# A PYROELECTRIC MATERIAL FOR A SENSITIVE ELEMENT IN GAS ANALYZERS

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#### ABSTRACT

The use of high performance pyroelectric materials as a sensitive element of catarometers in gas chromatographs enables us to decrease the gas detection limit to  $10^{-5} - 10^{-6}$  vol.%. The pyroelectric and dielectric properties of ferroelectric ceramic samples made of pure calcium leaden titanate as well as those modified by nickel and manganese have been studied. These results show that most of the parameters are affected both on the calcium quantity in the initial substance and on the nature and quantity of the modifying agent. The synthesized piezoelectric materials on that type of substances ensure improved physical parameters and stabilized optimal characteristics of the sensitive element of gas analyzers.

#### INTRODUCTION

Strengthened work in searching for possibilities and methods for increasing of the sensitivity of gas chromatographs has began since 60<sup>th</sup> years of the XX<sup>th</sup> century. Studies have been directed mainly in two directions: developing of an express chromatographic method (Leithe, 1980) and introducing of new perspective pyroelectric materials as sensitive elements (Novik, 1979). Because the signal of the pyroelectric catarometer is proportional to the speed of the change of the deposed mater concentration it is possible express methods for analyzing of the metallurgic, hole and other gases to be developed and combine them with step chromatography (Guglya et al., 1973; Guglya et al., 1984). Using of high effective pyroelectric materials in the catarometer sensitive elements ensures very low concentrations of the substances in the mix to be determined. In some cases they reach values of the order of magnitude of 10<sup>-5</sup> – 10<sup>-6</sup> vol. %. Because of these reasons the choice and synthesizing of suitable material are a stage of substantial meaning in creating of transformers that determine their transforming properties.

Pyroelectricity is a phenomenon observed for a group of piezoelectric crystals with low space symmetry (pyroelectrics). It is expressed in appearing of spontaneous polarization in dielectric crystals when there is no outer electric field. As the temperature varies the magnitude of the spontaneous polarization also changes. For difference from the ferroelectrics the sign of the polarization of pyroelectrics does not change when an outer electric field is applied.

Usually polarized charges, created as a result of the polarization, are compensated because of trapping of electrical charged motes and aerial ions as well as a result of pyroelectric own conductivity.

At regular heating or cooling of the pyroelectric crystals, however, change of the pyroelectric charge density, respectively spontaneous polarization  $P_s$  of the pyroelectric, can be observed. A direct proportional dependency exists between the temperature change  $\Delta T$  and the spontaneous polarization change  $\Delta P_s$ .

In dependence on the purpose of the transforming element the requirements to the materials are oriented to either the complex of physical properties, which ensure maximal exploitation characteristics to be achieved, or improving of their constructive and technological capabilities. Keeping and reproducing of the properties of the pyroelectric transformer at the work conditions (hits, concussions, irradiation, climatic factors etc.) depend strongly on the properties of the chosen material.

Among the existing three groups pyroelectric materials (monocrystals, polycrystals and organic polymers) the polycrystal pyroelectrics appeared to possess the best properties. They give possibility for flexible managing of their properties, 100 % using of the material, a low working cost (6 - 8 times less than the monocrystals working cost), a large specific surface (up to some thousands cm<sup>2</sup>/g). On the other hand, they suppose widely varying of their properties by changing their chemical composition and polarization regime. In these reasons the experiments considered in this work, were restricted only in studying of the pyroelectric ceramic polycrystal materials.

### EXPERIMENTAL

Pyroelectric and dielectric properties of basic ferroelectric ceramic material made only by calcium leaden titanate as well as the samples on this basic material with additives of nickel or manganese in given constant quantities were studied. The

stoichiometric composition of the basic material expressed in at. % is  $(Pb_{0.75}Ca_{0.25})[(Co_{0.5}W_{0.5})_{0.04}Ti_{0.06}]O_3$ . In comparison with other atomic ratios of the elemental composition the

The leaden titanate (PbTiO<sub>3</sub>) was used for synthesizing of the basic material. The structure was stabilized by substitution of some leaden atoms from the composition with calcium. The samples with calcium quantity between 23 and 27 at. % were studied - this means that the general formula of the basic material is  $(Pb_{1-x}Ca_x)[(Co_{0.5}W_{0.5})_{0.04}Ti_{0.06}]O_3$ , where x = 0.23, 0.24, 0.25, 0.26, 0.27. The samples were obtained using a standard method: hydraulic milling of the raw material in the ball mill, thermal synthesis at 900 °C for two hours, second milling of the product till its specific surface achieved a value  $\phi_v \ge 4000 \text{ cm}^2/\text{g}$ , double plasticizing using 10 % solvent of polyvinyl alcohol, pressing in the disc form with diameter of 20 mm and thickness of 2 mm and 2 hours baking at the temperature 1170 - 1210 °C with the rate of 200 °C / h for reaching of the temperature given. The sample composition was made in three variants: basic (without any modificator); with 1 mol. % modifying agent of NiO and with modifying additive of 1 mol. % MnO2. After cooling the discs down their thickness was going down to 1 mm. Then their surface was smeared with silver paste and baked at a temperature of 950 °C with an aim stabilizing of the silver layer on the sample surface. The polarization of the sample was performed in silicon oil at the temperature of approximately 100 °C and a field intensity of 6 kV / mm for 1.5 h. 24 h later the following dielectric parameters were measured:

Relative dielectric permeability  $\varepsilon_{33}^{T}$ , dielectric looses tg $\delta$ , resonant frequency trough the diameter  $f_{r}$ , antiresonant frequency trough the diameter  $f_{a}$ , resonant resistivity  $R_{r}$ .

shown one possess the highest pyroelectric activity, the least dielectric permeability and the highest thermostability.

resonant frequency trough the depth  $f_r$  and antiresonant frequency trough the diameter  $f_a$ . The samples were designated as follow: the first number shows the calcium amount in at. % and the figure after the dash - the type of the sample modification – "1" for nickel modification, "2" for manganese modification and "0" for unmodified samples (for example, "25 - 1" means that the sample is modified with NiO and contains 25 at. % calcium).

### EXPERIMENTAL RESULTS AND DISCUSSION

The mass looses were determined two hours after the thermal synthesis at 900  $^{\circ}$ C. The results show that they were not big and they are in the limits of 2 %.

In Table 1 the results of the relative dielectric permeability of the disc samples before polarization ( $\varepsilon_{33}^T$ )<sub>0</sub>, its change after polarization relative to its initial value  $\varepsilon_{33}^T/(\varepsilon_{33}^T)_0$  and the dielectric looses before (tg $\delta_0$ ) and after (tg $\delta$ ) polarization were shown.

Table 1. Effect of calcium Ca, nickel Ni and manganese Mn contents of the structure on the relative dielectric permeability and dielectric loses of the pyroelectrics. The designation of the sample is as follow: the first number shows the calcium quantity in the sample. The modification of the samples was shown by the figure after the dash:  $_{,0}^{,0}$  for row material, "1" – for material with nickel modificator and "2" - for material with manganese modificator. ( $\varepsilon_{33}^{,T}$ ) and  $\varepsilon_{33}^{,T}$  are relative dielectric permeability of the material before and after polarisation, and tg $\delta_{0}$  and tg $\delta$  - the material dielectric loses before and after polarisation, respectively.

Sample	Baking temperature	Relative dielectr	ic permeability	Dielectric loses		
	[°C]	Before polarisation ( $\varepsilon_{33}^{T}$ )0, x10 <sup>14</sup>	After polarisation $\mathcal{E}_{33}^{T}/(\mathcal{E}_{33}^{T})_{0}$	Before polarisation $\mathrm{tg}\delta_{\mathrm{o}}$	After polarisation $\mathrm{tg}\delta$	
24-0 25-0 26-0 27-0	1210 "	208 232 221 195	163 201 194 152	4.71 8.06 8.27 4.62	3.35 2.89 2.69 2.60	
23-1 24-1 25-1 26-1 27-1	1170 " "	196 225 227 225 235	166 208 216 214 225	6.45 6.14 4.27 5.30 4.75	6.08 6.18 6.10 7.93 723	
23-2 24-2 25-2 26-2 27-2	1200 " "	186 192 185 194 191	179 182 181 185 186	2.46 2.35 1.85 2.42 2.11	1.98 1.75 1.59 1.79 1.71	

Increasing of  $\varepsilon_{33}^{T}/(\varepsilon_{33}^{T})_{0}$  till and over 200 (for basic PbTiO<sub>3</sub> crystal, for example,  $\varepsilon_{33}^{T}/(\varepsilon_{33}^{T})_{0}$  is 78-80) is probably due, on one hand, to the different calcium quantity in the samples and on the other - to the type of the modifying agent. After substitution of the leaden atoms in the crystal cell with calcium ones, decrease of the tetragonal bending took places in the basic material, that is accompanied with the decreasing of the Curie temperature. When the ratio of PbTiO<sub>3</sub> to CaTiO<sub>3</sub> was 1 : 1, the T<sub>k</sub> became 80 °C and  $\varepsilon_{33}^{T}/(\varepsilon_{33}^{T})_{0}$  increased till 800. As the main purpose of this studying was producing of material possessing high sensitivity (that is material with low permeability) and better piezoelectric properties, introduction of calcium atoms should be limited to 27 at. %. The results for

chosen range of calcium amount presented in Table 1 show that the change of the dielectric permeability  $\varepsilon_{33}^{T}$  is in the range of 5 – 25 % for every at. % calcium quantity, depending on the nature of the modifying agent. Slight growing of the ratio  $\varepsilon_{33}^{T}$  for the sample with nickel additive could be seen, while  $\varepsilon_{33}^{T}$  for the manganese modified samples decreased and stabilized. Dielectric looses, tg $\delta$ , for the sample with manganese modifier are very low and almost did not depend on the calcium quantity, while for these one with nickel modifier they grew up with increase of the calcium quantity in the materials.

Table 2. Effect of the temperature on the deviation of the relative dielectric permeability and temperature coefficient of the dielectric permeability for different modifying additives.

Sample	Baking temperature	Deviation of the relative dielectric permeability, $\varepsilon_{_{33}}^{^T}$ , %			Temperature coefficient of the dielectric permeability, TK $\varepsilon_{33}^{T}$ , x10 <sup>-3</sup> , [K <sup>-1</sup> ]			
	[°C]	-25÷15 °C	15÷70 °C	-25÷70 °C	-25÷15 °C	15÷70 °C	-25÷70 °C	
23-1	1210	9.48	5.07	14.55	2.37	0.90	1.53	
24-1	1210	15.50	9.46	24.96	3.88	1.72	2.63	
26-1	1170	13.45	13.89	27.34	3.36	2.52	2.88	
27-1	1190	14.09	12.76	26.85	3.52	2.32	2.83	
25-2	1200	8.28	19.26	27.54	2.07	3.50	2.90	
27-2	1200	8.48	21.56	30.04	2.12	3.92	3.16	

The ratio  $\varepsilon_{33}^{T}/(\varepsilon_{33}^{T})_{0}$  in the different temperature intervals and the values of the temperature coefficient of the dielectric permeability, TK  $\varepsilon_{33}^{T}$ , are shown in Table 2. It was found destabilization of the ratio  $\varepsilon_{33}^{T}/(\varepsilon_{33}^{T})_{0}$  for the nickel-modified material when the calcium quantity changes. According us, this was due to the decrease of the Curie temperature when the calcium amount increased. Stabilization of this ratio was established for unmodified samples (not shown in the Table 2) and for the manganese-modified samples. The temperature

Table 3. Effect of the temperature on the value and sign of the resonant frequency deviation and the frequency temperature coefficient for manganese modified samples.

Sample	Deviation of the resonant frequency, fr, %			Temperature coefficien	It of the resonant frequencyTK $f_r$ , x10 <sup>-6</sup> , [K <sup>-1</sup> ]			
	-25÷15°C	15÷70°C	-25÷70°C	-25÷15°C	15÷70°C	-25÷70°C		
25-2 27-2	0.425 -0.492	0.159 -0.768	0.159 -1.250	1.062 -1.231	0.404 -1.402	0.631 -1.316		

coefficients of the dielectric permeability, different for the three kinds of samples were comparatively more stable.

In Table 3 data for the temperature coefficient of the radial vibrations for two of manganese-modified samples were presented. Similar values were found for nickel-modified samples as well. With increase of the temperature the values of  $f_r$  decreased. When the calcium amount was below 25 at. %, the resonant frequency  $f_r$  moved to the higher values, but at calcium quantity of 27 at. % it moved to the opposite direction ( $f_r$  decreased).

The results for the coefficient of the electromechanical connection for radial  $K_r$  and depth  $K_f$  vibrations at the baking temperature chosen were shown in Table 4.

Nature of the modifying additive as well as the number of the calcium atoms in the crystal lattice affected the material anisotropy. Adding of NiO and  $MnO_2$  into the basic matter caused qualitatively different properties of the ceramics. It was supposed that when nickel atoms displaced titan ones from their positions in the crystal lattice leaden vacations appeared that caused increase of the dielectric permeability and dielectric looses (see Table 1) and coefficient of the

Table 4. Effect of the electromechanical action on the radial  $K_r$  and depth  $K_t$  vibration.

Sample	Baking temperature	Kr	Kt	Kt/Kr	
23-0	1210	0.270	0.485	1.80	

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24-0 25-0 26-0 27-0	" "	0.137 0.096 0.096 0.110	0.450 0.450 0.438 0.483	3.28 4.62 4.56 4.39
23-1 24-1 25-1 26-1 27-1	1170 " "	0.094 0.153 0.176 0.116 0.136	0.522 0.502 0.498 0.483 0.462	5.55 3.28 2.83 4.16 3.40
23-2 24-2 25-2 26-2 27-2	1200 " "	0.142 0.125 0.125 0.129 0.197	0.352 0.428 0.442 0.434 0.466	2.48 3.42 3.54 3.36 4.31

electromechanical connection (see Table 4). The effect of manganese additive was not clear yet because manganese changed its valence in dependence on the conditions of the technological operations. Generally, one could conclude that the modified materials possessed less dielectric permeability, low dielectric looses and negligible changes of  $K_r$  and  $K_f$ . Bigger decrease of  $K_r$  and increase of  $K_f$  values could be expected if the technology for material producing improves and perfects and also if the nature and amount of the modifying agent change. The non-ferroelectric Pb(Co<sub>0.5</sub>W<sub>0.5</sub>)O<sub>3</sub> additive, compensating manganese valence, probably created additional leaden vacations and in that way the structure stabilized. The Pb(Co<sub>0.5</sub>W<sub>0.5</sub>)O<sub>3</sub> additive was the same in all samples studied.

The comparative characteristics' for the piezoelectric ceramic materials synthesized by us and for such, produced in Japan were shown in Table 5.One could see that as far as parameters used are concerned, materials synthesized by us achieve the Japanese ones. This conclusion is an indication for their eventually future application as sensitive elements in the catarometry. An object of the next experiment is studying of the piezoelectric ceramic materials as detectors for few inorganic gas components.

		5.4			Japanese			
Parameter		Bulgarien		Tosh	Hitachi			
	23-1	25-2	27-2	C-10	C-12	PC-11		
ε <sub>33</sub> <sup>⊤</sup> /ε₀	166	181	186	250	180	170		
tg $\delta$	6.08	1.59	1.71	-	-	1.00		
Kr	0.094	0.125	0.197	0.14	0.06	0.05		
Kt	0.522	0.422	0.466	0.45	0.47	0.5		
<i>N</i> t , Hzm	1874	2470	2022	2454	2358	2150		
<i>d</i> <sub>33</sub> .10 <sup>-12</sup> , C/N	80	90	95	61.6	55.6	52.8		
<i>g</i> <sub>33.</sub> 10⁻³, Ym/N	54.40	56.18	57.70	27.11	34.62	35.13		
$\sigma$ , N/m <sup>2</sup>	0.219	0.220	0.220	-	-	0.220		
<i>T</i> <sub>k</sub> , °C	325	308	309	360	340	355		

Table C	<b>^</b>	. <u></u>		h - h	Duda and an				
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### CONCLUSIONS

1. Three types of samples made by ferroelectric material based on the leaden-calcium titanate with nickel and manganese modifiers were synthesized and their dielectric and pyroelectric parameters were studied;

2. It is shown that in most of the cases the values of the parameters studied depended on calcium amount in the basic material as well as on the quantity and nature of the modifying additive;

3. It is established that dielectric looses of the samples are function of the nature of the modifying atom. For nickel additive they were negligible, while for manganese additive they depended on the calcium amount in the structure of the basic material; 4. Results from our studying of the piezoelectric materials produced indicated that improving and stabilizing of the specific physical parameters for these substances are possible to be obtained and optimal characteristics' for the sensitive elements of the chromatographic catarometer to be found.

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