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Effect of Ce and La substitution on dielectric properties of lead titanate ceramics.

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Abstract

Effect of cerium (Ce) on the microstructure and dielectric properties of lanthanum lead titanate (PLT) ceramics was investigated. Ce-doped lanthanum Lead titanate ceramics ($Pb_{0.86-x}La_{0.14}Ce_xTi_{0.965-x/4}O_3$) (x= 0, 0.01, 0.03, 0.06 and 0.1) with fixing La doped, were processed by sintering of pressed from nanopowder synthesized by the sol-gel route. Lanthanum lead titanate ceramics have single $Pb_{0.86}La_{0.14}Ti_{0.965}O_3$ (PLT14) phase of perovskite type, the same result is sonded then added cerium. No secondary phase was detected for all compositions. The effect of cerium addition to PLT14 on dielectric properties is analyzed. High values of dielectric constant are obtained of cerium doped PLT14. Temperature Tc, corresponding to the maximum value of dielectric constant, isn't shifted to higher temperature and the maximum value of the dielectric constant is decreased with increasing frequency, which indicates that relaxor behaviour is doesn't caused by Ce substitution.

Keywords: Sol-gel processes, Cerium, Dielectric properties, Perovskites

Introduction

The properties of lead-titanate based ferroelectrics are known to strongly depend on the stoichiometry and of substituent elements either on Pb^{2+}(A-site) and/or Ti^{4+} (b-site) sites. In this respect appropriate doping by different elements offers the possibility to perfect materials functional properties (dielectric, ferroelectric and piezoelectric properties).

Rare-earths (lanthanides) –including the cerium- constitute a series of chemically similar elements with gradually decreasing ionic radius [1]. Therefore, systematic investigations of cerium ions doped ceramics can reveal the effect of this substituent on the structural, electrical, ferroelectric and dielectric properties of the host material [2-5]. Moreover, correlation between doping level and performance of the materials must be established.

In this work, a modified sol-gel processes was adopted to synthesis lead titanate ceramics doped with Ce and La. We set the doping Lanthanum with 14 mol% and we was varied doping rate of cerium ions (0-10 mol %). The structural properties, phase composition and preferentially oriented state of the ceramics were analysed by means of X-ray diffractometry (XRD), scanning electron microscopy (SEM). The dielectric properties were investing in order to reveal the effects of oxidation type and concentration of doping cerium.

2. Experimental

Lanthanum lead titanate ($Pb_{0,86}La_{0,14}Ti_{0,965}O_3$) pur and doped with Ce ($Pb_{0,86-x}Ce_xLa_{0,14}Ti_{0,965-x/4}O_3$); corresponding to the samples PLT14, PLCTx where x= 0-01) were synthesized by the modified sol-gel route in a two-step process: first by controlled hydrolysis of Titanium isopropoxide with distilled water and lactic acid to fabricate the sol , and then on the second step by further reaction of the formed hydrated gel particles with

corresponding ions (Pb^{2+}, La^{3+}, Ti^{4+} and Ce^{3+}) [6-8]. The starting precursors in these syntheses are titanium alkoxide ($C_{12}H_{28}O_4Ti$, Sigma- Aldrich), lead-acetate trihydrate ($C_4H_6O_4Pb$. $3H_2O$, Aldrich), lanthanum-acetate hydrate ($C_6H_9LaO_6$, Fluka) and cerium-acetate hydrate ($C_6H_9O_6Ce$,xH_2O, Aldrich).
After calcinations at 700°C for 2 h powders were uniaxially pressed into disk of 10 mm diameter at pressure of 15 tonne. The pellets were sintered at 1100°C for 4 h in air atmosphere.

3. Results and discussion

X-ray diffraction patterns of powders calcined at 700°C for 2 h are illustrated in figure 1. XRD data for the powders samples PLT14 (($Pb_{0,86}La_{0,14}Ti_{0,965}O_3$)) revealed the existence of single lead titanate phase of perovskite type, similar as the powders with Ce addition PLCT ($Pb_{0,86-x}Ce_xLa_{0,14}Ti_{0,965-x/4}O_3$), and no secondary phases are present. However, good crystallization in the pure perovskite structure was obtained for these compounds. The 101 and 110 peaks of PT pattern are separated clearly, while they merge in the case of the other samples to form one broadening peak. The structure transforms from tetragonal to pseudo cubic. Occurrence of the cubic phase has been reported for concentrations higher than 25% [9,10].

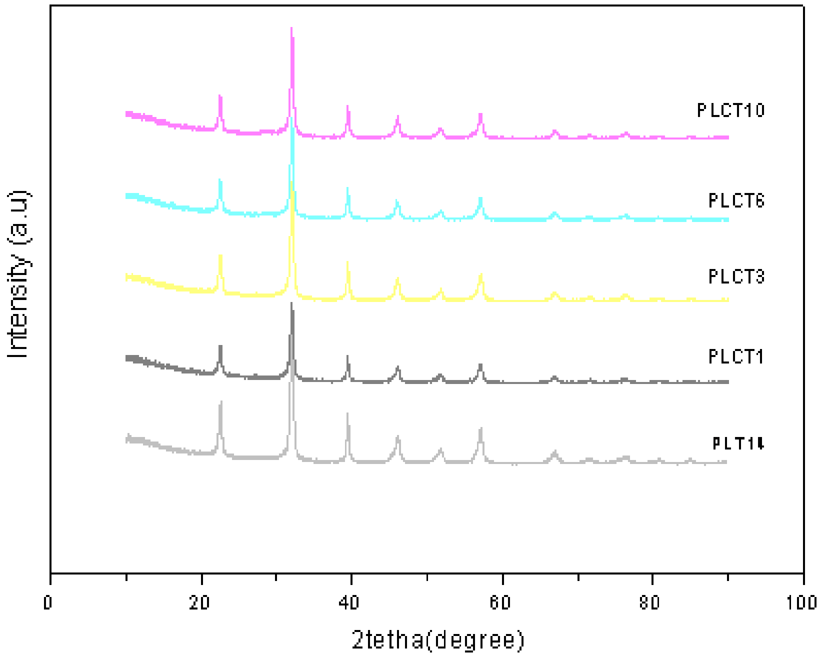

Figure 1: X-ray diffraction patterns of PLT14, PLCT1, PLCT3, PLCT6 and PLCT10 powders calcined at 700°C

The microstructure of the lead titanate based ceramics sintered at 1100°C is shown in figure 2. In the micrographs of the fracture surface of the PLT14, PLCT3, PLCT6 and PLCT10 platelike grains with the grain size of ~1µm are observed.
Another distint feature of the samples with Ce observed in the micrographs is that the fracture does not occurs through the large number of grains this characteristic is observed in several studies on ceramics doped with cerium [14,17]. The existence of transgranular fracture is probably due to preferable distribution of Ce in the boundary region [17].
Figure 3 shows the variation of dielectric constant and dielectric loss with temperature for selected compositions (PLCT3, PLCT6 and PLCT10). Increasing temperature resulted in a rapid increase in dielectric constant, attaining a peak at particular temperature (Tc) depending on Ce content. The minimum in the dielectric loss is coincident with maximum in the dielectric constant (figure 4). Therefore, it could be concluded that the ceramic samples undergo a structural phase transition at such temperature.
Addition of Ce^{3+} lead to an initial decrease in T_c from 292°C for undoped sample [6,8,11] to 230°C for 0.03mol% cerium doped one, and then increase to 254°C and slowly decrease to 251°C for 0.06 and 010 mol% cerium doped ones, respectively, as shown in figure 3. The two apparent stages in the Ce content dependence of Curie temperature for Ce doped PLT ceramics seemed to be in correlate to the substitution preferences.

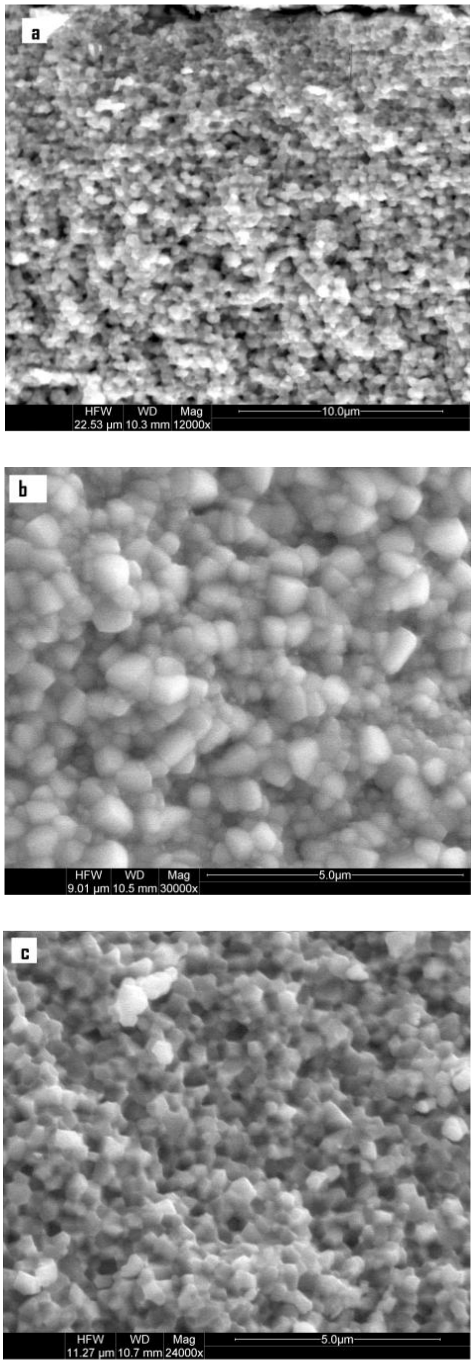

Figure 2: SEM micrographs obtained for the fracture surfaces of (a) PLCT3, (b) PLCT6 and (c) PLCT10 sintered at 1100°C/4 h

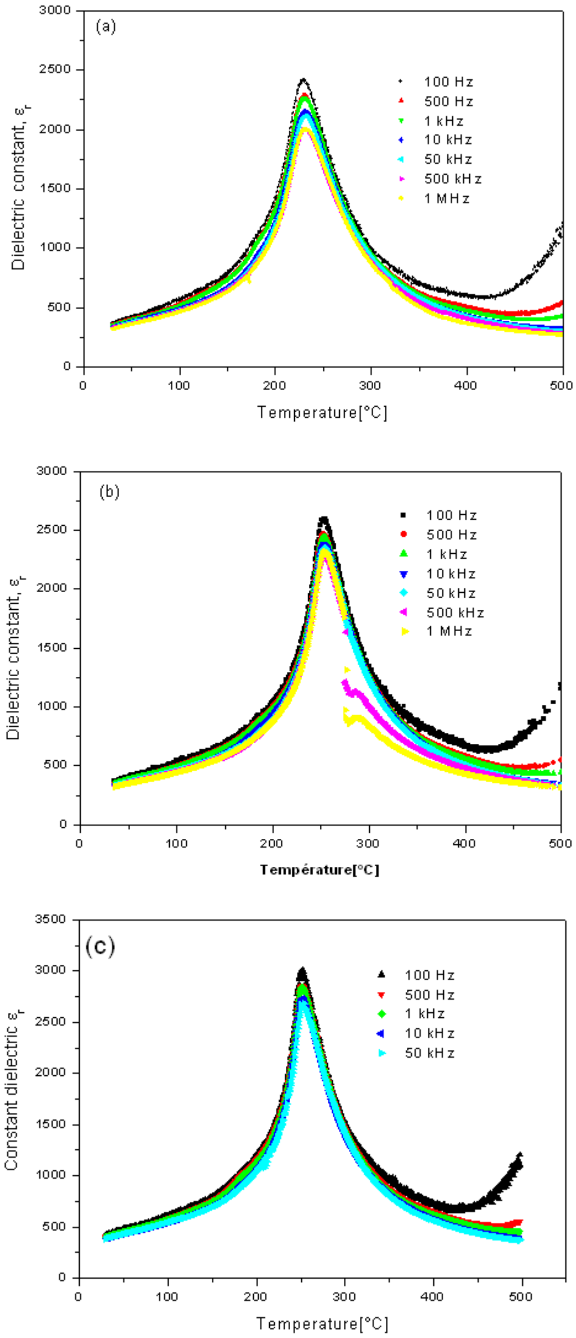

Figure 3: Dielectric constant of (a) PLCT3, (b) PLCT6 and PLCT10, as a function of temperature, for different frequencies.

In relaxor ferroelectric materials this law is valid only at temperatures much higher than temperatures of maximum relative dielectric constant Tm (typically by hundreds of degrees) [12]. Figure 5 shows the variation of reciprocal dielectric constant of the PLT3 and PLCT10 with temperature at 500 Hz. It was found that dielectric constant of lanthanum lead titanate with addition of Ce follows the Curie-Weiss law, which confirms that material shows normal ferroelectric phase transitions.

The changes in dielectric properties of Ce doped samples vs. doping level are shown in table 1. It can be noticed that ε tend to increase for all Ce concentrations from 2418 for PLCT3 to 2600 and 3006 for PLCT6 and PLCT10 ones, respectively. Loss factor generally also increased with increasing doing concentration.

The dielectric properties in perovskite ferroelectrics are also affected by their composition and crystal symmetry [13]. In particular, the dielectric properties of lead based perovskite doped with cerium is significantly enhanced by its oxidation states and substitution preferences [13]. The contiguity ε_{max} (in ε vs. Temperature curve) and its compliance from the Curie-Weiss law are the main characteristics of a normal ferroelectric phase transition. The broadness or diffusiveness in ε vs. temperature occurs mainly due to compositional fluctuation and structural disordering in the arrangement of cations in one or more crystallographic sites of the perovskite structure [12].

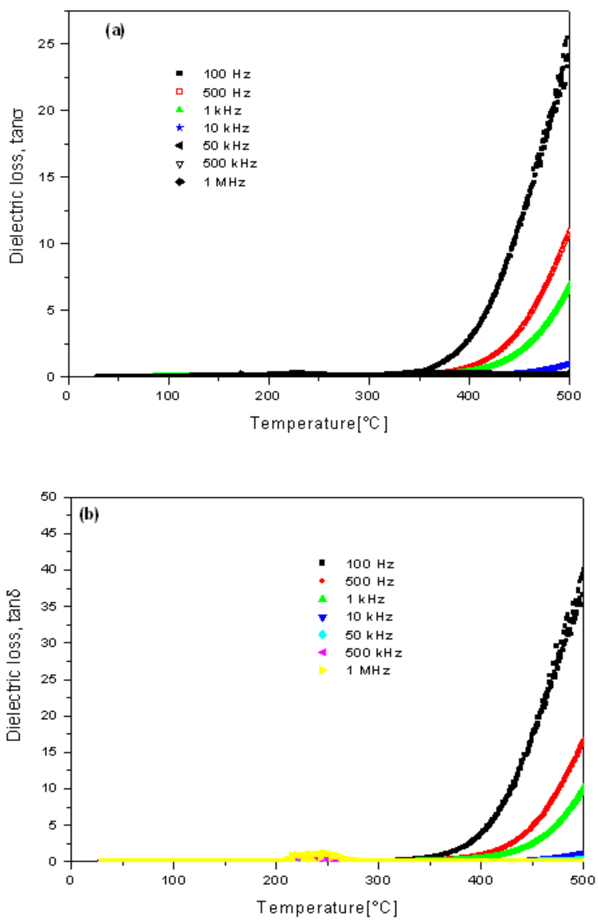

Figure 4: Dielectric loss tangent of (a) PLCT3 and (b) PLCT10, as a function of temperature, for seven frequencies.

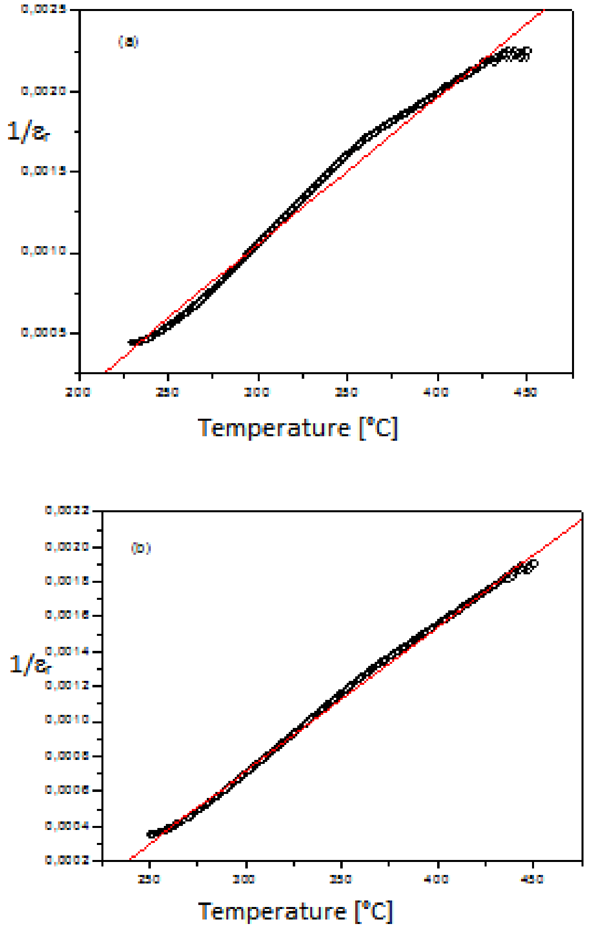

Figure 5: Inverse dielectric constant at 500 Hz as a function of temperature for: (a) PLCT3 and (b) PLCT10

Table 1: maximum dielectric constant and Curie temperature for PLCT3, PLCT6 and PLCT10 at 100 Hz.

x mol%	Tc (°C)	ε_{rmax}
3	230	2418
6	254	2600
10	251	3006

The decrease in T_c for PLCT3 and then increase for PLCT6, and next decrease for PLCT10 may be explained in terms of the appearance of second phase at grain boundaries which may act as pinning centers. The previous discussion was based on the supposition that Ce ions replace lead in A-sublattice as our studie. Stricltly speaking, distribution of Ce ions between A and B sites in the perovskite lattice is an object of controversy [13-20].

Among lanthanide metals Ce can change its oxidation states easily between +3 and +4 [13]. It can be expected that Ce ions preferably occupy Pb^{2+} site in the lead titanate ceramics due a similar ionic radii when the concentration of cerium addition is relatively low (x<0.06). Pb^{2+} (0.119 nm) ions are replaced by Ce^{3+} (0.101

nm) ions in this stage, which has a smaller ionic radii, and consequently, T_c decrease while the replacement of Pb^{2+} by Ce^{3+}. Thus, Ce^{3+} functions as a donor leading to some vacancies of A site in the lattice, which facilitates the movement of domain wall so as to improve the dielectric properties significantly. In contrast with Ce^{3+}, Ce^{4+} has smaller radius and occupies the Ti^{4+} site when the concentration of cerium addition relatively low (x > 0.06).

Conclusion

Cerium doped lanthanum lead titanate (PLCT) ceramics, $Pb_{0.86-x}La_{0.14}Ce_xTi_{0.965-x/4}O_3$ (x = 0-10 mol%) were obtained by a sol-gel method. The pure perovskite structure with the pseudo-cubic phase was obtained at calcining temperature. We speculate that the Curie temperature of our specimens is mainly controlled by doping level and the site occupancy of Ce-ions being changed from A to B sites with decreasing ionic radiis of doping ion. And that the effect of grain size, in the range of grain sizes obtained, can be neglected.

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