Polarization Processes in PZT Ceramics

V. D. Parvanova[1], **M. M. Nadoliisky**[2]

[1]Department of Inorganic Chemistry, University of Chemical Technology and Metallurgy, 8 Kliment Ohridsky Street, 1756 Sofia, Bulgaria

[2]Department of Physics, University of Architecture, Civil Engineering and Geodesy, 1 Hristo Smirnensky Blvd., 1421 Sofia, Bulgaria

Abstract. This paper studies the conditions for effective polarization of two compositions of PZT ceramics. The dependence of ε_r, $\tan\delta$, planar coupling factor K_r and the piezoelectric constant d_{31}, d_{33}, g_{31}, g_{33} on the polarizing DC-field is investigated. The values have been established of the polarizing DC field, where the ceramics demonstrates maximum piezoelectric properties. $Pb_{0.94}Ca_{0.04}Mg_{0.02}Zr_{0.53}Ti_{0.47}O_3 + 0.4\%$ B_2O_3 shows properties common for the ferrohard materials. $Pb_{0.94}Sr_{0.04}Mg_{0.02}Zr_{0.53}Ti_{0.47}O_3 + 0.4\%$ $5B_2O_3$ can be referred to the ferrosoft materials.
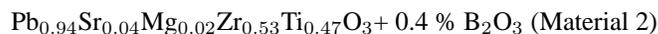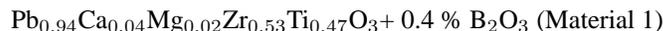
1 Introduction

Ferroceramics is a poly-crystalline body and in non-polarized condition does not possess piezoelectric properties. This fact can be explained by the chaotic orientation of the polar axes of the individual crystallites (grains) in it. Besides, the crystallites are divided into domains (areas) with various directions of the vectors of spontaneous polarization. Under the influence of an external constant electric field, a reorientation of the spontaneous polarization along the field direction occurs. As a result of this, the ferroceramics acquires piezoelectric properties.

The efficiency of the polarization depends on the values of the external electric field, on the duration of the impact and on the polarization temperature.

The present article studies the conditions for effective polarization of two compositions of ferroceramics of the PZT system, situated in the morphotropic phase border (MPB):

$Pb_{0.94}Ca_{0.04}Mg_{0.02}Zr_{0.53}Ti_{0.47}O_3 + 0.4\%$ B_2O_3 (Material 1)

$Pb_{0.94}Sr_{0.04}Mg_{0.02}Zr_{0.53}Ti_{0.47}O_3 + 0.4\%$ B_2O_3 (Material 2)

2 Experimental

The ferroceramic materials were prepared using a solid-state synthesis [1-8]. The input materials used were PbO, ZrO_2, TiO_2, $SrCO_3$, MgO and B_2O_3 with purity over 99%. The grinding and homogenizing of the input materials was carried out in a planetary ball mill for 35 min. The hard phase reaction of Material 1 took place at a temperature of 830°C, and that of Material 2 at a temperature of 870°C for two hours. After grinding it again for 55 min, the powders were pressed under pressure $P = 4.9 \times 10^5$ Pa. The plasticizer used was 10% polyvinyl alcohol. The sample materials in the shape of a disc 1 mm thick and 10 mm in diameter were sintered at a temperature of 1100 °C. The interim and final products were identified by means of X-ray phase analysis with TUR-U-62 device. The samples were poled in a silicon oil bath at 120°C with an applied DC-field for one hour. The electrodes in the samples were inserted using silver paste and firing followed. The relative dielectric constant ε_r and the dielectric losses $\tan \delta$ were measured together with LCR digital meter, at 1 kHz.

The planar coupling factor K_r and the piezoelectric constant d_{31}, d_{33}, g_{31}, g_{33} were determined by means of the resonance-antiresonance method [9].

3 Results and Discussion

Figure 1 shows the temperature dependence of the dielectric constant ε_r of the materials. Hence, the Curie temperature T_c of Material 1 is at 350°C, and that of Material 2 at 320°C. The Curie temperature transition of Material 1 is wider than that of Material 2. The lower value of T_c of Material 2 is due to the Sr^{2+}, which partially replaces Pb^{2+} and reduces T_c.
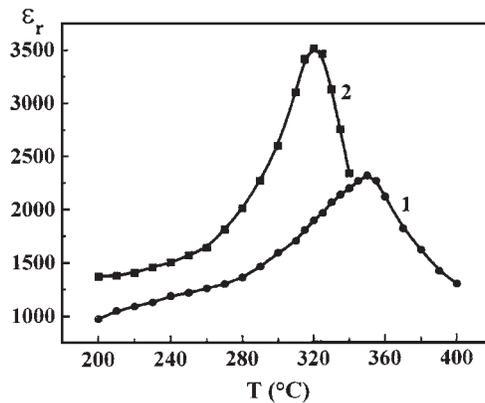

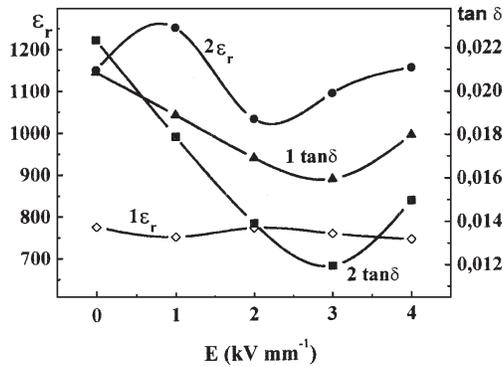Figure 1. Temperature dependence of the dielectric constant of Material 1 and Material 2.

Figure 2. Dependence of ε_r and $\tan \delta$ of the materials on the polarizing DC-field.

Figure 2 shows the dependence of the dielectric constant ε_r and dielectric losses $\tan \delta$ on the intensity E of the constant polarizing electric field. The dielectric constant of Material 2 is considerably higher than that of Material 1 and reaches a maximum at $E = 2 \, \text{kV mm}^{-1}$ and increases again.

The dielectric losses of the two materials decrease as E increases and have similar values.

The complex domain structure of the ceramics requires a static distribution of the domains by coercive fields. The reason for this is the difference in the crystal (grain) size, which may have one or more domains, the presence of a large number of defects in the crystal lattices and the existence of internal mechanical tensions. In terms of their composition, Materials 1 and 2 are in the morphotropic phase border and are a mixture of two phases – tetragonal and rhombohedral. Maximum polarization will be achieved if all 180°- and 90°-domain reorientarions (rotations) are realized in the tetragonal phase and 180°-, 71°- and 109°-reorientations in the rhombohedral phase, respectively. When applying a constant electric field to the ferroceramics fast polarizations are established in the initial moment. The stable polar state and piezoelectric properties stable in time are determined by the slow polarizations, characterized by a long time of relaxation. The processes related to the emergence of new domains and the mobility of domain walls have a major contribution to the creation of the polarized state.

In small polarizing fields, the first to reorient are the 180°-domains, as a result of which the effect of 'jamming' the domains is abolished and the dielectric constant ε_r of Material 2 increases (Figure 2). The increase of E results in the 90° reorientations of the domains, which have a greater contribution to the dielectric constant than the 180°-domains. That explains why the total dielectric constant of the material decreases (Figure 2). Further increase of E results in the increase of the number of reoriented domains and ε_r of Material 2 increases again.
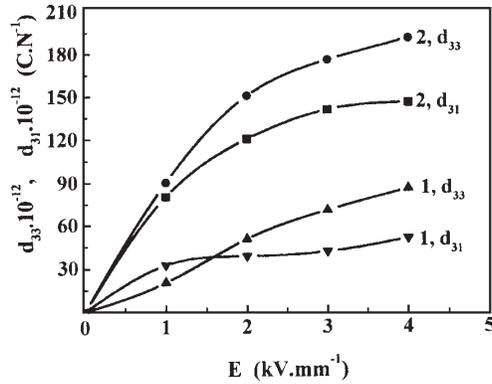
Figure 3. Dependence of piezomodules d_{31} and d_{33} on the polarizing DC-field.

It is interesting to note that the dielectric constant ε_r of Material 1 is higher before its polarization. This shows that in lower E, domain reorientations different from 180° prevail in this material.

The dependence of the coefficients of planar coupling factor K_r, of the piezomodules d_{31} and d_{33}, and the piezocoefficients g_{31} and g_{33} of the materials on the polarizing DC-field are shown in Figures 3, 4, and 5, respectively.

With the increase of E approaching the value of the coercive fields of the materials, a fast increase in piezoactivity is observed. With further increase of E, the increase in piezoactivity is slowed down and stops in fields with intensity of approximately $4 \, \text{kV mm}^{-1}$. Termination of the increase of piezoactivity is due to the decreased efficiency of the polarizing field because of it being shielded by a space charge accumulated in the near electrode areas and because of the increased conductivity of the materials.
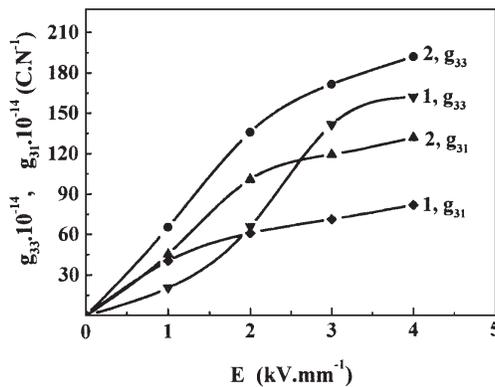

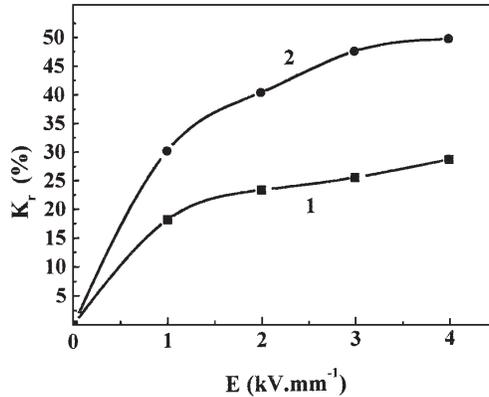Figure 4. Dependence of piezocoefficients g_{31} and g_{33} on the polarizing DC-field.

Figure 5. Dependence of the coefficients of the planar coupling factor K_r on the polarizing DC-field.

In the materials studied, the Sr^{2+} and Ca^{2+} ions are partially replaced by Pb^{2+}, and Mg^{2+} probably replaces $(Ti, Zr)^{4+}$, thus each replaced ion turns into an oxygen vacancy.

Material 2 demonstrates better piezoelectric properties and higher dielectric constant. In terms of these characteristics, it can be referred to the ferrosoft materials which are characterized by a smaller coercive field and are better polarized.

4 Conclusions

$Pb_{0.94}Ca_{0.04}Mg_{0.02}Zr_{0.53}Ti_{0.47}O_3 + 0.4\%$ B_2O_3 (Material 1) shows properties common for the ferrohardners. One of the possible reasons is the presence of higher concentration of defects in the crystal structure. They limit the movement of the domain walls and prevent the formation of new domains.

$Pb_{0.94}Sr_{0.04}Mg_{0.02}Zr_{0.53}Ti_{0.47}O_3 + 0.4\%$ B_2O_3 (Material 2) demonstrates better piezoelectric properties and higher dielectric constant. In terms of these characteristics, it can be referred to the ferrosoftners which are characterized by a smaller coercive field and are better polarized.

References

[1] B. Jaffe, W. Cook, H. Jaffe (1971) *Piezolectric Ceramic*, Academic Press, London and New York.

[2] Tajima Ken-ichi, Hwang Hae Jin, Sando Mutsuo, Nihara Koichi (2000) *Nippon Seramikkusu kyokai gakajutsu ronbunshi* **1258** 607.

[3] K. Okazaki (1976) *Technologia Keramicheskih Dielectrikov*, Energia, Moscow.

[4] M.D. Durruthy, L. Fuentes, . Hernandez, H. Camacho (2000) *J. Mater. Sci.* **9** 2311.

[5] Garg Ajai, D.C. Agrawal (1999) *Mater. Sci. and Eng. B* **1** 46.

[6] Purwasasmita Bambang Sunedar, Kimura Tochio (2000) *Nippon Seramikkusu kyokai gakajutsu ronbunshi* **1263** 996.

[7] E.A. Slonimskaia, A.B. Beliakov (2001) *Steklo i keramika* **2** 18.

[8] Hammer Marianne and Hoffmann Michael (1998) *J. Amer. Ceram. Soc.* **12** 3277.

[9] M. Nadoliisky, T. Vasileva, P. Vitkov (1992) *Ferroelectrics* **129** 141.