

Optical and electro-optical characteristics of hot-pressing (Pb_{1-x}La_x)TiO₃ ferroelectric ceramics

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La-modified PbTiO₃-based ceramics (PLT) are the subject of many studies in term of piezoelectric and pyroelectric applications, but the processing of PLT to optimize their transparency and electro-optical properties has not been studied in detail. Ferroelectric (Pb_{1-x}La_x)TiO₃ (PLT) ceramics, with 0.18 ≤ x ≤ 0.23, were produced by a solid state reaction and uniaxially hot pressing for 3h at a temperature of 1220° C, and a pressure of ~6,0 MPa. High density, translucent reddish color and high dc conductivity were observed for all compositions. Nevertheless appropriate thermal treatments in an O₂ atmosphere, after hot pressing, led to ceramics with good properties for dielectric, optical and electro-optical studies. The heat-treated samples revealed a homogeneous microstructure, absence of second phases, increased of the transmittance in the visible and infrared range and reduced dc conductivity. These features allowed the electro-optical coefficient of the (Pb,La)TiO₃ system to be calculated.

Keywords: Ferroelectric ceramics, electro-optics, hot-pressing, transparency.

Características ópticas y electro ópticas de cerámicas ferroelétricas del sistema (Pb_{1-x}La_x)TiO₃ obtenidas por prensado en caliente

Las cerámicas basadas en PbTiO₃ con adición de La, (PLT) han sido ampliamente estudiadas debido a sus aplicaciones piro y piezoeléctricas. Por otra parte, el procesamiento de PLT para optimizar su transparencia y sus propiedades electro-ópticas no ha sido estudiado con el mismo detalle. En el presente trabajo, se han preparado cerámicas ferroelétricas de (Pb_{1-x}La_x)TiO₃ (PLT) con 0.18 ≤ x ≤ 0.23, mediante síntesis en estado sólido y prensado uniaxial en caliente por 3 h a una temperatura de 1220° C, y una presión de ~6,0 MPa. En todas las composiciones se han observado una alta densidad, baja transparencia y conducción eléctrica elevada. Mediante adecuados tratamientos posteriores en atmósfera de O₂ se ha mejorado la calidad eléctrica y óptica de dichas cerámicas. La microestructura es homogénea, la transmitancia en las regiones visible e infrarroja crece y la conductividad DC disminuye. Estas características han permitido medir el coeficiente electro-óptico en muestras del sistema (Pb,La)TiO₃.

Keywords: Cerámicas ferroelétricas, efecto electro óptico, Prensado a caliente, transparencia.

1. INTRODUCTION

Since their discovery in 1940, lead titanate ferroelectric ceramics have been exploited in many applications, such as capacitors, sensors, piezoelectric transducers, electro-optic devices and thermistors (1-4). In general, ferroelectric ceramics are opaque, though at certain compositions. They can be suitably prepared to exhibit optical translucency or even transparency. Such materials are called transparent ferroelectric ceramics (TFC). The TFC perovskites were discovered in the late 1960s as a result of a study to find optimal processing and doping parameters for the lead zirconate titanate (PZT) system (5). In fact, the best known and commercialized TFCs are those from the lanthanum modified lead zirconate titanate (PLZT) solid solution system (6,7). This material can display excellent electro-optical properties, suitable for optical waveguides, infrared sensors, dynamic random access memories and non-volatile memories. The optical and electro-optical properties of the PLZT transparent ferroelectric ceramics have been investigated for many

decades, excepting those with compositions the Zr- and Ti-rich ends of the phase diagram, possibly due to the processing and reproducibility problems presented by them. In particular, lanthanum-doped lead titanate (PLT) ferroelectric ceramics have emerged as highly promising materials for piezomechanical and pyroelectric applications, owing to their high electro-mechanical anisotropy factor and large pyroelectric coefficient along the polarization axis, respectively (8,9). However, only Yamamoto et al. have investigated the entire tetragonal range of La-modified PT ceramics as a TFC system (10). Optical transmittance of 61 %, at wavelengths above 600 nm, was observed for the composition with tetragonality factor (c/a) of 1.010, in the case of a 300 μm-thick hot-pressing ceramic. However, to the best of our knowledge, their electro-optical properties have not been investigated until now.

Hence, in this study, the effects of the lanthanum content and of the annealing treatments in an atmosphere of oxygen on the dielectric, optical, and electro-optical properties properties

of the $(\text{Pb}_{1-x}\text{La}_x)\text{TiO}_3$ system, ($0.18 \leq x \leq 0.23$) were investigated in ceramic bodies prepared by uniaxial hot-pressing. High optical transmittance and a PLZT compatible Pockels electro-optical coefficient were found for the ceramics with 21 mol% of La (PLT21).

2. EXPERIMENTAL PROCEDURE

The raw materials PbO purity (99.3%), TiO_2 (99.9+%), and La_2O_3 (99.9%), were weighed according to the formula $(\text{Pb}_{1-x}\text{La}_x)\text{TiO}_3$, with $0.18 \leq x \leq 0.23$. Assuming mainly A-site vacancies, due to the replacement of Pb^{+2} with La^{+3} , this batch formula provides $x/2$ excess of PbO. However, it has been reported that vacancies might also be formed at the B-sites (11,12).

The primary oxides were ball-milled in distilled water, with zirconia as the grinding medium, for 3h. The resulting slurries were then dried at 120°C and later calcined at 850°C for 3 h in air. The calcined powders were ball-milled in distilled water for 3h and dried again. Binder was added to the powders, which were uniaxially cold-pressed into disks (10 mm in diameter and 10 mm thick), labeled according to nominal composition, from PLT18 ($x=0.18$) to PLT23 ($x=0.23$). Subsequently, isostatic pressure was applied to reduce the density gradients. After burning out the binder, the disks were hot-pressing at 1220°C , for 3h, under a uniaxial pressure of ~ 6.0 MPa, in O_2 atmosphere (30kPa). A program of heat treatments in O_2 was then performed, to obtain a material with appropriate characteristics for optical and electro-optical studies (Figure. 1). The test pieces were characterized after 5h(TT1), 10h(TT2) and 20h(TT3) of heating at 1220°C

Apparent densities were determined by the Archimedes method. The microstructure of the ceramics was observed with a scanning electron microscope (JEOL, JSM-5800 LV). The grain sizes were calculated from the SEM images of the polished thermally etched surfaces by the linear-intercept method. After polishing with $3\ \mu\text{m}$ diamond paste, the ceramics were thermally etched in air at 1100°C , for 1 min. in a sealed alumina crucible. The purity of the phases and the structural parameters were determined by X-ray diffraction (XRD) using a Rigaku diffractometer, with $\text{CuK}\alpha$ radiation. The lattice parameters were calculated by least-square fitting from the positions of the diffraction peaks. The ideal density was calculated from the unit cell volume found by XRD analysis and the molecular weight from the formula $(\text{Pb}_{1-3x/2}\text{La}_x)\text{TiO}_3$. For dielectric measurement, gold electrodes were deposited on both faces of the disk samples (5 mm diameter and ~ 1.0 mm thick). The relative permittivity was measured by impedance analysis (HP4194A). The transmittance was measured in a spectrophotometer (Micronal-B582), at wavelengths ranging from 200 to 1000 nm for optically polished samples, $600\ \mu\text{m}$ thick. The transversal electro-optical effect was observed in a system composed of two crossed polarizers, a high voltage source, a laser (633nm/20mW-JDS-UNIPHASE MODEL 1135) and an optical sensor (MELLES GRIOT). A high dc electric field, E , was applied, transversely to the laser beam changing the optical retardation, ($\delta(E)$), given by:

$$\delta(E) = 2\pi \frac{1}{\lambda} \Delta n(E) \quad (1)$$

that is a function of birefringence (Δn) and the optical path length (l) (7).

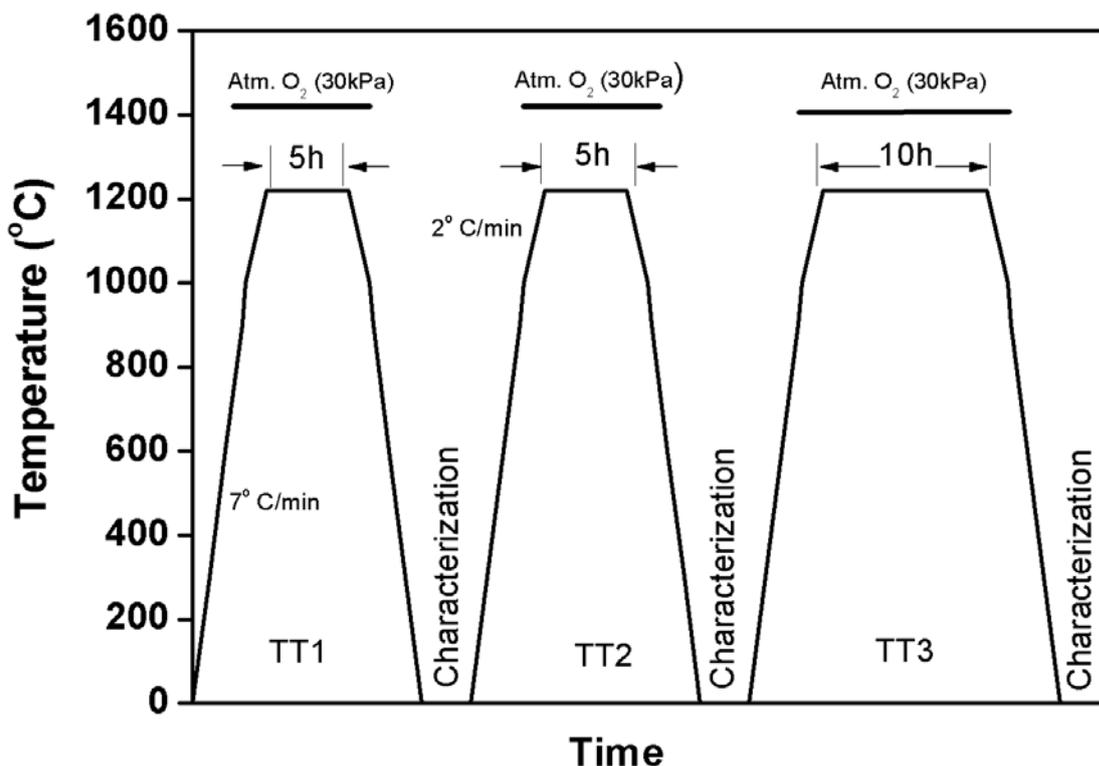


Figure 1. Temperature-time profile in program of heat treatments in atmosphere of oxygen (30 kPa pressure) applied to the PLT ceramic bodies.

TABLE I. COMPARISON OF THE THEORETICAL DENSITY WITH THAT MEASURED BY THE ARCHIMEDES METHOD FOR 0.18 ≤ x ≤ 0.23 IN THE CERAMIC Pb_{1-x}La_xTiO₃.

La Content x=	0.18	0.19	0.20	0.21	0.22	0.23
Theoretical (g/cm ³)	7.38	7.40	7.38	7.42	7.44	7.38
Archimedes (g/cm ³)	7.35	7.33	7.27	7.26	7.21	7.17
Relative (%)	99,6	99,1	98,5	97,8	97,0	97,2

The relative light intensity, I_{rel} , which reaches the optical sensor is them:

$$I_{rel} = \sin^2\left(\frac{\delta}{2}\right) \sin^2\left(\frac{\pi}{\lambda} \Delta n(E)\right) = \sin^2\left(\frac{\pi}{\lambda} (PE + KE^2)\right) \quad (2)$$

where K is the quadratic electro-optical coefficient and P , the linear coefficient.

3. RESULTS AND DISCUSSIONS

3.1 Physical Properties

Bulk density trend to increase with increasing La³⁺ content (Table I) as can be seen in the table I. As also, high relative densities values were found for (Pb_{1-x}La_x)TiO₃ ceramics (greater than 97% of the theoretical crystal density for uniaxially pressed ceramics). This fact is corroborated by the pore-free microstructure, with average grain size in the range 6-12 μm, observed for SEM in all samples, as shown in Figure 2 for the composition x=0.21.

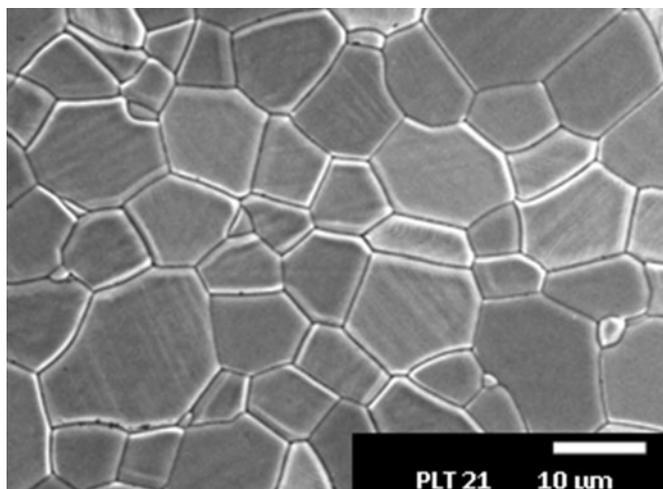


Figure 2. SEM micrographs of the polished and thermally etched surfaces of hot pressed and (Pb_{1-x}La_x)TiO₃ ceramics (x=0.21) after thermal treatment (1220 °C, 5h+5h+10h, O₂ atmosphere).

The relation between the average grain size and the lanthanum concentration, after three heat treatments applied to uniaxially hot-pressing PLT, is presented in Figure 3. In this illustration, a linear increase is observed in the grain size with increasing lanthanum content, for all heat treatments. If the results for the grain size are analyzed in relation to the thermal treatment, it is seen that longer time of heat treatment is needed for an effective change in grain size to occur.

X-ray diffraction patterns of the La-modified PbTiO₃ ceramics indicated the single tetragonal phase for all compositions, as shown in Figure 4.

3.2 Dielectric Properties

The temperature profile of real relative permittivity, of each test piece (for compositions with x=0.18 to 0.23), measured after treatment TT3, is shown in Figure 5. The peaks in the real relative permittivity ϵ' are diffuse, and they increase in height and shift to lower temperature as the La³⁺ content is increased. Real relative permittivity maxima, which occur at the temperature increase with increasing of La content (exception PLT23). In Figure 5, imaginary relative

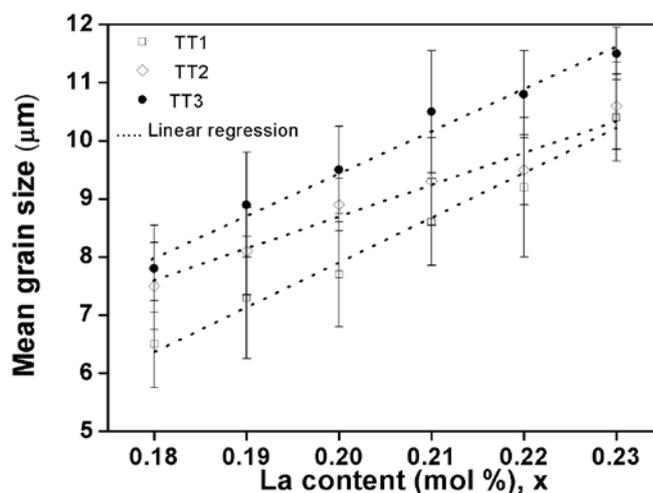


Figure 3. Mean grain size plotted against lanthanum content for the sequence of heat treatments (TT1, TT2 and TT3). The dotted lines are fitted by linear regression to the experimental points.

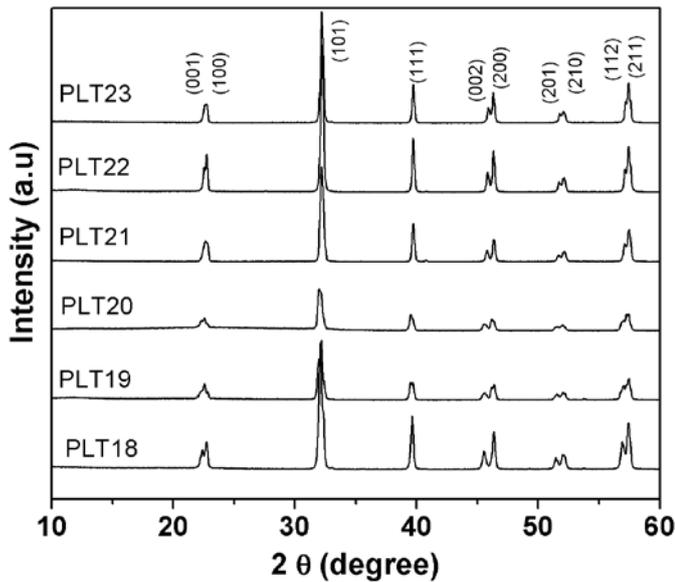


Figure 4. X-ray diffractograms of PLT ceramics with various La contents taken after hot-pressing.

permittivity, ϵ'' , is also plotted against temperature for all compositions. In general, ϵ'' for all La⁺³ contents were low at room temperature, increasing at high temperatures. At high temperatures the ceramics show high conductivity. In figure 5 also is possible to observe that the T_m is shifted to lower temperatures when the amount of

lanthanum is increased from PLT18 to PLT23 which is related to the decrease in tetragonality with the amount of lanthanum, as reported by Pinto et al (13).

The PLT is considered as an ideal model system for research on the nature of relaxor ferroelectricity and the spontaneous relaxor to normal ferroelectric transition discovered in several Pb-based perovskites (14,15,16). This is because a change

in the ferroelectric behavior from normal to relaxor can be induced by the addition of La⁺³ above a certain critical concentration (17).

The temperatures at which the maximum relative permittivity occurs are plotted in Figure 6 against the $\frac{c}{a}$. As can be seen, rises linearly with increasing the $\frac{c}{a}$.

A general characteristic of all the compositions of PLT studied here is the decrease of the conductivity with the sequence of thermal treatments, suggesting possible excess of PbO in the grain boundaries that would be eliminated during the thermal treatments (18). It is generally believed that trivalent La⁺³ ions replace for Pb⁺² ions, requiring a charge compensation process in the PT-based perovskite lattice. According to an early study by Hennings, (19,20) this charge compensation can be accomplished by the formation of either an -site vacancy (Pb site) or of a -site vacancy (Ti site). -site vacancy can give rise to a Ti-O octahedral strain field, whereas -site vacancies break Ti-O octahedral symmetry. The control of these defect processes should be considered an important step in the improvement of the electrical properties of Pb-based perovskite ferroelectrics. Pb-based perovskites is the PbO evaporation that occurs during the sintering stage. Since the evaporation of PbO produces -site vacancies, the control over these two distinct defect processes and the suppression of PbO evaporation are closely interrelated.

3.3 Optical and electro-optical properties

The optical transmittances of all optically polished and unpolarized samples of PLT are shown in Figure 7, in the wavelength range of 200 to 1000 nm and they became completely absorbing around 400 nm, indicating an optical absorption edge in near UV. This is similar to what absorbed for most oxygen-octahedral perovskites (21). All the samples show an increase in the transmittance with increasing wavelength. As can be seen, PLT21 possesses a higher transmittance than all the other test pieces.

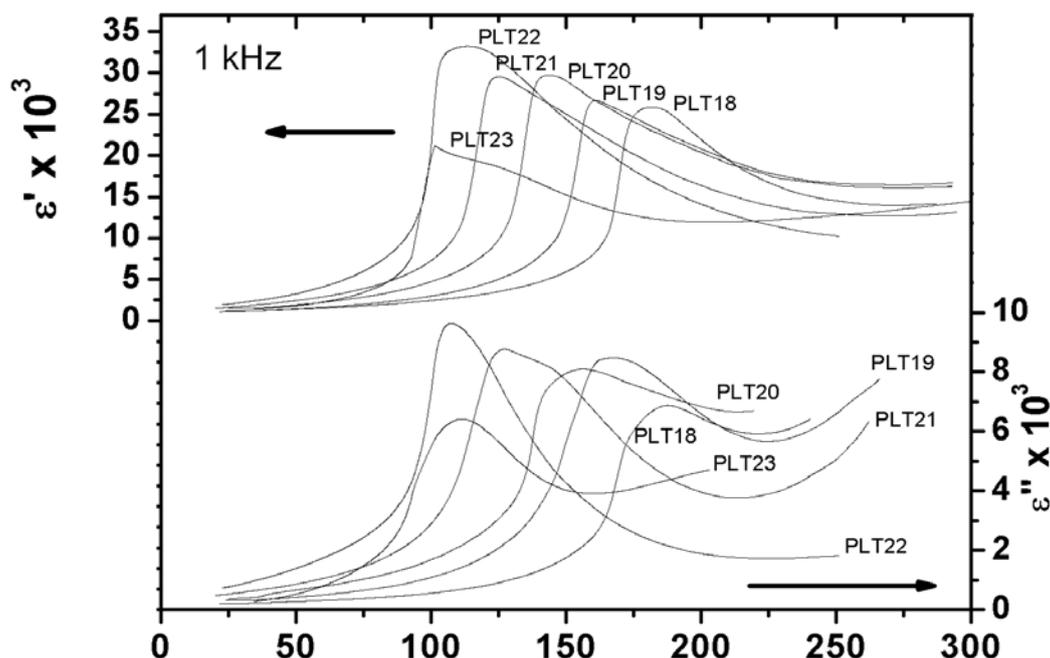


Figure 5. Temperature dependence of real (ϵ'), and imaginary (ϵ'') relative electrical permittivity at 1 kHz, for 6 PLT test pieces after heat treatment TT3.

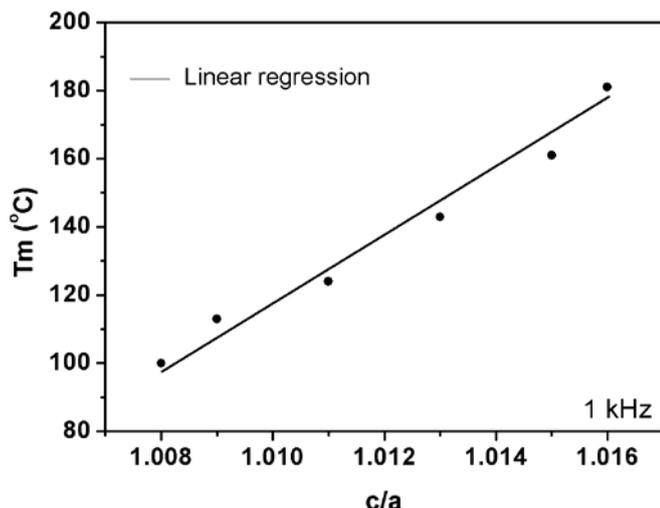


Figure 6. Plot of temperature at which relative electrical permittivity of PLT ceramics (after TT3) at 1 kHz is highest T_m , against tetragonality (c/a). The straight line is the linear regression of the experimental points.

A common characteristic of all the compositions is that the critical wavelength above which light transmission is observed is of the order of 400 nm, indicating a band gap of approximately 3.1 eV. This value is comparable to that expected for other TCF (around 3.3 eV). (22).

In Figure 7 high transmittance values can be seen for ceramics PLT20 and PLT21, which may be explained by the low scattering effects of domains and segregated phases, while samples with a low concentration of La show smaller transmittance, possibly due to the scattering effects of domains. The very low transmittance of sample PLT23 may be explained by the segregation phases, since the ferroelectric character of this specimen is too low to attribute scattering to domains (23).

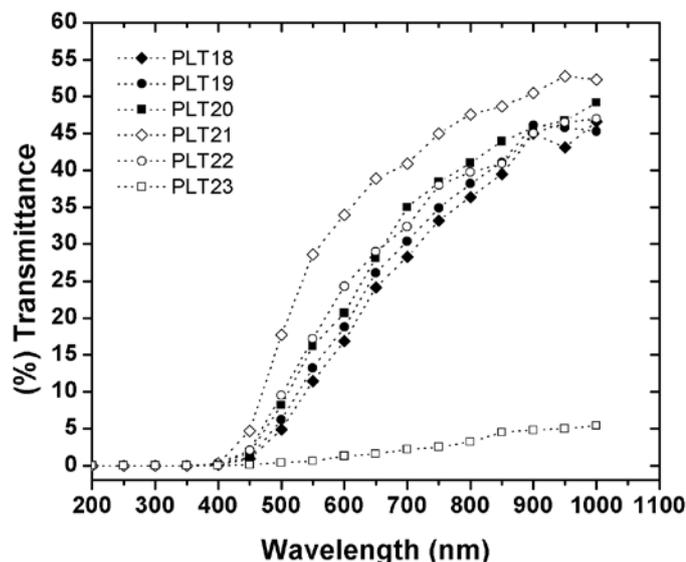


Figure 7. Variation of transmittance with wavelength for the various test-pieces of PLT, with heat treatments, (TT3). Thickness 600 μm .

It was observed that the transmittance of all the ceramic samples (except PLT23) increased with the thermal treatments (data not show), indicating that the excess of PbO was eliminated.

The values of the Pockels coefficients for the ceramics that showed high transmittance were measured: for PLT20, 0.6×10^{-10} m/V, and PLT21, 0.9×10^{-10} m/V. These values are lower than the electro-optical coefficients of PLZT 12/40/60 (1.2×10^{-10} m/V), but similar to those for fine films of PLT (0.5×10^{-10} m/V) (23).

The quadratic electro-optical Kerr coefficients for these ceramics were also calculated: PLT20= 0.10×10^{-16} m^2/V^2 and PLT21= 0.17×10^{-16} m^2/V^2 . These values are lower than those shown by PLZT 9.5/65/35 ($3.8 \times 10^{-16} \text{m}^2/\text{V}^2$) (7).

4. CONCLUSION

Analysis of X-ray diffraction patterns revealed that in all the ceramic test pieces obtained by uniaxial hot-pressing, the only obtained phase was perovskite, the incorporation of the lanthanum into the PT structure being proved by the reduction of the tetragonal factor.

The ceramics $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$ (PLT) were studied, for the compositions $0.18 \leq x \leq 0.23$. The microstructural results showed an increase in grain size with increasing lanthanum content.

The transmittance of the PLT ceramics was strongly dependent on subsequent thermal treatments in an atmosphere of oxygen, owing to the elimination of the PbO phase from the grain boundaries, not detected by the technique of XRD.

This work is the first determination of electro-optical coefficients of the ceramics $(\text{Pb}_{1-x}\text{La}_x)\text{TiO}_3$ with $x=0.18$ and $x=0.23$.

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