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Dielectric Properties of Hydrothermally Processed $Pb_{1-x}La_xTi_{1-x/4}O_3$ Ceramics

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In this work, ceramic compositions of a complex perovskite $Pb_{1-x}La_xTi_{1-x/4}O_3$ (PLTx) were prepared by hydrothermal process and their structure was characterized by X-ray diffraction. The morphology of the grains was investigated using a scanning electronic microscopy. In this work, we have chosen La^{3+} as a doping ion to improve dielectric properties of these ceramics. Dielectric measurements were performed using an impedance analyzer (LCR, HP 4284 A) in the frequency range from 100 Hz to 2 MHz.

Keywords: Ferroelectric, PLT, Dielectric permittivity.

INTRODUCTION

The perovskite-type compound $PbTiO_3$ exhibits ferroelectric ordering at a temperature near 490 °C. In the past, much effort has been made to prepare pure $PbTiO_3$ ceramics and corresponding ceramics with small grain size have been reported. Takeuchi *et al.* [1] have prepared pure $PbTiO_3$ ceramics with sub micrometer grains by spark plasma sintering. Crystalline $PbTiO_3$ (PT) has a tetragonal ABO_3-type structure. Studies of the optical characteristics of $PbTiO_3$ indicate that the emission of photons is related to $Ti^{3+} \rightarrow O^{2-}$ charge transfer in the [BO6–δ] octahedral [2].

Lead lanthanum titanate $(Pb_{1-x}La_x)TiO_3$ (PLT) is an important ferroelectric ceramic material that attracts much research interest currently [3-5]. $(Pb_{1-x}La_x)TiO_3$ is a very useful ferroelectric material that can be used for infrared micro-sensors, ferroelectric memories, electro-optical devices and piezoelectric micro-sensors (for biological applications) [6-11]. The structural development and control, ferroelectric behaviour, pyroelectric performance and piezoelectric properties of PLT have been studied.

Additions of lanthanum to $PbTiO_3$ improve the mechanical and ferroelectric characteristics of the material. Sei *et al.* [12] studied the refractive index of PLT prepared by sol-gel route and found that it increased with increasing crystal size of the PLT. This work is devoted to the study of dielectric properties of hydrothermally processed PLT ceramics.

EXPERIMENTAL

The synthesis of various compounds of lead titanate, doped with lanthanum PLT(x) corresponding to substitutions the Pb^{2+} by La^{3+} was performed by hydrothermally method.

Powders are prepared from the mixture of lead oxide (PbO), titanium dioxide (TiO_2) and lanthanum oxide (La_2O_3), taken in stoichiometric amounts according to the chemical reaction (1) and following the method for preparation (Fig. 1) [13].

$$(1-x)\ PbO + x/2\ La_2O_3 + (1-x/4)\ TiO_2 \rightarrow Pb_{1-x}La_xTi_{1-x/4}O_3 \quad (1)$$

RESULTS AND DISCUSSION

Analysis of the formed phases: Fig. 2 gives the XRD patterns of the as-prepared PLTx samples, for various lanthanum concentrations (0, 5, 7, 10, 12, 15 and 20 %), first heated at 180 °C during 24 h and then heat treated at 400 °C for 4 h.

It is observed that the splitting of the peaks observed in the pure $PbTiO_3$ disappears when lanthanum concentration is greater than or equal to 5 % [14,15].

Fig. 3 shows the variation of the tetragonality, c/a, as a function of concentration x, in La. It is observed that this parameter decreases abruptly until x near 5 % and then decreases slowly without reaching the value 1, preserving hence a pseudo cubic structure (Table-1); insertion of La reduces tetragonality leading to a phase transformation from quadratic to pseudo cubic structure [16-19].

TABLE-1
PARAMETERS: a AND TETRAGONALITY FOR PLTx PREPARED BY HYDROTHERMAL PROCESS

La	0	5 %	7 %	10 %	12 %	15 %	20 %
a (Å)	3.9021	3.9204	3.9243	3.9258	3.9263	3.9267	3.9271
c (Å)	4.1521	3.9449	3.9440	3.9354	3.9313	3.9285	3.9279
c/a (tetragonality)	1.0641	1.0062	1.0050	1.0024	1.0012	1.0004	1.0002

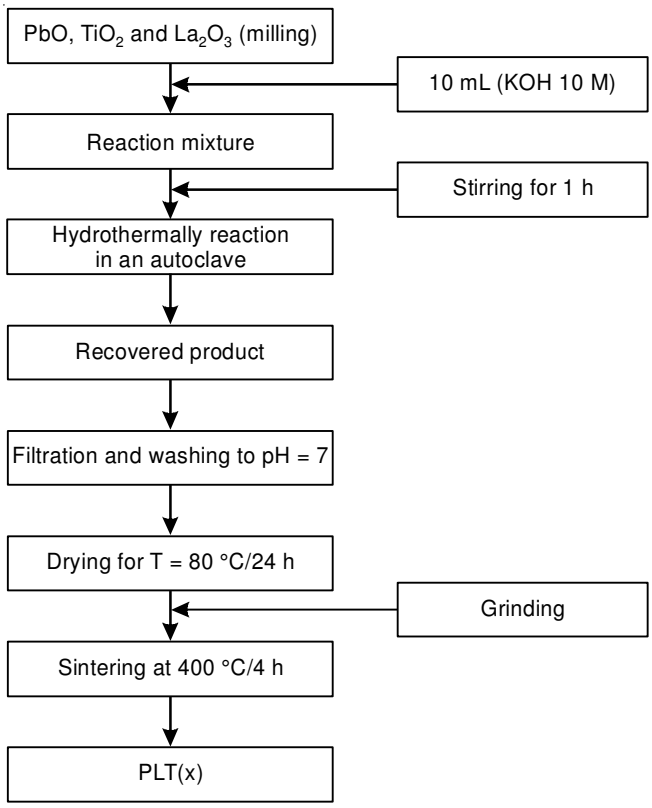

Fig. 1. Synthesis PLT(x) phase by hydrothermally process

Hennings and Rosenstein [20,21] showed that there is a charge compensation, which may be achieved by the filling of Pb vacant sites (Pb-site) or Ti vacant sites (Ti-site) resulting in an octahedron deformation field Ti-O.

Microstructure analysis: Fig. 4 shows the microstructure of the PLTx compounds (x).

The average grain size for the sample PLT(7) varies from approximately 1.09 to 1.2 μm and from approximately 1.53 and 1.72 μm from the samples PLT(12) and PLT(15) respectively (Fig. 5). The behaviour is according with the XRD patterns.

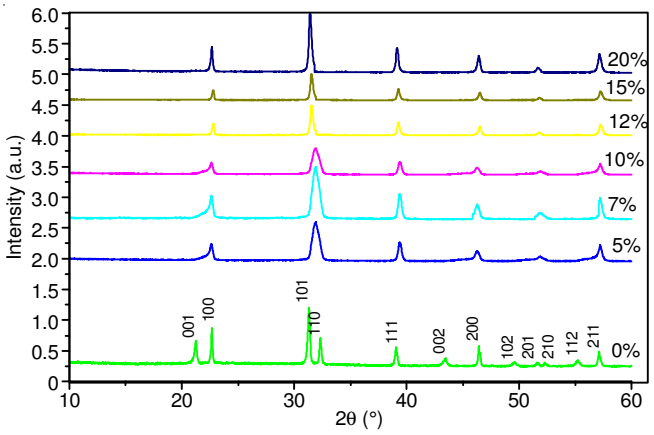

Fig. 2. XRD patterns of the PLTx phases, with various lanthanum concentrations [0, 5, 7, 10, 12, 15 and 20 %] synthesized at 180 °C/24 h and treated at T = 400 °C for 4 h.

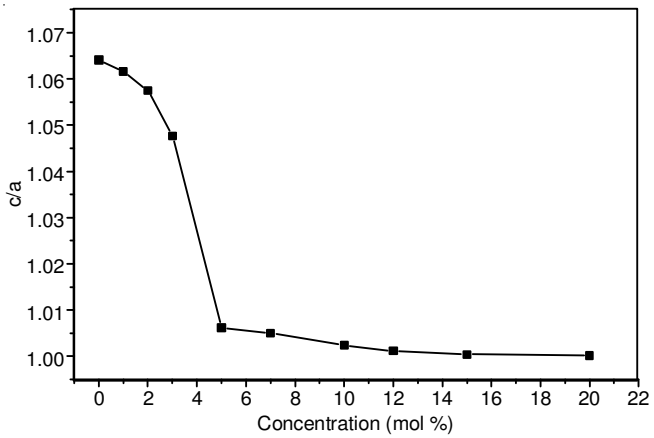

Fig. 3. Evolution of tetragonality (c/a) with various lanthanum concentrations

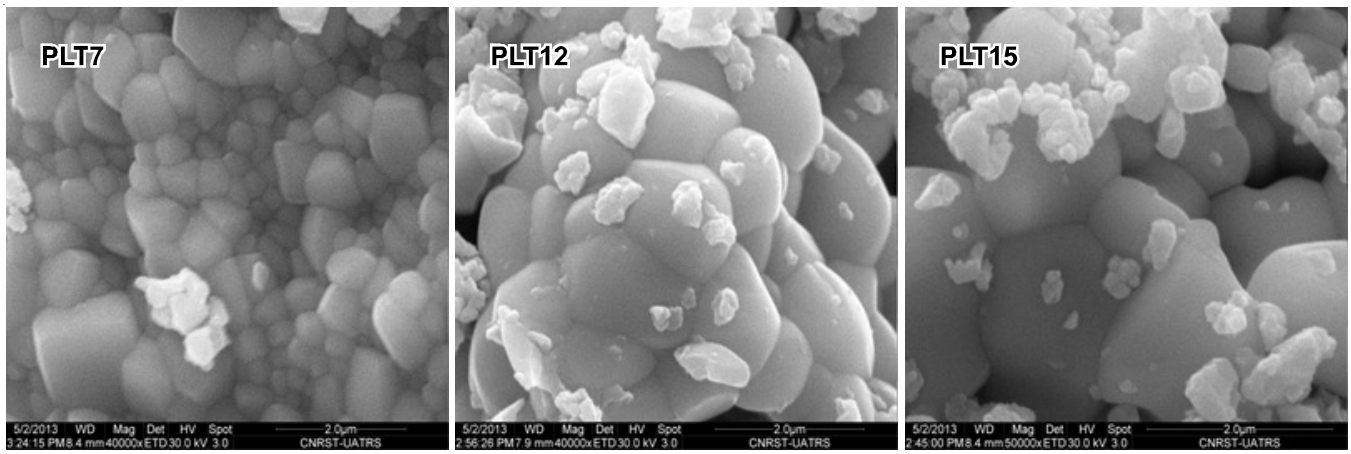

Fig. 4. Microstructure of PLT7, PLT12 and PLT25, synthesized by the hydrothermal process

The grain size increases linearly with increasing La content, as shown in Fig. 5.

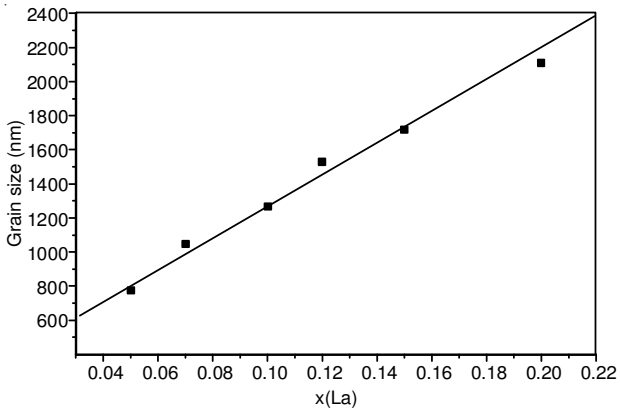

Fig. 5. Variation of the grain size of PLT(x) as a function of La content

Dielectric properties: Thermal behaviour of the dielectric permittivity (ε_r), for frequencies ranging from 1 kHz to 500 kHz is shown on Fig. 6.

It is found that when the temperature increases, the dielectric permittivity (ε_r) increases with lanthanum doping and that the temperature of the maximum of ε_r shifts toward lower values (Table-2).

TABLE-2
VARIATIONS OF DIELECTRIC PERMITTIVITY (ε_r) AND OF TEMPERATURE OF ITS MAXIMUM, T_m, AS FUNCTIONS OF La CONCENTRATION FOR FREQUENCY OF 1 KHz

x % (La^{3+})	T_c (°C)	ε_r
5	413	3437.508
7	353	4082.302
10	316	4809.011
12	272	5527.748
15	231	6175.719
20	168	6453.924

Electrical conductivity: Table-3 summarizes the conductivity (σ), of the PLTx samples, recorded in the para-electric phase at the frequency of 1 KHz, as determined from measurements of dielectric losses and the real part of the dielectric permittivity, according to the following relation: $\sigma = \varepsilon_r\varepsilon_0\omega tg\delta$.

TABLE-3
CONDUCTIVITY FOR PLT(x) AT T_m AND FREQUENCY 1 KHz

x (%) of lanthanum	Conductivity T_m ($s\ m^{-1}$)
5	1.9120×10^{-4}
7	1.1960×10^{-4}
10	1.0980×10^{-4}
12	2.7670×10^{-5}
15	1.4460×10^{-5}
20	1.3105×10^{-5}

For all concentrations of PLTx, the conductivity values are low and are consistent with those found in the literature, which is a sign of good densification of grains [22].

Activation energy: Activation energies of the electric conduction were evaluated using the Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E_a/k_BT)$$

σ stands for conductivity. σ_0 is the pre-exponential factors, k_B is the Boltzmann factor, T is the absolute temperature and E_a the activation energy which was calculated from the slope of the plot of ln σ as a function of 1/T (Fig. 7).

The activation energy increases with increase of La concentration, then shows a slight decrease for x = 20 % lanthanum. This increase may be due to the increased rate gaps (Table-4).

Diffuse phase transition: Fig. 8 shows the fitting simulation of ε_r by the modified Uchino' law, depending on the temperature of the different compounds PLTx at a frequency of 1 KHz.

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m}\left(1 + \frac{(T - T_m)^{\gamma}}{2\delta^2}\right) \text{ [Ref. 23]}$$

γ and δ are the relaxor and diffuse parameters respectively.

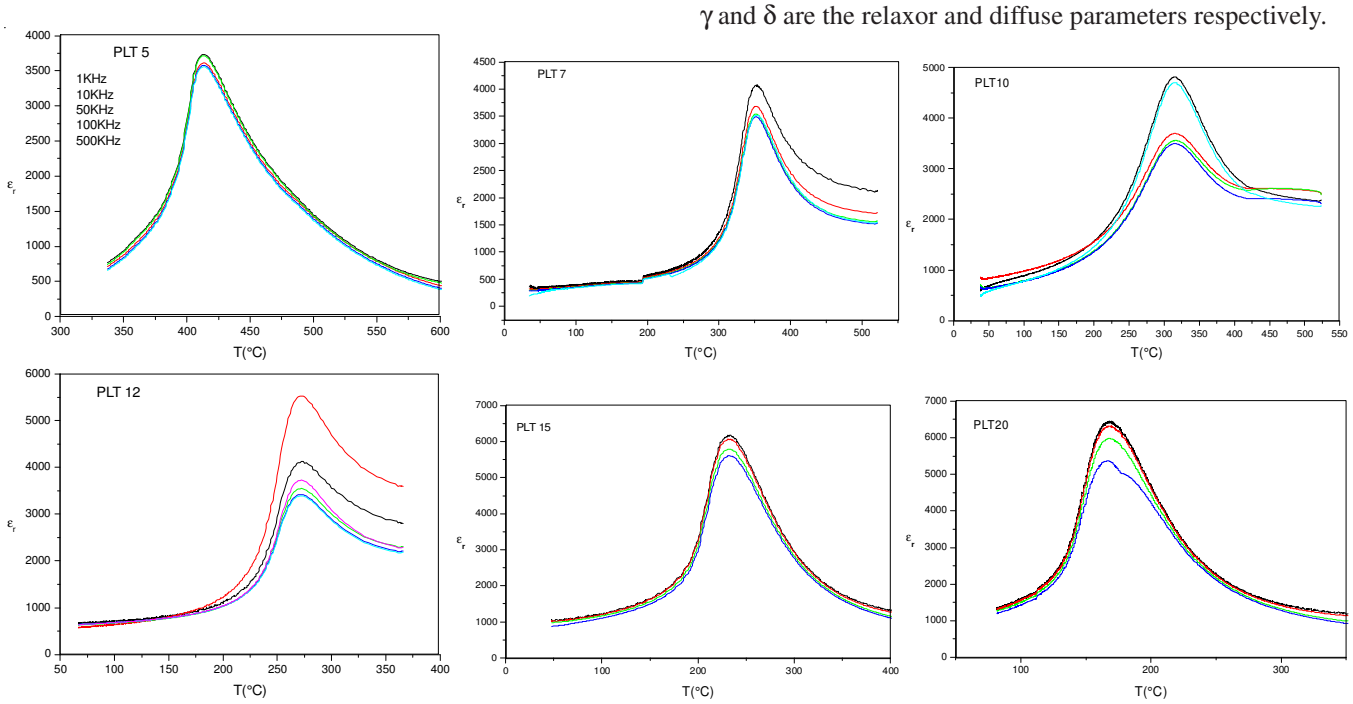

Fig. 6. Thermal variations of the relative permittivity, ε_r of PLT(x) (x = 5, 7, 10, 12, 15 and 20 %) heat treated at 900 °C/4 h

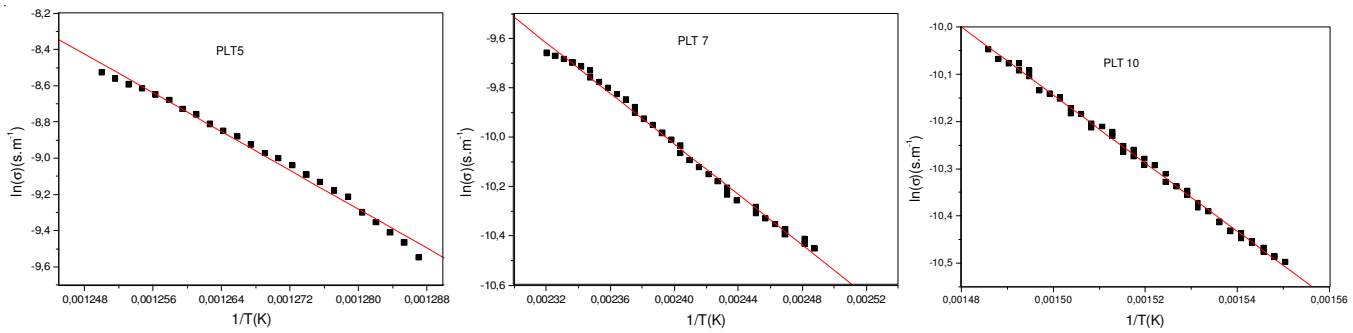

Fig. 7. Plot of ln σ as function of ln [1/T(1/k)]

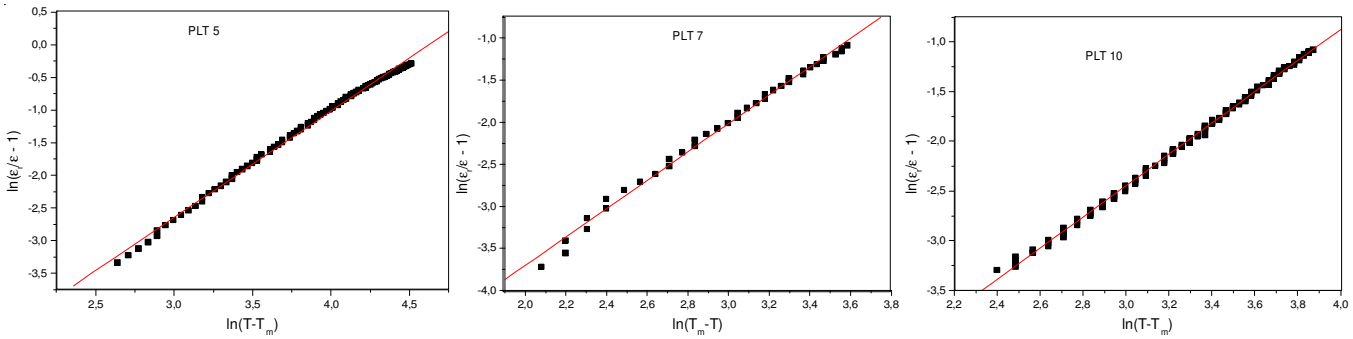

Fig. 8. Plot of $\ln\left(\frac{\varepsilon_m}{\varepsilon}-1\right)$ as a function of ln $(T-T_m)$

TABLE-4
E_a VALUES FOR SAMPLES AT 1 KHz

Concentration (%) of lanthanum in PLTx	E_a (eV)
5	0.152
7	0.221
10	0.622
12	1.394
15	1.544
20	1.470

δ and γ values obtained are given in Table-5. The values show that these constants increase with lanthanum concentration and the transition shows a diffuse character $(1 < \gamma < 2)$.

TABLE-5
PARAMETER VALUES (δ, γ) FOR PLTx
FOR A FREQUENCY 1 KHz

Lanthanum (%)	γ	δ
5	1.572	37.52
7	1.680	37.53
10	1.660	44.03
12	1.690	44.08
15	1.750	61.18
20	1.840	69.35

Conclusion

Doping hydrothermally processed $PbTiO_3$ samples with La showed that the perovskite phase is obtained from a concentration of 5 %, as identified by XRD analysis. Dielectric measurements showed a diffuse character of the ferro-to-paraelectric transition together with a relaxation behaviour, which may be seen as a direct result of local structural fluctuations of the composition and the non-uniform distortion is random positions occupied by the lanthanum in the crystal structure. The increase and decrease of the permittivity, ε_r and transition temperature depend on lanthanum concentration.

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