

# Phase development and dielectric properties of $(1-x)\text{Pb}(\text{Ni}_{1/3}\text{Ta}_{2/3})\text{O}_3-x\text{PbTiO}_3$ ceramics

Zhenrong Li<sup>a,b</sup>, P.M. Vilarinho<sup>a,\*</sup>

<sup>a</sup> Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>b</sup> Electronic Materials Research Laboratory, Key Laboratory of Education Ministry, Xi'an Jiaotong University, Xi'an 710049, China

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## Abstract

$(1-x)\text{Pb}(\text{Ni}_{1/3}\text{Ta}_{2/3})\text{O}_3-x\text{PbTiO}_3$  ( $x=0.00-0.80$ ) ceramics were prepared by the columbite/wolframite method. The phase stability was studied by XRD analysis. No perovskite phase was formed for  $x=0.00$ . As PT content increases in the solid solution, the perovskite phase becomes dominant at room temperature. When  $x \geq 0.60$ , a pure perovskite phase was obtained. The temperature dependence of the dielectric properties was evaluated. A maximum of the dielectric constant of about 28,000 is observed for  $x=0.60$  ceramics.

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## 1. Introduction

Lead-based relaxor ferroelectrics are widely used in microelectronic applications such as capacitors, tunable transducers, and memory devices.<sup>1</sup> Most of the researches have been mainly focused on the study of lead-based niobate  $\text{Pb}(\text{B}_{1-x}\text{Nb}_x)\text{O}_3$  materials, in which  $\text{B} = \text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ , and the solid solution with  $\text{PbTiO}_3$ . Lead-based tantalate  $\text{Pb}(\text{B}_{1-x}\text{Ta}_x)\text{O}_3$  is another family of ferroelectric relaxors, but not too much attention has been paid to this system. However, the low phase transition temperature of some of the members make  $\text{Pb}(\text{B}_{1-x}\text{Ta}_x)\text{O}_3$ , ( $\text{B}$  is  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ) important candidates for utilization in devices operating at cryogenic conditions, like low temperature capacitors and actuators for space applications. Moreover, the perovskite phase stabilization is difficult in these systems.

According to the literature, Nb tends to stabilize the perovskite phase in  $\text{Pb}(\text{B}_{1-x}\text{Nb}_x)\text{O}_3$  system more effectively than Ta in  $\text{Pb}(\text{B}_{1-x}\text{Ta}_x)\text{O}_3$ .<sup>2</sup> It is well known that two basic requirements should be fulfilled to obtain a stable perovskite phase: a tolerance factor,  $t$ , comprised between 0.8 and 1.09

and strong ionic bonds.<sup>3</sup> Due to the electronic configuration of  $\text{Ta}^{5+}$ , when compared with  $\text{Nb}^{5+}$ , the degree of covalent bonding in tantalum compounds is higher. In addition, the stabilization of the perovskite phase is different for different B site ions. It is relatively easy to obtain a pure perovskite phase for  $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ <sup>4</sup> and  $\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ .<sup>5</sup> However, and similarly to  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PZN), it has been reported that it is impossible to prepare  $\text{Pb}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  (PZTa) with a pure perovskite structure.<sup>6</sup> Several attempts were conducted to obtain the perovskite stabilization in PZTa by adding 80 mol%  $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ ,<sup>7</sup> 35 mol%  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ ,<sup>8</sup> and 80% of  $\text{PbTiO}_3$  (PT).<sup>9</sup> It is known that the tolerance factor and electronegativity difference in PZTa systems are increased by the solid solution formation with these compounds and consequently the stabilization of the perovskite phase. Recently, a new methodology to stabilize the perovskite phase in PZTa ceramics that combines the maximization of the crystal-chemical and thermodynamic requirements, and optimization of the kinetics of the reaction of perovskite phase formation by using highly reactive PT nucleus was reported.<sup>10</sup> A pure perovskite phase was obtained at  $x=0.60$  by PT seeds method and the dielectric constant of 0.40PZTa-0.60PT ceramics was reported to be 13,800, at 1 kHz, compared with 5800 at 1 kHz for ceramics prepared by oxide mixture sample.<sup>10</sup>

\* Corresponding author. Tel.: +351 234 370354; fax: +351 234 425300.  
E-mail address: paulas@cv.ua.pt (P.M. Vilarinho).

$\text{Pb}(\text{Ni}_{1/3}\text{Ta}_{2/3})\text{O}_3$  (PNT) system has not been widely reported in the literature. PNT single crystal is ferroelectric relaxor with a maximum of dielectric constant of 2400 at 450 kHz and  $-160^\circ\text{C}$ .<sup>2</sup> Ling et al.<sup>2</sup> investigated the perovskite phase formation of PNT ceramics. The results showed that only pure pyrochlore phase was obtained when conventional mixed oxide method was used. No other systematic investigations were reported on this system to the author's knowledge.

In this paper, the phase development and the perovskite phase stabilization of PNT induced by PT is studied.  $(1-x)\text{PNT}-x\text{PT}$  ( $x=0.00-0.80$ ) powders were prepared by the columbite method.<sup>11</sup> The phase structure development was investigated by XRD analysis. The temperature dependence of the dielectric properties was measured. From these preliminary results, the relationship between phase structure and dielectric properties is presented and discussed.

## 2. Experimental procedure

$(1-x)\text{PNT}-x\text{PT}$  ( $x=0-0.80$ ) powders were prepared by the columbite method. The starting raw materials were reagent grade  $\text{PbO}$  (Merck, purity >99.0%),  $\text{NiO}$  (Merck, purity >99.0%),  $\text{Ta}_2\text{O}_5$  (Merck, purity >99.8%) and  $\text{TiO}_2$  (Merck, purity >99.0%).  $\text{NiO}$  and  $\text{Ta}_2\text{O}_5$  oxides were firstly mixed in teflon pots with alcohol in 1:1 mol ratio. The mixture was dried and calcined at  $1200^\circ\text{C}$  for 2 h to form  $\text{NiTa}_2\text{O}_6$ .  $\text{PbO}$ ,  $\text{NiTa}_2\text{O}_6$ , and  $\text{TiO}_2$  were then mixed according to the formula  $(1-x)\text{PNT}-x\text{PT}$  ( $x=0-0.80$ ), for 4 h and calcined at  $900^\circ\text{C}$  for 3 h in a covered alumina crucible. The phase formation process was followed by XRD analysis. The relative amount of the perovskite phase was determined from the relative intensities of the major XRD peaks of perovskite (1 1 0) and pyrochlore (2 2 2) (according to the relation:  $I_{\text{perov}(110)}/(I_{\text{perov}(110)} + I_{\text{pyro}(222)})$ ).

$(1-x)\text{PNT}-x\text{PT}$  powders were uniaxially and then isostatically pressed at 200 MPa. The pellets were sintered between  $1100$  and  $1150^\circ\text{C}$  for 3 h in air. For the evaluation of the dielectric properties, gold electrodes were sputtered on both sides of the sample. Dielectric measurements were performed with a HP4284A LCR meter, from room temperature to  $300^\circ\text{C}$ , at a heating rate of  $2^\circ\text{C}/\text{min}$  and in a frequency range from 1 to 1000 kHz.

## 3. Results and discussion

Fig. 1 depicts the XRD patterns of calcined powders of  $(1-x)\text{PNT}-x\text{PT}$  system. For  $x=0.00$  composition, the main phase is a pyrochlore type, of unidentified composition, confirming the results reported by Ling.<sup>2</sup>  $\text{PbO}$  and an unknown phase are also visible. The perovskite phase is almost not found. When  $x=0.10$ , the perovskite phase is clearly observed, but the main phases are still pyrochlore and  $\text{PbO}$ . As

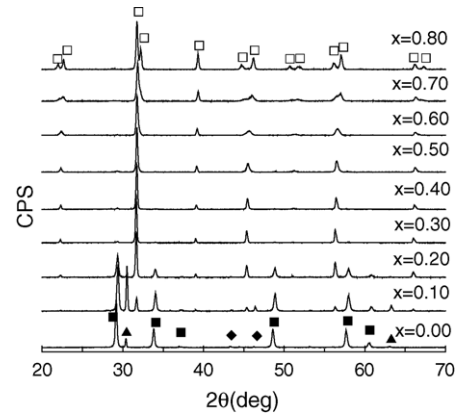


Fig. 1. XRD pattern of  $(1-x)\text{PNT}-x\text{PT}$  powders calcined at  $900^\circ\text{C}$  ( $\square$ ) perovskite; ( $\blacksquare$ ) pyrochlore; ( $\blacktriangle$ )  $\text{PbO}$ ; ( $\blacklozenge$ ) unknown phase).

$x$  increases the perovskite phase becomes the dominant one and the amount of pyrochlore and other extra phases gradually decreases, as expected. The variation of the amount of the perovskite phase formed at  $900^\circ\text{C}$  with PT content is shown in Fig. 2. When  $x \geq 0.30$ , the perovskite phase content is more than 97%. For  $x \geq 0.60$ , a pure perovskite phase was obtained. Comparing the perovskite phase formation in  $\text{Pb}(\text{Ni}_{1/3}\text{Ta}_{2/3})\text{O}_3$  and  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PNN) systems, single perovskite PNN phase was prepared by the reaction of  $\text{NiNbO}_6$  with  $\text{PbO}$ ,<sup>12</sup> however, it is impossible to obtain pure perovskite phase through the reaction of  $\text{NiTaO}_6$  and  $\text{PbO}$ . From the results presented in this work, the formation of the pyrochlore phase in PNT can be completely avoided by adding 60 mol% of PT. The tolerance factor and electronegativity difference of PNT are around 0.99 and 1.8, respectively.<sup>13</sup> The higher tolerance factor (1.02) and electronegativity difference (1.9) of PT correlated with the perovskite phase formation and stabilization in PNT, as verified for other lead-based systems. Like in PZN and PZTa systems, these results also indicate that Nb tends to stabilize the perovskite phase more effectively than Ta.

From Fig. 1, the change of some diffraction peaks with the PT content can be observed. For compositions with

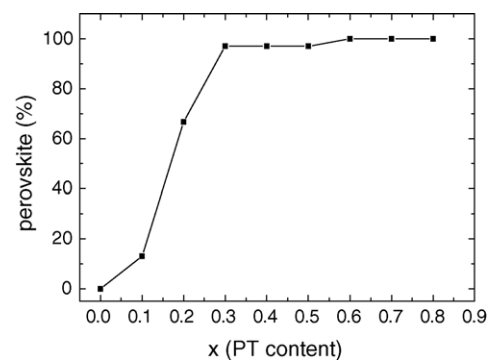


Fig. 2. The amount of the perovskite phase in  $(1-x)\text{PNT}-x\text{PT}$  powders as a function of PT content.

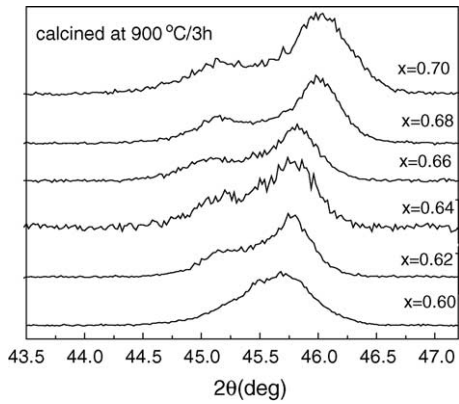


Fig. 3. XRD pattern of  $(1-x)\text{PNT}-x\text{PT}$  powders around  $2\theta = 45^\circ$ .

$x = 0.60-0.80$ , a visible splitting of the diffraction peak around  $2\theta = 45^\circ$  is detected though for the compositions with  $x = 0.30-0.50$ , no splitting is observed, demonstrating that the structure is changing to a tetragonal symmetry, as the PT content increases. A detailed analysis of the phase transition for compositions with  $x = 0.60-0.70$  is presented in Fig. 3. The unsplit  $(200)$  line indicates that the cubic structure remains for  $x = 0.60$ . For compositions with  $x = 0.62-0.70$ ,  $(200)$  peaks undergo a gradual splitting, which corresponds to a phase transition to a tetragonal structure.

The variation of the dielectric constant with temperature for ceramics with  $x = 0.50-0.70$  ceramics is shown in Fig. 4. With increasing  $x$  (PT content), the transition temperature shifts to higher temperatures and the dielectric peak becomes sharper, indicating the increasing behaviour as a first-order ferroelectric. A maximum dielectric constant of about 28,000 is observed for  $x = 0.60$  ceramics. The relationship between the transition temperature ( $T_m$ , corresponding to the maximum dielectric constant) and composition represented in Fig. 5 is almost linear.

The frequency dependence of the dielectric properties for  $x = 0.50$  and  $0.60$  ceramics is shown in Fig. 6. A diffuse phase

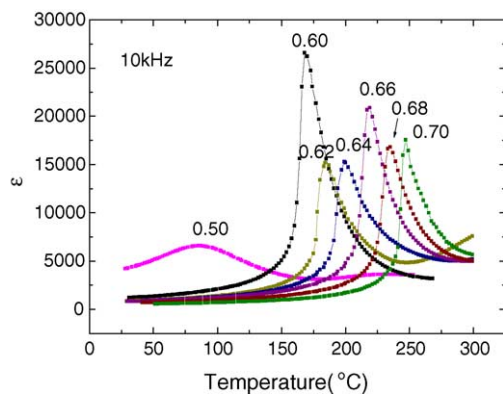


Fig. 4. Variation of dielectric constant with temperature for  $(1-x)\text{PNT}-x\text{PT}$  ceramics ( $f = 10$  kHz).

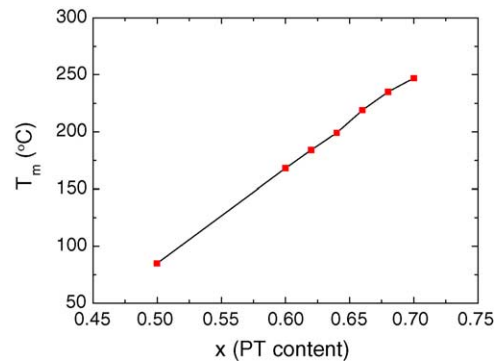
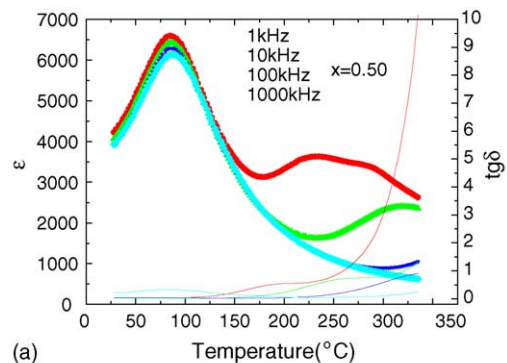
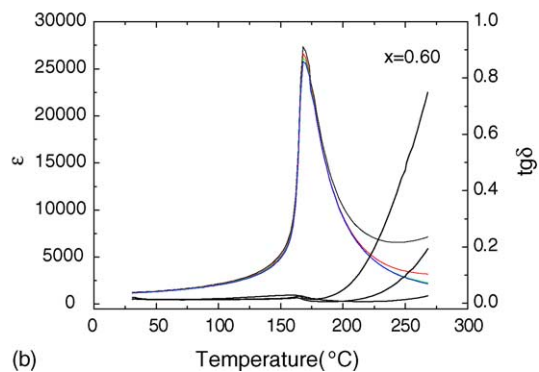


Fig. 5.  $T_m$  vs. composition in  $(1-x)\text{PNT}-x\text{PT}$ .

transition and a small frequency dispersion of the dielectric maxima are presented for  $x = 0.50$  ceramics, indicating a relaxor-type behaviour. Differently,  $x = 0.60$  ceramics exhibits sharp dielectric constant peaks with almost no dependence on the frequency of measurement, implying a classical ferroelectric behaviour. It is also found that the losses increase and dielectric constant rises with increasing temperature in the range of high temperature for these two ceramics. For  $x = 0.50$  composition, a second dielectric peak is clearly observed in the dielectric constant curve at the lowest frequency (Fig. 6). Similar results were observed in  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  (PNN-PT) ceramics and attributed to the partial



(a)



(b)

Fig. 6. Temperature dependence of dielectric properties for: (a)  $x = 0.50$ ; (b)  $x = 0.60$  ceramics.

oxidation of  $\text{Ni}^{2+}$ . Under these conditions, polar defect pairs created and may be related to such dielectric anomaly.<sup>14</sup> Annealing treatments in different atmospheres will be conducted in order to contribute to the clarification of the nature of such dielectric dispersion.

#### 4. Conclusions

The perovskite phase stabilization of PNT induced by PT was studied. For  $x=0.00$  composition, the main phase is pyrochlore. When  $x \geq 0.30$ , the perovskite phase content increases, becoming dominant as PT content increases (>97%). For  $x \geq 0.60$ , a pure perovskite phase was obtained. The crystalline structure changed gradually to a tetragonal symmetry with increasing PT content in the range of  $x=0.60$ – $0.70$ . A diffuse phase transition and a dependence on the frequency of the temperature of the dielectric maxima was observed for  $x=0.50$  ceramics. When  $x > 0.60$ , the samples show sharp dielectric peaks characteristic of a classical ferroelectric behaviour. A maximum dielectric constant of about 28,000 was detected in  $x=0.60$  ceramics.

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