

DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF MODIFIED PbTiO_3 CERAMICS

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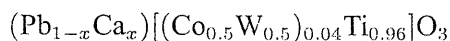
Abstract. This article deals with the results from the studies of the relative dielectric constant ε_r , the dielectric losses $\tan \delta$, the planar coupling factor K_p , the thickness coupling factor K_t , as well as the temperature stability of ε_r in the temperature range from -25°C to 70°C of $(\text{Pb}_{1-x}\text{Ca}_x)\text{TiO}_3$ ceramics modified with $\text{Pb}(\text{Co}_{0.5}\text{W}_{0.5})\text{O}_3$, NiO and MnO_2 . Maximum anisotropy coefficient $K_t/K_p = 5.55$ and best temperature stability of ε_r are registered for the composition with $x = 23$ at. % CaTiO_3 with additives of NiO and $\text{Pb}(\text{Co}_{0.5}\text{W}_{0.5})\text{O}_3$.

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1. Introduction

The present research is a continuation of an earlier research [1] on the optimum composition of the modified PbTiO_3 ceramics for practical applications. There are many researchers working in this field, who have studied similar materials for the preparation of IR detectors [2, 3], for piezoelectric transducers [4] and for compositions with suitable values of ε_r and low dielectric losses [5-7].

The following system was studied



where $x = 0.23, 0.24, 0.25, 0.26$ and 0.27 .

Each composition was developed in three variants: without additive, with additive of 1 mol % NiO and with additive of 1 mol % MnO_2 . The ceramics were produced using the standard technology [8], and the input raw materials were described in [1]. The methods of research are also given there. We would add also that the coefficients of the electromechanical coupling K_t and K_p

were determined by means of the resonance-antiresonance method. Poling of the samples was made at 100 °C and dc-field 6 kV/mm for 1 hour.

2. Results and Discussion

Figures 1 and 2 show the dependence of ϵ_r and $\tan \delta$ respectively on the concentration of Ca²⁺ ions. In the not polarized samples the permittivity and dielectric losses are at maximum at 23 at. % Ca. The additives of NiO and MnO₂ stabilize the properties of ceramics, and this tendency is more clearly expressed for MnO₂.

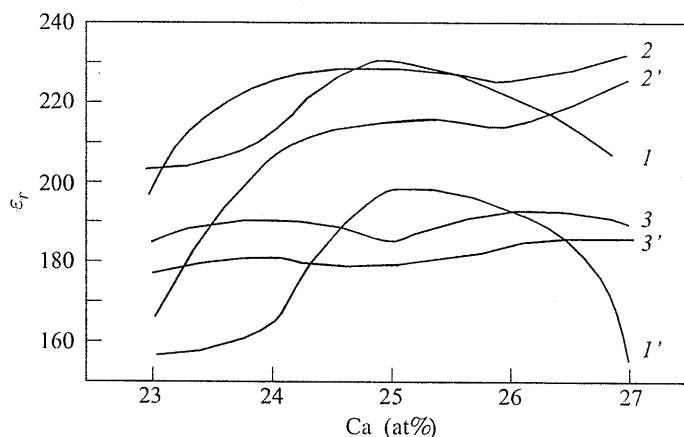


Fig. 1. Dependence of the relative dielectric constant ϵ_r on the concentration of Ca in $(\text{Pb}_{1-x}\text{Ca}_x)[(\text{Co}_{0.5}\text{W}_{0.5})_{0.04}\text{Ti}_{0.96}]\text{O}_3$ ceramics

The curves refer respectively: 1 and 1' to the material without additive; 2 and 2' with an additive of 1 mol % NiO; 3 and 3' to the material with an additive of 1 mol % MnO₃. The curves 1, 2 and 3 refer to non-polarized samples; the curves 1', 2' and 3' refer to polarized samples

Figure 3 shows the dependency of the radial coefficient of the electro-mechanical coupling K_p and the thickness coefficient of electro-mechanical coupling K_t on the concentration of Ca²⁺ ions. The coefficient K_t is higher than K_p for all studied compositions and has a maximum value for the samples with NiO additive.

Temperature stability of ϵ_r of the composition with the additive of NiO is shown in Table 1. The stability of permittivity increases as the volume of Ca²⁺ ions is increased mainly because of the lower Curie temperature T_c .

It is interesting to point out that all polarized samples have lower ϵ_r and $\tan \delta$ values than the not polarized ones. The change in ϵ_r after the poling is determined by two factors: the change in direction of the polarized axes in

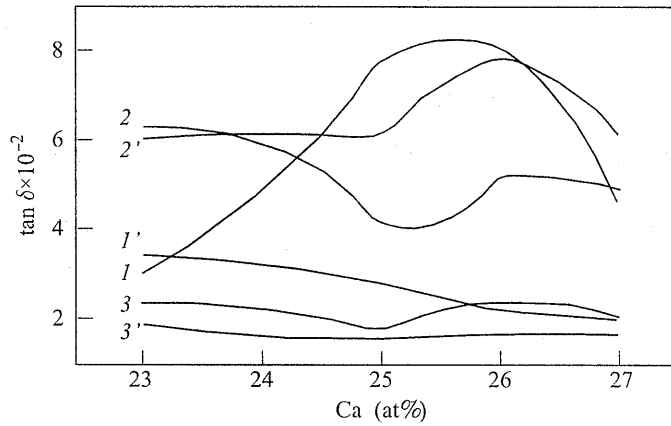


Fig. 2. Dependence of $\tan \delta$ on the concentration of Ca in $(\text{Pb}_{1-x}\text{Ca}_x)[(\text{Co}_{0.5}\text{W}_{0.5})_{0.04}\text{Ti}_{0.96}]\text{O}_3$ ceramics
The curves refer respectively: 1 and 1' to the material without additive; 2 and 2' with an additive of 1 mol % NiO; 3 and 3' to the material with an additive of 1 mol % MnO_3 . The curves 1, 2 and 3 refer to non-polarized samples; the curves 1', 2' and 3' refer to polarized samples

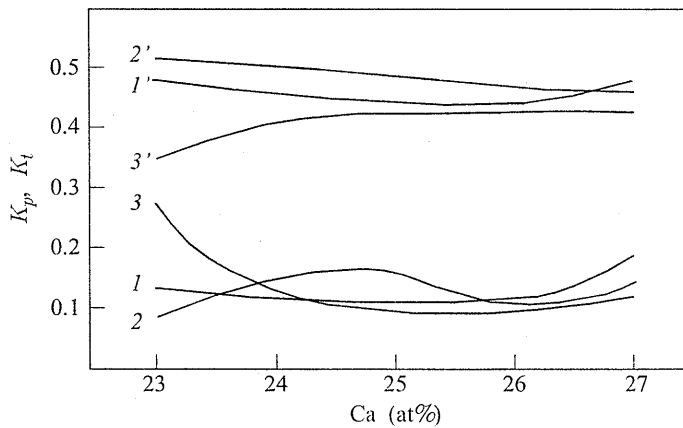


Fig. 3. Influence of the planar coupling factor K_p and the thickness coupling factor K_t of $(\text{Pb}_{1-x}\text{Ca}_x)[(\text{Co}_{0.5}\text{W}_{0.5})_{0.04}\text{Ti}_{0.96}]\text{O}_3$ ceramics on the concentration of Ca
The curves 1, 2 and 3 refer to K_p ; the curves 1', 2' and 3' refer to K_t respectively: 1 and 1' about materials without additive; 2 and 2' about materials with added NiO; 3 and 3' about materials with added MnO_2

the crystals in domain orientations different from 180°, which leads to reducing the permittivity as a result of dielectric anisotropy; elimination of the 'pressing' effect in the 180° domain orientations, as a result of which ϵ_r increases. Since in the tetragonal phase the 180° domain re-orientations prevail, the lower values of ϵ_r are determined by the first factor.

Table 1. Temperature stability of ϵ_r of $(\text{Pb}_{1-x}\text{Ca}_x)[(\text{Co}_{0.5}\text{W}_{0.5})_{0.04}\text{Ti}_{0.96}]\text{O}_3 + 1 \text{ mol } \% \text{ NiO}$ ceramics

x (at. %)	Deviation of ϵ_r (%)		
	-25 °C to 15 °C	15 °C to 70 °C	25 °C to 70 °C
23	9.48	5.07	15.55
24	15.04	11.36	26.40
25	15.50	9.46	24.96
26	13.45	13.89	27.34
27	14.09	12.76	26.85

The additive of compensated valence $\text{Pb}(\text{Co}_{0.5}\text{W}_{0.5})\text{O}_3$, in this case assumed to a permanent quantity, has cubic perovskite structure and is not ferroelectric. Its role is to stabilize the crystal structure and improve the mechanical strength of the ceramics. Besides, it probably creates additional lead vacancies.

The Ni^{2+} ion most probably substitutes the Ti^{4+} , as a result of which new lead vacancies are created. That leads to increasing the mobility of the domain walls, relieving the domain re-orientations and increasing ϵ_r , $\tan \delta$, K_p and K_r .

The effect of the additive MnO_2 is the opposite. In the presence of other additives and high temperature processing, the manganese can change its valence from Mn^{4+} to Mn^{3+} , which creates additional oxygen vacancies limiting the mobility of the domain walls [1]. In comparison with NiO, adding MnO_2 has the effect of a hardener.

References

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