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Influence of Structural Disorder on the Photoluminescence Emission of PZT Powders[†]

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Intense and broad visible photoluminescent (PL) band was observed at room temperature in disordered $Pb(Zr_{0,53}Ti_{0,47})O_3$ powders. Structural order−disorder was evaluated by different methods. XANES results pointed to the presence of different coordination modes of disordered Ti powders, and in the ordered sample the local structure around titanium atoms is characteristic of the structurally ordered PZT with only TiO_6 units. Only samples containing simultaneous structural order and disorder in their network present the intense visible PL emission at room temperature.

1. Introduction

The ABO_3 perovskites are among the most important classes of materials with nonlinear electro-optical properties. The development of new materials with optical properties such as electroluminescence and photoluminescence (PL) may lead to new high-performance optoelectronic devices. PL property has been observed from earlier works in semiconductors pervovskite-type titanate compounds. Canham[1] was the first to observe visible PL at room temperature. The PL emission in the visible spectrum wavelengths is an attractive property due to the possibility of high-efficiency, long-lifetime, solid-state lighting using the blue to complement existing longer-wavelength sources for white lighting.[2] A PZT nanorod with strong blue-light emission was studied by Pan et al.[3]

PZT is a solid solution of lead zirconate and lead titanate that presents piezoelectric behavior with important technological applications.[4−6] This perovskite structured material presents ferroelectric properties originating from displacive transitions of Ti^{4+}/Zr^{4+} cations between two stable off-centered sites of $TiO_6.ZrO_6$ octahedra, respectively, in response to an external field.[7] There is considerable interest in ferroelectric PZT system for their potential wide range applications in microelectronics.

PZT ceramics are very sensitive when excited with laser light in the visible spectra region. As a consequence, PL emission is observed in these ceramics depending on their structural order−disorder state.

Disorder in materials can be manifested in many ways, as for instance: vibrational, spin and orientation disorder (all referred to a periodic lattice) and topological disorder. We will concentrate principally on the latter, which is the type of disorder associated with the structure of glassy and amorphous solids in which the structure can not be defined in terms of a periodic lattice. PL is a powerful probe of certain short-range order aspects in the range 2−5 Å and medium range 5−20 Å, such as clusters, where the degree of local order is such that structurally inequitable sites can be distinguished on account of their different types of electronic transitions and because they are linked to a specific structural arrangement.

Our proposal regarding the use of these clusters is to offer a simple scheme enabling to understand the effect of structural deformations on the electronic structure, because the most intense PL emission is evidenced in PZT samples containing structural order−disorder in the lattice. In the case of the perovskite titanates−zirconates the cationic environments had 5-fold MO_5 ($M = Ti, Zr$) and 6-fold MO_6 coordinations.

In this work, our main objective is not to explain all the possible mechanisms that occur during the photon excitation and decay processes, because the literature already offers many valid hypotheses,[8,9] but to discuss the conditions that favor the generation of intense PL emission before the excitation process in PZT powders.

2. Experimental Procedure

Ordered and Disordered $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) powders were synthesized by the polymeric precursor method.[10] The disordered powders were annealed in pure alumina crucible at 300 °C at three different periods: 4 h (PZT4h), 8 h (PZT8h), and 16 h (PZT16h). The ordered powder was obtained by heat treatment at 700 °C for 3 h (PZTc).

The PZT powders were characterized by X-ray diffraction (XRD), electronic paramagnetic resonance (EPR), reflectance spectra (UV−vis), XANES spectroscopy and PL spectra measurements. All the measurements were taken at room temperature. Microstructural and morphological characterization was performed by field emission scanning electron microscopy (FE-SEM, Zeiss Supra 35), using 2 to 4 kV in different magnification.

The XRD (Cu Ka radiation) was taken in the $\theta-2\theta$ scan mode on a Rigaku RINT2000 diffractometer (42 kV × 120 mA).

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EPR spectra were recorded on a Varian E-109 Spectrometer, operating at X-band (9 GHz) and operating at microwave power 0.5mW and modulation frequency 100 kHz. The g-factor were referenced with respect to MgO:Cr^{3+} ($g = 1.9797$) as the external standard. The EPR spectra were evaluated using the SimFonia program.

Reflectance measurements (the spectral dependence of the optical absorbance/UV−vis) of powders were obtained in the total reflection mode, using a Cary 5G equipment. The same quantity of powder is used in all measurements. The powder is compacted inside the Teflon Support (with one central hole) to form a well compacted smooth surface like a pellet.

The PL spectra were collected with a digital monochromator internally integrated to a CCD with optical resolution of 1 nm and accuracy of 0.1 nm (Newport, OSM-400UV/VIS-U), using a time integration of 4 s (2.9×10^{-17} W per count/s) coupled to a fiber optic. The 355 nm exciting wavelength of a third harmonic of a Nd:YAG Q-switched laser (Brilliant B from Quantel) with a pulse duration of 4 ns and a repetition rate of 10 Hz was used, with an average energy of 4 mJ per pulse. The laser line was filtered out by a high pass glass filter, i.e., LP 385 to avoid signal saturation of the CCD. For the homogeneous powders we used a Carbon Graphite Support (which presents no luminescence and minimizes laser scattering) with a 3 mm diameter and 1 mm deep hole to compact the powders inside this aperture.

The same quantity of powder is used in all PL measurements. The powder is compacted inside the carbon graphite hole to form a well compacted smooth surface like a pellet. The optical alignment is made using micrometrics displacement devices. Once aligned and the PL signal maximized, all positions are fixed. The laser beam (~2 mm diameter) is focused onto the powder compacted inside the carbon graphite hole. The circular photoluminescence image formed in the compacted powder surface is collected with a fiber optic and focused on the CCD. This procedure is the same for all the samples, with all the alignments fixed and only one sample exchanged and returned to the aligned original position of the carbon graphite support.

The titanium K-edge X-ray absorption spectra were collected at the LNLS (National Synchrotron Light Laboratory) facility using the D04B-XAS1 beam line. The LNLS storage ring was operated at 1.36 GeV and 100−160 mA. XANES spectra of grounded samples were collected at the Ti K-edge (4966 eV) in transmission mode at room temperature using a Si(111) channel-cut monochromator. Ionization chambers were used to detect the incident and the transmitted flux. XANES spectra at the Ti K-edge were recorded for each sample between 4910 and 5100 eV using energy steps of 0.5 eV. To provide good energy reproducibility during the XANES data collection, the energy calibration of the monochromator was checked during the collection of the sample data using a Ti metal foil. For comparison purposes among different samples, all spectra were background removed and normalized using as unity the first EXAFS oscillation.

3. Results and Discussion

Figure 1 presents the field emission scanning electron microscopy (FE-SEM) image. There are no morphological differences among the PZT powders annealed at 300 °C for 4, 8 and 16 h. The FE-SEM images for PZT powder annealed at 300 °C for 16 h (Figure 1a) are typical of structurally disordered powders without structural definition.

On the other hand, PZT annealed at 700 °C for 3 h present a typical image (Figure 1b) for structurally ordered materials. It is possible to define that the morphology of the polycrystalline particles are spherical and well defined. In detail, it is possible to visualize the formation of particles. The diameter of the particles ranges between 93 to 175 nm.

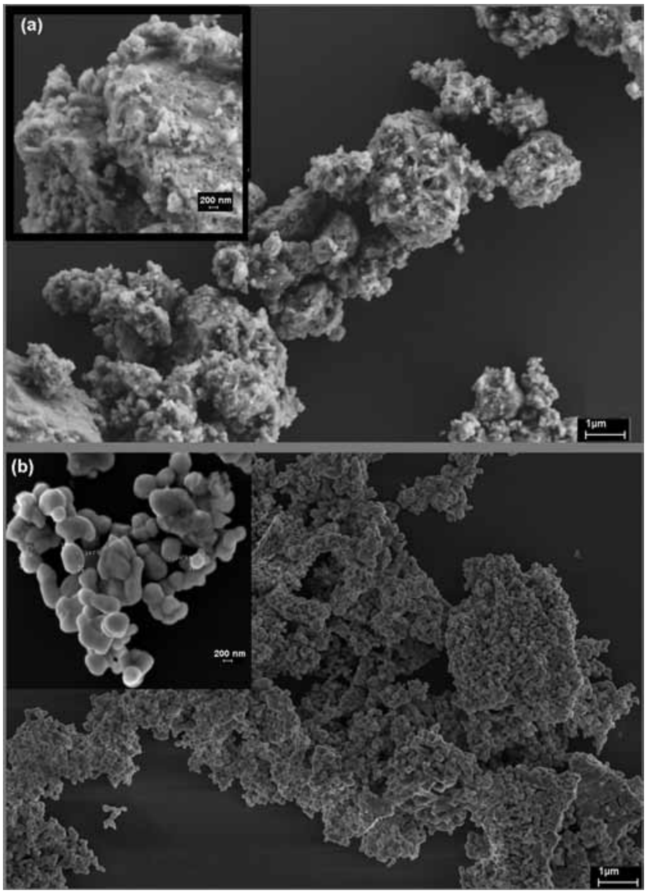

Figure 1. FE-SEM image of the PZT powder annealed at (a) 300 °C for 16 h and (b) 700 °C for 3 h.

Figure 2 shows PL spectra for the PZT powders annealed at 300 °C for 4, 8, and 16 h and annealed at 700 °C for 3 h. The PZT powders annealed at 300 °C for 4 h present a more intense PL emission. The PL emission reduces with the increase of the thermal treatment time. In addition, the PZT annealed at 700 °C does not show PL emission.

The PZT samples disordered at long-range order (annealed at 300 °C for different times) do not present morphological differences. However, the PL measurements indicate significant changes in the intensity of emission and short changes in the Stoke shift (difference between the excitation and the emission maximum). The rearrangement of the lattice was clearly detected through PL experimental measurements and strongly indicates that this measurement is highly sensitive to structural changes.

Using the Gaussian method, the PL spectra of the PZT sample annealed at 300 °C for 4, 8, and 16 h were deconvoluted into three components, herein called the blue component (maximum below 430 nm), green component (maximum below 600 nm), and red component (maximum below 730 nm), corresponding to the regions where the maximum intensity for each component appeared. These deconvolutions represent different types of electronic transitions and are linked to a specific structural arrangement.[11] Such electronic transitions are due to the existence of electronic levels in the band gap of a material, which are possibly due to structural disorder.[12] Figure 2b shows results obtained with such deconvolution. The bar graph shows that with increase of the thermal treatment time the red

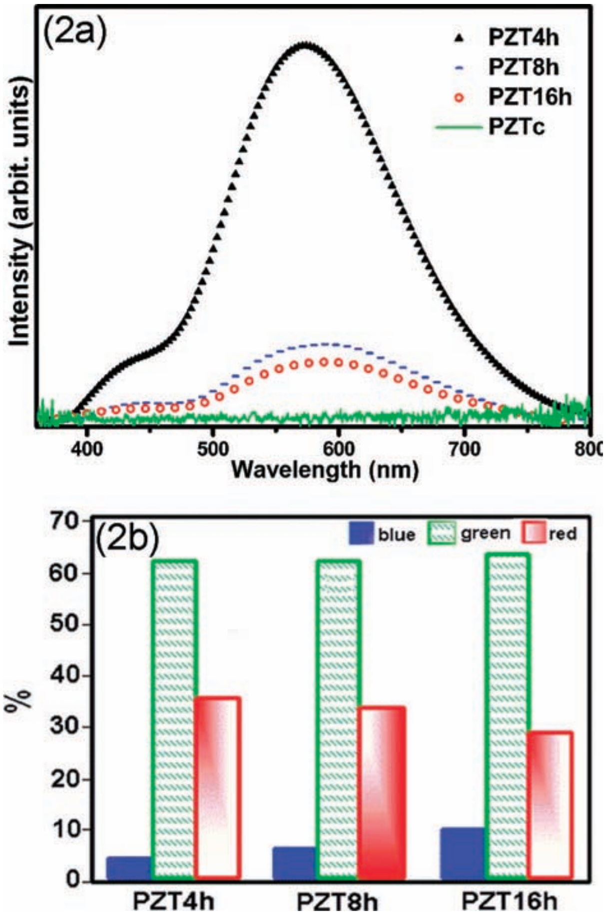

Figure 2. (a) PL spectra for PZT annealed at 300 °C for 4, 8, and 16 h annealed at 700 °C for 3 h. (b) Deconvolutions obtained by dividing the area of each deconvoluted PL curves by the total PL area.

component of PL decreases and the blue component of PL increases. This behavior pointed to changes in the localized states inside the band gap linked to the increase in the structural order.

The red component represents the less energetic electronic transitions that occur in the band gap and are thus linked to states that are deeply inserted in the band gap. Conversely, the blue component, more energetic, can be linked to shallow defects in the band gap.[13] In the annealing process the disorder powders become more ordered with increased annealing times and this structural change also alters the electronic levels in the band gap allowing for the predominance of shallow defects and the increase of blue light emission. With the crystallization process at 700 °C, the defects vanish as well as the PL emission.

The photoluminescence spectra at room temperature for materials present a line shape typical of the multiphonon process; i.e., they have several relaxation channels indicative of a broad energy band gap. Although these are disordered materials, it is also well-known that the details of a band structure in solids are mainly determined by their potential within the unit cell rather than by long-range periodicity. Thus, the broadband PL emission consists of the sum of individual emissions (Figure 2). Such emissions arise from a radiative recombination between trapped electrons and trapped holes in the gap states. Then, the transitions for disordered titanates occur at energies far less than the band gap of these materials.

The effect of structural order in the photoluminescent property of materials has been studied in recent years.[14,15] The PL at room temperature occurs due to structural disorder of the system. Therefore, if the system is totally disordered, then the PL does not exist; moreover, a totally ordered system does not exhibit PL.[12,14] The analysis of structural disorder in these PZT powders helps to understand the origin of PL emission.

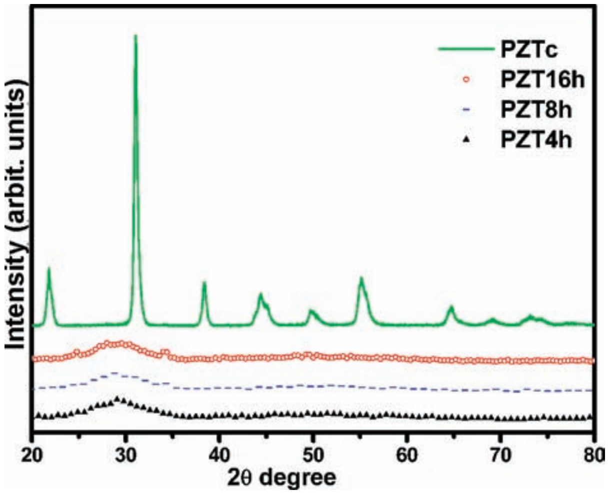

Figure 3. XRD diffractograms for PZT annealed at 300 °C for 4, 8, and 16 h and annealed at 700 °C for 3 h.

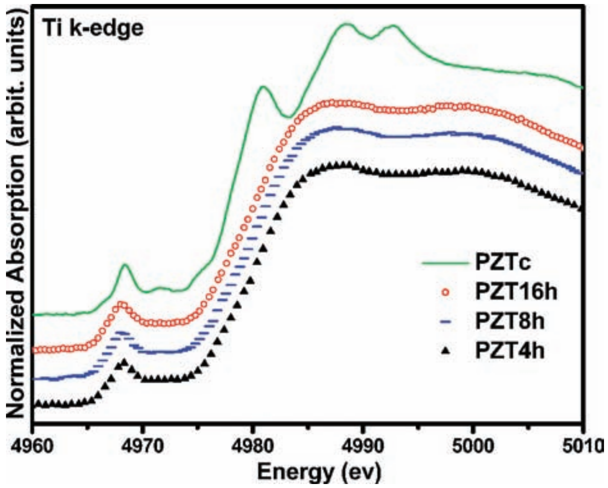

Figure 4. Results Ti K-edge XANES spectra for PZT powders annealed at 300 °C for 4, 8, and 16 h and annealed at 700 °C for 3 h.

Figure 3 presents X-ray diffractograms of the PZT powders annealed at 300 °C for 4, 8 and 16 h and annealed at 700 °C. XRD analysis shows that all powders annealed at 300 °C are structurally disordered in the long-range, once they do not show diffractions peaks. On the other hand, PZT annealed at 700 °C is structurally ordered, once the presence of diffractions peaks in the XRD evidence structural ordered at long-range structure at distances ≥20 Å.

The XRD analysis corroborates with PL results. The structurally ordered PZT (annealed at 700 °C) does not show PL emission; on the other hand, the structurally disordered PZT (annealed at 300 °C) presents PL emission.

The system is influenced by short-range structural order. Such order can be available by XANES spectroscopy,[16−18] while providing information about the electronic state and chemical bond of a specific atom. Previous XANES results for titanate powders pointed out the coexistence of two types of environments for the titanium, namely, a 5-fold (TiO_5) square-base

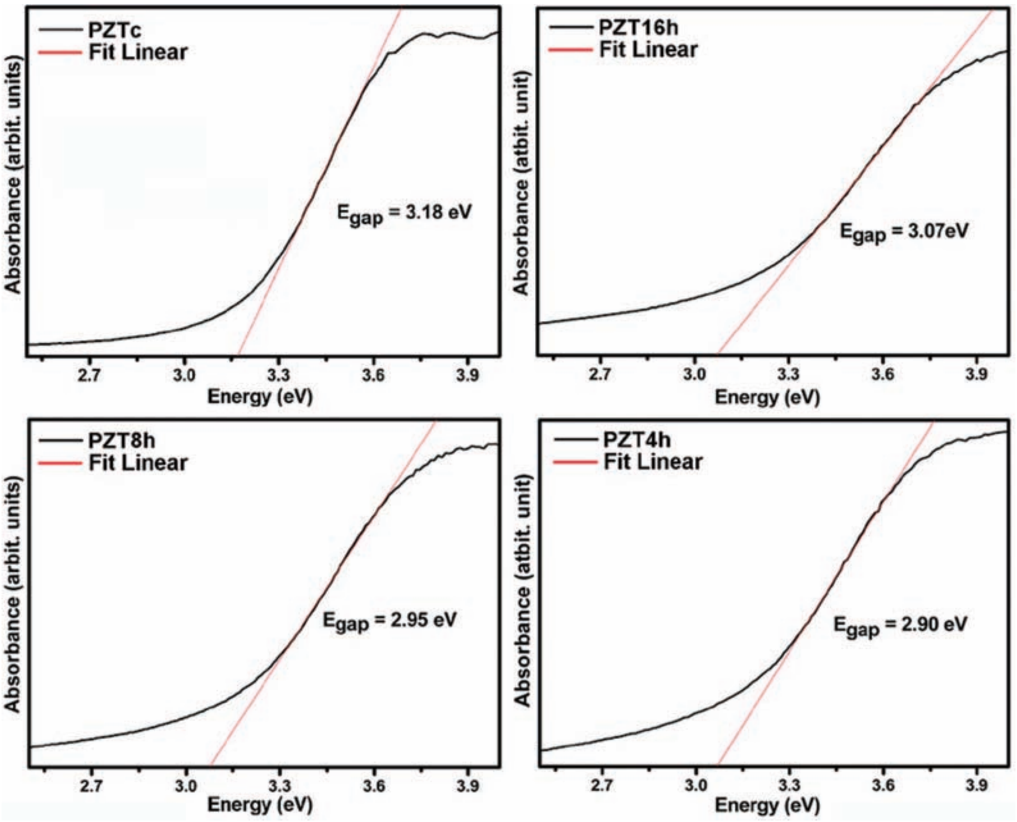

Figure 5. Spectral dependence of the absorbance for the PZT powders heat treated at 300 °C for 4, 8, and 16 h and annealed at 700 °C for 3 h.

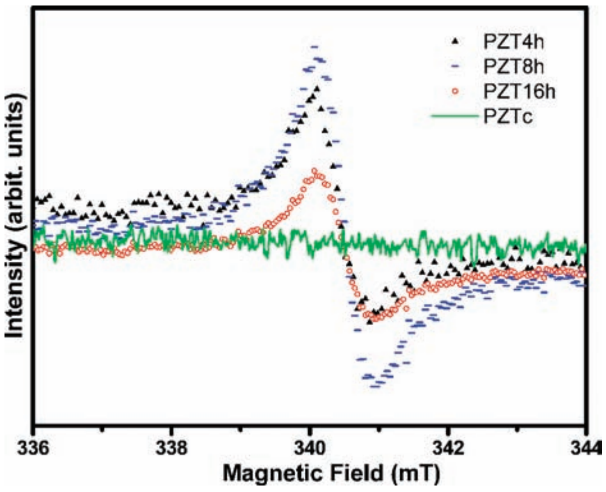

Figure 6. EPR spectra for the PZT powders heat treated at 300 °C for 4, 8, and 16 h and annealed at 700 °C for 3 h.

pyramid and a 6-fold coordination (TiO_6) octahedron. The structural order is related to the presence of TiO_6 clusters, whereas the structural disorder is related to the presence of TiO_5 clusters. PL emission occurs due to interaction of the TiO_5-TiO_6 pair.[14]

The results for Ti k-edge XANES are shown in Figure 4. The XANES spectrum for PZT annealed at 700 °C reveals that the local structure around titanium atoms is characteristic of the structurally ordered PZT with only TiO_6 units, in good agreement with XRD and PL data. However, the PZT powders annealed at 300 °C do not present this kind of order. In these powders there is more than a single coordination mode for titanium. These results are in agreement with PL and XRD results. The observation of a large peak after the edge of the spectra of these samples could also be interpreted as the existence of a certain degree of disorder at the environment around titanium atoms when compared to structurally ordered ones.[14,16−18]

Figure 5 shows the spectral dependence of the absorbance measured for PZT powders annealed at 300 °C for 4, 8, and 16 h and annealed at 700 °C. The absorption spectra of the samples treated at 300 °C for 4, 8, and 16 h present the typical shape of the spectra of structurally disordered semiconductors with absorption tails below the exponential part of the edge.

Wood and Tauc[19] associated these absorption tails with localized states in the band gap linked to structural defects in the lattice. The value of the experimental gap energy at room temperature for structurally ordered PZT heat treated at 700 °C calculated by Silva et al. is 3.16 eV.[20] According to Liu et al.[21] the energy gap was estimated to be about 3.2 eV for the structural ordered PZT. The value gap obtained by theoretical calculus for PZT is 3.03 eV.[10] In this work, the value gap for structural ordered PZT is 3.18 eV.

For the structurally disordered powders, the curve presents a continuous smooth absorption increase as a function of the energy, suggesting the presence of localized states inside the band gap.[12] The creation of these localized sates can be provoked by the presence of oxygen vacancies.[22,23] The presence of oxygen vacancies in structurally disordered PZT powders is supported by a coexistence of different types of environments for titanium, evidenced by XANES results, given that the reduction of the TiO_6 cluster to TiO_5 cluster may be accompanied by the creation of electron-captured oxygen vacancies. Oxygen vacancies there are not alone, they are bonded to neighbors. In this case, oxygen vacancies are bonded to TiO_5 cluster and this bonding can form three different species with distinct charge states: the [$TiO_5 \cdot V_O^x$] complex states which have captured electrons and are neutral with respect to the lattice, the singly ionized [$TiO_5 \cdot V_O^{\bullet}$] complex state, and the [$TiO_5 \cdot V_O^{\bullet\bullet}$] complex state which did not trap any electrons and is doubly positively charged whith respect to the lattice.

EPR spectroscopy was used to investigate the presence of singly ionized [$TiO_5 \cdot V_O^{\bullet}$], due to the sensitivity of this technique to the presence of unpaired electrons. Figure 6 shows EPR spectra for PZT powders annealed at 300 °C for 4, 8, and 16 h and annealed at 700 °C. PZT annealed at 700 °C present silent EPR; thus this powder does not present paramagnetic species. On the other hand, PZT annealed at 300 °C for 4, 8, and 16 h shows EPR signal, confirming the presence of paramagnetic species, which are attributed to singly ionized [$TiO_5 \cdot V_O^{\bullet}$]. These data are in agreement with the results of PL, XRD, UV−vis and XANES presented in this work.

To rationalize the links between PL and structural disorder (TiO_5 or ZrO_5 and TiO_6 or ZrO_6 clusters), a detailed theoretical study of the electronic structure in two model compounds was performed, a crystalline (TiO_6-TiO_6/ZrO_6-ZrO_6) and a disordered (TiO_6-TiO_5/ZrO_6-ZrO_5) cluster.[24]

The proposed hypothesis from studies on the origin of PL in disordered PZT is that to exhibit room temperature PL, a system must fulfill two conditions: (i) possess at least two types of differently charged clusters creating a polarization of the structure and (ii) present some localized levels inside its band gap, levels that for the most part a result from some structural disorder.

The junction of these two conditions allows an easy trapping of electrons and holes during excitations and thus favors the radioactive decay causing PL emission.

4. Conclusion

The PL emissions in ordered PZT powders were nonexistent. For the samples containing a high structural disorder degree, the intense PL emission is also not favorable. The intense and broad visible PL emissions were evidenced in PZT powders simultaneously containing order and disorder in the structure. PL behavior for the PZT compound can be summarized as follows: the intensity of the PL emission, previously discussed, undergoes alterations according to the evolution of the structural short- and long-range order in the structure of the material. The structural order−disorder was available by different methods. Analyses of broadband PL emission and XANES spectra have shown that it is possible to relate the PL emission of PZT to short- and long-range structural ordering based on the order−disorder concept.

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