

Studies on PZT–Nb modified piezoceramic materials

A. M. MOISIN*, A. I. DUMITRU, E. ANDRONESCU^a, C. GHITULICA^a
National R&D Institute in Electrical Engineering, 313 Splaiul Unirii, Bucharest, Romania
^a*University Politehnica, 313 Splaiul Independentei, 77206 Bucharest, Romania*

PZT with aliovalent Nb⁵⁺ substitutions in Ti⁴⁺/Zr⁴⁺ positions have been obtained through a conventional mixed oxide method. Advanced milling by using two different milling systems has been performed in order to get fine grained ceramic powder. The ceramic grains growth has been limited by choosing the optimized sintering parameters. The investigation of the distribution of the mean dimensions of the ceramic powder grains as well as their dimensional increasing after sintering by both granulometric and SEM analysis has been performed. XRD analysis and electrical parameter measurements have been performed too.

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1. Introduction

Lead zirconate-titanate ceramics - Pb(Zr_{1-x}Ti_x)O₃ (PZT) - is the mostly used piezoelectric ceramic material due to its excellent electromechanical properties. It is a solid solution of ferroelectric PbTiO₃ and antiferroelectric PbZrO₃ in different Zr/Ti ratios. The structure is of perovskite type with the general formula ABO₃ (A – mono-trivalent, B – tri-hexavalent ions) that gives the possibility to make various substitutions in the A and/or B sites resulting the modified PZT material [1]. The substitution with some dopants and the value of the Zr/Ti ratio provide different structural modifications and influence the properties of the ceramic material.

In the present paper PZT with Nb⁵⁺ substitutions and a Zr/Ti ratio of 52/48 have been investigated. The Nb⁵⁺ dopants are donor type creating Pb vacancies in PZT (soft PZT). Their effect is to increase the values of both the piezoelectric coefficient and the permittivity and to decrease the coercive field and mechanical quality factor. The Zr/Ti ratio value is important for situating PZT near the morphotropic phase boundary.

Another aspect we considered was the influence of the ceramic particle size on the properties of the material. Excepting the densification of the bulk piezoelectric active elements, the dimension of the ceramic grains influences the electrical properties of the material [2]. Several techniques were used in the elaboration process in order to obtain fine grained ceramic powder and then to control their increase mainly during the high temperature sintering.

2. Experimental

Soft Pb_{1-x/2}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO₃ with x=0.024 (PZTN-2) and 0.025 (PZTN-1) and ε=x/2 were prepared by the conventional mixed oxide process. The oxides – TiO₂, ZrO₂, PbO, Nb₂O₅ – were homogenized in water in a planetary Fritsch mill. Two types of milling have been used: advanced milling in a planetary mill and attritor milling. In order to get fine grained ceramic powder we used longer milling time, from 1 to 3 hours. Calcination at 850 °C and the sintering between 1180 °C and 1230 °C have been performed. The active piezo elements have been obtained after electrical poling at 5 kV/mm.

3. Results

The distribution of the ceramic grains dimensions has been determined by using a laser granulometer (Fritsch Particle Sizer Analysette type). Some results obtained in different milling conditions are shown in Fig. 1. The difference obtained in the two milling processes is evident: the grains mean dimension of a powder obtained in an Attritor mill is under 1 μm while in a Planetary mill is between 1 and 3 μm.

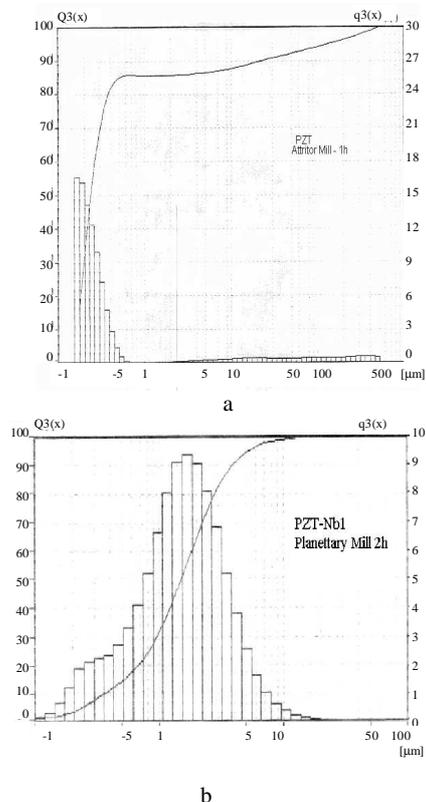
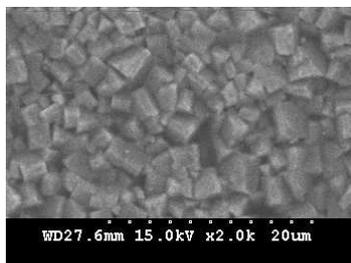


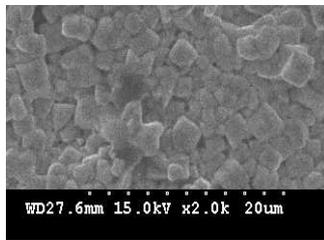
Fig. 1. The distribution of the ceramic grains dimensions after two milling processes: (a) 1 h in an Attritor mill and (b) 2 h in a planetary mill.

To get fine grained ceramic powder is important to obtain high density and pore less piezoceramic bulk. The further processing of the ceramic powder produces, mainly during sintering, a growth of the ceramic grains. In a technology using a normal planetary milling the dimension of the grains in the bulk is under $5 \mu\text{m}$. By advanced or attritor milling to get the ceramic powder we obtained smaller values of the grain's dimension in the bulk: $2\text{-}3 \mu\text{m}$ and respectively $< 1 \mu\text{m}$. To see the growth of the ceramic grains after sintering, SEM measurements on bulk material at different sintering temperatures were performed.

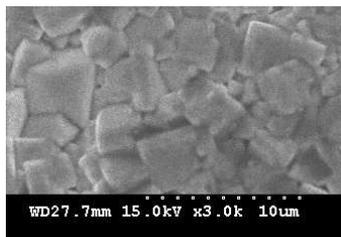
Some SEM images obtained on PZT-Nb samples at different compositions and sintered at two different temperatures are given in Fig. 2. The bulk ceramic has been obtained from Planetary milled powder.



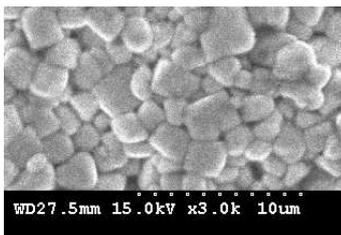
(a)



(b)



(c)



(d)

Fig. 2. The SEM micrographs of PZTN-1 sintered at $1.230 \text{ }^\circ\text{C}$ (a) and $1.180 \text{ }^\circ\text{C}$ (b) and PZTN-2 sintered at $1.230 \text{ }^\circ\text{C}$ (c) and $1.180 \text{ }^\circ\text{C}$ (d).

The micrographs show a dense microstructure with a uniform grain distribution; the dimension of the grains increases with the temperature achieving $2\text{-}3 \mu\text{m}$ at $1.230 \text{ }^\circ\text{C}$. In the case of PZTN-2 one observes the formation of bigger plates too (c).

XRD measurements showed a majoritary perovskite phase with an tetragonality $c/a=4.09/3.94=1.038$ for PZT-N₁ composition.

Electrical measurements has been performed and some characteristics such as the dielectric losses $\text{tg } \delta$, relative permittivity ϵ_{33}/ϵ_0 and electromechanical coupling factor k_p are given in Table 1.

Table 1.

Sample	$\text{tg } \delta$ at 1 kHz	$\text{tg } \delta$ at 10 kHz	ϵ_{33}/ϵ_0	k_p
PZTN-1	0.013	0.014	342	0.5
PZTN-2	0.017	0.016	446	0.45

These characteristics have been determined because the PZT-Nb material has been used as substrate for a SAW resonator [3]. All the measurements have been performed on piezoceramic samples obtained by using planetary advanced milling. The dielectric losses $\text{tg } \delta$ have low values and this fact is correlated with the fine dimensions of the ceramic grains.

4. Conclusion and discussion

PZT- modified with Nb has been elaborated by a mixed oxide route. Different type of milling has been used in order to get fine grained ceramic powder. The optimum sintering temperature, namely $1.180 \text{ }^\circ\text{C}$ has been determined from SEM measurements. SEM investigation showed the evolution of the microstructure with the sintering temperature and the formation of a dense bulk, poreless microstructure. The dimension of the ceramic grains were between $2\text{-}3 \mu\text{m}$ when the powder was obtained by a planetary milling and under $1 \mu\text{m}$ in a attritor milling case.

The PZT-Nb piezoceramic has been developed in order to be used as substrate for SAW components.

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*Corresponding author: ammoisin@icpe-ca.ro