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Short Communication

Effects of Ti on dielectric and piezoelectric properties of $(Pb_{0.985}La_{0.01})_{1+y}(Nb_{1-y}Ti_y)_2O_6$ ceramics

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ABSTRACT

Piezoelectric ceramics $(Pb_{0.985}La_{0.01})_{1+y}(Nb_{1-y}Ti_y)_2O_6$ ($0 \leqslant y \leqslant 0.1$) (PLNT) were fabricated by a conventional solid-state reaction method. The crystal structure and microstructures of specimens were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). All PLNT ceramics sintered at temperatures from 1250 °C to 1290 °C are shown to be a single orthorhombic phase. The formation of orthorhombic phase is promoted by excess PbO existed in the Ti-bearing samples during calcination processing. The increasing of the tolerance factor due to substitution of Ti^{4+} for Nb^{5+} is also responsible for the stability of orthorhombic phase. The high density of ceramics (relative density >95%) with the equiaxed grains and a minor porosity have been obtained. The measurement of dielectric and piezoelectric properties of PLNT ceramics reveals that Ti reduces the dielectric loss (tan δ) and dielectric constant (ε_r) of PLNT ceramics, and enhances the piezoelectric constant (d_{33}) and Curie temperature (T_c). The optimum component with $y = 0.075$ possesses the excellent electrical properties: $\varepsilon_r = 182$, tan $\delta = 0.0018$, $d_{33} = 84$ pC/N and $T_c = 564$ °C.

1. Introduction

Lead metaniobate $PbNb_2O_6$ (PN) is considered as one of excellent ferroelectrics for applications at high temperature conditions due to its high Curie temperature ($T_c \sim 570$ °C), low dielectric constant (ε_r), and very low mechanical quality factor (Q_m) [1–3]. Usually, the dense PN ceramics with a single orthorhombic phase are very difficult to be obtained. Firstly, by a conventional solid-state reaction method, PN ceramics are often formed with the mixtures of rhombohedral and orthorhombic phases [4–6]. Secondly, abnormal grain growth, cracks, and undesirable phases (promoted by PbO losses) affected the densification of PN ceramics [4]. It is well known that the electrical properties of PN ceramics are obviously influenced by microstructures [5].

In order to obtain the PN ceramics with a single orthorhombic phase and a high density, the green pellets of PN ceramics were often heated at 1300 °C and then quenched quickly [4,5]. This procedure is inconvenient for a practical processing. Element substitutions at Pb site of PN compound by Ca, Ba, La, Sm and Nb site by Mn, Zr and Ti were used to improve the sintering behavior and electrical properties of this material. However, most of these elements usually decrease the Curie temperatures of PN ceramics [7–9]. It was reported that the addition of Ti in pure PN ceramics, not only increased the densification of the PN ceramics, but also increased the T_c [8–10]. Furthermore, the Ca and Ti co-doped PN ceramics possess well-behaved electrical properties ($T_c = 582$ °C and $d_{33} = 76$ pC/N) [10].

Recently, we have investigated the dielectric and piezoelectric properties of La and Ti co-doped $Pb_{1-x}La_{2x/3}(Nb_{0.95}Ti_{0.0625})_2O_6$ novel ceramics [11]. The previous work mainly focused on the effects of various La modifications on the electrical properties of the ceramics. In this work, Ti content y on crystal structure, microstructures, dielectric and piezoelectric properties of $(Pb_{0.985}La_{0.01})_{1+y}(Nb_{1-y}Ti_y)_2O_6$ ceramics will be reported.

2. Experimental

The powders with the nominal formula $(Pb_{0.985}La_{0.01})_{1+y}$-$(Nb_{1-y}Ti_y)_2O_6$ ($y = 0.025, 0.050, 0.075, 0.1$) were prepared by a conventional solid-state reaction method. The powders of PbO (99%), Nb_2O_5 (99%), TiO_2 (99.99%) and La_2O_3 (99.99%) were used as starting raw materials. They were ball milling for 24 h in a polyethylene jar with ZrO_2 balls using alcohol as a medium. To compensate the loss of PbO during the calcinations process, which usually results in the formation of a $Pb_5Nb_4O_{15}$ pyrochlore phase [6], 2 wt.% PbO were added to the mixed powders. Mixtures were dried and calcined at 900 °C for 4 h. The calcined PLNT powders show a rhombohedral structure with a minor PbO as a secondary phase (Fig. 1). The calcined powders were re-milled for 12 h and ground with PVA solution as a binder. Pellets with 15 mm in diameter and 1.5 mm in thickness were pressed under 160 MPa using an uniaxial pressing. These green pellets were sintered in closed alumina crucibles at temperatures from 1210 °C to 1290 °C for 4 h, and then

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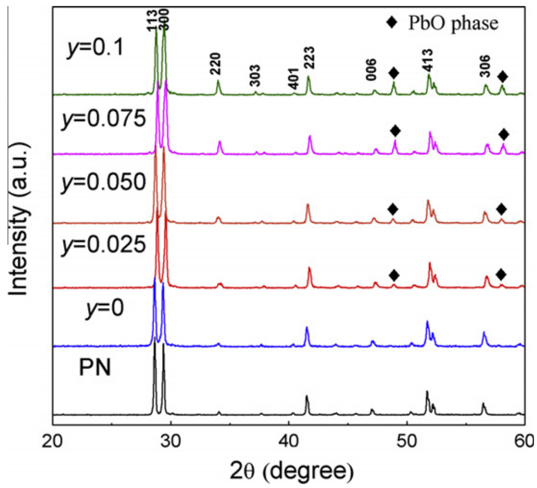

Fig. 1. X-ray diffraction patterns of the pure PN and $(Pb_{0.985}La_{0.01})_{1+y}(Nb_{1-y}Ti_y)_2O_6$ ($0 \leqslant y \leqslant 0.1$) powders calcined at 900 °C for 4 h soaking time.

cooled to the room temperature in the furnace. A lead rich atmosphere was maintained with the corresponding powders to minimize the lead loss during firing. Then, the sintered ceramics were mechanically polished. Silver paste was fired on both faces of the disks at 800 °C as electrodes. The ceramics for measurement of piezoelectric properties were polarized in silicone oil at 180 °C under the electric field of 4.5–5 kV/mm for 20 min.

The bulk density of the sintered ceramics was measured by using the Archimedes method. Relative density was calculated through the bulk density divided by the pure $PbNb_2O_6$ theoretical density (6.64 g/cm^3) [5]. X-ray powder diffraction (XRD, Rigaku D/max 2250, Japan) with Cu Kα radiation (40 kV and 50 mA) was used for the identification of phases. The microstructures of the sintered ceramics were investigated by using a Scanning Electron Microscopy (Quanta 200 SEM, Holland). The dielectric measurement was performed at various temperatures by using an Agilent E4980A precision LCR in a temperature range of 30–650 °C and a frequency range of 1 kHz–1 MHz. Piezoelectric constant d_{33} of the ceramics was measured using a quasistatic d_{33} meter (ZJ-3A Institute of Acoustics, Chinese Academy of Sciences, Beijing, China) based on Berlincourt method at 110 Hz. The remanent polarization P_r was determined from P–E hysteresis loops obtained by Radiant Precision Workstation ferroelectric testing system at 50 Hz. Piezoelectric properties were measured by means of the resonance–anti-resonance method using a precision impedance analyzer (HP4294A, Santa Clara, CA). The electromechanical coupling factors K_t and K_p were calculated from the resonance and anti-resonance frequencies based on the Onoe's formula [12].

3. Results and discussion

Fig. 1 shows the XRD patterns of pure PN and PLNT powders calcined at 900 °C for 4 h. It can be found that all powders are shown to be the rhombohedral phase structure, with two main diffraction peaks of (1 1 3) and (3 0 0) occurring at 2θ of 28.7° and 29.4°. For PLNT powders, two diffraction peaks at 48.8° and 58.0° indicate appearance of a secondary phase PbO and the intensity of the diffraction peaks becomes stronger with an increase of Ti content y. The excess PbO was advantageous to the formation of the orthorhombic ferroelectric phase of pure PN compound [6].

Fig. 2a and b shows the XRD patterns of PLNT ceramics sintered at 1210 °C and 1250 °C for 4 h, respectively. As shown in Fig. 2a, the sample with y = 0.025 remains rhombohedral structure, but a single orthorhombic phase was formed in the specimens with Ti

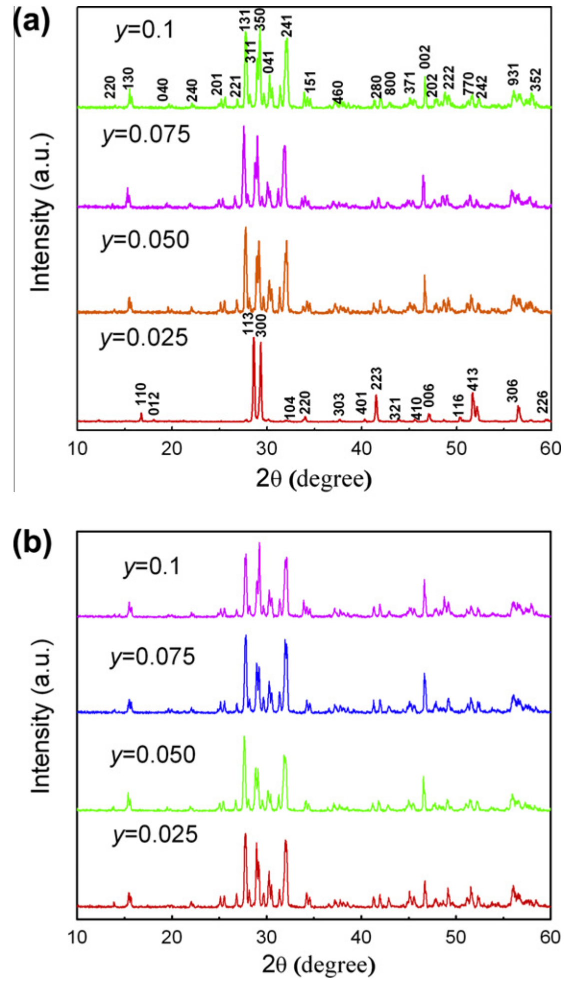

Fig. 2. The XRD patterns of $(Pb_{0.985}La_{0.01})_{1+y}(Nb_{1-y}Ti_y)_2O_6$ ($0.025 \leqslant y \leqslant 0.1$) ceramics sintered at 1210 °C (a) and 1250 °C, (b) for 4 h.

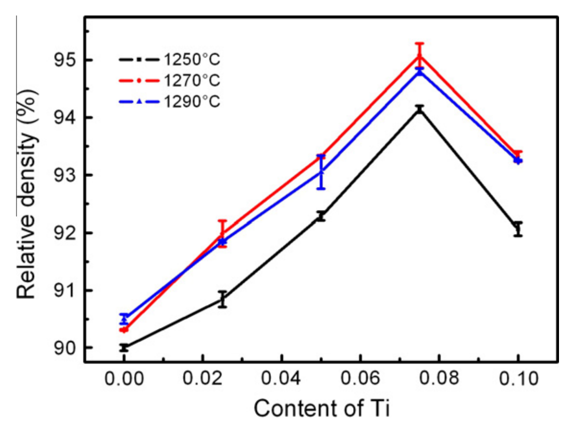

Fig. 3. Relative density as a function of the Ti content y of $(Pb_{0.985}La_{0.01})_{1+y}(Nb_{1-y}Ti_y)_2O_6$ ceramics sintered at 1250 °C, 1270 °C and 1290 °C for 4 h.

content $y \geqslant 0.05$. This means that titanium ($y \geqslant 0.05$) stabilizes the orthorhombic phase of PLNT compound. The good effect of Ti on the formation of orthorhombic phase may be related to the excess PbO found in the Ti-bearing samples [6]. In addition, the stability of crystal structure can be evaluated by tolerance factor of tetragonal tungsten bronze structure [13]. The substitution of Ti^{4+} for Nb^{5+} results in a larger tolerance factor due to a smaller