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Processing - structure – dielectric and piezoelectric properties correlation in PbO- based ceramics

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Effects of trace impurities and additives on physical properties of piezoelectric ceramics are discussed. Experimental results are presented in the case of ceramics with the composition $(Pb,Ca)TiO_3$ - $Pb(Co,W)O_3$, doped with lithium and manganese ions. The nanostructure of the materials has been evidenced by HRTEM technique. Dielectric and piezoelectric properties have been measured on samples poled under an electric field of 5.5 – 7.5 kV/mm. Electromechanical coupling factors k_t up to about 0.7 have been obtained. The dependence on temperature of dielectric, piezoelectric and electromechanical properties was recorded. The presence of anisotropy in the $(Pb,Ca)TiO_3$ - $Pb(Co,W)O_3$ -type materials was evidenced.

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1. Introduction

PbO based piezoelectric ceramics, with the general formula ABO_3 and perovskite structure, are still largely studied and used for various applications. The lead titanate crystalline lattice of perovskite type supports a lot of substitutions in A- or/and B-site positions, and a great variety of chemical compositions are obtained. There are several types of possible modifications of the ABO_3 compounds: a) by partial substitution of A- or/ and B ions with isovalent ions, higher- or lower valence ions, pairs of isovalent ions, pair of ions with compensating valence; b) by addition of compounds to a stoichiometric composition; c) by mixing with other $PbBO_3$ (where B is Zr, Hf, Sn) or $PbB'B''O_3$ compounds (where B' is one of the atoms: Nb, W, Ta, and B'' could be Ni, Mg, Zn, Mn, Sc, Co, In, Yb). The resulted materials show different physical properties and characteristics as compared to those of $PbTiO_3$ ceramics. The mixture of $PbTiO_3$ with the $PbB'B''O_3$ compounds, known also as end members, allows the formation of the relaxor type materials [1, 2].

The amount, the nature and some properties of the substituents, such as electronegativity, ionic radius, valence, mass, etc. is related to the introduction of point defects in the crystalline structure of the new materials. The point defects include A-site vacancies, oxygen vacancies, Pb-O vacancy pairs, electron holes, dislocations. Obviously, relationships between the chemical composition, crystal structure and physical properties should exist. Additives introduced in perovskites produce different effects on the crystalline lattice and their physical properties. Some additives contribute to a modification of crystalline lattice, followed by an increase of the relative dielectric constant, ε_{33}^T, and electromechanical coupling factor, k_P, up to a specified concentration and a decrease of them over this concentration. This is the case of CeO_2 addition (0.03, 0.05, 0.1, 0.3, 0.5, and 0.7 wt %), in the ternary system $0.03Pb(Sb_{0.5}Nb_{0.5})O_3$- $0.03Pb(Mn_{1/2}Nb_{2/3})O_3$- $(0.94-x)PbZrO_3$- $xPbTiO_3$. Over the concentration of 0.1 wt% Ce ions, a decrease of the ε_{33}^T, and k_P values are observed [3]. On the same solid solution system a decrease of dielectric constant is reported with the increasing concentration of Y_2O_3 or MnO_2 content. The authors suggested that the polarization could be decreased as a consequence of the pinning of domain walls when Y^{+3} or Mn^{2+} substitute B-sites in ABO_3 perovskite lattice [4]. A threshold Li ions concentration was also observed for the compounds $Pb\ Nb_{3x}\ Li_x\ Zr_{0.51}\ Ti_{0.49-4x}O_3$, with x = 0.015, 0.03, 0.06, 0.09, 0.12, 0.15: the dielectric constant increases up to x = 0.07 lithium content and decreases over this concentration.[5] It is well known that the substitution of Sr and Ba for Pb increases piezoelectricity. [1] In the case of ferroelectric relaxor $(Pb_{1-x}Sr_x)(Zr_yTi_{0.95-y}(Mg_{1/3}Nb_{2/3})_{0.05})O_3$ + MnO 1.5 mol% (x = 0, 0.05, 0.15, 0.20), the increasing of Sr content decreases the Curie point [6]. Sintering conditions are also important for the properties of ceramics with complex substitutions: the electric properties of $Pb_{0.76}Ca_{0.24}(Co_{0.5}W_{0.5})_{0.04}Ti_{0.96}O_3$ ceramics, prepared by conventional sintering techniques (1200°C - 2 hr) are superior to those prepared using the microwave sintering method (1150°C-15 min) [7]. The anisotropy of piezoelectric properties of calcium modified PT ceramics depends on the poling conditions: while the thickness coupling factor, k_t, increases with increasing electric field from 2 kV/mm to 9 kV/mm, the planar coupling factor was negligibly influenced in the $Pb_{0.76}Ca_{0.24}(Fe_{2/3}W_{1/3})_{0.04}Ti_{0.96}O_3$ ceramics [8]. A decrease of tetragonality (c/a) with increasing Ta content, was reported for samples with compositional formula $Pb_{0.76}Ca_{0.24}Mn_{0.02}Ti_{0.98-5x/4}Ta_xO_3$ with the variation in x from 0 to 0.04 in steps of 0.01 [9].

Impurity ions serving as acceptors or donors significantly affect the conduction process and dielectric and piezoelectric behavior of $Pb_{0.85}Sr_{0.15}Zr_{0.55}Ti_{0.45}O_3$ material with various amounts of Mn and (Sb, Nb) dopants. V_{Pb} vacancies (generated when partial Sb^{3+} entered the Pb^{2+} sites or certain amounts of Sb^{5+} occupied the B site), V_O vacancies (created for charge compensation when doped $Mn^{3+/2+}$ ions substituted for B-sites), and V_{Pb}-V_O pairs were evidenced by positron annihilation [10]. A complex substitution in A- and B-site positions, together with other additives like MnO and NiO, in the ceramic with the formula: $(Pb,Me)(Co_{1/2}W_{1/2})_{0.04}Ti_{0.96}O_3$, (where Me = Ba, Sr or Ca) was reported in ref. [11]. Large piezoelectric constant k_t and high anisotropic ratio of k_t/k_P was observed in these materials. The amount of MnO additive influences the electrical and piezoelectric properties of the ceramic $Pb_{0.76}Ca_{0.24}(Co_{1/2}W_{1/2})_{0.04}Ti_{0.96}O_3$: the electrical resistivity increases up to 1.0 mol%, but decreases for higher concentrations, while for 2.0 mol% MnO the anisotropic ratio k_t/k_P was infinite [12]. A high piezoelectric anisotropy (d_{33}/d_{31} = 34/1) and an increased dielectric constant is reported in the $Pb_{0.65}Ca_{0.31}Sr_{0.04}Ti_{0.94}(Co_{0.5}W_{0.5})_{0.06}O_3$ + 0.01 mol% MnO system. [13]

The aim of this work is to prepare and characterize calcium-doped PT ceramics, containing $Pb(Co,W)O_3$, as end member. The concentration of lead and calcium was maintained as in ref. [12] ($Pb_{0.76}Ca_{0.24}(Co_{1/2}W_{1/2})_{0.04}Ti_{0.96}O_3$), but that of the titanium ions was decreased up to 95 at%. The concentration of the additive MnO_2 is 1 wt%. In this material, considered as a reference material, small amounts of lithium carbonate were added as dopant, to obtain other two materials.

The first part of this study refers to the influence of the sintering temperature and lithium ions on microstructure, the dielectric and piezoelectric properties. The variation of physical properties with the temperature in the range 20^{0}C - 300^{0}C is also presented. The changes in the anisotropy of electromechanical properties are evidenced as a function of the lithium concentration.

2. Experimental

The modified lead titanate ceramics with the chemical formula: $Pb_{0.76}Ca_{0.24}Ti_{0.95}(Co_{0.5}W_{0.5})_{0.05}O_3$ + 1.0 wt% MnO_2 + *a* wt% Li_2CO_3, where *a*= 0; 0.14; 0.28, were prepared by solid-state reaction from reagent-grade oxides and carbonates with purity better than 99%. Materials are denoted CaPT0, CaPT1 and CaPT2, respectively. Disc of about 15 mm diameter were pressed, and sintered in a narrow range of temperatures, between 1000^{o}C and 1050^{o}C, for 3-4h. Silver paste was deposited on the ceramic samples for poling and electrical characterization. The sample poling was achieved in silicone oil bath at a maximum field of 70 kV/cm. The microstructure investigation of poled samples was performed using HRTEM and scanned area electron diffraction (SAED) techniques.

The dielectric and piezoelectric properties were obtained from the measurements of capacitance, resonance and antiresonance frequency for radial modes, conducted with a HP 4194A Impedance/ Gain-Phase Analyser [14]. The coupling factor k_t has been calculated from the resonance and antiresonance frequencies of thickness mode of a thin disc. [15]

The variation of dielectric and electromechanical properties with the temperature was conducted according the following procedure. The sample is maintained at the measurement temperature, while the impedance spectra are acquired around the resonance and antiresonance frequencies, and harmonic frequencies. The capacitance, C, and dielectric loss, tanδ, are also recorded around 1kHz. The sample is heated again, until a new chosen temperature and the procedure is repeated over the whole temperature range established for study. These values are used for piezoelectric constants calculation.

A different procedure is used to evidence possible phase transitions and thermal activated relaxation processes. The capacitance and dielectric loss are recorded during heating and cooling (with a rate of about 1.5^{o}C/min) for a set of five frequencies: 0.2, 1, 2, 20 and 100 kHz.

3. Results and discussion

3.1 Microstructure

The sintering temperature, the complexity of composition, gradient of element concentration, and the poling conditions favour the coming out of inhomegeneities, and nanodomains are developed inside or at the boundary of normal domains. The HRTEM images, shown in Figure 1, evidence the influence of sintering temperature on the microstructure of poled CaPT0 samples. Typical contrast (dark fields), proving the existence of the lattice strain in the crystal lattice, is observed in the HRTEM images. Small nanodomain zones are present in the CaPT0 material sintered at 1000^{o}C (Figure 1.a). Larger regions containing nanodomains can be seen in the CaPT0 materials sintered at higher temperatures even at smaller magnitude of the micrographs (Figs. 1b-1d).

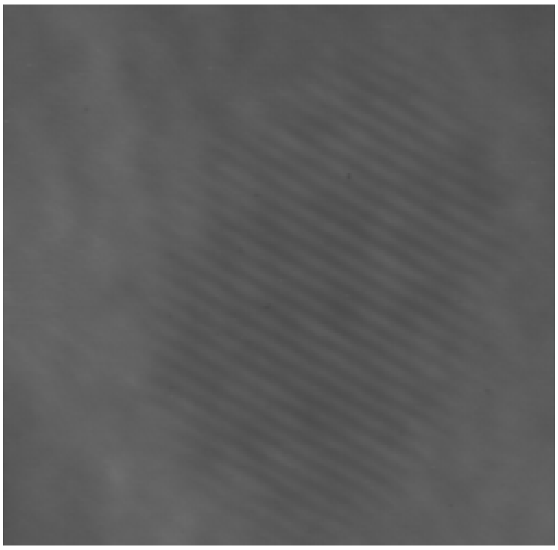


Fig. 1a.Nnanodomain zone (height=10 nm; width=5 nm) in CaPT0 material sintered at 1000^{o}C:

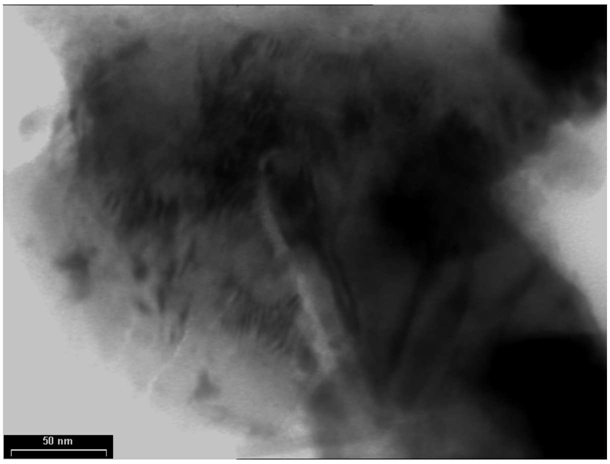


Fig 1b. Nano domain areas in CaPT0 material sintered at 1010^{o}C. HRTEM image - scale bar: 50nm

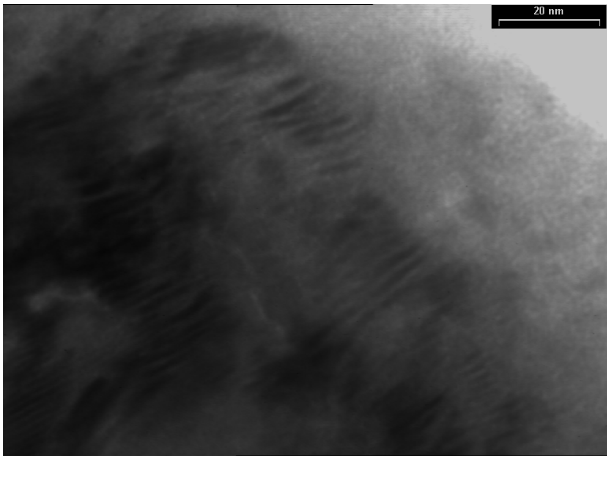


Fig. 1c. Nanodomain area in CaPT0 material sintered at 1010^{o}C. HRTEM image - scale bar: 20nm

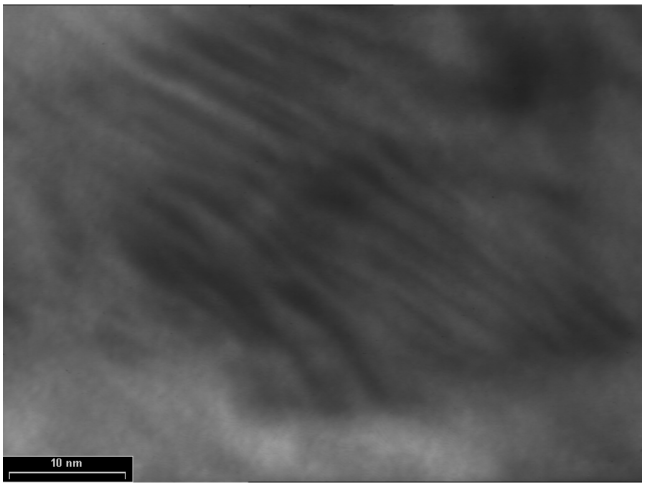


Fig. 1d. Nanodomain area in CaPT0 material sintered at 1010^{o}C. HRTEM image- scale bar: 10 nm

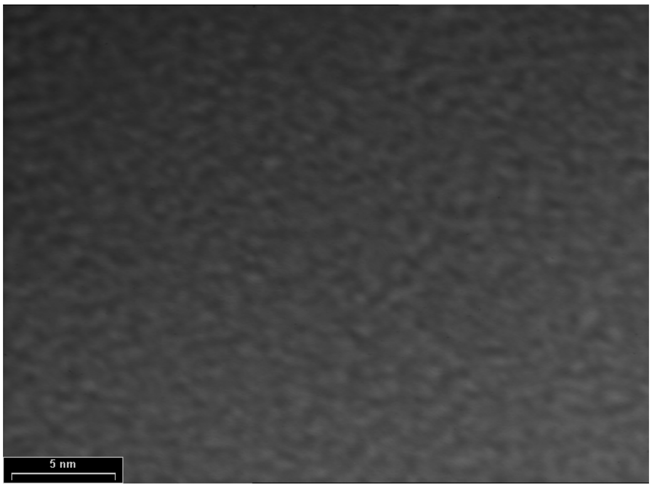


Fig. 1e. HRTEM images in CaPT0 material sintered at 1010^{o}C. Scale bar: 5nm

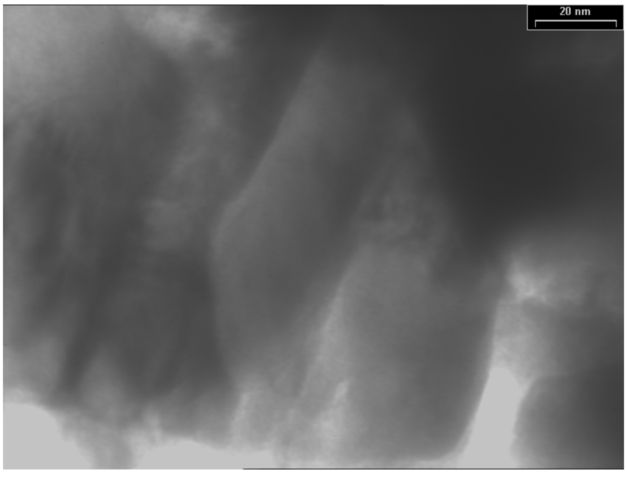


Fig. 1f. HRTEM images in CaPT0 material sintered at 1030^{o}C. Scale bar: 20nm

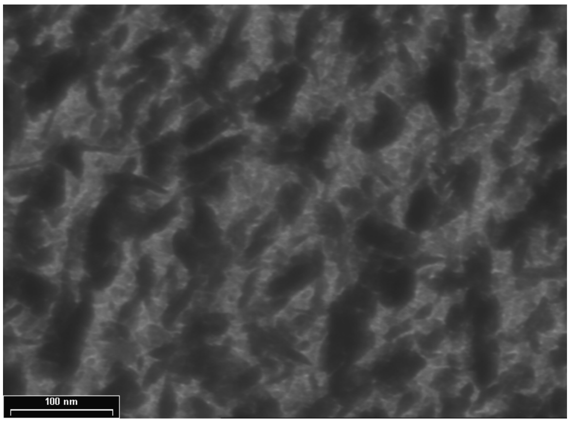


Fig. 1g. HRTEM images in CaPT0 material sintered at 1030°C. Scale bar: 100nm

Fig. 1. HRTEM images in CaPT0 material sintered in the temperature range between 1000°C and 1030°C.

The nanodomains are included in the matrix of the CaPT material, shown in Fig. 1e.

The corresponding selected area electron diffraction (SAED) pattern, presented in Fig. 2, confirms the tetragonal crystallization system of CaPT0 materials. The lattice constants of samples sintered at 1010°C are: a = b = 3.94 and c = 4.06.

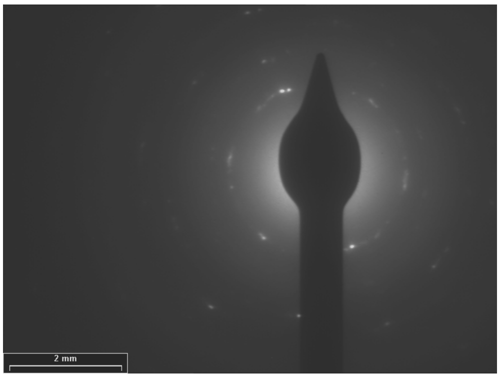


Fig. 2a. SAED image of the CaPT0 ceramic sintered at 1000°C.

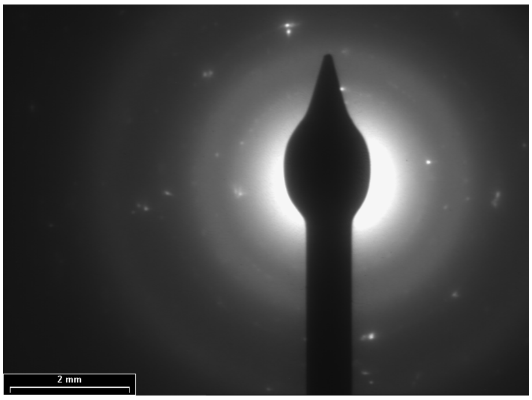


Fig. 2b. SAED image of the CaPT0 ceramic sintered at 1010°C

Fig.2c. SAED image of the CaPT0 ceramic sintered at 1030°C.

Fig. 2. SAED pattern of CaPT0 samples sintered in the temperature range 1000°C-1030°C. Scale bar: 2mm

The crystalline anisotropy factor of the prepared CaPT materials doped with Co and W (c/a=1.0304), is lower than that of the tetragonal $Pb_{0.6875}Ca_{0.3125}TiO_3$ material (ASTM reference code 00-043-0303): c/a=1.03618.

The spot doubling in SAED images indicates that the diffraction pattern is a result of the superposition of two diffraction patterns corresponding to the domain walls rotated from each other. The undistorted ABO_3 perovskite structure consists of a network of corner-sharing BO_6 octahedra that extends infinitely in the three orthogonal directions, creating cubic symmetry. Each octahedra is composed of small cation (B) surrounded by six anions (Oxygen).

At the center of every cube of eight octahedra sits a larger divalent cation (A). The A-cations sit in a symmetric environment of twelve anions. In the real case of the CaPT-type materials two types of modifications are made on $PbTiO_3$ compound: isovalent substitution in A-site with Ca^{2+}, aliovalent substitution in B-site position with Co^{2+} and W^{6+}.

At the stoichiometric raw materials necessary for preparing $Pb_{0.76}Ca_{0.24}Ti_{0.95}(Co_{0.5}W_{0.5})_{0.05}O_3$ compound, manganese oxide and lithium oxide are added. As compared to the substituted ions, namely lead and titanium, the substituents and adatoms are characterized by different ionic radius, oxidation state, and electronegativity. Although Pb^{2+} and Ca^{2+} have the same oxidation state, Ca^{2+} ions have smaller ionic radius and electronegativity than lead. Two oxidation states are possible for the substituents of titanium ions: divalent and trivalent ions for cobalt ions; IV and VI as stable oxidation states for tungsten. By comparison with the ionic radius of lead, Co^{2+} ions have a higher ionic radius while W^{6+} ions have a smaller one. In general, charge disproportionation is possible in solid state for transition elements with partially filled 3d subshell.

If one considers tungsten ions in the oxidation state VI, its substitution for titanium ions induce the formation of oxygen vacancies.

On the other hand, manganese dioxide is subjected to different transformations during the sintering process: in Mn_2O_3 at 500°C; in Mn_3O_4 at 950°C; in MnO over 950°C. Manganese ions could cause a partial reduction of tetravalent titanium ions to Ti^{3+} ions. The second adatom is lithium with a small ionic radius (0.60 Å), but a very close ratio charge/ionic radius as compared to that of the lead: 1.666 for Li^+ and 1.68 for Pb^{2+}.

The CaPT-type materials have a complex composition. Dopants are randomly placed in the crystalline lattice and involve changes in the interaction between ions. Around the dopants short range potentials contribute to the total energy of the system. All these perturbations, together with the oxygen vacancies and other point defects influence the dielectric and piezoelectric properties of the material.

3.2 Principal properties

The mechanical, electrical and electromechanical properties of the materials are studied as a function of temperature and lithium content. All results are presented in Table 1 and Figs. 3- 6.

Table 1. Material constants of CaPT0 – CaPT2 ceramics. The additional index 1 or 2 or 3 attached to labels CaPT0, CaPT1 and CaPT2 correspond to the sintering temperatures of 1000 °C, 1010 °C and 1030 °C, respectively.

CaPT	ρ (g/cm^3)	k_t	ε_{33}^T	d_{33} (pm/V)
0.1	6.9	0.569	150.2	71
0.2	6.9	0.590	161.7	48
0.3	6.95	0.675	173.2	68
1.1	6.9	0.372	235.5	30
2.1	6.9	0.387	258.1	52

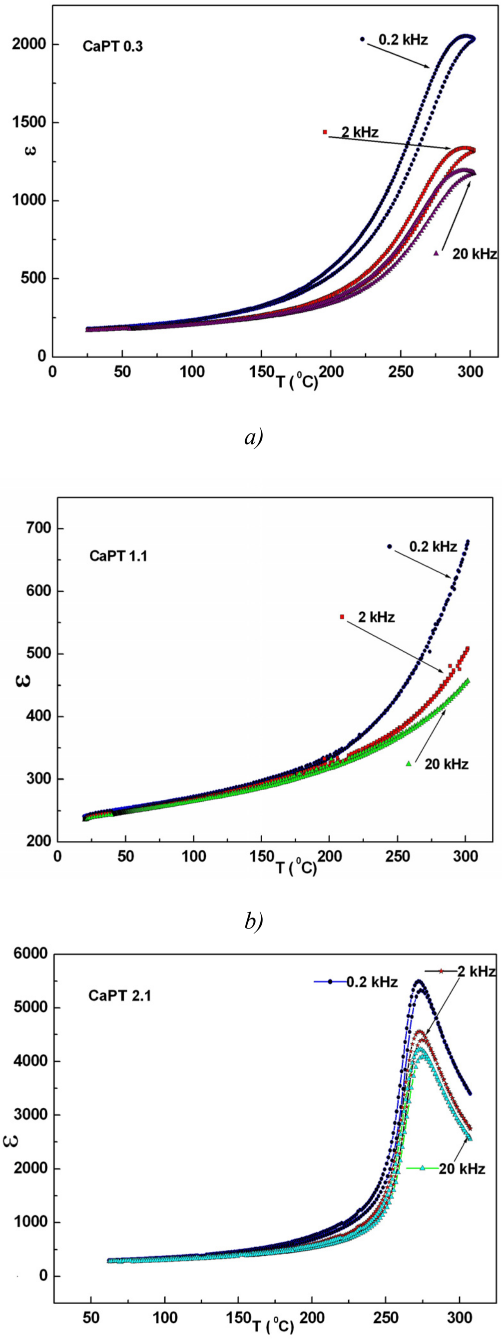
The density of the samples is around 96% of the theoretical density. There are not high differences between the densities of the three materials; the amount of Li_2CO_3 added does not influence their values.

No planar resonance was found for all the samples made on CaPT0 and CaPT2 materials, therefore the coupling planar factor was considered null. Thus for these samples the anisotropy k_t/k_p factor is infinite. Unlike this behaviour, the sample CaPT1.1 has a finite planar coupling factor (k_P=0.134) and only a modest anisotropy factor (k_t/k_P=2.8).

The dielectric constant of the CaPT0 ceramics increases with the increasing sintering temperature (see Table 1).

As can be seen from Figs. 3 and 4, the temperature of ferroelectric transition from cubic to tetragonal phase was also influenced by Li dopant. Thus it strongly decreases from 490 °C (pure $PbTiO_3$) to about 300 °C (CaPT0) and it is further deployed to about 270 °C for Li-doped CaPT2 sample (Fig.3c). A small hysteresys between the heating and cooling curves is also observed for the samples in Fig. 3.

A remarkable stability of the dielectric loss with the variation of temperature until 150°C is observed in Fig. 4.b for the CaPT1material, while increased values are observed for all other samples. The effect of the temperature on the dielectric constant as a function of composition and sintering temperature is shown in Figure 5. A very good stability with the temperature is observed for the material CaPT1 with 0.14 wt% Li_2CO_3.

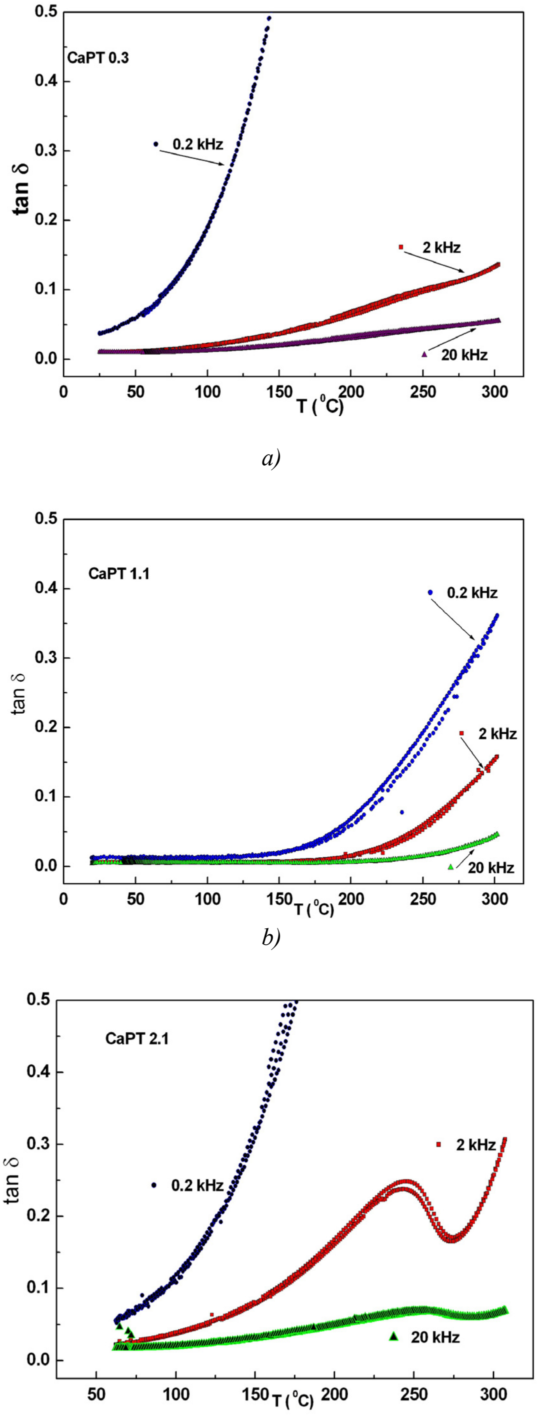


a)

b)

c)

Fig. 3. Variation of dielectric constant with temperature for CaPT0(a), CaPT1(b) and CaPT2(c) materials



a)

b)

c)

Fig. 4. Variation of dielectric loss tangent with temperature for CaPT0 (a), CaPT1 (b) and CaPT2 (c) materials

A high increase of maximum dielectric constant at the transition temperature (270 ^{0}C) is registered for the sample CaPT21 doped with 0.28 wt% Li_2CO_3, with respect to CaPT0.3 sample, whose transition temperature is about 300 ^{0}C (for the other samples the transition temperatures are above the experimental set up temperature limit).

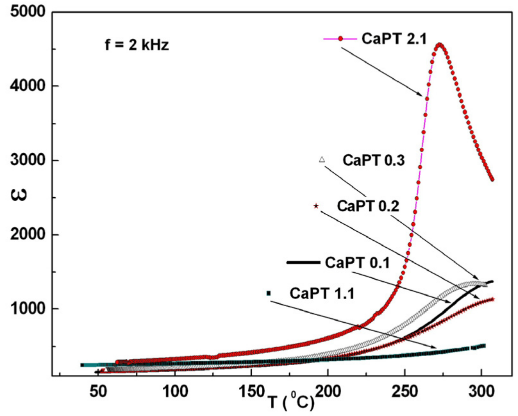


Fig. 5 . Influence of the temperature on the dielectric constants of CaPT-type materials

A good stability with the temperature is observed for piezoelectric thickness coupling factor, k_t, of all materials (Fig. 6).

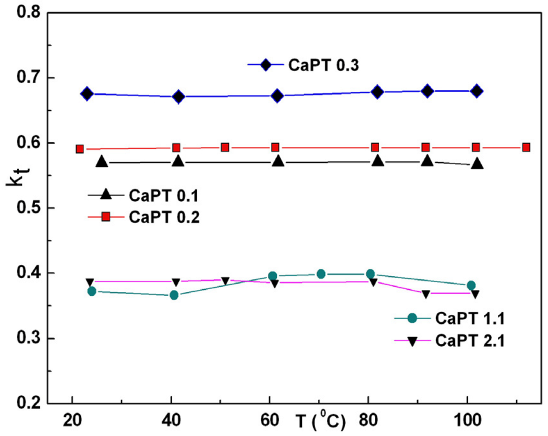


Fig. 6. The piezoelectric thickness coupling factor, k_t vs. temperature variation

4. Conclusions

Anisotropy in crystalline lattice is observed in the CaPT-type materials. Lithium ions addition in $(Pb,Ca)TiO_3$ - $Pb(Co,W)O_3$ materials reduces the sintering temperature of ceramics, and modify their physical properties. The transition temperature from tetragonal to cubic phase is decreased by the addition of 0.28 wt% Li_2CO_3. The dielectric constants increase with the sintering temperature in materials with the same chemical composition. The influence of Li addition is not linear: thus a small amount of Li_2CO_3 added (0.14 wt %) bring about a modification in the nanostructure of the material, with implications in its piezoelectric behaviour: resonance both in planar and thickness modes is present. Consequently, the anisotropy factor is reduced. However, a huge anisotropy in electromechanical properties is observed in the reference material, $Pb_{0.76}Ca_{0.24}Ti_{0.95-}$

$(Co_{0.5}W_{0.5})_{0.05}O_3$ + 1.0 wt% MnO_2, and the ceramic containing 0.28 wt% lithium carbonate. For these materials a zero planar coupling factor k_p is observed.

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