

Effect of Li addition in (Pb,Ca)(Ti,W,Co)O₃ piezoelectric ceramics

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(Pb,Ca)(Ti,W,Co)O₃ + x Li₂CO₃ preparation and properties are reported. We have found that the substitutions of 24 at% of Pb²⁺ ions in A-site positions by Ca²⁺ and 5 at% of Ti⁴⁺ by cobalt and tungsten ions decrease the transition temperature to around about 300°C. A further decrease is obtained by Li addition of to the Pb_{0.76}Ca_{0.24}Ti_{0.95}W_{0.025}Co_{0.025}O₃ basic composition. A sintering process at relatively low temperatures (1000-1050°C) has been employed. The effect of Li content (x wt% Li₂CO₃, x = 0, 0.14 and 0.28) and sintering temperature on structural, dielectric and piezoelectric properties and their temperature dependence has been investigated. The grain growth process and densification of samples with x = 0.28 Li addition was stabilized at a lower sintering temperature compared to those without Li addition. In both cases similar microstructure and physical properties were obtained. However, in samples with x = 0.14, it seems that the presence of lithium ions reduces the sintering temperature, but favours the abnormal growth of the grains and defects formation in the crystalline lattice, thus leading to very different physical properties.

(Received February 25, 2009; accepted March 19, 2009)

Keywords: Piezoceramic, (Pb,Ca)(Ti,W,Co)O₃, Li dopant, Microstructure, High anisotropy

1. Introduction

In PbTiO₃ materials a large tetragonal distortion is accompanied by high electromechanical anisotropy, a feature that makes them very attractive for applications in array transducer elements with high directionality. However, these materials are difficult to sinter and polarize, since cooling down through the paraelectric-ferroelectric transition at 490°C invariably causes cracking, while polarizing process requires high electric field due to the high coercive field. As a result, the modified PbTiO₃ materials with high k_t and k_t/k_p ratio, prepared by an easier and reliable process of sintering and poling, are used in these applications. Pure and modified PbTiO₃ (PT) ceramics and composites have widely been used as transducer material due to their large piezoelectric anisotropy. Different isovalent or off-valence A-site substitutions like Ca²⁺, Sr²⁺ and La³⁺, lower the Curie point and reduce the tetragonal distortion [1], [2]. For example, a Pb_{1-x}Ca_xTiO₃ composition with x=0.5 has the Curie point at 80°C and ratio c/a about 1 [3]. A high piezoelectric anisotropy ($d_{33}/d_{31} = 34/1$) and an increased dielectric constant is reported for the system (Pb_{0.65}Ca_{0.31}Sr_{0.04}Ti_{0.94})(Co_{0.5}W_{0.5})_{0.06}O₃ + 0.01 mol% MnO [4]. Yamashita proposed first the Co-, W-, Mn-doped (Pb_{0.76}Ca_{0.24})Ti_{0.94}(Co_{1/2}W_{1/2})_{0.06}O₃ compound [5, 6].

The aim of this work is to investigate the microstructure and the dielectric and elastic properties of (Ca, Co, W) - modified PT ceramics doped with Li ions. The effect of lithium doping on the properties of PbTiO₃ ceramics is discussed.

In a previous paper [7] we have discussed the correlation of microstructural aspects (revealed by HRTEM images) and dielectric and piezoelectric properties. In this paper we emphasise the microstructural differences as revealed by SEM images of samples prepared in diverse conditions and discuss thermal stability of the piezoelectric and elastic properties.

2. Experimental

The investigated compositions are as follows: Pb_{0.76}Ca_{0.24}Ti_{0.95}(Co_{0.5}W_{0.5})_{0.05}O₃ + 1.0 wt% MnO₂ + x wt% Li₂CO₃. They are labelled CaPT0, CaPT1 and CaPT2 for dopant concentration of x=0, 0.14 and 0.28 respectively.

The ceramics were prepared by solid-state reaction from reagent-grade oxides and carbonates with purity higher than 99%. Using the preparation technique described in [8], ceramics with a homogeneous distribution of dopants have been obtained. Disc shape samples of about 15mm diameter were pressed and sintered for 3-4 h, in a narrow range of temperatures from 1000°C to 1050°C. After sintering, silver paste electrodes were applied and the samples were poled in silicon oil bath at a maximum field of 70 kV/cm.

The microstructure was investigated using SEM techniques. The dielectric and piezoelectric properties were calculated from the measurements of capacitance, resonance and anti-resonance frequency for radial modes, as recommended by ANSI/IEEE Standards [9]. An HP 4194A Impedance/Gain-Phase Analyser was used. The

coupling factor k_t was calculated from the resonance and anti-resonance frequencies of thickness mode of a thin disc [10]. A Delta Design 9023 controlled temperature chamber was employed to investigation of temperature dependence of dielectric and electromechanical properties. The poled samples were heated from room temperature until the first step of e.g. 40°C was reached and maintained at this temperature until the impedance spectra were recorded around the resonance, anti-resonance and harmonic frequencies. The capacitance, C , and dielectric loss, $\tan\delta$, were also recorded, with frequency sweep between 100 Hz and 1 MHz. Then, the sample was heated again, until a new chosen temperature was reached, and the procedure was repeated again, over the temperature range of interest. The capacitance C of poled samples recorded at 1 kHz was used for dielectric constants calculation. The capacitance and dielectric loss were recorded during heating and cooling while the temperature was varied with 1.5°C/min. The data were acquired for a set of five discrete frequencies: 200 Hz, 1 kHz, 2 kHz, 20 kHz and 100 kHz. Due to heating chamber temperature range, the maximum measurement temperature is limited to 310°C.

3. Results and discussion

3.1 Microstructure

A Siemens D5000 system was used for XRD. The XRD patterns, illustrated in Fig. 1, show that only tetragonal perovskite-type structures were found, demonstrating a high degree of crystallization in the material CaPT2 with lithium content, sintered at 1000°C. For the same sintering temperature, the CaPT0 material shows a rather amorphous structure, even if the principal

tetragonal peaks are present. As compared with the reference $\text{Pb}_{0.6875}\text{Ca}_{0.3125}\text{TiO}_3$ compound (ASTM reference code 00-043-0303 and crystallographic parameters such as crystal system - tetragonal, space group - P4, space group number - 123, $c/a=1.03618$), a lower crystalline anisotropy factor $c/a=1.0304$ was calculated for the Mn doped and with Co- and W- substituted for titanium CaPT-type materials [7].

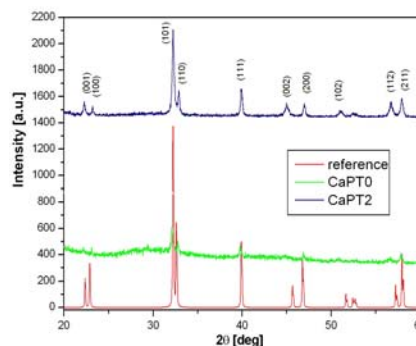


Fig. 1. XRD pattern of CaPT-type materials sintered at 1000°C. The reference is $\text{Pb}_{0.6875}\text{Ca}_{0.3125}\text{TiO}_3$.

Hitachi S3400 and S4500 were used for SEM. The morphology and dimensions of grains for the materials sintered at 1000 °C and 1030 °C are presented in Figs. 2(a) – (h). An additional second Figs. 1, 2, or 3 was attached to labels CaPT0, CaPT1, and CaPT2, to indicate the sintering temperatures of 1000°C, 1020°C and 1050°C, respectively. These new labels are CaPT0.1, CaPT1.1, and CaPT2.1, CaPT0.2, CaPT0.3, CaPT1.1, and CaPT2.1.

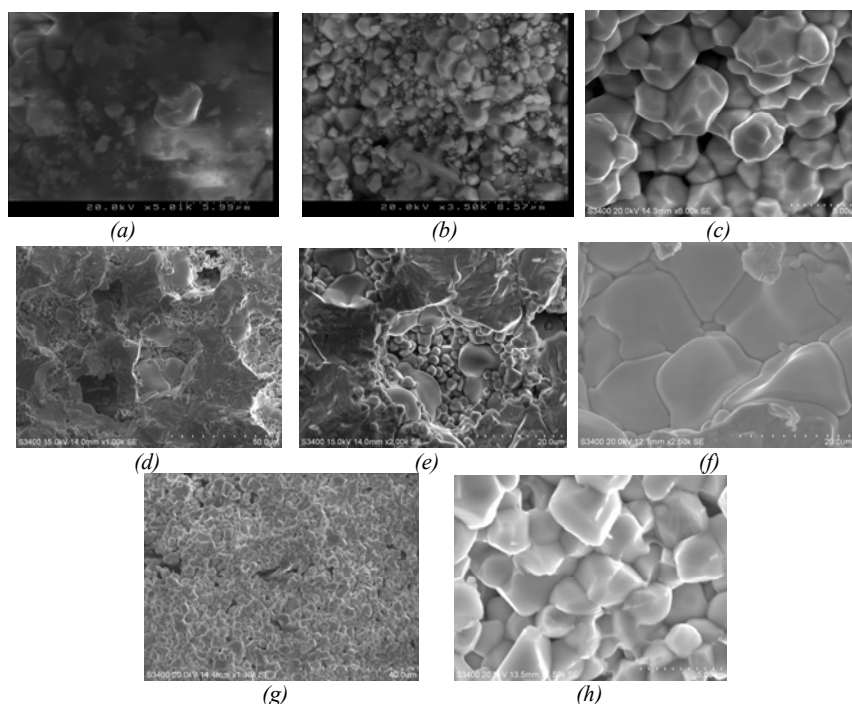


Fig. 2. SEM images of CaPT0 – CaPT2 poled sample: (a) CaPT0.1; (b) CaPT0.2; (c) CaPT0.3; (d)–(f) CaPT1.1; (g) and (h) CaPT2.1.

Different evolution stages of the densification process are revealed from Figs. 2(a)-(c) for the considered sintering temperature range.

In the solid solution of CaPT0 without Li ions material, sintered at 1000°C, there are lots of small particles with sizes between 0.15 μm and 0.56 μm and few grains of about 2 μm . With a small increase in temperature, the isolated grains grow and strongly interact with their neighbours [11], thus leading to a higher degree of densification, as it is observed in Fig. 2(b). However, the sintering process is not yet stabilized and a complex pore network surrounds the grains with various sizes and shapes. For the samples CaPT0.3, a further increase in temperature diminishes the number of pores and more uniform grains in size and shape are obtained. Polyhedron-like grains between 0.5 μm and 2.5 μm , together with aggregates with maximum size of 6 μm are observed in the material CaPT0 sintered at 1050 °C (as shown in Fig. 2(c)).

A different morphology is found in material CaPT1 sintered at 1000°C. Round and lamellar shaped, together with agglomerated particles, of different form, and sizes between 1 μm and 17 μm , embedded in a glass-like matrix, are present in Fig. 2(d). It seems that the presence of lithium ions reduces the sintering temperature, but favours the abnormal growth of the grains and defects formation in the crystalline lattice. One can assume that in the CaPT1 system, with the smallest amount of lithium ions, at least two mechanisms of the grain growth are possible. These are the grain boundary migration (diffusion based-continuous) and grain rotation coalescence (discontinuous) or a linear combination of the two. Other types of events may happen. For example small three-sided grains disappear, or grains moving toward each other to form a new common grain boundary, as discussed in ref [12]. In this model of grain growth, the rate of change of an individual grain depends on the mobility constant for grain boundary migration and the local critical grain size. Another model [13] takes into account the anisotropic grain boundary energy and grain boundary mobility. According to this model, the grain boundary energy is determined by misorientation between the two neighbouring grains. This feature could be a possible explanation of the microstructure from Figs. 2(d) and (e).

A further increase of the lithium content improves the crystallization process, as one can see in Figs. 2(f) and (h). The grains growth process is stabilized at 1000°C only for the CaPT2.0 samples. Grains with sizes in the range from 1.2 μm to 3.8 μm are obtained in the CaPT2 material. Some grains are grown on one side of another grain and form agglomerates of about 14 μm long. The microstructure of the CaPT2.0 samples resembles that of CaPT0.3 samples, therefore it is expected that also some of their physical properties are similar. Moreover, from analogous considerations, we expect CaPT1 samples to be very different.

3.2 Physical properties

The dielectric and piezoelectric properties, together with the thermal coefficients of the main physical properties, are listed in Tables 1 and 2.

Table 1. Electromechanical and dielectric properties of CaPT0 - CaPT2 materials (The additional attached figure to the samples name indicates the different sintering temperature, as previously stated).

Sample	k_t	k_p	k_t/k_p	ϵ_{33}^T	$\tan \delta$
CaPT0.1	0.569	0	∞	150.2	0.0198
CaPT0.3	0.675	0	∞	173.2	0.0171
CaPT1.1	0.372	0.134	2.8	235.5	0.0051
CaPT2.1	0.387	0	∞	258.1	0.0178

The dielectric constant of the materials increases with increasing sintering temperature and lithium content. For CaPT0 and CaPT2 materials no planar resonance was found, and the planar coupling planar factor was considered null. Thus, for these samples, the ratio of the thickness and planar coupling factors, known as the electromechanical anisotropy k_t/k_p factor, is infinite. However, in agreement with the evidenced microstructural differences, the sample CaPT1.1 behaves very differently. It has a finite planar coupling factor and only a modest anisotropy factor.

The temperature of the ferroelectric transition from cubic to tetragonal phase depends on the material composition. Thus, it strongly decreases from 490°C (pure PbTiO₃ [3]) to about 300°C (CaPT0) (Fig. 3a,b) and to about 270 °C for Li-doped CaPT2 sample, as illustrated in Fig. 3(d). Again, Li-doped CaPT1 sample behaves differently. The transition temperature seems to be well-above 300°C (Fig. 3c).

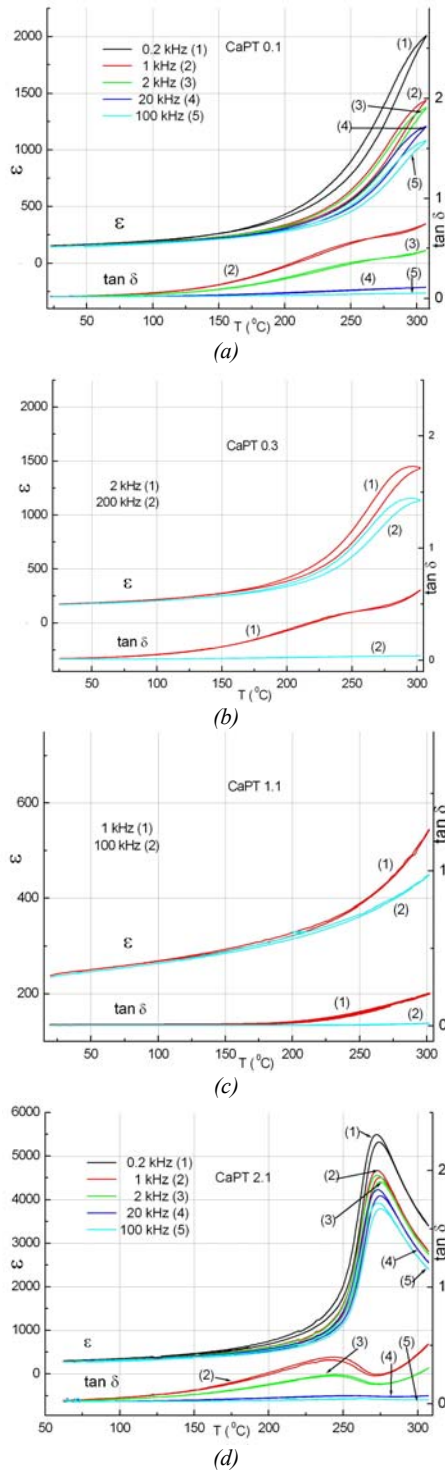


Fig. 3. Temperature dependence of dielectric permittivity and dielectric loss, recorded in the frequency range from 0.2 kHz to 100 kHz, for the CaPT0-CaPT2 materials: (a) CaPT0 material sintered at 1000°C (sample CaPT0.1); (b) CaPT0 material sintered at 1050°C (sample CaPT0.3); CaPT1 material sintered at 1000°C (sample CaPT1.1); (d) CaPT2 material sintered at 1000°C (sample CaPT2.1).

A small hysteresis between the heating and cooling curves is observed in all samples.

All studied materials are characterized by a high thermal stability, as one can see in Table 2. The temperature coefficients are defined as the percentage variation of the corresponding parameter, as the temperature changes by 1 °C.

Table 2. Temperature coefficients of resonance frequency $T(fr)$, coupling constant $T(k_t)$; dielectric loss $T(\tan \delta)$, and elastic constant $T(c_{33}^E)$.

Sample	$T(fr)$ ($^{\circ}\text{C}^{-1}$)	$T(k_t)$ ($^{\circ}\text{C}^{-1}$)	$T(\tan \delta)$ ($^{\circ}\text{C}^{-1}$)	$T(c_{33}^E)$ ($^{\circ}\text{C}^{-1}$)
CaPT0.1	-1.01E-4	3.69E-5	0.0206	-2.06E-4
CaPT0.3	-2.52E-4	7.77E-5	0.0415	-5.12E-4
CaPT1.1	-1.02E-4	0.00127	0.00626	-2.72E-4
CaPT2.1	2.95E-5	-1.29E-5	0.0211	5.97E-5

The dielectric constant presents a slight increase with the increased sintering temperature and lithium content as can be seen in Fig. 4.

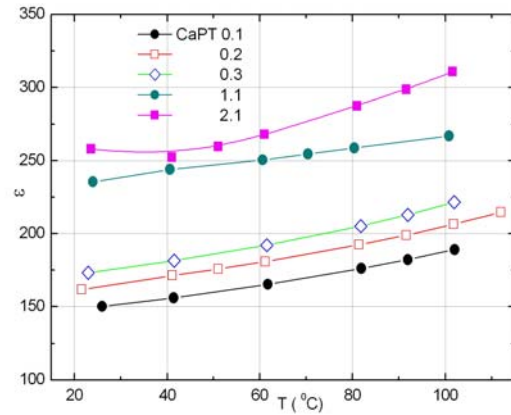


Fig. 4. Dielectric constant of the CaPT0-CaPT2 materials vs. temperature.

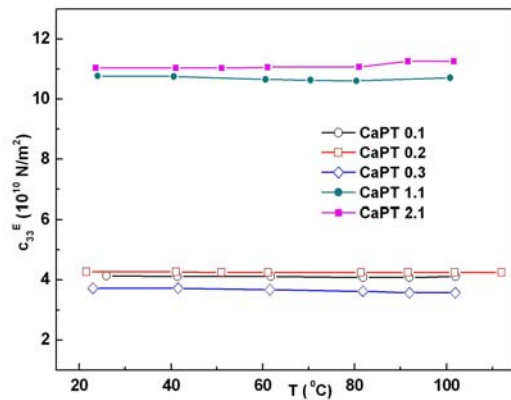


Fig. 5. Elastic stiffness constant, c_{33}^E , of the CaPT0-CaPT2 materials vs. temperature.

The elastic stiffness constant, c_{33}^E , is characterized by a high stability with the temperature, as it is also illustrated in Fig. 5.

A remarkable effect of the Li addition in the CaPT materials is the increase of the elastic constant up to typical values of pure PbTiO₃. Thus lithium addition has an opposite effect on dielectric and elastic behaviour, making the modified CaPT compound a soft dielectric, but a stiff elastic material.

4. Conclusions

Lithium ions addition in (Pb,Ca)TiO₃ - Pb(Co,W)O₃ materials reduces the sintering temperature of ceramics and modifies their microstructure. The concentration of lithium has a threshold value. A small amount of Li₂CO₃ added up to 0.28 wt%, brings about a modification in the microstructure of the material, with implications to its piezoelectric behaviour. A good stability under changing temperature is observed for dielectric constant, dielectric loss, thickness coupling factor and elastic constant c_{33}^E . A huge anisotropy in electromechanical properties is observed in undoped materials and in those containing 0.28 wt % lithium carbonate.

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