

SPONTANEOUS STRAIN AS ORDER PARAMETER TO DESCRIBE THE PHASE TRANSITION IN La^{3+} DOPED PbTiO_3 FERROELECTRIC PEROVSKITE

LA DEFORMACIÓN ESPONTÁNEA COMO PARÁMETRO DE ORDEN PARA DESCRIBIR LA TRANSICIÓN DE FASE EN LA PEROVSKITA FERROELÉCTRICA PbTiO_3 DOPADA CON La^{3+}

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Spontaneous strains of lanthanum doped PbTiO_3 compound were determined from the temperature dependence of the unit cell parameters. The critical temperature was determined by using the spontaneous strain as order parameter. The calculated value of the critical temperature agrees with that obtained through differential scanning calorimetric measurements. The temperature dependence of the spontaneous polarization was also estimated through the components of the uniform elastic deformations parallel and perpendicular to the [001] crystallographic direction of the perovskite structure.

Las deformaciones espontáneas en el compuesto PbTiO_3 dopado con lantano han sido determinadas a partir de la dependencia de los parámetros de red con la temperatura. La temperatura crítica ha sido determinada haciendo uso de la deformación espontánea como parámetro de orden. El valor calculado para la temperatura crítica se corresponde con el obtenido a través de mediciones de calorimetría de barrido diferencial. La dependencia de la polarización espontánea con la temperatura ha sido igualmente estimada a través de las componentes de las deformaciones elásticas uniforme paralela y perpendicular a la dirección cristalográfica [001] de la estructura perovskita.

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INTRODUCTION

Lead titanate (PT) is one of the most important ferroelectric systems for technological applications due to their excellent piezoelectric properties [1]. The PT is characterized by its high anisotropy, resulting in a good candidate for high frequency transducers [2]. On the other hand, the PT system exhibits high $c/a = 1,064$ ratio value (tetragonality), leading to a highly fragile material [3,4]. This brittleness can be reduced by the partial substitution of Pb^{2+} with lanthanum ions (La^{3+}), preserving the good properties in the piezoelectric material [4].

PbTiO_3 (PT) crystal exhibits a cubic symmetry above its critical temperature (T_c). The centrosymmetric crystal structure (Pm3m) collapses to tetragonal (P4mm) below the T_c , providing a paraelectric-ferroelectric phase transformation. During this reduction of symmetry, variations in the crystal structure parameters carried out, i.e. from $a = b = c$ for $T > T_c$ to $a = b \neq c$ for $T < T_c$, being invariant the angles between the crystallographic axes. The structural change leads to distortions in the crystal structure, basically along the crystallographic direction [001]. These distortions can be evaluated through

magnitudes as the spontaneous strain. The evaluation of the tetragonal distortion of the lattice, given through the c/a ratio, allows determining the spontaneous polarization (P_s) which is a fundamental ferroelectric property in PT crystals [5].

The ferroelectric properties of PT samples vary once doped with La^{3+} . The effect of the addition of La^{3+} on intrinsic properties, as the critical temperature and the spontaneous polarization can be determined through the spontaneous strain [6]. Previous studies on this system [7] have showed a suppression of the tetragonality and cell volume, and a concomitant decrease in the ferroelectric to paraelectric transition temperature, compared to undoped lead titanate, which is consistent with substitution of La^{3+} ions at the A-site. Consequently, it has been realized high resolution X-ray diffraction experiments as function of temperature in order to estimate these magnitudes for the studied composition. The use of synchrotron X-ray sources allows improving the quality of the diffraction data due to high intensity and resolution of the diffracted beam. Similar studies in PT doped with other lanthanides are currently being conducted. Additionally, the experimental spontaneous polarization

value at room temperature was determined in order to calculate the electrostrictive constants.

EXPERIMENTAL PROCEDURE

The samples were prepared by a ceramic conventional method with the nominal composition $(\text{Pb}_{0.88}\text{La}_{0.08})\text{TiO}_3$. The powders were calcined at 900 °C for two hours in air and the sintering is carried out at 1220 °C for two hours, also in air [7]. The high resolution X-ray diffraction experiments were conducted at the XPD beam line of the LNLS, Campinas, Brazil. A Hubber diffractometer with Bragg-Brentano geometry was equipped with a crystal monochromator of Si (111) and a Ge crystal (111) as analyzer. The measurements were made on a disk like sample from room temperature until well above the critical temperature. The used wavelength was 1.76042 Å and the patterns were collected with a fixed counting time and a step of 0.02 degrees. A LaB_6 sample was used as external standard to remove instrumental contributions to the diffraction profile. The spontaneous polarization value at room temperature was obtained from the hysteresis loops, at 1 Hz, by using a Precision Ferroelectric Tester System (Radiant Technologies INC). The critical temperature, i.e. the ferroelectric-paraelectric transition temperature ($T_c^{\text{DSC}} = 618 \text{ K}$), was determined by using differential scattering calorimetric measurements (DSC) [7].

RESULTS AND DISCUSSION

Figure 1 shows a region of the X-ray diffraction (XRD) patterns of $(\text{Pb}_{0.88}\text{La}_{0.08})\text{TiO}_3$ at several temperatures from room temperature until well above the critical temperature ($T_c^{\text{DSC}} = 618 \text{ K}$). This 2θ region suggests clearly a phase transition to a higher symmetry. Above the T_c^{DSC} the $(100)_T$ and $(001)_T$ peaks merge into a single peak $(100)_C$ as result of the phase transition 4mm – m3m. The diffraction patterns show an anisotropic broadening, dependent on (hkl) value, below the T_c^{DSC} . The integral breaths of the peaks $(00h)_T$ are larger than that of the peaks $(h00)_T$. It is illustrated by the behavior of the $(100)_T$ and $(001)_T$ reflections in Figure 1. In general, this behavior is observed for the reflections of the type $(00h)_T$ in relation to $(h00)_T$ and $(hk0)_T$. The observed profile broadening is known as *anisotropic microstrain type broadening* [8]. Additionally, the relative intensity of the peaks $(00h)_T$ and $(h00)_T$ is inverted as result of certain texture in the disk like sample, but it does not affect any analysis based on peak positions.

At T_c^{DSC} , the peak $(100)_C$ shows an asymmetry especially on its left side due to some kind of diffuse background. This asymmetry occurs for all peaks in the diffraction pattern and disappears for a higher temperature. This effect could be interpreted as results of remaining regions with a distorted tetragonal structure at this temperature. Previously, some studies on this system have shown that local distortions remain in the cubic phase [9-11].

The degree of the anisotropic microstrain, which is associated with the observed profile broadening is a result of the strain

components perpendicular and parallel to the tetragonal c axis of the perovskite structure. The relations, which are used to determine the spontaneous polarization, and indirectly, the critical temperature from the components of the uniform strains have been previously developed within the framework of the Landau-Ginsburg-Devonshire formalism for the Gibbs free energy [5,2-14] and applied to the particular case of the undoped PT compound [14] and for La^{3+} doped PT considering a different composition [6].

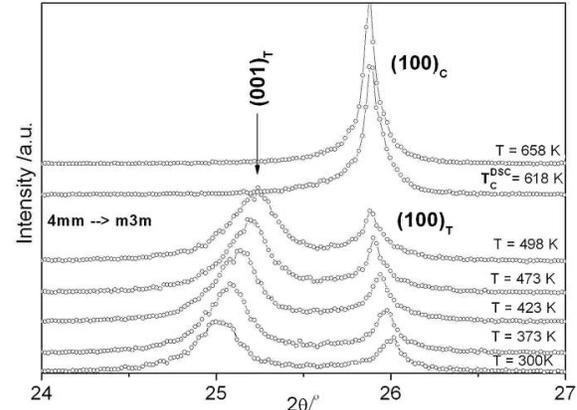


Figure 1. Fraction of the XRD patterns of $(\text{Pb}_{0.88}\text{La}_{0.08})\text{TiO}_3$ as function of temperature. The $(100)_T$ and $(001)_T$ peaks of the tetragonal phase merge into a single peak $(100)_C$, cubic phase, as result of the phase transition 4mm – m3m.

The La^{3+} doped PT paraelectric cubic phase is taken as reference with zero spontaneous strain and spontaneous polarization values. In its tetragonal structural modification the following relations for uniform deformations holds [6]

$$\begin{aligned} x_1 = x_2 = Q_{12}P_3^2 \\ x_3 = Q_{11}P_3^2, \quad x_4 = x_5 = x_6 = 0 \end{aligned} \quad (1)$$

where x_i are the components of the deformation tensor and Q_{ij} the electrostrictive constants. P_3 is the spontaneous polarization in the $[001]$ direction of the perovskite structure.

On the other hand, the spontaneous deformation values x_1 and x_3 can be determined by using the unit cell parameters calculated for each temperature through the following relations

$$\begin{aligned} x_1 = (a_T - a'_C) / a'_C \\ x_3 = (c_T - a'_C) / a'_C \end{aligned} \quad (2)$$

where a_T and c_T are the unit cell parameters of the tetragonal phase for a given temperature and a'_C is the extrapolated cubic unit cell parameter into the tetragonal region.

The unit cell parameters were calculated from the diffraction patterns by using a least square fit with an external standard and after deconvolution of the diffraction profiles for instrumental broadening and zero correction. To calculate the temperature dependence of the deformation values, the lattice constant of the cubic phase must be extrapolated into the tetragonal region (a'_C). Performing a linear extrapolation of the cubic cell parameter from the region above the critical temperature through a wide temperature range into the room temperature can introduce errors in the determination of a'_C . The former

is a result of the nonlinear behavior of the thermal expansion coefficient reported for many oxides [15].

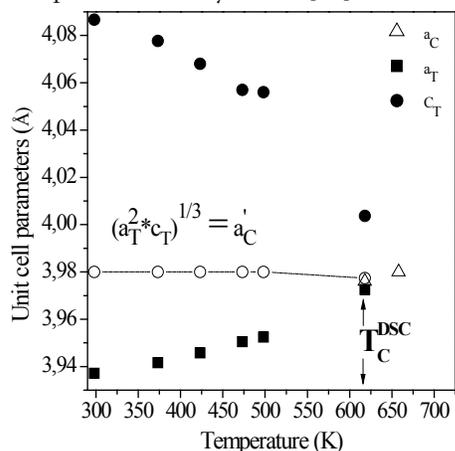


Figure 2. Unit cell parameters and $(a_T^2 c_T)^{1/3}$ as function of the temperature.

On the other hand, in our experiments only a single temperature value above the critical temperature could be measured as result of experimental limitations. Thus, it was not possible to carry out an extrapolation as described above. In this case an alternative method has been used, which consists in determining the magnitude $(a_T^2 c_T)^{1/3}$ [5]. It should not vary with the temperature, as it represents a no volumetric strain in the tetragonal state. In our case a'_c has been assumed as $(a_T^2 c_T)^{1/3}$ in equation (2). Figure 2 shows the temperature dependence of the unit cell parameters and $(a_T^2 c_T)^{1/3}$. The unit cell parameters begin to converge more rapidly by approaching the phase transition temperature, while the parameter $(a_T^2 c_T)^{1/3}$ remains constant in the studied temperature range until the critical temperature. Only from the pattern measured at the critical temperature, $T_C^{DSC} = 618$ K, two set of unit cell parameters were calculated, one for the tetragonal phase and the other one for cubic phase.

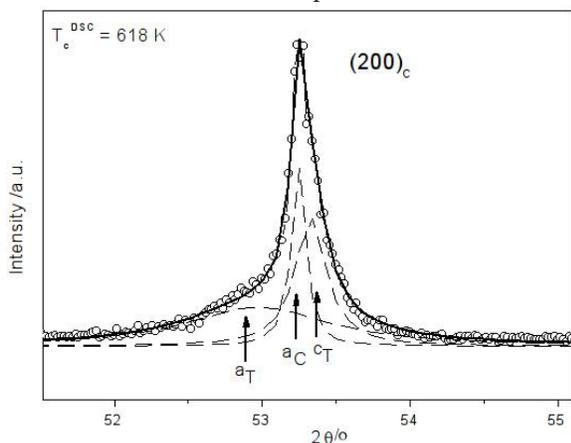


Figure 3. Fitting of the peak $(200)_c$. The experimental data is represented with open circles, the components of the peak, a_T , c_T and a_c with dashed lines, and the calculated peak profiles from the components with solid lines.

Figure 3 shows the fitting result of the peak $(200)_c$ using three functions, which were used to calculate the values of these unit cell parameters. The calculated $(a_T^2 c_T)^{1/3}$ value for the pattern measured at the critical temperature agree with the value of a'_c which supports the idea of having three components in the peak $(200)_c$. The spontaneous strain was calculated using (2)

and is showed in Figure 4 as function of $|T - T_C^{DSC}|^{1/2}$.

The components of the spontaneous strain decrease with increasing temperature, being x_3 the component which decreases faster; hence it determines the spontaneous polarization state of the material. The solid curves represent the linear fit and the dashed one the extrapolation of both x_3 and x_1 . The point where the extrapolated curves intersect can be interpreted as the temperature at which the uniform deformation disappear (T_C^{DRX}). At this temperature the crystal structure goes into a paraelectric state recovering its centrosymmetric nature. However, it should be noted that the interception point is shifted slightly from the horizontal dashed line representing a non-deformation state; but this displacement is of the order of 10^{-3} , which is within the error made determining the spontaneous strain from the unit cell parameters due to some systematic error. The value obtained graphically for the T_C^{DRX} is 623 K, which is only 5 K higher than that of T_C^{DSC} .

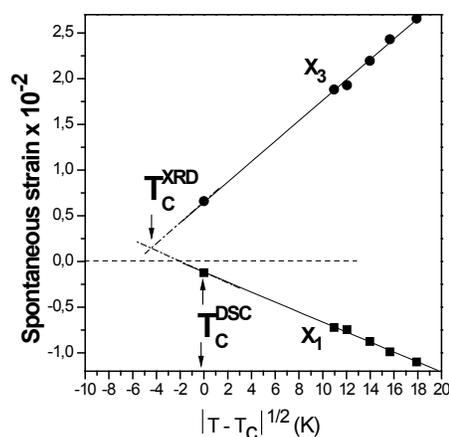


Figure 4. Components of the spontaneous strain values as function of temperature. The intercept point of the curves represents the value of the critical temperature determined from the spontaneous strain (T_C^{DRX}).

The experimental spontaneous polarization value at room temperature, which was obtained from the hysteresis loops, is $P_s = 0.144$ C/m². This value is very shorter than that of the previously reported for undoped single crystal and powder PT [5,14,16] as result of La incorporation in the structure.

Using the spontaneous strain determined by X-ray diffraction experiments at room temperature as well, it was then possible to calculate the electrostrictive constants through equation (1). The coefficients Q_{12} and Q_{11} are known to vary slightly with temperature for a fixed composition, but usually they are assumed to be independent of temperature [5,14,17]. In our case $Q_{12} = -0.53$ m⁴/C² and $Q_{11} = 1.28$ m⁴/C². Under this assumption, the temperature dependence of the spontaneous polarization was determined (Figure 5). As expected, P_s decreases as the temperature approaches the T_C^{DSC} . As previously stated, it seems that at T_C^{DSC} regions with a distorted tetragonal structure still remain. From the crystallographic data, which was obtained at T_C^{DSC} , the value for the spontaneous polarization at the critical temperature was calculated ($P_0 = 0.05$ C/m²), which is one order shorter than that reported for the pure lead titanate at the same temperature [5].

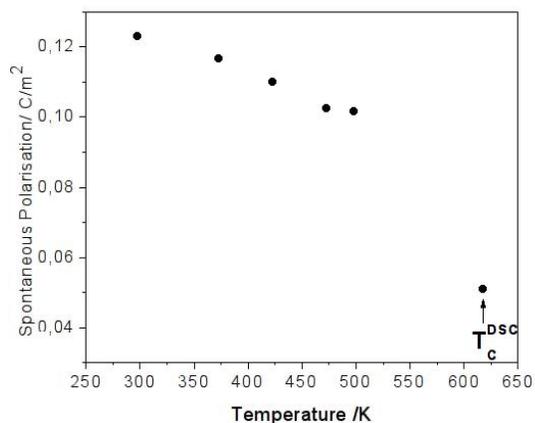


Figure 5. Spontaneous polarization as function of temperature. At the T_c^{DSC} a very low value of the spontaneous polarization could be determined.

Using crystallographic methods it has been possible to study the effect of the La^{3+} addition on intrinsic properties of PT without measuring them directly. As expected, T_c and P_s decrease respect to pure PT compound after La^{3+} addition. The study shows the effective coupling between the spontaneous polarization and the components of the spontaneous deformation.

The method used allows estimating values of P_s as a function of temperature. Usually, for a more accurate calculation, it should be taken into account the fact that the microstructure of the sample varies with temperature. The width of the ferroelectric domain walls increases with the temperature [18]. The domains are regions of crystal imperfections that influence the shape of the diffraction profiles, e.g. asymmetry [19]. The variations in the profile can lead to shifts of Bragg positions and thus to errors in the determination of the unit cell parameters of the crystal structure of ferroelectric domains regions. In the studied polycrystalline disc-shaped sample, asymmetric effects were not significant below the Curie temperature. In the case of the pattern measured at the Curie temperature, the effect of asymmetry was taken into account as referred previously (Figure 3). Furthermore, it has been assumed that crystal defects of other nature, such as vacancies and dislocations, do not contribute to asymmetry effects. It has been shown that the calculated T_c and P_s values could be a guide in tailoring the ferroelectric properties of this kind of perovskite compounds.

CONCLUSIONS

Fundamental ferroelectric properties in La^{3+} doped PT crystals were determined from crystallographic data. The spontaneous strain was used as order parameter to estimate the Curie temperature of the studied system, being in correspondence with the value determined by using the DSC technique. The electrostrictive constants were assumed to be temperature independent and were calculated from the experimental values of the spontaneous strain and spontaneous polarization at room temperature. It was possible to determine the evolution of the spontaneous polarization as function of the temperature. At T_c^{DSC} a very low value of the spontaneous polarization

was calculated suggesting that the structure was not truly centrosymmetric for this temperature.

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