DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF MODIFIED PbTiO₃ CERAMICS

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Abstract. This article deals with the results from the studies of the relative dielectric constant εᵣ, the dielectric losses tan δ, the planar coupling factor Kᵢ, the thickness coupling factor Kᵣ, as well as the temperature stability of εᵣ in the temperature range from -25 °C to 70 °C of (Pb₁₋ₓCaₓ)TiO₃ ceramics modified with Pb(Co₀.₅W₀.₅)O₃, NiO and MnO₂. Maximum anisotropy coefficient Kᵣ/Kᵢ = 5.55 and best temperature stability of εᵣ are registered for the composition with x = 23 at. % CaTiO₃ with additives of NiO and Pb(Co₀.₅W₀.₅)O₃.

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1. Introduction

The present research is a continuation of an earlier research [1] on the optimum composition of the modified PbTiO₃ 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 εᵣ and low dielectric losses [5-7].

The following system was studied

(Pb₁₋ₓCaₓ)(Co₀.₅W₀.₅)₀.₀₄Ti₀.₉₆O₃

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 % MnO₂. 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 Kᵢ and Kᵣ,
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 $\varepsilon_r$ and $\tan \delta$ respectively on the concentration of Ca$^{2+}$ ions. In the not polarized samples the permittivity and dielectric losses are at maximum at 23 at. % Ca. The additives of NiO and MnO$_2$ stabilize the properties of ceramics, and this tendency is more clearly expressed for MnO$_2$.

![Graph showing $\varepsilon_r$ vs Ca concentration](image)

**Fig. 1.** Dependence of the relative dielectric constant $\varepsilon_r$ on the concentration of Ca in (Pb$_{1-x}$Ca$_x$)3[(CO$_{0.5}$W$_{0.5}$)0.04Tl$_{0.06}$]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.

Figure 3 shows the dependency of the radial coefficient of the electro-mechanical coupling $K_r$ and the thickness coefficient of electro-mechanical coupling $K_t$ on the concentration of Ca$^{2+}$ ions. The coefficient $K_t$ is higher than $K_r$ for all studied compositions and has a maximum value for the samples with NiO additive.

Temperature stability of $\varepsilon_r$ of the composition with the additive of NiO is shown in Table 1. The stability of permittivity increases as the volume of Ca$^{2+}$ ions is increased mainly because of the lower Curie temperature $T_c$.

It is interesting to point out that all polarized samples have lower $\varepsilon_r$ and $\tan \delta$ values than the not polarized ones. The change in $\varepsilon_r$ 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 (Pb$_{1-x}$Ca$_x$)[(Co$_{0.5}$W$_{0.5}$)$_{0.04}$Ti$_{0.96}$]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 (Pb$_{1-x}$Ca$_x$)[(Co$_{0.5}$W$_{0.5}$)$_{0.04}$Ti$_{0.96}$]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 $\varepsilon_r$ increases. Since
in the tetragonal phase the 180° domain re-orientations prevail, the lower values
of $\varepsilon_r$ are determined by the first factor.

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

<table>
<thead>
<tr>
<th>$x$ (at.%)</th>
<th>Deviation of $\varepsilon_r$ (%)</th>
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<tbody>
<tr>
<td></td>
<td>-25°C to 15°C</td>
</tr>
<tr>
<td>23</td>
<td>9.48</td>
</tr>
<tr>
<td>24</td>
<td>15.04</td>
</tr>
<tr>
<td>25</td>
<td>15.50</td>
</tr>
<tr>
<td>26</td>
<td>13.45</td>
</tr>
<tr>
<td>27</td>
<td>14.09</td>
</tr>
</tbody>
</table>

The additive of compensated valence Pb(Co$_{0.5}$W$_{0.5}$)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 $\varepsilon_r$, $\tan \delta$, $K_p$ 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 va-

tence 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
   Russian).