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Infralow-frequency Dispersion of Piezoelectric and Dielectric Constants in $PbTiO_3$-based Ferroelectric Ceramics

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Abstract

The direct piezoelectric constant d_{33} *and dielectric permittivity* ε_{33} *of* $PbTiO_3$*-based ferroelectric ceramics were measured in a frequency range from* 10^{-2} *to 10 Hz under acting weak alternative mechanical and electric fields. Debye-type dispersion was observed for* d_{33} *and* ε_{33}' *of (Pb, Ca)* TiO_3 *(PCT) ceramics. Obtained results were compared with those published by other authors, and it was shown, that similar behaviour is kept in the strong electric and mechanical fields. The dispersion frequencies were determined. In all the frequency range* d_{33} *and* ε_{33}' *of* $Pb(Zr,Ti)O_3$ *(PZT) ceramics remained frequency independent. The possible origins of observed effects are discussed.* *© 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

One of the most useful properties of ferroelectric ceramics for engineering is the piezoelectric effect. Recently interesting phenomena as for instance frequency dependence and distinctions of the direct and reverse piezoelectric constants were found.[1] The piezoelectric response of ferroelectric ceramics appearing by using alternative mechanical stresses with large amplitudes (1–5 MPa) within the frequency range from 10^{-2} to 10^2 Hz was studied in detail.[2–5] It was found[3–6] that Rayleigh law which is widely used for magnetic hysteresis loops and magnetic permeability can be used for describing the piezoelectric and dielectric properties within the region of middle-amplitude electric and mechanical fields ('intermediate' fields).[3–6] Conformity of the piezoelectric constants behaviour with Rayleigh law was displayed in PZT piezoelectric materials[2–4] and violations were observed by arriving the large amplitude values of the ac stress. It was obtained[6] that dielectric permittivity in PZT ferroelectric ceramics submits to Rayleigh law in the sub-switching electric fields. A frequency behaviour of the piezoelectric constants in the PCT ferroelectric ceramics indicates the presence of a Debye-type process.[5] It was suggested that the Rayleigh-type behaviour of the piezoelectric and dielectric constants can be caused by presenting pinning centres of the domain walls.

Properties of the ferroelectric ceramics under weak values of the ac mechanical and ac electric fields have not yet been studied well. Very limited numerous experimental data[7] such as increasing piezoelectric constants when frequency increases and changing signs of the d_{31} and d_{33} constants are controversial. In our opinion it is improbable that frequency dependence of piezoelectric properties of the PZT and PCT ferroelectric compositions differ such considerably in the weak and 'intermediate' fields. Thus, to obtain the total notion concerning the properties of those ferroelectric ceramics in the mechanical and electric fields of different values an additional information on their frequency-dependence properties is necessary.

The present paper is devoted to studying the piezoelectric and dielectric properties of the PCT and PZT compositions. We present experimental results of investigation of the frequency behaviour of the direct piezoelectric constant d_{33} and dielectric permittivity ε_{33} for two compositions of $(Pb_{1-x}Ca_x)TiO_3$: (PCT) with $x = 0{\cdot}24 \div 0{\cdot}25$ and PZT-type ferroelectric ceramics in the ac electric fields and ac pressure with small amplitude.

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2 Experimental

The direct piezoelectric constants d_{33} were measured at the fixed static stress (60 kPa) and the fixed amplitude of the harmonic one-dimensional stress (10 kPa), in an infralow-frequency range from 10^{-2} to 10 Hz. The device for measurements of the piezoelectric constants was designed and tested at quartz crystal. The error of the measurements was not more than 5%.

The dielectric permittivity measurements were carried out by using a special designed device, which allowed to compare an impedance (capacity and resistance) of the ceramic samples with parametra of the equivalent RC-scheme. Measurements were fulfilled within the same frequency range by using the electric field having the small amplitude ($5\,kV\,m^{-1}$). The method of the equivalent schemes permitted to separate the real and imaginary parts of the complex dielectric permittivity $\varepsilon^*_{33}=\varepsilon'_{33}-i\varepsilon''_{33}$. Samples of the PZT and PCT ferroelectric ceramics were taken for the investigations.

3 Results and Discussion

Figure 1 shows piezoelectric constant d_{33} as a function of the frequency of the ac stress for three compositions. Within the frequency range from 10^{-2} to 10 Hz, d_{33} of PCT-1 composition decreased 45%. Dispersion within this range has character of the Debye-type relaxation with a relaxation frequency $f_r \approx 2$ Hz. The frequency dependence of PCT-2 piezoelectric constants also has the Debye-type behaviour; d_{33} of this composition decreased 40% as the frequency increased from 1 to 10 Hz. It is found, that d_{33} for PCT-1 and PCT-2 compositions decreased from static values and approached to dynamic values which were measured by resonance-antiresonance method. As seen from Fig. 1, d_{33} was independent on frequency in the PZT ceramics.

Data, concerning frequency dependence of the real part ε'_{33} of the room-temperature dielectric permittivity for the same samples as in Fig. 1 are shown in Fig. 2. In the frequency range from 10^{-2} to 10 Hz ε'_{33} of PCT-1 decreased 80% with frequency (from 1400 to 300). Decreasing ε'_{33} is connected with a Debye-type relaxation that is conformed with Damjanovic data for (Pb, Sm) TiO_3 ceramics,[6] and can be successfully described by Debye formulae with the relaxation frequency $f_r \approx 0{\cdot}1$ Hz. In PCT-2 samples ε'_{33} showed a decrease of about 10%. Frequency behaviour also resembles Debye-type relaxation with $f_r \sim 4$ Hz. Perhaps the smaller relaxation frequency in (Pb, Sm) TiO_3 ceramics can be connected with the smaller ionic radius of the Sm ion in comparison with the corresponding radius of Ca one. In PZT-ceramics ε'_{33} remained frequency independent on frequency variation. The relaxation frequency f_r for dielectric permittivity ε'_{33} in PCT-2 ceramics is close to the relaxation frequency of the piezoelectric constant d_{33}. However, centres of the relaxation for ε'_{33} and d_{33} in the PCT-1 composition are situated not very closely. The cause of these phenomena is yet unknown. As seen from Fig. 2, in the PZT ceramics ε'_{33} was independent on frequency; it is similar to the d_{33} behaviour in these compositions.

Because of a very large resistance of the samples of PCT-2 and PZT compositions, imaginary part ε''_{33} of the dielectric permittivity was measured only for PCT-1 composition, which had the small resistance as compared with other samples. The frequency behaviour of ε''_{33} of this ferroelectric ceramics is presented in Fig. 3. Relaxation maximum is not observed due to large conductivity of the sample. As the result, ε''_{33} is proportional to $1/f$ that is agreed with Debye formula when dc-conductivity gives the main contribution in ε''_{33}. The similar frequency behaviour of ε'_{33} and d_{33} for $PbTiO_3$-based ferroelectric ceramics with substitutions in the Pb-sublattice by ions of Sm had

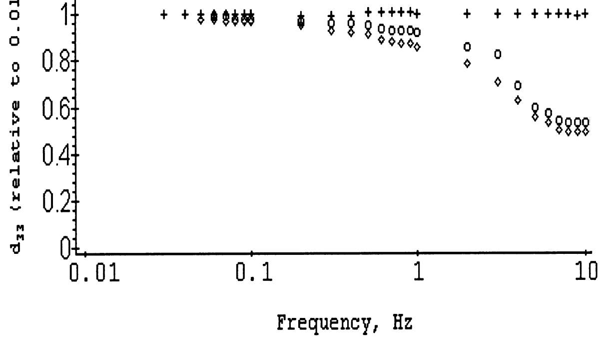

Fig. 1. Direct piezoelectric constant d_{33} versus frequency in the PCT-1 (◇), PCT-2 (○) and PZT (+) ceramics.

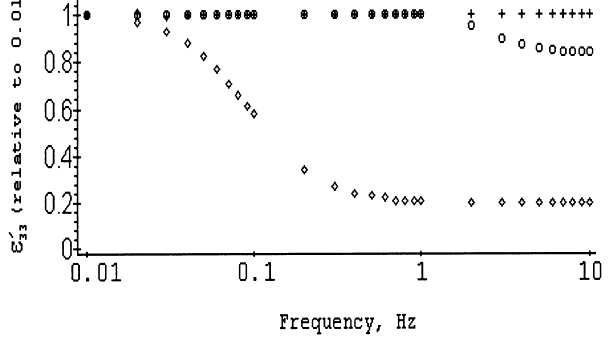

Fig. 2. Frequency dependence of the ε'_{33} in the PCT-1 (◇), PCT-2 (○), and PZT (+) ceramics.

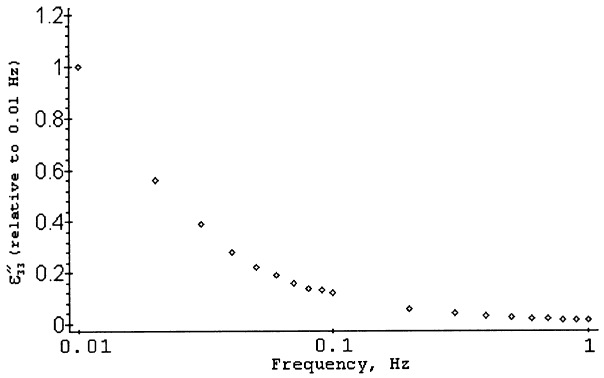

Fig. 3. Frequency behaviour of ε''_{33} in the PCT-1 ceramics.

been obtained by Damjanovic.[6] Relaxation frequency, obtained from his data also equals to 0·1 Hz.

According to above-mentioned results, it can be confirmed that in PZT ceramics the Rayleigh type frequency behaviour[5] in the weak electric and mechanical fields is not realized. The Debye-type behaviour of d_{33} and ε'_{33} in such the fields is typical of the $PbTiO_3$-based ferroelectric ceramics with substitution in the Pb-sublattice by ions with the lesser ionic radius. The reverse piezoelectric constants d_{33} in these materials are similar to direct ones frequency behaviour as shown in preliminary measurements under the strong electric fields with the amplitude of about $8\times10^5\,V\,m^{-1}$.

Thus, the Debye-type dispersion of the dielectric permittivity ε'_{33} and piezoelectric constant d_{33} of the PCT compositions takes place as well in the weak as in the 'intermediate' and strong mechanical and electric fields. In our opinion such the behaviour is associated with a peculiarity of potential energy of the modifying ions.

We did not see the d_{33} constant increasing of PCT-ceramics with frequency and in this aspect our data have a principal difference from results.[7]

4 Conclusion

It was obtained that infralow-frequency dispersion of piezoelectric constants is typical of $PbTiO_3$-based ferroelectric ceramics with small-radius ions substituting a part of Pb ions. The infralow-frequency dispersion of dielectric permittivity is observed in the same ceramics simultaneously with the piezoelectric dispersion. Piezoelectric and dielectric dispersions can be described in the Debye dispersion law terms. Within the frequency range from 10^{-2} to 10 Hz under acting weak amplitude values of the alternative pressure, the piezoelectric d_{33} coefficients in PZT-type ferroelectric ceramics do not show the frequency dependence. Such the behaviour is typical of ε'_{33} in PZT compositions under the weak ac electric field.

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