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Hot-Pressed Transparent PLZT Ceramics from Low Cost Chemical Processing

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Lanthanum-modified lead zirconate titanate (PLZT) ceramics were obtained with high transmittance in the visible range by a combination of an inexpensive chemical processing and hot pressing. Optical, microstructural, pyroelectric, ferroelectric and dielectric properties characterized in this study attested the applicability of the employed method in the production of PLZT transparent ferroelectric ceramics. In fact, the corresponding analyzed physical parameters are in very good agreement with those obtained in samples traditionally prepared by other methods. Furthermore, due to high sample quality, a phenomenological analysis of the PLZT 10/65/35 relaxor features was performed in these ceramics.

Keywords: *PLZT, transparent ferroelectric ceramics, chemical processing*

1. Introduction

Transparent ferroelectric ceramics (TFC) were produced by Haertling and Land in 1969 at the Sandia National Laboratories after about ten years of extensive work based on lead titanate zirconate (PZT)[1]. The composition was $Pb_{0.92}La_{0.08}(Zr_{0.65}Ti_{0.35})_{0.98}O_3$ or simply PLZT 8/65/35. The incorporation of aliovalent lanthanum into the lattice enhanced the densification rates of the PZT ceramic bodies, leading to pore-free homogeneous microstructures. In 1971, a detailed work on the preparation and characterization of PLZT transparent ceramics, obtained by conventional mixed oxides technique and hot-pressing densification stage, was published[2]. Only one year later, Haertling and Land reported a novel powder processing of PLZT by chemical routes[3]. This process was based on co-precipitation of alkoxides in presence of PbO and proportioned high chemical and optical uniformity of the hot-pressed PLZT slugs, which started to be produced in commercial scale. Up to that date, many researches had reported routes to obtain TFC with better characterization and cost benefits, resulting in a list of different processing techniques and hundreds of compositions (most of them with lead and lanthanum elements). However, hot-pressed PLZT ceramics from co-precipitated powders have maintained themselves at the top of the most utilized ceramics for electro-optic devices[4].

Menegazzo and Eiras[5] have developed an alternative two-stage calcination process to obtain high chemical homogeneity in lead titanate zirconate ceramics. It was developed a chemical method in which all constituents are dissolved and co-precipitated from the same source solution. PZT powders were obtained from mixed oxides method and pre-calcined before dissolution. Thus, precipitation was carried out by aqueous ammonium hydroxide addition, followed by rinsing and drying of the slurry. A second calcination stage completed the powder crystallization. Differential thermal analysis and X-ray diffraction patterns showed that the PZT phase is formed at temperatures as low as 823 K. Recently, Menegazzo, Garcia and Eiras[6] showed that this method, under optimized preparation conditions, can be applied to lanthanum modified lead zirconate titanate ceramics reaching fine single phase powders.

In this work, the goal is the production of transparent PLZT ferroelectric ceramics combining the chemical method developed by Menegazzo and Eiras and uniaxial hot-pressing. Although, the focus is the microstructural, optical, pyroelectric, ferroelectric and dielectric characterizations of the synthesized PLZT ceramic bodies to discuss their physical features and potential quality for applications.

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2. Experimental

The ceramic powders were prepared following the experimental route proposed in Refs. 5,6 which can be basically described as follow. Firstly, $Pb_{0.90}La_{0.10}(Zr_{0.65}Ti_{0.35})_{0.9975}O_3$ powders (hereafter PLZT 10/65/35) were produced by conventional mixed oxides method, being submitted to the first calcination stage at 1173 K/3 h. Then, the calcined powder was dissolved in a solution of nitric acid under controlled pH at 343 K. After that, precipitation was promoted by addition of HNO_3 to the solution up to pH ~9-10. The slurry, after rinsing, filtering and vacuum drying, was submitted to the second calcination stage at 1173 K/3 h. Thus, cold-pressed ceramic pellets were prepared from the ball-milled powders. Prior the milling, 2 wt% excess of PbO was added to compensate further losses by volatilization.

Green disc shape samples, with 20 mm in diameter, were densified for 4 h at 1523 K, under uniaxial pressing of 5MPa in an alumina die. Partial O_2 atmosphere was kept during the heating and cooling. Density measurements, by Arquimedes method, revealed apparent density of ~7.9 g/cm^3, showing that hot-pressed slugs reached densities closer to 100% of the expected theoretical values. Optically polished samples presented yellow-orange color and high transparency. Examples of PLZT 10/65/35 samples obtained in this work are presented in the Fig. 1.

X-ray diffraction (XRD) analysis was performed in the ceramic (crushed) powder, using a Rigaku diffractometer with rotatory anode, CuK$_\alpha$ radiation, and 2θ from 10° to 80°, at room temperature. Scanning electronic microscopy (Jeol, model JSM 5800LV) was carried out for the microstructure observation of the polished and thermally attacked surface.

Gold electrodes were sputtered on the polished disc faces for pyroelectric, ferroelectric and dielectric measurements. The pyroelectric current was measured with an electrometer Kethley 619 in a rate of 6 K/min. Before the pyroelectric measurement, the PLZT sample was heated up to 440 K and let to cool down to low temperatures in the presence of an electric field of 10 kV/cm. Prior measurement and after the electric field removal, the sample was short-circuited for 15 min. to avoid space charge building-up. Hysteresis loops measurements were performed employing a Sawyer-Tower bridge in a temperature range from 240 K to 350 K. A triangular electric field of 10 kV/cm and 1.0 Hz was applied on the sample. This frequency of the electric field assured that the sample temperature was kept constant, avoiding a possible self-heating that could change drastically the ferroelectric properties[7]. Dielectric characterizations were performed as a function of frequency (from 100 Hz to 1 MHz), employing an Impedance Gain Phase Analyzer HP 4194A. The amplitude of the probe oscillating electric field was 5 V/cm for all measuring frequencies. For temperature measurements, the samples were kept in a cryogenic system (APD Cryogenics Inc.) that can be operated from 450 K to 20 K, with a precision of ±0.1 K in all covered temperature ranges. Taking in mind the influence of the aging effects on the physical properties of PLZT ceramics, the data were collected using samples aged for one day, following a procedure employed by Kutnjak *et al.*[8] in similar studies.

A Carry 4G spectrophotometer was used to measure the relative transmittance in the region of ultraviolet to near infrared, at room temperature. The scanning rate was 250 nm/min.

3. Results and Discussions

The X-ray diffraction pattern of the hot-pressed PLZT 10/65/35 ceramic, which may be observed in Fig. 2, reveals a single-phase material with pseudo-cubic perovskite structure. The lattice parameter is a = 4.16 Å, in a good agreement with the reported values for the same composition[1-4].

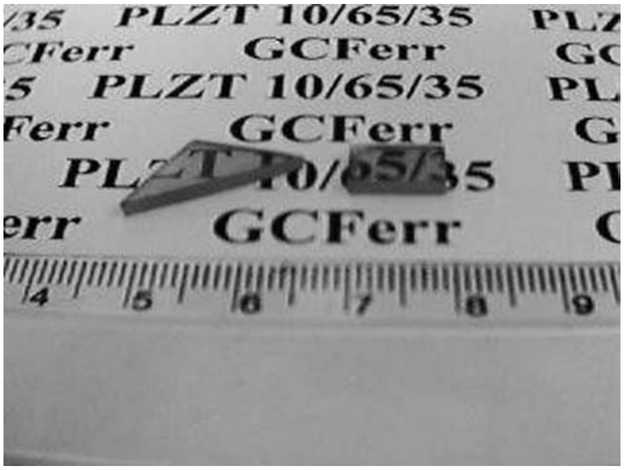

Figure 1. Hot-pressed PLZT 10/65/35 ceramics.

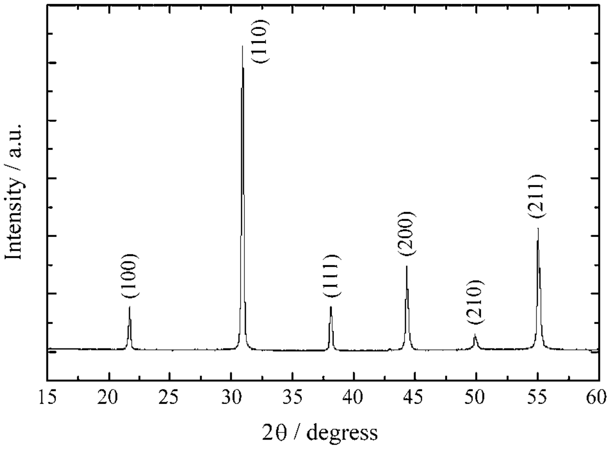

Figure 2. X-ray diffraction pattern of the PLZT 10/65/35 ceramic.

Figure 3 shows a SEM micrograph of the hot-pressed PLZT 10/65/35 ceramic. As can be observed, the high densification achieved in this material is confirmed by its non-porous and straight grain boundary microstructure. In fact, no segregated or liquid phases are noticeable even for higher magnifications (around 15000x). This fact might indicate that PbO excess, added to the precursor powder, was practically consumed. Microstructure such as this obtained here justifies the high transparency observed. For 0.9 mm thick samples, transmittance in the visible range is around 60% (without excluding multiple reflection losses, which are ~28%), as presented in Fig. 4.

The pyroelectric current I_p and the remanent polarization P_r are shown in Fig. 5. The I_p peak arises at 249 K, where the remanent polarization presents an inflection point. In fact, at temperatures few degrees above T_p (temperature of the pyroelectric current peak) the remanent polarization reaches values approximately close to zero. This result also agrees with other previously reported for PLZT 10/65/35 ceramics[8]. The sharpness of the pyroelectric current curve clearly indicates the single-phase nature of this sample. Nevertheless, the I_p *vs.* T curve do not reach zero values until 320 K. This effect may be related to some spurious conductivity, certainly originated from spatial charge building up during the heating.

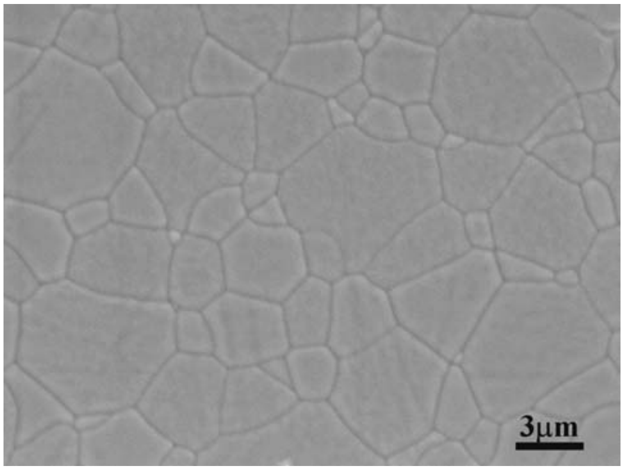

Figure 3. SEM micrograph of a PLZT 10/65/35 polished and thermally attacked surface. (5000x).

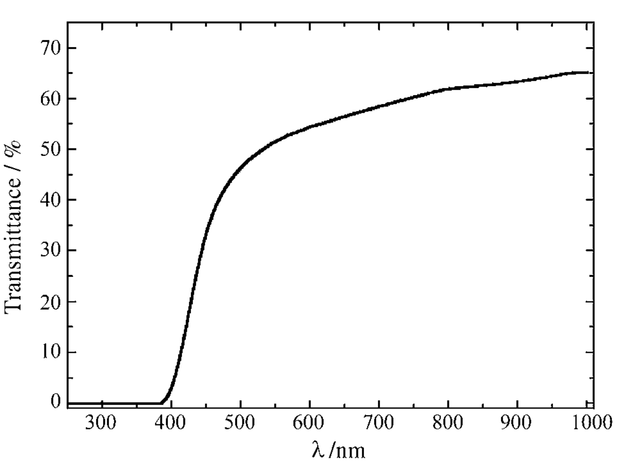

Figure 4. Transmittance spectrum of a 0.9 mm thick PLZT 10/65/35 ceramic.

Figure 6 shows the temperature dependence of the hysteresis loops for the PLZT 10/65/35 sample. The results show that, increasing the temperature, the coercive field and the remanent polarization gradually decrease. At 350 K the hysteretic behavior disappears completely and the P *vs.* E curve becomes a so-called slim loop, as commonly observed for ferroelectric relaxor materials[9]. The coercive field and remanent polarization reach their highest values at 240 K ($E_c = 3.5$ kV/cm, $P_r = 4.4$ μC/cm^2). The hysteresis loops observed in our measurements present a slight rounded shape that is attributed to conduction mechanism effects. The origin of this conduction comes either from point defects, introduced in the lattice, as by a PbO layer in the grain boundary. Nevertheless, the later could not be observed at SEM micrographs, as above mentioned.

The temperature dependence of the polarization for the static case (pyroelectric current measurement) is different from the dynamic case (P *vs.* E measurement) due to the different measurement regimes. At temperatures higher than 240 K, remanent polarization gradually decreases in hysteresis loops while an abrupt change is observed in the pyroelectric measurement. In the pyroelectric measurement a static electric field was applied during cooling, while in hysteresis measurement, an ac (time dependent) field was applied at fixed temperatures. Therefore, in the former, the sample ferroelectric state is reached and, by heating, a consequent depolarization is observed. In the latter, the polar ferroelectric clusters (ferroelectric domains) can be reoriented under field driving. In fact, the square-to-slim-loop transition of the hysteresis curves dur-

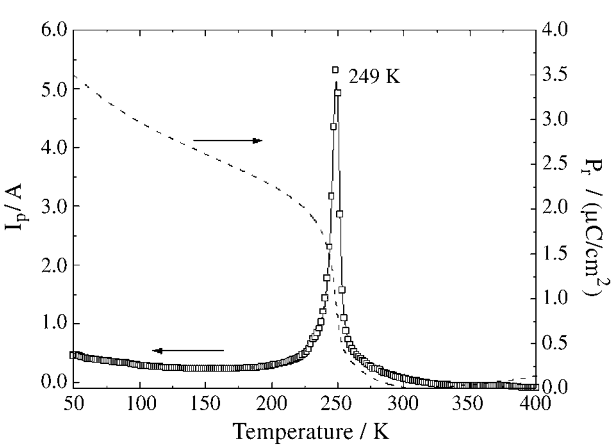

Figure 5. Pyroelectric current (I_p) and remanent polarization (P_r) for the PLZT 10/65/35 hot-pressed ceramic.

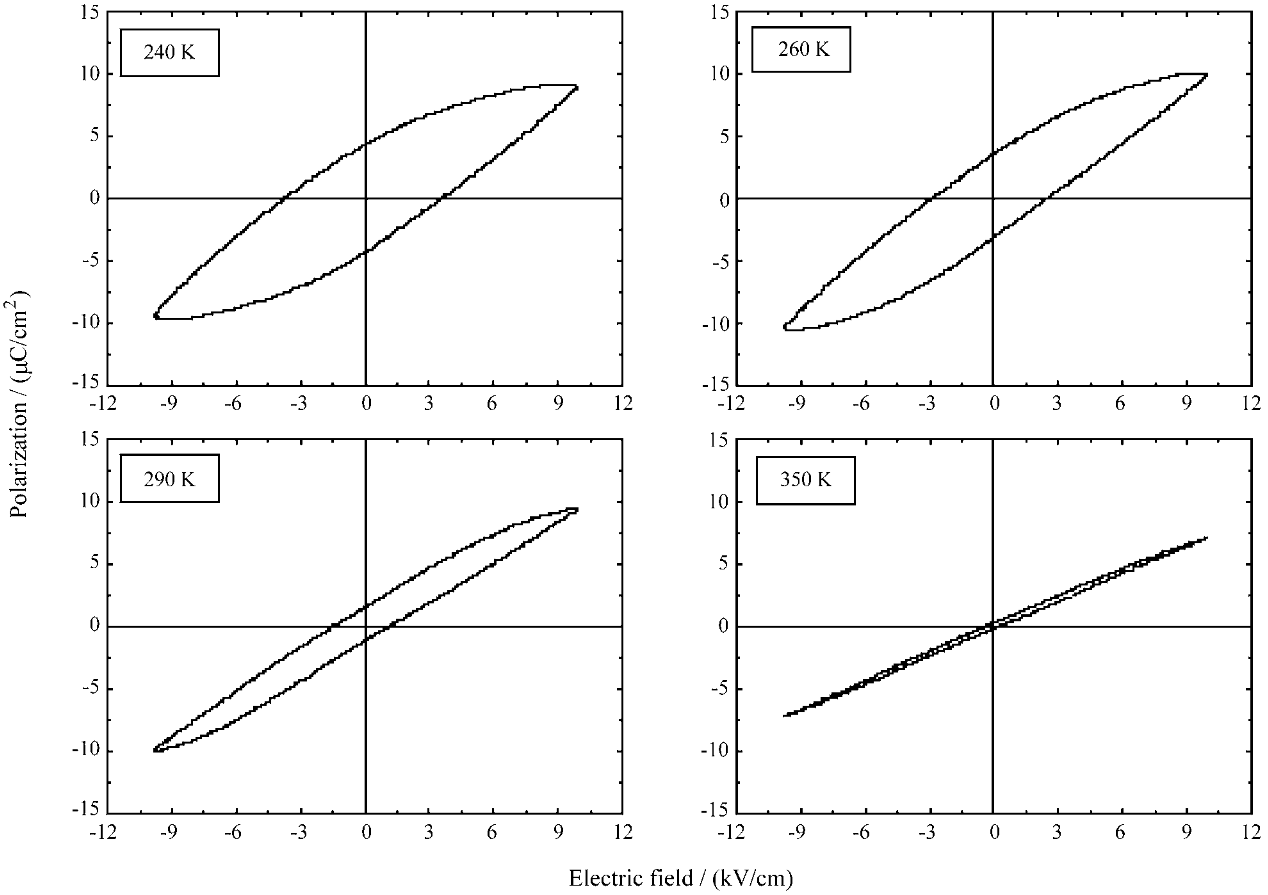

Figure 6. Temperature dependence of the hysteresis loops for the PLZT 10/65/35 ceramic.

ing heating (Fig. 6) can be associated with ferroelectric clusters interactions controlling the kinetics of the polarization reversals and the consequent freezing process[10,11] (see discussion below).

The dielectric characterization of the hot-pressed PLZT 10/65/35 ceramic, as a function of temperature and frequency, is shown in Fig. 7. Lower values for the dielectric constant at room temperature ($\varepsilon'_{RT(1kHz)} = 2879$) and higher values for the maximum dielectric constant temperature ($T_{m(1KHz)} = 339.6$ K) in comparison with those obtained from other studies are observed. This fact might be a consequence of a certain compositional deviation from the batch stoichiometry formula. By the results, it may be a concentration of La lower than 10 mol % or a Zr/Ti ratio lower than 65/35. Zirconium oxide segregation at the grain boundary can be preferential than titanium oxide, when PbO losses occurs in lead-based perovskites[12,13]. Since no segregated phases were observed in the SEM and XRD analysis, probably the Zr or even La precipitation can be rejected. Lin e Chang[14] reported the formation of the phase $La_2O_3.4PbO$ at the PLZT grain boundary after quenching procedures. They proposed that a possible concentration gradient of lanthanum could be rising into the grain during the hot-pressing. Higher concentrations of La would be found closer to the grain boundary and could react with the PbO excess when thermal treatments are applied. This lanthanum concentration gradient could explain our results (on the dielectric parameters), since a lower La effective content into the whole grain is assumed. Qualitative energy dispersive X-ray spectrometry (EDS) analysis showed

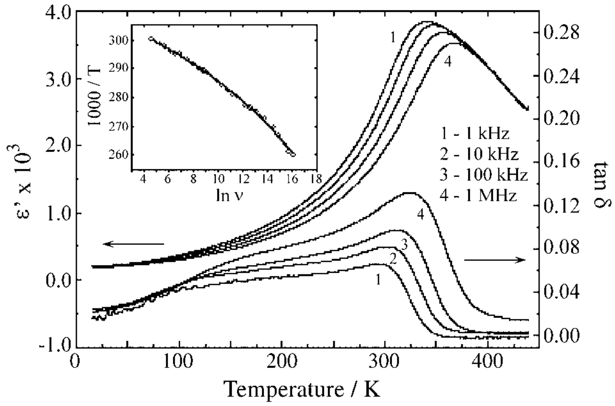

Figure 7. PLZT 10/65/35 dielectric constant (ε') and dielectric losses (tan δ) as a function of both temperature and frequency. Inset: Vogel-Fulcher analysis.

fluctuations on the La concentration along the grain. Although, those variations were observed within the equipment resolution, becoming the EDS analysis inconclusive. Further transmission scanning microscopy analysis might aid in this study.

As it can be observed, the PLZT ceramic shows a typical relaxor dielectric behavior (Fig. 7). When the measurement frequency increases, the maximum dielectric constant, ε'_m, decreases, but increasing the temperature of the maximum, T_m. On the other hand, for dielectric losses, when the frequency increases, tan δ increases, as well as its temperature of maximum, T'_m. The frequency dependence of the dielectric constant can provide direct information on the dynamic processes occurring in ferroelectric relaxors. In this way, it was performed the Vogel-Fulcher analysis[11] of the frequency dependence of the dielectric constant maximum temperature (T_m) in the PLZT 10/65/35 ceramic (inset in the Fig. 7). The attempt frequency $\nu_0 = 1.48 \times 10^{15}$ Hz, the average activation energy $U = E_a/k_B = (2512 \pm 100)$ K and the freezing temperature $T_f = (251 \pm 3)$ K, were obtained fitting the $1/T_m$ *vs.* ln ν curve with the following expression:

$$\nu = \nu_0 \exp\left(-\frac{U}{T - T_f}\right) \quad (1)$$

Independently of the analyzed frequency, the maximal dielectric constant and dielectric loss temperatures are not coincident with the freezing temperature (T_f), which is the temperature where the ergodicity is effectively broken. However, T_f coincides with the pyroelectric current peak temperature (T_p = 249 K). This is a typical feature of the relaxor ferroelectric materials, where the ergodic state (where the long-range interaction between the ferroelectric clusters is practically absent) is effectively broken at T_f, and not at T_m or T'_m. In fact, the ergodicity is broken due to the divergence of the longest relaxation time in the vicinity of 251 K, *i.e.*, the temperature where the ferroelectric state, with long-range interactions, can also be induced by applying sufficiently high electric fields, as in pyroelectric or dielectric measurements with high applied bias electric fields[15,16].

4. Conclusions

Hot-pressed transparent lanthanum modified lead titanate zirconate (PLZT) ceramics were obtained from powders prepared by a low cost chemical method. The results clearly indicates that this powder processing is very efficient to obtain transparent PLZT ceramics. Moreover, the analyzed physical properties showed very similar values to those reported in the literature. The high quality samples obtained with this alternative chemical route permitted a phenomenological study of the PLZT relaxor features. Indeed, the Vogel-Fulcher analysis of the dielectric data indicated the ergodicity breakdown at T_f, which is a typical relaxor characteristic.

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