Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of the European Ceramic Society 25 (2005) 2443–2446
www.elsevier.com/locate/jeurceramsoc

Piezoelectric properties of undoped and titanium or barium-doped lead metaniobate ceramics

M. Venet [a,*], A. Vendramini [a], F.L. Zabotto [a], F. Guerrero [b], D. Garcia [a], J.A. Eiras [a]

[a] *Ferroelectric Ceramics Group, Physics Department, Federal University of São Carlos, Rod. Washington Luiz. km 235, São Carlos 13565905, SP, Brasil*
[b] *Physics Department, University of Oriente, Patricio Lumumba. C.P. 90500. Santiago de Cuba, Cuba*

Available online 30 March 2005

Abstract

Ferroelectric materials with high Curie temperature are highly desirable to construct transducers for high temperature piezoelectric applications. Among the ferroelectric materials $PbNb_2O_6$ (PN) is one that display such characteristic. However, the fabrication of high density PN ceramics is very difficult, which limited the use in piezoelectric transducers. In this paper high density (~95%) Ti- and Ba-doped PN ceramics were prepared through the conventional ceramic method. The electromechanical coefficients, such as coupling (k_{31}, k_{33}) and quality factors (Q_m), were measured and compared in the investigated materials. The properties of "pure" PN were comparable to those observed in Ti- and Ba-modified PN ceramics. The addition of Ba to the PN ceramics decreased the Curie temperature (as compared to the pure PN), limiting the applicability in piezoelectric transducers for temperatures below 350 °C. On the other hand, the addition of titanium not only increases the Curie temperature, but also contributes to the increase of the densification of the PN ceramics. Results showed that Ti doped PN ceramics present a high potential to be used in high temperature applications as piezoelectric transducers.

Keywords: Piezoelectric properties; Dielectric properties; Lead metaniobate

1. Introduction

Lead metaniobate $PbNb_2O_6$ (PN) is a ferroelectric material with a tungsten–bronze structure and orthorhombic symmetry in the ferroelectric phase.[1–3] Due to its high Curie temperature (T_c) and low quality factor (Q), this material has potentiality to be used in the fabrication of ultrasonic transducers, for high temperature applications, such as flow detectors devices (where the $Pb(Zr,Ti)O_3$ and other piezoelectric materials can not be used).[4]

Although the PN ceramics have excellent industrial applicability, they fabrication is extremely difficult. First, because the orthorhombic ferroelectric phase is only obtained after appropriates heat treatments.[3,5,6] Second, abnormal grain growth, cracks and the formation of undesirable phases (promoted by the PbO losses) may affect the densification of the PN ceramics, difficulting the polarization[5,6] and, consequently, their use in ultrasonic transducers.

In order to avoid the aforementioned difficulties some elements may be used as additives in the PN structure. For example, the addition of barium[7–9] ($Pb_xBa_{1-x}Nb_2O_6$ or PBNx) contributes for the densification of this material, but highly reduce the Curie temperature, harming the high temperature applications. Others elements also added to the PN structure, such as Pb, Ca, Mn La and Ti,[3,4,10] have been used to increase the densification rate of the PN. An important characteristic is that the addition of Ti, not only increases the densification of the PN ceramic, but also increases the T_c,[3] which is a desirable property for high temperature transducers. However, to obtain a single phase compound with orthorhombic ferroelectric phase, some authors[5,6] needed to use a quenching by dropping the sample into an empty beaker surrounded by pieces of ice. This procedure may be inconvenient in high quantities processing.

* Corresponding author. Tel.: +55 16 260 8227; fax: +55 16 261 4835.
E-mail address: venet74@df.ufscar.br (M. Venet).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.03.079

In this work, highly densified Ti- and Ba-doped PN ceramics were prepared. The main piezoelectric properties were measured and compared between the studied materials, viewing the potential of these materials for high temperature applications.

2. Experimental

Ceramic powders with nominal formula $PbNb_2O_6$ (PN), $Pb_{0.75}Ba_{0.25}Nb_2O_6$ (PBN75) and $Pb_{1+x}Ti_xNb_{2-x}O_6$ (PTNx) were prepared by the solid-state reaction method. Analytical graded precursors (with an excess of 2 wt.% PbO, in the case of PN and PTN), were mixed in a ball mill, containing isopropyl alcohol and stabilized ZrO_2 cylinders, during 20 h. The mixture was dried, and calcined at 1050 °C for 3.5 h and ball milled again for 20 h. The powders of PN and PTN were heat treated at 1300 °C for 1 h in order to obtain the room temperature orthorhombic ferroelectric phase. After the thermal treatment, 3 wt.% of PbO was added to compensate the lead losses during the sintering process, at 1270 °C/4.5 h. Similar sintering process was used for the PBN75 sample, where the addition of PbO excess and thermal treatment was not necessary to obtain the ferroelectric phase. This sample was prepared mainly to compare the effect of both dopants. X-ray diffraction technique was performed to a qualitative phase analysis and to determinate the lattice parameters at room temperature, using a Rigaku diffractometer and Cu Kα radiation. Computer assisted dielectric characterization was realized as a function of the temperature, using an HP 4194A impedance gain phase analyzer. The measurements were performed over a temperature range of 24 °C < T < 650 °C, during heating and cooling process, at a constant rate of 2 °C/min. The samples were cut with different geometries (bars and discs) to enable the piezoelectric characterization through the Gain–Bandwith method.[11] Measurements of electrical resistivity versus temperature allowed to choose the poling temperature, which was 150 °C. All samples were poled in this temperature with an electric field of 4 kV/mm for 30 min.

3. Results and discussion

As mentioned in Section 1, the fabrication of a PN ceramic with a single phase is a difficult task. Lee and Kimura[5,6] studied the phase evolution of the PN ceramics, obtaining the ferroelectric phase through a thermal treatment at 1300 °C and an appropriate quenching before the sintering of the ceramic bodies. In this work, the orthorhombic phase was obtained without the quenching. The addition of PbO in excess, during the fabrication process, allowed us to obtain PN ceramics with a single orthorhombic phase, as illustrated in Fig. 1.

In Fig. 2 can be observed the variation of the Curie temperature and the density of the sintered samples as a function of the Ti content. The density of PTN ceramics increases gradually with the increasing of the Ti content. The Curie temperature also increases with the Ti content, from approximately 520 °C (for $x = 0$) up to 560 °C (for $x = 0.1$). On the other hand, the addition of Ba ($x = 0.25$) allows the fabrication of higher densified ceramics when compared with PTNs, but decreases, in considerably form, the Curie temperature (∼360 °C). This result, as mentioned above, practically destroys the high temperature potentiality of PN as piezoelectric materials.

Fig. 3 illustrates the behavior of the room temperature mechanical quality factor, for the thickness vibration mode, of a thin disc (Q_m) and the relative dielectric permittivity ($\varepsilon_{33}/\varepsilon_0$),

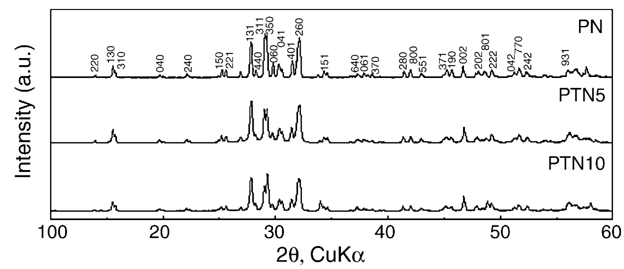

Fig. 1. X-ray diffraction patterns of the PN and PTN powders, heat treated at 1300 °C during 1 h, with orthorhombic structure.

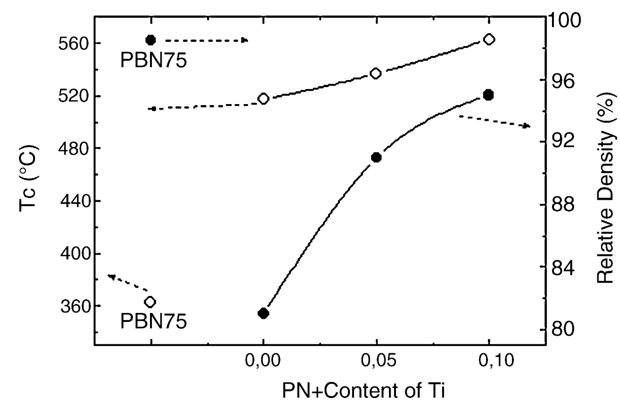

Fig. 2. Curie temperature (T_c) and relative density, as a function of the Ti content, for the PTN ceramics and for PBN75.

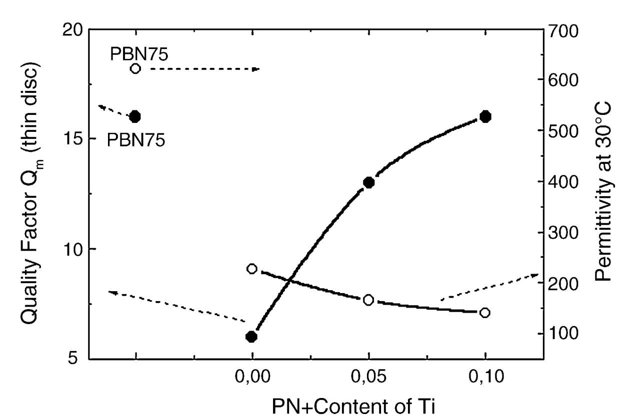

Fig. 3. Quality factor (Q_m) and permittivity at room temperature, as a function of the Ti content, for the PTN ceramics and for PBN75.