EFFECT OF TEMPERATURE ON THE MAIN PROPERTIES OF HARD AND SOFT TYPE LEAD-TITANATE-ZIRCONATE CERAMICS

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1. INTRODUCTION

Modern transducers must be capable to operate in a wide range of modes and environmental conditions. The performance requirements for transducers continues 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 typicaly 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 g_{33} and g_{31}, as well as the dielectric constant ε_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 g_{33} and g_{31}, Relative dielectric constant ε_r

3. EXPERIMENTAL

MATERIAL PREPARATION

Two piezoelectric materials were chosen for the experiment: a soft material with the formula $PbNb_{0.02}Li_{0.007}Zr_{0.51}Ti_{0.463}O_3$ and a hard material $PbMn_{0.017}Sb_{0.033}Zr_{0.48}Ti_{0.47}O_3$. They were prepared by the conventional mixed oxide route by using p.a. purity raw oxides. The mixed powders were doubled calcined at 850 and 900 ^oC 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 results showed the formation of the well known perovskite single phase 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 ^oC (soft material) and 1300 ^oC (hard material) respectively. Densities of 7.72 and 7.70 g/cm^3 for the soft and hard material respectively were obtined. The electroded samples were poled in a silicon oil bath at 220 ^oC under an electric field of 30 kV/cm. The piezoelectric measurements were carried out after 48 h of relaxation at room temperature.

MEASUREMENTS

The piezoelectric parameters were measured by the resonance-antiresonance method using a HP4194A Impedance Analyzer interfaced to a Quantum Design Physical Properties Measurement System (PPMS) by means of which the temperature varied from very low values (about 2 K) up to room temperature (300 K). The temperature step was set to 5K. For the measurements from room temperature up to 600-700 ^oC we used a home made temperature chamber, as shown in figure 1, so that the whole temperature range of measurements covered 2-700 K. A special software was designed for automatic data acquisition and processing which was adapted to the HP 4194A analyzer in order to directly record the behaviour of the piezoelectric parameters versus temperature. Specific heat measurements between 2 and 300 K were performed by means of a relaxation method, employing the same Quantum Design PPMS. The sample masses for this measurement were 104.84 mg for the soft specimen and 188.36 for the hard one. The samples were attached to the specific heat platform using Apiezon N grease. The addenda (including the platform and the grease) were carefully subtracted from the raw data.

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_p(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 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 increased steadily reaching about the same value as that at 2 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 2K 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 room temperature where k_p shows rather constant values for a wider temperature range. Figure 5 shows how mechanical quality factors Q_m changes with temperature. For the hard material it increases drastically by about 500% between 2 and 250 K, then very slowly and steadily up to 460 K after which it suddenly drops. The behaviour of Q_m for the soft material is quite different. At first, between 2 and 80 K, it decreases more than twofold then increases linearly by 350% up to 400 K, remains constant up to thr nearby of the Curie point and then suddenly drops to zero. It is as if at lower temperatures 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 6 and 7 respectively, but at different values. If for the hard material d_{33} increases about threefold 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 g_{33} and g_{31} 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 ε_r on temperature. As one can see there is no noticeable difference for the two materials at least up 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^o domain walls are not ferroelastic and the other non 180^o are ferroelastic active one may consider that the main contribution to the dielectric and piezoelectric properties is given by this non 180o domain wall movement. On the other hand the enhancement of the 180o 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^o and non 180^o domain walls should be active in PZT materials and that temperature represent the main factor of influence for domain wall mobility with consequences on improving or diminishing the material properties.

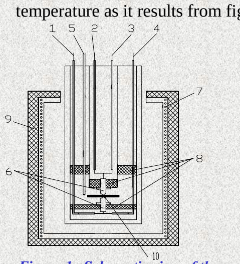

Figure 1 Schematic view of the chamber for piezoelectric measurements above room temperature;

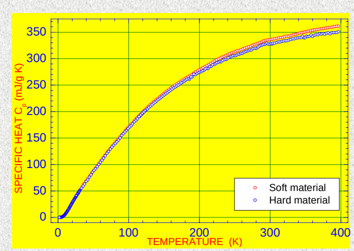

Figure 2 Temperature dependence of the specific heat

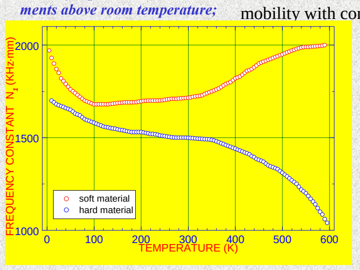

Figure 3 Temperature dependence of the frequency constant N_1

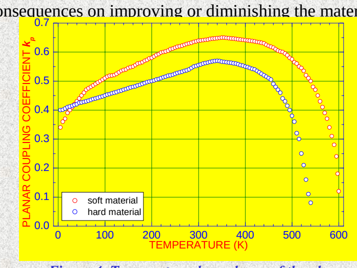

Figure 4 Temperature dependence of the planar coupling coefficient k_{tr}

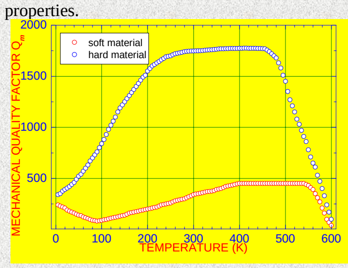

Figure 5 Temperature dependence of the mechanical quality factor Q_m

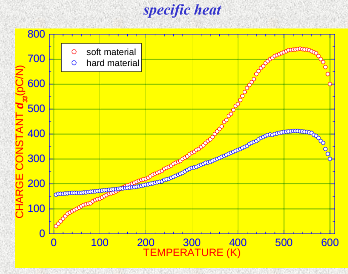

Figure 6 Temperature dependence of the charge constant d_{33}

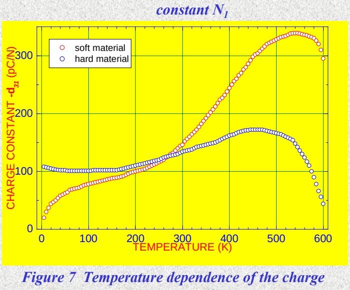

Figure 7 Temperature dependence of the charge constant d_{31}

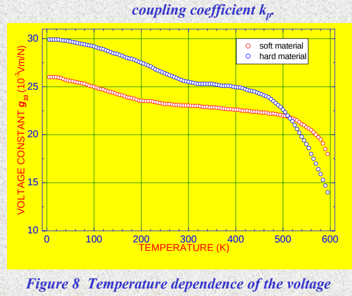

Figure 8 Temperature dependence of the voltage constant g_{33}

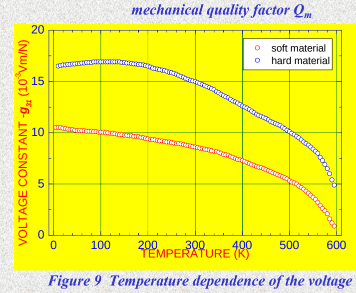

Figure 9 Temperature dependence of the voltage constant g_{31}

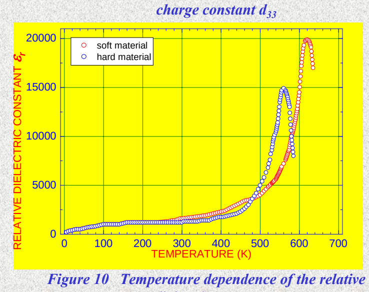

Figure 10 Temperature dependence of the relative dielectric constant ε_r

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 strongly harder showing a plateau of the highest values of Q_m 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 g_{33} and g_{31} 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^o domain wall activity which is controlled by the temperature through the domain wall mobility.