

Study of structural modifications in a ferroelectric material by means of two optical methods

Estudio de las modificaciones estructurales en un material ferroelétrico por medio de dos métodos ópticos

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Resumen- Las intensidades de las líneas Raman del cerámico complejo (titanato de plomo) se han investigado como una función de la relación de las áreas de los modos Raman de baja frecuencia $E(1TO)$ y silenciosos. Un cambio de fase tetragonal dentro del material cúbico fue observado por espectroscopía Raman. Las muestras fueron sometidas a las mismas condiciones en el momento de realizar las mediciones de Raman. Los espectros UV-vis de absorción sugirieron un cambio en los niveles de energía al aumentar la concentración del elemento de lantano (La). La intención de este estudio es observar cambios estructurales en el material mediante intensidades Raman sin utilizar la posición central tradicional del ancho máximo en las bandas.

Palabras Clave- Espectroscopía Raman, material ferroelétrico, métodos ópticos

Abstract- The intensities of the Raman lines of the ceramic complex (lead titanate) have been investigated as a function of the relation of the areas of the low Raman frequency modes $E(1TO)$ and silent. A change of tetragonal phase into cubic material was observed by Raman spectrjky. The samples were subjected to the same conditions at the time of making the Raman measurements. The UV-vis spectra of absorption suggested a change in energy levels with increasing concentration of lanthanum element (La). This study's intention is to observe

structural changes in the material by means of Raman intensities without using the traditional central position of the peak width in the bands.

Keywords- Raman spectroscopy, Ferroelectric material, Optical methods.

1. INTRODUCTION

Ceramic materials can be defined as all inorganic solids, except for pure metals, formed by metallic and nonmetallic elements. Linked together by ionic or covalent bonds [1]. Generally in a perovskite structure the larger ions occupy the position of the vertices in the cube and the smaller ions, occupy the octahedral position and the oxygen is located on the cube faces. This material has many ferroelectric properties and a high phase transition temperature, an ideal material for many electronic elements [2, 3, 4, 5]. The big problem with this material is its lead composition which makes the material environmentally hazardous. Because of this, we should search for a material similar in ferroelectric properties, but environmentally friendly. The conventional method of solid state reaction, also known as mixture of oxides, has been a me-



thod employed for obtaining the material in many papers [1, 6]. The basic procedure in this method is the stoichiometric mixture of the starting reagents and their subsequent homogenization. In this procedure the mixture must be subjected to heat treatment at high temperatures. The method of the polymeric precursors or Pechini method is based on chelation or complexation of cations by a hydroxycarboxylic acid such as citric acid. The process of chelation occurs when the salts and citric acid are mixed in an aqueous solution. A glycol, such as etiniglicol, is added and is immediately heated to a temperature lower than 100° C [1]. These are some of the methods found in the literature for the creation of the material.

In fact, replacing the ion (*Pb*) in the material can cause defects such as vacancies, both in the higher ion and in the minor. This replacement is presented in the literature usually using lands rare trivalent (Ln^{3+}) at the site occupied by a lead bivalent ion (Pb^{2+}). A charge compensation is necessary in the crystalline network of the material in the study of lead titanate [1, 14, 15].

The relative intensity for each line varies with temperature. With higher temperatures more molecules exist in the energy level $\nu = 1$, where ν is the vibrational quantum number. Quantitatively, the population of molecules is determined by the Boltzmann distribution [7, 8, 9, 10, 11, 12].

$$\frac{N_i}{N_o} = e^{-\frac{\Delta E}{kT}} \quad (1)$$

Where N_i is the number of molecules in the energy state E_i and N_o is the number of molecules in the energy state E_o ; K is the Boltzmann constant and T is temperature in Kelvin and ΔE is the energy difference between E_i and E_o states. The intensity of the Stokes line decreases when the temperature rises [12].

The intensity of the scattered light also depends on the following factors: - The size of the particle or molecule illuminated. - The position of observation. - Angle of scattering in relation to the incident beam. - The frequency of the incident light. - The intensity of incident light [11, 12].

The Raman displacement $\Delta w = w_i - w_f$ is usually measured with wavenumber per centimetre cm^{-1} . The displacement is characteristic of the material as it coincides with the vibration frequency thereof, and not dependent on the incident light. In perfect crystals phonons are only seen the Brillouin zone centre, so that the Raman spectra are narrow and intense. In amorphous materials all the phonons and the spectra show long bands and little intensity that reproduces the density of the vibrational states. The intensity of a Raman mode, in contrast to their frequency, varies with the frequency of the incident light. In principle it is proportional to w^4 . But when w_i approximates a band of electronic absorption of the material, the Raman intensity can increase in an order of magnitude (resonant Raman). The number of Raman modes is related to the number of atoms and their symmetries. In this way, the Raman intensity also depends on the nature of the links, with increasing covalent character and symmetry [13].

The Raman modes studied here are reported in the literature in other studies [14, 15, 16]. From these spectra, we made in a careful study of modes $E(1TO)$ and silent to see if it was possible to detect changes in the crystalline structure of the material only by changes in the intensity of the Raman modes in study. Many studies of the material are found in the literature explaining the phase transition of the *PLT* material [14, 15]. But few studies on this other material are reported that look at structural changes at the beginning of the intensities of Raman modes. So our goal in this paper is to report the importance of Raman intensities in the material lead titanate doped lanthanum, but can also be extended to other materials. In this study, we show changes in Raman intensities with increasing concentration of *La* and temperature applied to the material.

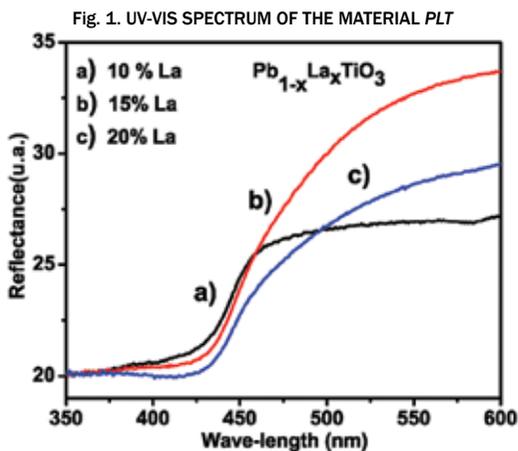
2. EXPERIMENTAL DETAILS

The *PLT* samples were prepared using the mixture of oxides in the conventional method. Samples were analysed at room temperature using XRD to confirm its structural characteristics. Measurements scattering Raman were performed using a triple monochromator Jobin Yvon T64000 with a CCD detector. The excitation light was an argon

laser. The optic used in the samples was a microscope with a 50X objective long working distance. For low-temperature measurements from 10K to 300K, a closed-cycle helium cryostat was used. For the high temperatures from 300K to 850K the measurements were made in an oven with an optical window. The UV-vis spectra were made using a Cary 5000 spectrometer (Varian) in diffuse reflection mode.

3. RESULTS AND DISCUSION

Figure 1 shows the optical reflectance of the samples 10%, 15% e 20% of La doping the $PbTiO_3$ material. Optical reflectance spectra of the samples were studied at room temperature. UV-vis analysis can be thought of as a quality check for the optical behaviour of the studied ceramic material. In this study, we did not make lower concentration samples for lack of sample quantity in the study. As can be seen in Fig. 1 the samples have an energy gap (E_{gap}) very similar to those found in the literature. Other experimental and theoretical papers say that the E_{gap} of energy of the PLT material varies between 3.0 and 4.53eV [17]. As can be seen in Fig. 1 a) 10% La, 15% La and c) 20% La energy gap this close to 3eV. The results indicate that the material behaves according to the literature [17]. The energy levels are dependent on the degree of structural order-disorder in the network. The gap increases with crystal size, but decreases with the extent that the perovskite phase is formed [17]. It is said that an increase in energy of the interval of band Eg increases the dielectric properties of the material. The UV-vis absorption spectra of the samples were measured in a wavelength of 350 to 600nm.



Source: the authors

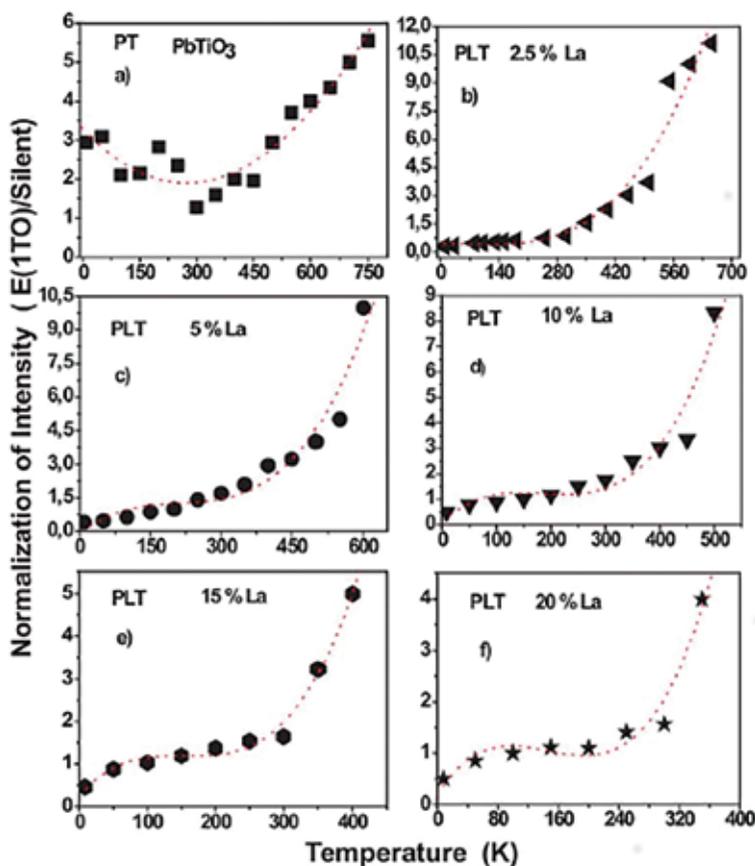
When a new crystalline material is discovered, one of the first fundamental properties to be determined is the atomic structure defined by the minimum in the free energy with respect to the positions of atoms. Another key feature of interest is the curvature of the free energy minimum in the neighbourhood, and this was manifested in the elastic constants for the material. As these are derived from free energy, they are closely linked to the thermodynamic properties of the material. They can be related to the specific heat, the Debye temperature and parameter Grüneisen [14, 18]. Thus, there are many methods to study the characterization of materials. But few of those study the characterization for the change in Raman intensity in the spectra of materials. Isomorphous substitution of lead by lanthanum atoms induces some interesting changes in the physical properties of lead titanate (PT); for example, at a linear reduction of the Curie temperature (T_c) [19], which follows a change in the transition phase. The Raman intensity measurements are used primarily to quantitatively determine the amount, distribution and degree of crystallization of different phases of a material, i.e., the Raman mapping.

The intensities of vibrational spectra of the ceramic material were obtained for the PT pure 2.5, 5, 10, 15 and 20% of La. The efficiency of the method presented herein, shows great promise for evaluating vibration intensities reliably for a wide range of materials. These results clearly show the efficiency of the Raman intensity with respect to analyse the behaviour of the phase transition. Fig. 2 shows the evolution of the temperature of the intensities of the Raman modes $E(1TO)$ /Silent. As can clearly be seen, the intensity of all modes begins to significantly decrease with increasing temperature and dopant concentration in the PT network. This suggests that with increasing temperature the structure continuously evolves towards cubic symmetry. Raman intensities depend on the square of the polarization. It is true that doing the math to calculate the Raman intensity is very expensive and tiring and we believe this is the reason there are so few studies on the subject in the literature. The complete assignment of ceramic PTL modes of vibration was performed by analysing the dependence of Raman intensities of the modes $E(1TO)$ low frequency and the

silent mode. The temperature dependence of the Raman modes, wavenumber positions and intensities provide clear evidence of the occurrence of the phase transition. Fig. 2 shows that as the concentration increases in the material the T_c temperature decreases. However, one can also observe the phenomenon of the behaviour of the intensi-

ty as it approaches the phase transition. In Figs. 2. a) to f) shows that the intensity has a regular behaviour with increasing temperature, but as it becomes close to the phase transition the behaviour is abrupt indicating the phase transition of the material.

Fig. 2. NORMALIZATION OF THE INTENSITY $E(1TO)=SILENT$ FOR SAMPLES A) 0%, B) 2.5%, C) 5%, D)10%, E) 15% E F) 20% LANTHANUM. RAMAN SPECTROSCOPY SPECTRA AT DIFFERENT TEMPERATURES [16]. THE LINE OF EXCITEMENT AND CONDITIONS OF MEASUREMENTS WERE THE SAME FOR ALL THE SAMPLES



Source: the authors

The significant differences of the absolute intensity values are detected in the pure and doped material. That is, the increase in intensity is observed after the partial replacement of Pb by La. Once measured, intensity allows the evaluation of the distortion of the crystal structure, which shows that doping and vacancies of oxygens associated help distortions of the host network. In our opinion, the study of relative intensity Raman also is a very powerful tool in the characterization of materials.

4. CONCLUSIONS

The example of the material discussed above clearly shows that the analysis of the Raman intensity is a very powerful tool to deepen the understanding of different materials and their properties. All the samples are subjected to the same conditions at the time of making the Raman measurements. The UV-vis measurements in the samples are consistent with the values found in the literature.

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