Ca was in favor of fabricating dense PN ceramics with good piezoelectric property [6]. The doping of Ba into PN enhanced densification, but reduced Curie temperature [3,7,8]. Venet et al. found that the incorporation of La into the $Pb_{0.56}Ba_{0.44}Nb_2O_6$ ceramics modified grains morphology and decreased Curie temperature [9]. Men et al. prepared the La and Ti co-doped PN ceramics by conventional solid state reaction method and found that their densification was improved and grain growth was restrained, compared to pure PN ceramics [10].

In this work, La doped PN ceramics with high relative density and relatively small grain size were obtained by solid state reaction of high energy ball milled precursor powders. Crystallite structure, microstructure and dielectric properties of the ceramics were studied in detail.

2. Experimental procedure

The $Pb_{0.94}La_{0.06}Nb_2O_6$ (PLN) ceramics were prepared by solid state reaction of high energy ball milled precursor powders. Analytical grade PbO, Nb_2O_5 and La_2O_3 powders in stoichiometric ratio of the composition with agate balls were put in two agate vials and milled for 12 h with a Fritsch Vario-Planetary high energy ball milling system in air. The rotation speed of the disk was 300 rpm and that of the vials was 450 rpm. To compensate the strong loss of PbO at calcination process, 2 wt% excess PbO was added to the mixed powders. The milled powders were subsequently calcined at 850 °C for

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2 h. Then the calcined powders were re-milled for 5 h and ground with approximately 5 wt% polyvinyl alcohol as a binder. Pellets of 11.5 mm in diameter and approximately 1.5 mm in thickness were pressed at uniaxial pressure of 200 MPa. The pellets were burned out at 500 °C for 2 h and sintered at 1180, 1205, and 1230 °C for 4 h, respectively. Heating and cooling rates were 3 °C/min. In order to prevent the volatility of lead, a lead rich atmosphere was maintained during sintering.

Bulk density of the ceramics was measured by the Archimedes method and relative density was calculated. X-ray diffraction (XRD) measurement was carried out by using a Rigaku D/Max 2550 with Cu Kα radiation. Scanning electron microscopy (SEM) was performed with a scanning electron microscope (Quanta 200, FEI Co., Eindhoven, Netherlands). Silver electrodes were coated and fired at 650 °C for 15 min for electrical characterization. Dielectric measurement was performed by using an Agilent E4980A precision LCR from room temperature to 600 °C. The ceramics were polarized in a silicon oil bath at 150–170 °C at an electric filed of 3.5 kV/mm for 30 min. Piezoelectric constant (d_{33}) was measured by using a quasistatic d_{33} meter (ZJ-4A Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). Electromechanical coupling factor (K_p) was calculated by means of resonance and anti-resonance method.

3. Results and discussion

Fig. 1 shows XRD patterns of the as-milled and calcined powders. The diffraction peaks of the as-milled powders can be attributed to PbO and Nb_2O_5, indicating that no reaction has yet been triggered by the milling. No trace of La_2O_3 is observed, which may be due to its small amount. The calcined powders show a rhombohedral phase (JCPDS No. 74-2221) [11] with minor PbO excessive. Calcination temperature in fabricating PN-based ceramics by conventional solid state reaction method is always ≥900 °C [4,10,12,13]. It is well known that high energy ball milling can improve reaction activity of the milled powders [14]. Here, the calcination temperature of 850 °C is lower than that required by the conventional solid state reaction process. The low calcination temperature is believed to be beneficial to PLN ceramics with fine grains [14].

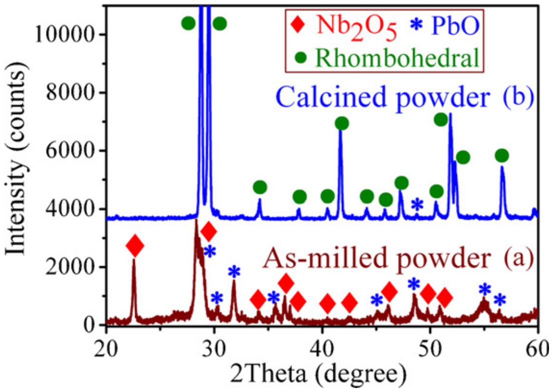

Fig. 1. XRD patterns of the as-milled (a) and calcined powders (b).

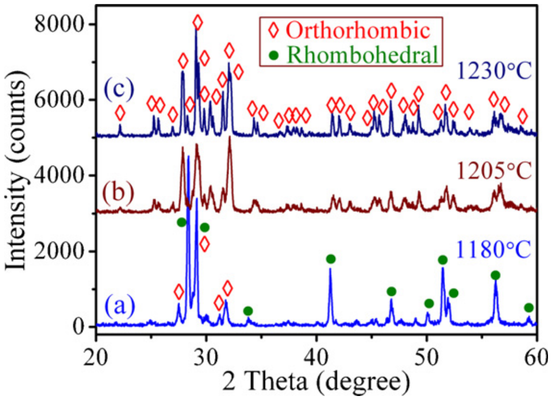

Fig. 2. XRD patterns of the ceramics sintered at 1180 °C (a), 1205 °C (b) and 1230 °C (c).

Fig. 2 shows XRD patterns of the ceramics sintered at different temperatures. Rhombohedral and orthorhombic phases coexist in the ceramic sintered at 1180 °C. For the ceramics sintered at 1205 and 1230 °C, a single orthorhombic phase is observed (JCPDS No. 70-1388) [11]. No second phase is observed, suggesting that single phase PLN has been formed. The loss of PbO usually results in the formation of $Pb_5Nb_4O_{15}$ pyrochlore phase [2]. Here, no pyrochlore phase is found, which can be attributed to the excess PbO. On the other hand, it

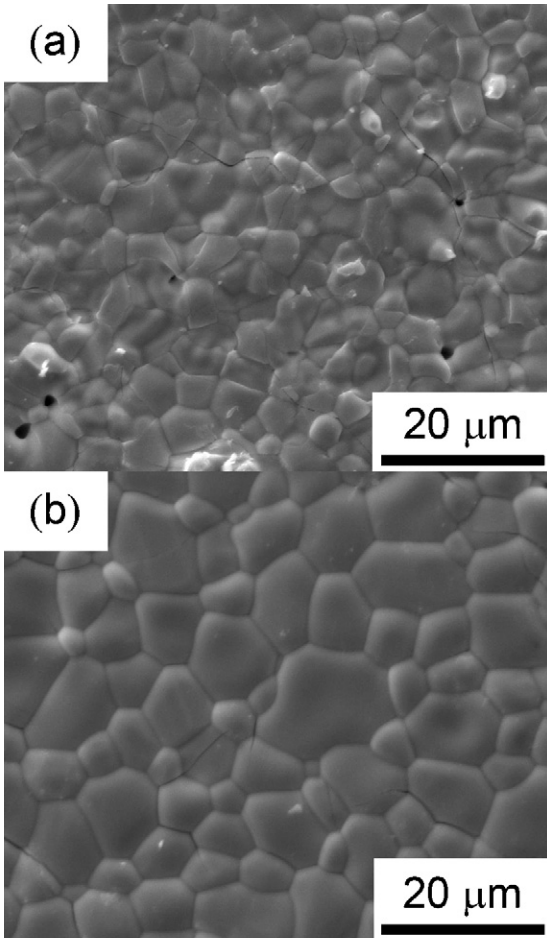

Fig. 3. SEM images of the ceramics sintered at 1205 °C (a) and 1230 °C (b).

is known that fabrication of pure PN ceramics with a single orthorhombic phase is very difficult using the conventional solid-state reaction method [4,6,12]. In order to obtain orthorhombic phase, quenching is usually used [4,12]. It is believed that the doping of La stabilizes the orthorhombic phase of PLN, as well as the excess PbO.

Lattice parameters (*a*, *b*, *c*) of the PLN ceramics with single orthorhombic phase were obtained by whole pattern fitting using the least-square approach. Peak shapes were modeled by a Pearson-VII function, taking into account both Lorentzian and Gaussian functions to obtain smaller values of residual factor. *a*, *b*, and *c* of the ceramic sintered at 1205 °C are 17.664, 17.974, and 3.887 Å, respectively; and those of the ceramic sintered at 1230 °C are 17.697, 18.029, and 3.889 Å, respectively. The change in lattice parameters with sintering temperature is related to an increase in internal stress in the ceramics when the paraelectric–ferroelectric phase transition occurs [15,16]. On the other hand, internal stress can be relieved by pores and grain boundary sliding [17]. Pores and grain size in the PLN ceramics are related to sintering temperature, as verified by scanning electron microscopy. So, the competing effects among internal stress, pores and grain size are responsible for the change in lattice parameters.

Fig. 3 shows SEM images of the PLN ceramics sintered at 1205 and 1230 °C. Some pores are observed in the ceramic sintered at 1205 °C, corresponding to its low relative density of 88.9%. After sintering at 1230 °C, few pores are found and the ceramic becomes dense with high relative density of 95.3%. Mean grain size of the ceramic sintered at 1205 °C is about 5.7 μm. The ceramic sintered at 1230 °C has a bimodal microstructure consisting of large grains with a mean size of ∼11.9 μm and smaller grains of ∼5.9 μm. The grains of the conventionally fabricated PN-based ceramics are always very large [10].

Temperature dependences of dielectric constant (ε_r) of the PLN ceramics sintered at 1205 °C and 1230 °C are shown in Fig. 4a and b. Obvious dielectric peaks are observed. The dielectric constant data are fitted with the Curie–Weiss law $1/\varepsilon_r = (T - T_0)/C$, where T is temperature, T_0 is Curie–Weiss temperature, and C is Curie constant. The parameters obtained from the fitting are shown in Table 1. A normal Curie–Weiss dependence, i.e., linear dependence with temperature, is observed above T_c (Fig. 4c and d). Therefore, the PLN ceramics are typical ferroelectrics with normal ferroelectric–paraelectric phase transition. For the ceramic sintered at 1205 °C, a strong frequency dispersion of ε_r is observed in a wide temperature interval around T_c (Fig. 4a), while the dielectric dispersion weakens greatly for the ceramic sintered at 1230 °C (Fig. 4b). Correspondingly, the temperature dependence of reciprocal ε_r shifts with frequency for the ceramic sintered at 1205 °C, but does not shift for the ceramic sintered at 1230 °C (Fig. 4c and d). The temperature dependences of dielectric loss in the phase transition temperature range are shown in the insets of Fig. 4a and b. The loss peaks corresponding to the ferroelectric–paraelectric phase transition locate at temperatures below T_c. Dielectric loss of the ceramic sintered at 1205 °C is higher than that of the ceramic sintered at 1230 °C, which may be due to the difference in relative density

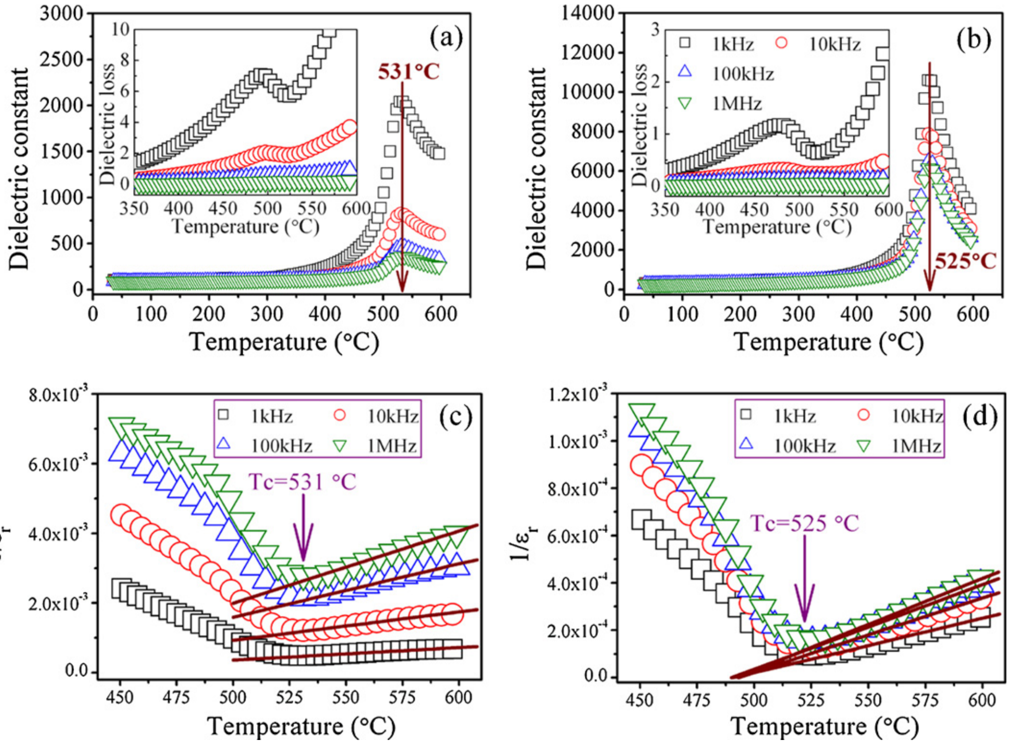

Fig. 4. Dielectric constant of the ceramics sintered at 1205 °C (a) and 1230 °C (b) vs. temperature. Plots of reciprocal of dielectric constant ($1/\varepsilon_r$) vs. temperature and the fitting plots by the Curie–Weiss law for the ceramics sintered at 1205 °C (c) and 1230 °C (d). The symbols denote experimental data, while the solid lines denote the least-squared fitting line to the Curie–Weiss law. The insets in (a) and (b) show dielectric loss vs. temperature in the temperature range of phase transition.

Table 1
Parameters from Curie–Weiss law fitting and main piezoelectric properties at room temperature of the PLN ceramics.

Sintering temperature (°C)	T_0/C (°C/10^5, °C)				d_{33} (pC/N)	K_p	Q_m
	1 kHz	10 kHz	100 kHz	1000 kHz			
1205	398.72/2.80	386.42/1.22	392.45/0.65	402.69/0.48	–	–	–
1230	490.54/4.31	493.29/3.21	490.02/2.80	493.06/2.57	62.3	0.3342	11.64

of the two ceramics. For both samples, dielectric loss decreases with increasing frequency from 1 kHz to 1 MHz, especially at high temperatures. This temperature dependence of dielectric loss is typically associated with losses by conduction [18]. At low frequencies, dielectric loss increases with increasing temperature above T_c, which may be associated with point defects originated by Pb^{2+} losses during sintering [19].

For a given sample, T_c does not shift with frequency. As sintering temperature increases from 1205 °C to 1230 °C, T_c decreases from 531 °C to 525 °C. It has been reported that Curie temperature of ferroelectrics with tungsten bronze structure is affected by internal stress [17,20]. Internal stress can increase free energy of ferroelectric phase and decrease Curie temperature [21]. On the other hand, internal stress can be relieved by pores and grain boundary sliding [17]. The ceramic sintered at 1205 °C has more pores and small grains. As a result, internal stress was easily relieved by pores and grain boundary sliding in the ceramic. Thus, its T_c is higher than that of the ceramic sintered at 1230 °C.

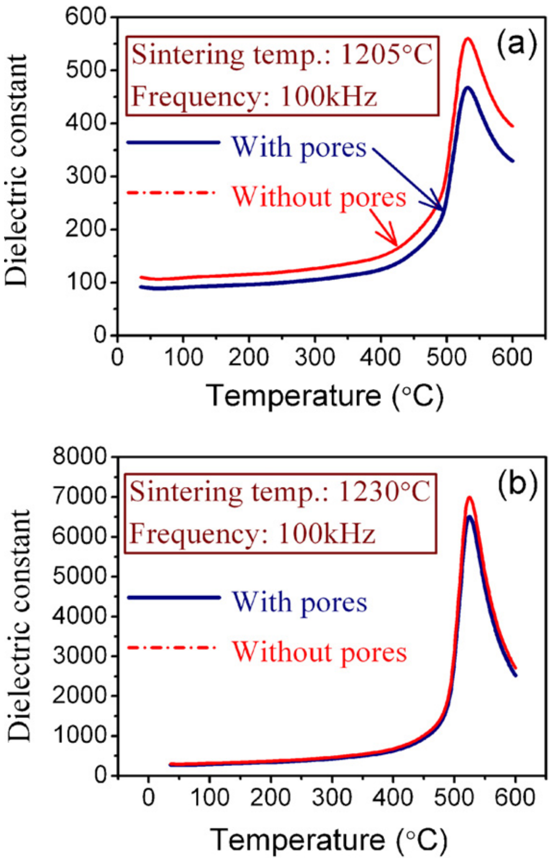

Fig. 5. Measured (with pores) and calculated (without pores) dielectric constant using Bruggemans model vs. temperature for the ceramics sintered at 1205 °C (a) and 1230 °C (b) at 100 kHz.

For both samples, ε_r values remain nearly unchanged from room temperature up to about 450 °C (Fig. 4a and b), which provides high temperature stability for their application as transducers. The maximum values of dielectric constant (ε_m) of the ceramic sintered at 1230 °C are higher than those of the ceramic sintered at 1205 °C. The influence of pores on dielectric constant can be accounted by using Bruggeman's model: $\varepsilon_{r\,\mathrm{exp}} \approx \varepsilon_{r\mathrm{th}}\ (1\text{–}1.5V_p)$ [2,22], where, $\varepsilon_{r\,\mathrm{exp}}$ denotes measured ε_r (with pores); $\varepsilon_{r\mathrm{th}}$ denotes theoretical ε_r (without pores); V_p is volumetric pore fraction and can be obtained from the formula, $V_p = 1 - \rho_r$; ρ_r is relative density. Temperature dependences of $\varepsilon_{r\,\mathrm{exp}}$ and $\varepsilon_{r\mathrm{th}}$ for the both samples are shown in Fig. 5. As is observed, the presence of pores results in low dielectric constant. $\varepsilon_{r\,\mathrm{exp}}$ values of the ceramic sintered at 1205 °C are obviously lower than $\varepsilon_{r\mathrm{th}}$ values because of its large porosity. For the ceramic sintered at 1230 °C, $\varepsilon_{r\,\mathrm{exp}}$ values almost equal to $\varepsilon_{r\mathrm{th}}$ values because of its high relative density. However, it should be noted that $\varepsilon_{r\,\mathrm{exp}}$ values of the ceramic sintered at 1230 °C are still much larger than $\varepsilon_{r\mathrm{th}}$ values of the ceramic sintered at 1205 °C. This suggests that the difference in dielectric constant between the two ceramics is mainly due to the differences in grain size rather than a porosity variation.

The PLN ceramic sintered at 1230 °C was polarized and its main piezoelectric properties are listed in Table 1. The ceramic has d_{33} of 62.3 pC/N, K_p of 0.3342 and Q_m of 11.64, making it a potential candidate as piezoelectric transducers.

4. Conclusions

Dense PLN ceramics with single orthorhombic phase were obtained by solid state reaction of high energy ball milled precursor powders. Lattice parameters and microstructure of the PLN ceramics were affected by sintering temperature. Curie temperature decreased and maximum dielectric constant increased with increasing sintering temperature. The changes in dielectric properties of the ceramics are related concurrently to internal stress, porosity and grain size. The PLN ceramic sintered at 1230 °C showed $d_{33} = 62.3$ pC/N, $K_p = 0.3342$ and $Q_m = 11.64$, which make it suitable for high temperature piezoelectric transducers.

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