1. INTRODUCTION

Modern transducers must be capable to operate in a wide range of modes and environmental conditions. The performance requirements for transducers continue to grow so that the demand for high quality piezoelectric materials increases too. All dielectric, piezoelectric and mechanical properties of these functional materials are temperature dependent so that it is necessary to have knowledge about the behaviour of material properties over a larger temperature interval. In the literature there are just a few works dealing with the change of some piezoelectric properties with temperature. Therefore, in the present paper we carried out a systematic evaluation of the behaviour of the main piezoelectric parameters with temperature, over the whole temperature interval from 2 K up to 600 K i.e. near their Curie temperatures for two typically soft and hard PZT ceramics respectively which are the most used ceramics as sensors and transducers. The parameters investigated were those of the largest interest such as the planar coupling coefficient \( k_p \), the mechanical quality factor \( Q_m \), the frequency constant \( N_1 \), the charge constants \( d_{33} \) and \( d_{31} \), the voltage constants \( R_1 \) and \( R_0 \), as well as the dielectric constant \( \varepsilon_r \).

2. OBJECTIVES

The main objectives of this experimental investigation are:

- To prepare two piezoceramic materials, the most used ones in application: a soft and a hard PZT types;
- To fully characterize their main piezoelectric and dielectric parameters over the whole temperature interval between 2 K and 700 K.

The parameters measured were:

- Frequency constant \( N_1 \)
- Electromechanical coupling factor \( k_p \)
- Mechanical quality factor \( Q_m \)
- Charge constants \( d_{33} \) and \( d_{31} \)
- Voltage constants \( R_0 \) and \( R_1 \)
- Relative dielectric constant \( \varepsilon_r \)

3. MATERIAL PREPARATION

Two piezoelectric materials were chosen for the experiment: a soft material with the formula \( \text{Pb(Nb}_{0.017}\text{Sb}_{0.033}\text{Zr}_{0.48}\text{Ti}_{0.47}O_3} \) and a hard material \( \text{PbMn}_{0.017}\text{Sb}_{0.033}\text{Zr}_{0.48}\text{Ti}_{0.47}O_3 \). They were prepared by the conventional mixed oxide route by using p.a. purity raw oxides. The mixed powders were double calcined at 850 and 900 °C respectively with an intermediate milling for 1 h, and a final wet milling of 6 h. The calcined powders were checked by X-ray and the resulting double calcined values of \( Q_m \) for temperature of 200 °C for both materials. Disc shaped samples of 12 mm diameter and 1.5 mm thick were next uniaxially pressed at about 50 MPa from the milled powders and sintered for 3 hours at 1250 °C (soft material) and 1300 °C (hard material) respectively. Densities of 7.72 and 7.70 g/cm³ for the soft and hard material respectively were obtained. The hard material was poled in a silicon oil bath at 220 °C under an electric field of 30 kV/cm. The piezoelectric measurements were carried out after 48 h of relaxation at room temperature.

4. RESULTS

Modified PZT type ceramics show substantially strong piezoelectric properties for those compositions situated within the morphotropic phase boundary where tetragonal (T) and rhombohedral (R) distorted cells coexist. The lower temperature zone investigated so far was not complete, so that there is no information about the existence or inexistence of any transition at temperatures down to 2 K. To clarify this we carried out measurement of specific heat with temperature over a large temperature interval. Figure 2 shows the behaviour of specific heat with temperature from 2 to 400 K for both materials investigated. One can see that there is no anomaly of \( C(T) \) over the whole temperature interval which confirms the inexistence of any other phase transition which could possible influence the behaviour of the basic piezoelectric parameters with temperature. Figure 3 illustrates the behaviour of the frequency constant \( N_1 \) with temperature. For the hard material \( N_1 \) decreased between 2 and 600 K with about 60%, the rate of change being more pronounced at temperatures over 400 K approaching the Curie point. For the soft material \( N_1 \) decreased pronouncedly for the first 100 K then remains nearly constant up to 350 K and then it exhibits a steady increase with increasing temperature up to 400 K. The behaviour of the planar coupling coefficient with temperature is shown in figure 4. The \( k_p \) for the hard material increases steadily from 0.4 at 2 K to about 0.57 at 350 K then drops drastically by approaching the Curie temperature. A similar behaviour is also recorded for the soft material with the only exception that the initial increase between 2 and 80 K is much more pronounced after which the increase becomes continuously steady up to about 450 K. Maximum values for \( k_p \) are attained around 250 K for both materials and then temperature the hard material softens and the soft one becomes just a little harder. The both charge constants \( d_{33} \) and \( d_{31} \) exhibit an entirely similar behaviour namely a steady increase with increasing temperature as it results from figures 5 and 7 respectively, but at different values. If for the hard material \( d_{33} \) increases by about 300% between 2 and 550 K, the increase for the soft one is thirty fold greater. The corresponding figures recorded for the increase of \( d_{31} \) were 1.7 times for the hard and 10 times for the soft one respectively. The voltage constants \( R_1 \) and \( R_0 \) show a steady and continuous decrease with temperature up to the vicinity of the Curie point, where they start to drop much more rapidly, as can be seen in figures 8 and 9. Figure 10 illustrates the dependence of the relative dielectric constant \( \varepsilon_r \) on temperature. As one can see there is no noticeable difference for the soft material at all to 450 K. The dielectric constants increase rather constantly at a large rate from 200 at 2 K up to about 3600 around 470 K, which represent an increase by 18 times. From this temperature on the dielectric constants increase at much higher rates, reaching maximum values of 15000 and 20000 for the hard and soft materials respectively, at their Curie points of 520 K and 620 K respectively. Since the 180° domain walls are not ferroelastic and the other non 180° are ferroelastic active one may consider that the main contribution to the dielectric behaviour comes from the increase of piezoelectric properties is given by this non 180° domain wall movement. On the other hand the enhancement of the ferroelastic and the other non 180° are ferroelastic active one may consider that the main contribution to the dielectric constants increase at much higher rates, reaching maximum values of 20000 and 25000 for the hard and soft materials respectively, at their Curie points of 690 K and 710 K respectively. Since the 180° domain walls are not ferroelastic and the other non 180° are ferroelastic active one may consider that the main contribution to the dielectric behaviour comes from the increase of ferroelastic and non 180° domain wall movement. On the other hand the enhancement of the 180° domain walls activity will improve the dielectric response of material and the high increase of dielectric constant may probably prove that. Therefore the general behaviour of the properties suggest that both 180° and non 180° domain wall movements should be active in PZT materials and that temperature represents the main factor of influence for domain wall mobility with consequences on improving or diminishing the material properties.

CONCLUSION

The experimental results obtained on the two PZT materials investigated reveals the following aspects:

- There is no phase transition from 2 K up to 400 K; The planar coupling coefficients \( k_p \) shows a continuous increase with increasing temperature, having maximum values around room temperature; The soft material has the tendency to become a little harder with increasing temperature, and the hard one to become slightly harder showing a plateau of the highest values of \( k_p \) for temperatures just a little above room temperature. Dielectric charge constants \( d_{33} \) and \( d_{31} \) increase steadily with temperature showing humps with the highest values at temperatures around 540 K; The voltage constants \( R_0 \) and \( R_1 \) decreases constantly with increasing temperature up to temperatures in the vicinity of the Curie point; High dielectric activity was recorded for both materials with a constant increase up to 450 K and a drastic increase above it showing maximum values at the Curie point; The behaviour of these properties over a large temperature interval from 2 K up to 600 K seems to be due to the 180° domain wall activity which is controlled by the temperature through the domain wall mobility.