Effect of porosity on the electrical properties of PZT ceramics

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Abstract. In the present work the effect of porosity ceramics PZT on the dielectric properties was studied. It is shown that the presence of pores leads to decrease of the real part of the dielectric permittivity in the frequency range of 25 Hz – 1 MHz also as to non-stability of the dielectric characteristics in the phase transition region.

1. Introduction
Ferro-piezoelectric ceramics on the basis of lead zirconate titanate perovskite solid solutions PbZr₁₋ₓTixO₃ (PZT) continue to be the most important ferroelectric and piezoelectric materials in commercial devices [1]. Curie temperature Tc of these materials more than 250 °C. Above this temperature ceramics is in the paraelectric cubic phase. Below the Curie temperature the PZT components have a ferroelectric (PbTiO₃, PbZrO₃) or antiferroelectric (PbZrO₃) ordering. This is confirmed by experimental data on crystals and ceramics of similar composition [2-4]. PZT materials systems have high and stable piezoelectric properties in a broad temperature range. For improving the piezoelectric properties of ceramics PZT it introduce various modifying agents.

The properties of PZT-based materials as well as of other solid solutions depend strongly on the preparation conditions, in particular on the porosity formed during sintering [5,6]. As a consequence both new techniques are developed and old technologies are improved to obtain materials with desired properties.

2. Experimental
The samples of PZT ceramics (PZT system with the addition of niobium pentoxide), which were produced with a given percentage (25%) of the pores were investigated. The PZT ceramics without pores for comparison electrical properties was used.

The dispersion of capacitance and dielectric loss tangent were measured at room temperature in the frequency range 25 Hz - 1 M Hz using immittance meter E7-20. Also the temperature dependence of the dielectric permittivity were measured in the temperature range 25-400°C at 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz. The heating rate was 2K/min, cooling – 3.4 K/min.

To confirm percent of porosity the grain size and porosity were examined with the aid of scanning electron microscopy (JEOL JSM 6510LV). The images of the cross sections of the PZT samples obtained in secondary electrons on the SEM are shown in Figure 1. As can be seen from the pictures, samples greatly differ in the number and size of pores. In addition, the porosity ceramics have larger grains (about 3-4 microns) compared with normal (non–porosity), ceramics (about 1-2 microns). The results for the porosity sample coincide with a number of published data for PZT ceramics [7].
3. Results and Discussion

The frequency dependence of the complex dielectric characteristics for PZT ceramics were obtained from experimental data (Fig. 2). The real part the dielectric permittivity $\varepsilon'(f)$ PZT ceramics, as may be seen from the graphs, decreases with increasing percentage content of pores in the sample [8]. Thus there are the dispersion in the frequency range under investigated is the same for both samples. The dielectric loss $\varepsilon''(f)$ ceramics without pores are weakly dependent on the frequency, except for the high-frequency range ($10^5$–$10^6$ Hz). The absence of maximum of dielectric loss for both samples is probably related to the fact that the process of relaxation polarization corresponds to frequencies more than $10^6$ Hz. Therefore for the two samples we do not see the arcs of semicircles on the diagrams of the dielectric dispersion (Fig.3).

Behaviors of the temperature dependence of the dielectric permittivity for the heating and cooling processes are different (Fig.4). The temperature of the maximum dielectric permittivity was observed during the cooling is less than during heating. The difference in temperature ranges is from 3 to 13 degrees. While that in all experiments the temperature change rate were the same both for heating and cooling, depending on given quantity on the frequency was not observed. It should be noted that just as at room temperature the magnitude $\varepsilon'$ at the maximum for the porosity sample is less than the pore-free ceramics.
Figure 3. The diagrams of the dielectric dispersion $\varepsilon''(\varepsilon')$ of PZT pore-free ceramics (1) and that with porosity of 25% (2).

Figure 4. The temperature dependence of the permittivity PZT ceramic, pore-free (3, 4) and with porosity of 25% (1, 2) by heating (1, 3) and cooling (2, 4) at the frequency 1kHz.

Temperature dependences of the real part of the dielectric permittivity that occur during cooling at different frequencies are shown in Fig.5, a. In pore-free ceramic the positions of dielectric permittivity maximum, which corresponding to the phase transition, does not depend on the frequency measurement. It occurs at a temperature of 330 °C. In contrast, the maximum on the temperature dependence of the dielectric permittivity for ceramics containing pores of 25% (Fig.5, b) varies with the measuring frequency. At the same time, depending on the direction of displacement of these maximum from the frequency as it is proper to relaxors not observed. Such a difference in the behavior of the temperature dependence of the permittivity for a sample with porosity 25 % and pore-free ones is observed during heating.

Figure 5. Temperature dependences were measured during cooling for the real part of the dielectric permittivity of PZT pore-free ceramics (a) and that with porosity of 25% (b)

The study of the dielectric hysteresis loops by the Sawyer-Tower method also showed the existence of differences between the properties of pore-free and porosity (25 %) ceramics (Fig.6). Calculated according the dielectric hysteresis loops were obtained remanent polarization of the pore-free sample is 16 $\mu$C/cm$^2$. For porosity (25 %) ceramics this value is about two times less (7 $\mu$C/cm$^2$). The values of the coercive fields are 4.4 kV/cm and 6 kV/cm for pore-free ceramics and that with porosity of 25% correspondingly.
4. Conclusions

Thus, the porosity of ceramics directly affects the dielectric characteristics such as permittivity and spontaneous polarization. Whereas the magnitudes of the above parameters decrease with the increase of porosity, the types of their frequency dependence remain the same. Therefore, specifying certain percent of porosity for the ceramic during the production process, it is possible to obtain samples with the dielectric properties that are necessary for a specific application. This is particularly important when ferroelectrics ceramics are used at high frequencies. In that frequency range, as shown above, increasing the porosity reduces dielectric loss.

The presence of porosity in the ceramic is not promoted to the arisen the relaxor properties, although it leads to instability of the dielectric properties of the phase transition region.

References

[1] ET-102 Piezoelectric Operated Actuators and Motors – A Global Industry and Market Analysis (Web: www.innoresearch.net)
[2] Yaffe B, Cook WR, Yaffe R 1971 Piezoelectric ceramics (London–NY: Academic Press)
[3] Heywang W, Lubitz K, Wersing W 2008 Piezoelectricity Evolution and Future of Technology Springer – Verlag Berlin Heidelberg
[4] Guo R, Wang C A, Yang A K, Fu J T 2010 J. Appl. Physics 108 124112
[5] Praveenkumar B, Kumar H H, Kharat D K 2005 Bull. Mater. Sci. 28 453-455
[6] Ting R Y 1985 Ferroelectrics 65 11-20
[7] Mercadelli E, Sanson A and Galassi C 2010 Porous piezoelectric ceramics Piezoelectric ceramics ed E Suaste Gуmez (Rijeka, Croatia – Sciyo) pp 111-128 (www.intechopen.com)
[8] Piazza D, Galassi C, Barzegar A, Damjanovic D 2010 J Electroceram 24 170-176