

## EFFECT OF Nb DOPPING ON PIEZOELECTRIC PROPERTIES OF PZT TYPE CERAMICS

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*Abstract:* The effect of niobium doping on the piezoelectric properties of the compositions  $\text{Pb}[(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.975}\text{Nb}_{0.025}]\text{O}_3$  and  $\text{Pb}_{0.988}[(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.975}\text{Nb}_{0.024}]\text{O}_3$  was investigated. The materials were prepared by the usual mixed oxide ceramic technique starting from high purity raw materials. Disc shaped samples of each composition were sintered 2 hours at a temperature of 1230°C. The perovskite structure was determined by X-ray diffraction and the piezoelectric properties were determined by means of a resonance – antiresonance method and the influence of the Nb doping on the electrical parameters has been established.

*Key words:* ferroelectric ceramic, dopants, piezoelectric, dielectric properties

### 1. INTRODUCTION

The lead zirconate-titanate  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  ceramics (PZT) is widely used in piezoelectric applications, because of its superior piezoelectric properties.

Lead zirconate titanate (PZT) has the perovskite structure (the general formula  $\text{ABO}_3$ ) with the A-site ( $\text{Pb}^{2+}$ ) occupying the cubo-octahedral interstices described by the  $\text{BO}_6$ - site octahedral. Above the Curie temperature, the unit cell is cubic, but below, it is distorted to either tetragonal or rhombohedral. The boundary between these two phases (Zr:Ti~52:48) at room temperature is known as the morphotropic phase boundary (MPB), where the tetragonal and rhombohedral phases coexist and the most of the properties show their maximum values.

A solid-state reaction process using oxides as the starting materials traditionally prepared PZT powders.

The conventional method requires high calcinations temperature.

Many olivaleant compositional alterations to PZT have been studied either with higher valence substitutions (donors), either with lower valence ions (acceptors). Several modified PZT materials have found applications such as piezoelectric and electrostrictiv devices in the bulk form: multi-layer capacitors, electro-optic shutters and piroelectric senzors in the thin film form.

In the case of niobium doping, PZTN materials, some recent works deal with several improvements when produced as thin film: an increase in the electrical rezistivity and an enhancement of hysteresis squareness and fatigue behaviour. Niobium,  $\text{Nb}^{5+}$  can be considered as a donor dopant for PZT materials, since it substitutes the  $\text{Ti}^{4+}/\text{Zr}^{4+}$  ions.

In the present paper, we intend to present a study of the effects of the niobium doping on the electrical properties.

## 2. EXPERIMENTS

The materials were prepared by conventional powder processing technique, i.e. starting from high purity raw materials: TiO<sub>2</sub> (Loba purum) ZrO<sub>2</sub> (Merck 99%), Nb<sub>2</sub>O<sub>5</sub> (Fluka 99.9%) and PbO (Aldrich 99.9%).

The stoichiometric amount of the oxide was weighted according to the general formula of PZTN 52/48/x where x is the Nb content.

After 10 h of ball milling with agate balls, the mixed powders were calcinated in the air for 2 h at a temperature of 850°C. The calcinated powders were then pressed into a disk form with 10 mm in diameter and about 1mm thickness.

The compacts were sintered at 1230°C for 2 hours. The phase content of the samples was monitored by X-ray diffraction (XRD) using CuK<sub>α</sub> radiation. The sintered compacts density was measured by the Archimedes method, using water.

The dielectric properties of the ceramics were investigated using inductance-capacitance –impedance-meter (model Hewlett Packard).

## 3. THE INFLUENCE OF NIOBIUM ON THE SINTERING

The compacts were sintered in air at 1230°C for 2 h. The sintered samples are polished and all the samples are covered with a silver paste.

Fired-on silver paste was used as the electrode for electrical measurements such as dielectric and piezoelectric measurements. Table 1 shows the measured density, absorption and porosity of the doped PZT prepared using two niobium concentrations. The Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)<sub>0.975</sub>Nb<sub>0.025</sub>O<sub>3</sub> composition has been replaced with PZTN<sub>1</sub> while instead of Pb<sub>0.988</sub>(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)<sub>0.976</sub>Nb<sub>0.024</sub>O<sub>3</sub> we will use PZTN<sub>2</sub>.

It is noted that the niobium concentration has an insignificant effect on the sintered density.

*Tabel 1*

The physical properties of the studied materials.

Type of materials	$\rho$ [g/cm <sup>3</sup> ]	P [%]	Absorption [%]
PZTN <sub>1</sub>	7.12	0.047	0.065
PZTN <sub>2</sub>	7.46	0	0

## 4. PIEZOELECTRIC CHARACTERISTICS

The poling process has been realized in a silicon oil bath under a DC electrical field of 2 KV/mm applied for 30 min. All the measurements were made at 24 h after the poling. The wide range dielectric response of any material is defined by several polarization mechanisms. Piezoelectric properties were measured by means of a resonance-antiresonance method. The electro-mechanical coupling factor K<sub>p</sub> was calculated from the resonance and antiresonance frequencies.

Table 2 shows the piezoelectric and dielectric characteristics.

Table 2

Piezoelectric properties						
Materials type	$F_r$ [kHz]	$F_a$ [kHz]	$K_p$	$T_c$ [ $^{\circ}$ C]	$\epsilon_{33}$	$\tan \delta$
PZTN <sub>1</sub>	162.72	179.84	0.51	420	343	0.013
PZTN <sub>2</sub>	162.05	168.19	0.28	400	447	0.017

The permittivity and the Curie point increase for doped PZT with niobium, if we are to compare with the case of undoped PZT.

Niobium oxide is a good sintering aid for PZT based materials. The addition of Nb increases the dielectric constant and the Curie point.

Fig. 1 shows the plots of relative permittivity versus temperature. The Curie point ( $T_c$ ) increases at 420 $^{\circ}$ C, respectively 400 $^{\circ}$ C by PZT doping with Nb. These values are in good agreement with the requirement of practical application.

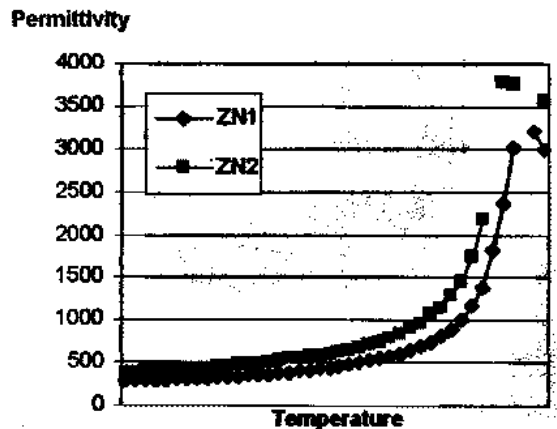


Fig.1. – Dielectric constant as a function of temperature.

## 5. CONCLUSIONS

The niobium oxide is a good sintering aid for PZT based materials (high density, low grain size). The addition of Nb increases the dielectric constant and the Curie point comparing with the same properties of the undoped PZT material. The transition temperatures of the PZTN material are generally higher than the ones of the PZT material. This means that the PZTN material has a good stability of the properties with the temperature variation and a good stability in time, but the coupling piezoelectric coefficients are smaller.

## REFERENCES

1. Wanda C Las, Priscila D. Spagnol, Marial A Zaghete, M. Cilense- *Electrical characterization of lead zirconate titanate prepared by organic solution route*, *Ceramics International* 27 (2001)
2. C Tanasoiu, E Dimitriu and C Miclea, *Effect of Nb, Li Doping on Structure and Piezoelectric Properties of PZT Type Ceramics* *Journal of The European Ceramic Society*, p 1187, 19 (1999).
3. B.M. Jin, J. Kim, S.C. Kim, *Effects of grain size on the electrical properties of  $PbZr_{0.52}Ti_{0.48}O_3$  ceramics*, *Applied Physics*, A 65, p. 53-56 (1997)