

Electrical properties of Lead Titanate Zirconate ceramics doped with niobium

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Ceramics with composition of $Pb_{(1-x/2)}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ with $x = 0.01 - 0.025$, were prepared by conventional mixed oxide route were investigated. A microstructure with mean grains sizes of 1–3 μm were found and the apparent density of 7.1–7.6 g/cm^3 . The dielectric and piezoelectric properties were determined on ceramic discs with a diameter of 10 – 18 mm and 1mm thick. Dielectric constant and losses have been measured in the range of frequencies at 40 Hz - 400 kHz using impedance analyzer. The piezoelectric constant k_p were calculate using the resonance and antiresonance values. It showed that the Nb additives were helpful in improving both of the dielectric and piezoelectric properties.

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1. Introduction

Lead zirconate titanate ceramics $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) is the mostly used piezoelectric ceramic material due to it's the excellent electromechanical properties. PZT piezoceramic, contiguous to morphotropic phase boundary (MPB) composition, i.e., the rhombohedral and tetragonal phase coexisting, is well known to have superior piezoelectric properties [1]. Modifications of the PZT ceramics and the effects of dopants have been researched extensively to improve its piezoelectric properties for various applications in actuators, piezoelectric resonators, transducers, etc [2]. One significant benefit of PZT piezoceramics is that doping foreign ions, substituting part for the host atoms, can modify their piezoelectric characteristics. Hirose and coworkers [3] reported that the Nb doping as a donor dopant improved the piezoelectric properties of PZT ceramics.

Therefore, some of the critical properties of PZT were optimized by the addition of donor dopant ions. Nb^{5+} can be considered as a donor dopant for PZT materials, since it substitutes Zr^{4+}/Ti^{4+} ions. Using donor dopant such as Nb^{5+} on the B-site is one of mechanisms thought to promote domain wall motion in PZTs [4.].

Pereira et al. reported that the Nb oxide is a good sintering aid for PZT (65/35)-based materials (high density, small grain size) and the solubility limit of Nb in PZT materials (perovskite structure) is about 7% [5]. Above this concentration, a secondary phase is formed, containing also Pb and Ti. [6].

In this paper, we prepare $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$, ($x=0.01-0.025$) system with additional dopants of Nb, probing into microstructure and ferroelectric characteristics with the sintering temperature dependence. The sample is noted PZT-N1 ($_{0.995}Pb(Zr_{0.52}Ti_{0.48})_{0.99}Nb_{0.01}O_3$), PZT-N2

$(_{0.988}Pb(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3)$ and PZT-N3 ($(Pb(Zr_{0.52}Ti_{0.48})_{0.975}Nb_{0.025}O_3)$).

2. Experimental

2.1 Sample preparation

A conventional ceramics preparation procedure was used to prepare the sample. The oxide PbO , ZrO_2 , TiO_2 and Nb_2O_5 (> 99.0% purity) were homogenized in water in a planetary Fritsch mill. Additionally, an excess of 5% of lead oxide related to the stoichiometry amount was used for all samples. The powders were obtained in Zr/Ti stoichiometry equals to 52/48, which is near the morphologic phase boundary. After 16 h milling with ZrO_2 balls in presence of the water, and dried at 80°C in oven, the materials is pressed and calcined at 850°C for 4h. The powders were milled and dried with 5%wt% of a 5% polyvinyl alcohol (PVA) solution. Then, the powders were pressed into disc with diameter 20mm and 1mm thickness, for bulk measurements, using a pressure of 2tf. Specimens were sintered at a 1120 °C, 1150 °C and respectively 1220 °C for 2h.

2.2. Measurements

The distribution of the ceramic grains has been determined using a laser granulometer (Fritsch Particle Sizer Analysette type). The grains dimension of a powder obtained is between 1 and 3 μm . To get fine grained ceramic powder is important to obtain high density and pore less piezoceramic bulk.

But, during sintering ceramics, the grains grow. The grain shape and size, for two sintering temperature, 1120 and 1180°C are given by SEM microscopy by Fig. 1.

The microscopy shows a dense microstructure with a uniform grain distribution.

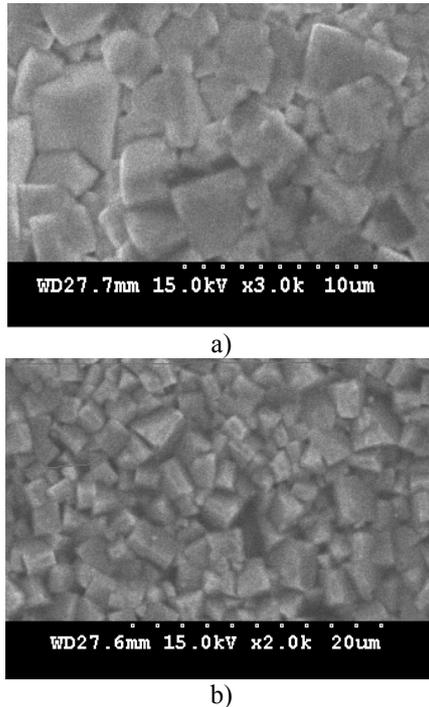


Fig. 1. SEM images for sintered composition of the PZT-N2 a) at 1120°C and b) at 1150°C.

The X-ray diffraction for two composition $0.988\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.976}\text{Nb}_{0.024}\text{O}_3$ (PZT-N2) and $0.995\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.99}\text{Nb}_{0.01}\text{O}_3$ (PZT-N1) sintered at 1120°C is shown in Fig. 2. X-Ray Diffraction for two composition sintered at 1120°C a) PZT-N1 and b) PZT-N2

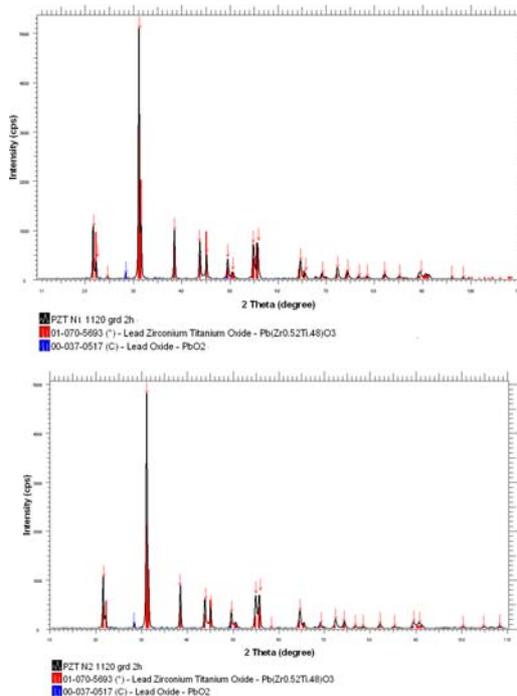


Fig. 2. X-Ray Diffraction for two composition sintered at 1120°C a) PZT-N1 and b) PZT-N2.

The XRD analysis performed on sintered samples and the indexing procedure showed the presence of a major tetragonal crystalline phase indicated by arrows in xrd spectra and a minor rhombohedral phase at $2\theta = 28.5^\circ$.

In order to measure the electrical properties, silver paste was coated to form electrodes on both sides of the samples, then subsequently fired at 650 °C for 30 min. Polarization was performed in a silicon oil bath at 160°C at 30kV/cm with a period of 30 min. After 72 h from polarization the piezoelectric properties were measured.

Dielectric, piezoelectric and electromechanical properties for ceramics were determined 72h after poling using HP 4294 A Impedance analyzer. The capacitance and the dissipation factor D were measured at 1kHz, then dielectric constant ϵ_{33} was calculate from the relation $\epsilon_{33} = Ch/\epsilon_0 A$, where h is the sample thickness and A the electrodes area.

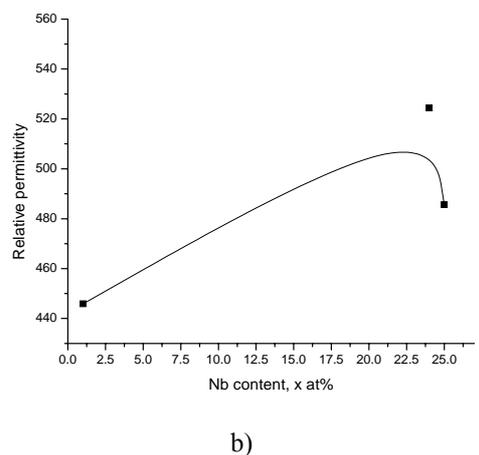
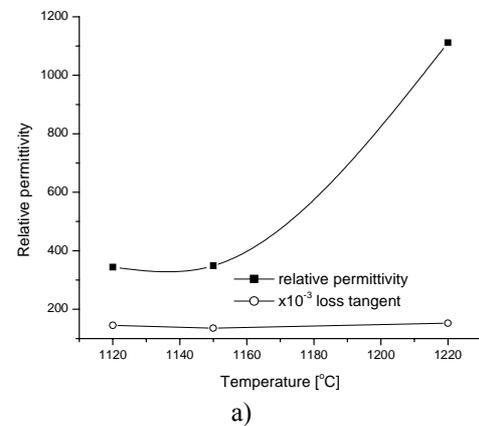


Fig. 3. Relative permittivity vs a) temperature and b) Nb content, at %.

The relative permittivity for PZT doped with Nb increase with the sintering temperature, and the Nb content (Fig. 3). For Nb content under $x = 0.024$, the dielectric properties are better and increasing over this value.

Curie temperature determinates by this variation is in all case over 400°C, with means that the electrical properties in three types of ceramics have a good stability which temperature (Fig. 4).

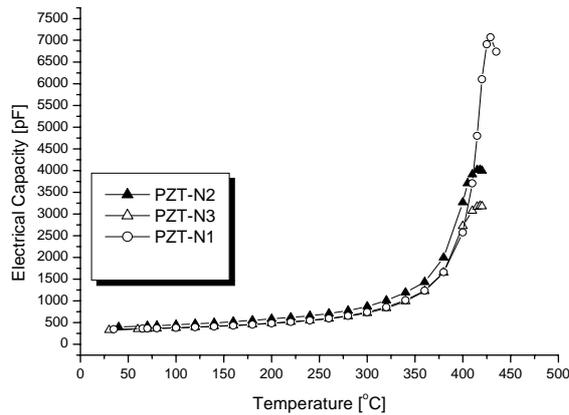
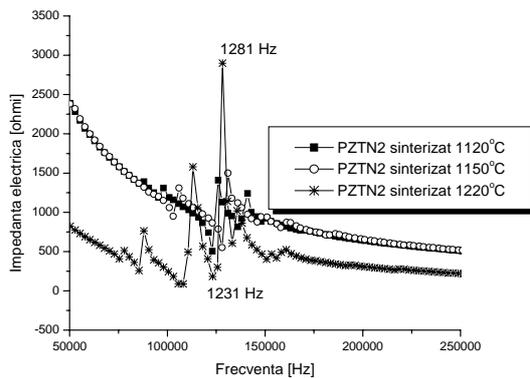
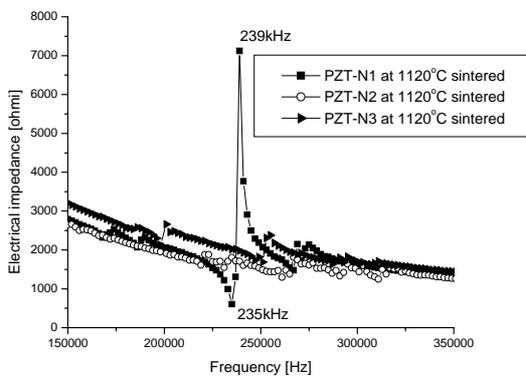


Fig. 4. Electrical capacity versus temperature for PZT-N ceramics.

Polarization degree evaluation was performed by resonance and anti-resonance frequency measurements and the electromechanical coupling coefficient was calculated according to the IEEE standard. [7].



a)



b)

Fig. 5. Electrical impedance versus a) sintering temperatures and b) frequency.

Fig. 5a) shows the electrical impedance versus temperature for PZT-N2 ceramic sintered at 1220 °C. The 1220 °C temperature is the optimum temperature for sintering. Resonance frequency is 1281 Hz and anti-resonance frequency is 1231Hz and the electromechanical coefficient k_p is 0.32. Fig. 5b) shows the electrical impedance versus frequency at 1120°C. The piezoelectric characteristic, the resonance frequency and antiresonance frequency 239kHz, respectively 235kHz is optimum for PZT N1, $x = 0.025$. Electromechanical coupling factor $k_p = 0.21$, which means that a Nb dopant concentration below 0.025, and 1220°C temperature is better.

P-E hysteresis loops of the PZT-N samples with different dopant contents are shown in Fig. 6. *Hysteresis loop versus electric field for PZT -N*. The doped PZT ceramics exhibit a typical hysteresis loop and have a relative high values in saturation polarization (P_s) and remanent polarization (P_r). The values decrease with increasing dopant concentration and maximum values for $P_r = 10.6 \mu\text{C}/\text{cm}^2$ is for PZT -N1, $x=0.01$ and minimum values is for PZT-N3, $x = 0.025$, $P_r = 6.31 \mu\text{C}/\text{cm}^2$.

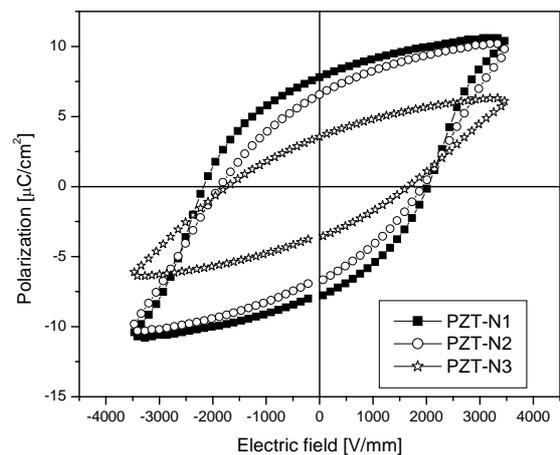


Fig. 6. Hysteresis loop versus electric field for PZT -N.

3. Conclusions

Nb doped PZT ceramics, with a composition of $\text{Pb}_{1-x}[(\text{Zr}_{0.52}\text{Ti}_{0.48})_{1-x}\text{Nb}_x]\text{O}_3$ ($x = 0.01 - 0.025$), have been prepared by the conventional solid-state reaction method, using high purity (>99.9%) commercial PbO , ZrO_2 , TiO_2 , and Nb_2O_5 powders as starting materials. The doping of Nb^{5+} ions leads to a significant difference in the electrical properties of PZT. According to the experimental results, Nb dopant is helpful increasing the dielectric constant, planar electromechanical coupling coefficient of PZT ceramics.

Acknowledgements

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