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Investigation of the relaxor behavior of sol gel processed lanthanum lead titanium ceramics

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ABSTRACT

A series of La doped lead titanate samples, with composition $Pb_{1-x}La_xTi_{1-x/4}O_3$ (PLTx), where x=0.00; 0.02; 0.04; 0.06; 0.07; 0.08; 0.10; 0.12; 0.14; 0.16; 0.18; 0.21 and 0.22 was prepared using the sol–gel process.

Addition of La gives rise to the two well-known phenomena: diffuseness and relaxation around the ferro-to-paraelectric transition; the two parameters related to these phenomena, and which give a satisfactory interpretation of them, have been estimated using the **Uchino's** quadratic law. This diffuse phase transition (DPT) has been investigated with the help of the Landau–Devonshire cluster theory and the model of Cheng et al., to show that polar regions may be generated around the DPT and far from the temperature, T_m, of the maximum of the dielectric permittivity, which have as a direct consequence a non vanishing polarization even if $T > T_m$.

1. Introduction

Lead titanate ($PbTiO_3$; PT), a ferroelectric material, is known for its interesting properties; high Curie temperature, pyroelectric coefficient and spontaneous polarization, and low permittivity. These properties make it suitable for numerous applications: ultrasonic transducers [1], thermistors, optical electronic devices and satellite detection [2], etc. At room temperature, PT has a tetragonal perovskite structure [3], and combined with other oxides it forms materials such as (Pb, La)TiO_3, (PLT), Pb (Zr, Ti)O_3, (PZT), and (Pb, La)(Zr,Ti)O_3, (PLZT) whose very wide range of applications is well known: nonvolatile random access memory (NVRAM) and dynamic random access memory (DRAM) devices [4], infrared sensors [5], etc. In fact, these materials belong to what is called Smart materials, materials (and structures) which may give information about their environment to an observer or monitoring device, especially those exhibiting two or more ferroic features such as ferromagnetism/magnetostriction, ferroelectricity/piezoelectricity or ferroelasticity/shape memory effects due to their unusual responses, which are benefiting of a growing interest due to the possibility of their applications and integrations into industrial systems including civilian, industrial, medical and military applications. PLT ceramics belong to the family of **relaxor ferroelectrics (RF):** non-Debye dielectric dispersion, deviations from the Curie–Weiss law in the paraelectric phase, zero spontaneous macroscopic polarization, frequency dispersion of the permittivity, ε_r, and a large maximum ($\varepsilon_{r\ max}$) of ε_r at a temperature, T_m, which is shifted towards high values with increasing frequency; the corresponding phase transition is called diffuse phase transition (DPT); relaxor character has also been also investigated in a large number of Pb-based perovskite such as $PbB_1B_2O_3$, Pb $Mg_{1/3}$ $Nb_{2/3}O_3$ [6,7], $Pb(Fe_{0.5}Nb_{0.5})O_3$ [8] and Pb $Fe_{2/3}$ $W_{1/3}O_3$ [9,10]. Several models and approaches have been developed to interpret this DPT involving different mechanisms: chemical heterogeneities, superparaelectric behaving due to mesoscopic heterogeneities,… [11–15]. However, details concerning the physical process of the DPT remain not completely clear. Moreover, it has been reported that properties of such systems may be explained by the existence of polar *nanoregions* with non-zero local polarization and short range order [16].

Indeed, at high temperature relaxor ferroelectrics exist in a non-polar paraelectric phase which is similar to the paraelectric phase of ferroelectric in all the aspects.

However upon cooling they transform into ergodic relaxor state in which polar regions of nanometer size with randomly

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distributed directions of dipole moments appear. The temperature corresponding to the transformation is called Burn's temperature (T_B) [12,17]. At temperature close to T_B polar *nanoregions* (PNR) are mobile and their behavior is ergodic. The dielectric behavior of these materials at temperature lower than T_B is mainly dependent on the concentration of the polar regions and the dipole moment of each polar region, and the dynamics of the PNR associated with the thermally activated flips is considered to be responsible for the relaxor behavior. Moreover, PNR are believed to play an important role in the appearance of particular properties and phenomena in many relaxor systems strong piezoelectric and electromechanical properties [18], electrostriction phenomena [19]; PNR have been directly observed in these materials such as $Pb(Mg_{1/2}Nb_{3/2})O_3$ [20].

Both experimental and theoretical works have been devoted to the study of the relaxor behavior in ferroelectric materials. From theoretical point of view, different approaches and models have been established to clarify the mechanisms involved in the normal-to-relaxor behavior [21–26], taking also into account, besides the existence of PNR mentioned above, the effect of compositional (or chemical disorder) disorder as no relaxor ferroelectric behavior was observed among completely compositionally ordered crystals, which destroys a normal ferroelectric phase and creates the relaxor state by mechanisms which remain unclear**.** Different experimental methods have also been used to elucidate the origin of relaxor ferroelectricity [27–32], including extended x**-**ray absorption (EXAFS) [27], high-resolution transmission electron microscopy [29,33], neutron diffraction [30]; synchron x-ray scattering [31], and nuclear resonance [32]. Structural investigation of the ferroelectric phase transition in La-doped lead titanate (PLT) revealed that for La contents in excess of 5 at%, local polarization persists until temperatures significantly above that of the average phase transformation [34]. Moreover, transmission electron microscopy (TEM) studies showed the presence of sub-domain modulation along the mechanically soft tetragonal c axis [34]. As the dopant content was further increased between 5 and 20 at%, the degree of modulation increased suggesting a relaxation of the lattice. At La content of 25 at%, the ferroelectric domain structure was found difficult to define, rather the bright-field image consisted of a cross-hatched or “tweed” microstructure; the latter has also been observed in the incipient relaxor state of rhombohedral [35] and tetragonal PLZT materials [36]. Besides, it has been suggested that La modification of PT gives rise to the development of a spatially varying polarization within the normal microsized ferroelectric domain structure [34]. These structural changes appear to be directly related to the nature of the phase transition, the latter transforms from a conventional first order to a diffuse transition as the La content is increased between 5 and 10 at% [37]. As the La content is increased to above 20 at%, an extreme broadening of the permittivity has been reported.

As mentioned above, it is widely accepted that the behavior of the polar regions around the maximum of the permittivity in the material is a key to the behavior of the ferroelectric relaxation. Therefore, in this context, Attempts have been done to quantitatively describe the transition from ferroelectric (with long range order) to relaxor behavior (with short range order).This work aims to study and discuss the role played by polar regions in the relaxation process which takes place in relaxor ferroelectrics, using the modified Landau–Devonshire cluster theory and the model of Cheng et al. [38,39] taking into account contributions of macroscopic and local polarizations; the former was applied in the study of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ [40,36], and $(1-x)PbFe_{2/3}W_{1/3-x}PbTiO_3$ [41] systems.These two approaches have been applied to our experimental results concerning the sol gel processed (Pb, La)TiO_3 (PLTx, where x is the concentration in La) ceramics [42]. Moreover, we have observed on our samples PLTx an anomaly, in the ferroelectric phase, on the thermal behavior of the dielectric permittivity, for compositions $x \leq 0.16$ (indicated by an arrow as FA in Fig. 1(a)) [42]. Existence of such anomaly has been reported in Pb(Zr,Ti)O_3 (PZT) compounds. Ragini et al. [43] have observed two anomalies at low temperatures (191 k and 253 k) on PZT systems ($PbZr_xTi_{1-x}O_3$, $x=0.52$ and $x=0.515$) which they explained based on the work of Noheda et al. [44], to a transition from tetragonal to monoclinic phase for the first anomaly (around 197 k) and to a cell-doubling transition [44] for the second anomaly (around 253 k). Sheen and Kim [45] have also observed an anomaly on PZT films which they interpreted as a transition from tetragonal to monoclinic symmetry with decreasing temperature ($PbZr_{1-x}Ti_xO_3$, $x=0.46$, 0.48, 0.49, where anomalies occur at about 490 k, 325 k and 235 k, respectively). From dielectric measurements, Bouzid observed two anomalies, at relatively high temperature, on undoped PZT54/46 samples and on those doped Nb and K. these two anomalies were interpreted as due to a rhombohedral to quadratic phase transition for that located at the temperature of 180 °C (undoped sample), and to a quadratic to cubic phase transition for that occurring at about 370 °C (undoped sample).This interpretation was based on the correlation made between mechanical losses and dielectric losses [46]. Work is in progress to determine the origin and the nature of the anomaly observed in our samples.

2. Experimental

The experimental procedure of fabrication of $Pb_{1-x}La_xTi_{1-x/4}O_3$(PLTx) samples, with $\boldsymbol{x}$ ranging from 0.00 to 0.22, has been detailed elsewhere [42]. The sol gel method was used for the sample preparation due to its many advantages in the possibility of elaborating high pure mixed oxides at relatively low temperature with an excellent control of the stoichiometry and a good homogeneity [47,48].

The corresponding curves of the thermal variation of the permittivity, $\boldsymbol{\varepsilon_r}$, reveal, for $\boldsymbol{x} < 0.16$, the presence of a sharp peak corresponding to the ferroelectric to paraelectric transition (FPT), and diffuse anomalies in both the ferroelectric and paraelectric regions, and relatively broad peaks for the FPT. For $\boldsymbol{x} \geq 0.16$, samples exhibit relaxor characteristics as shown on Fig. 1. One can also observe on this figure that below the FPT, low values of dielectric losses are recorded and that above the transition these losses increase rapidly as a consequence of the conducting nature of the samples in the paraelectric phase.

Temperature and character of the phase transitions are influenced by La doping.With increasing La content, the character of the phase transition changes from a sharp transition to a diffuse one, the width of the dielectric peak of the transition characterized by the parameter, Δ, increases with increasing La concentration as illustrated on Fig. 2 by plot of reduced dielectric constant $\boldsymbol{\varepsilon_r/\varepsilon_{r\ max}}$ versus reduced temperature $\boldsymbol{(T-T_m)/T_m}$ for different PLT compositions. Indeed the temperature, $\boldsymbol{T_m}$, of the maximum of the FPT is shifted linearly toward low values (Fig. 3). This lowering of $\boldsymbol{T_m}$ may be attributed to the increase of the internal stress resulting from the lattice distortion due to the La occupancy of A-site [49] and the comparatively large ionic radius [50]. These results agree well with other studies [51–54].

3. Results and discussions

As said in the introduction, we have applied the approach based on the Landau–Devonshire theory and the model of Cheng et al. [38,39] to our PLTx ($\boldsymbol{x} \geq 0.16$) samples [42], and we give in the two following sections the obtained results.