



## The nature of the photoluminescence in amorphized PZT

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### Abstract

The polymeric precursor method was used to synthesize lead zirconate titanate powder (PZT). The crystalline powder was then amorphized by a high-energy ball milling process during 120 h. A strong photoluminescence emission was observed at room temperature for the amorphized PZT powder. The powders were characterized by XRD and the percentage of amorphous phase was calculated through Rietveld refinement. The microstructure for both phases was investigated by TEM. The optical gap was calculated through the Wood and Tauc method using the UV–Vis. data. Quantum mechanical calculations were carried out to give an interpretation of the photoluminescence in terms of electronic structure.

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### 1. Introduction

Ever since Canham [1] first observed visible photoluminescence at room temperature in porous silicon, the study of photoluminescence (PL) in disordered or nanostructured materials has focused on the development of new materials, owing to their potential technological applications including piezo-electric sensors, dynamic random-access memory

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(DRAM) and non-volatile ferroelectrics random-access memory (NFRAM) devices [2,3].

The  $\text{ABO}_3$  perovskites form one of the most important classes of materials with non-linear electro-optical properties [2]. In the semiconducting titanates perovskite-type compounds, various luminescence phenomena have been detected during the past decades. They have mostly been studied in crystalline samples at liquid nitrogen temperature [4–9]. PL at room temperature in amorphous titanates synthesized by low-temperature routes in the form of thin films or powders has been reported only recently [10–18].

Liu et al. [19] are, to our knowledge, the only ones to have reported the room temperature photoluminescence of PZT. They synthesized PZT films by RF-sputtering technique followed by a heat treatment at 750 °C in  $\text{Ar}/\text{H}_2$  atmosphere to create oxygen vacancies. However, although Lanciotti et al. and Santos et al. [13,15] recently reported intense visible PL at room temperature in amorphized  $\text{PbTiO}_3$  compounds by high-energy mechanical milling, PL of amorphized PZT has not yet been studied.

In this paper, we present an alternative method to process PL in PZT and aim to explain why this phenomenon depends on the crystalline structure of the material.

## 2. Experimental

In this work, crystalline PZT powder was synthesized by the polymeric precursor method. This process is based on the chelation of cations (metals) by citric acid in a water solution. The citrate solution is mixed with ethylene glycol to promote polymerization through a polyesterification reaction maintaining the cations homogeneously distributed. The organic part is subsequently eliminated at low-temperature forming reactive oxides with well-controlled stoichiometry [16,20]. Pure PZT, with composition  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ , was prepared from the metal-citrate complex polyesterified in ethylene glycol at 90 °C. Next, the temperature is increased to 140 °C, yielding to a high-viscosity polyester resin. Most of the organic material was decomposed in a

box furnace by carefully heating the polyester from room temperature up to 300 °C for 2 h. Then, the temperature was increased to 400 °C for 2 h and 500 °C for 2 h to eliminate the residual organic material. At each temperature step, the powder was crushed in mortar. Further calcination was conducted at 700 °C for 3 h to promote crystallization. The crystalline PZT powder was mechanically milled in a high-energy attritor for varying lengths of time and the amorphization process was followed by X-ray diffraction (XRD) ( $\text{Cu K}_\alpha$  radiation) in the  $2\theta$ – $\theta$  scan mode recorded on a Rigaku<sup>®</sup> RINT2000 diffractometer (42 kV  $\times$  120 mA). The amorphous crystalline phases fractions were calculated through Rietveld refinements [21,22] using  $\text{Cu K}_\alpha$  radiation ( $\lambda_{\text{k}\alpha 1} = 1.5405 \text{ \AA}$ ,  $\lambda_{\text{k}\alpha 2} = 1.5443 \text{ \AA}$ ,  $I_{\text{k}\alpha 1}/I_{\text{k}\alpha 2} = 0.5$ ), in the  $2\theta$  range between 20° and 70°, step 0.02° ( $2\theta$ ) with 3.5 s per point. The divergence slit was 0.5 mm and the receiving slit 0.3 mm.

The Rietveld refinements were performed using the General Structure Analysis System (GSAS) package [23]. The peak profile function was modeled using a convolution of the Thompson–Cox–Hastings pseudo-Voigt [24] with the asymmetry function described by Finger et al. [25], which accounts for the asymmetry due to axial divergence. X-ray diffraction analysis with internal standard was performed to determine the percent of amorphous phase.  $\text{CeO}_2$  was used as the internal standard. The powder mixture was prepared from 90 wt% of PZT sample and 10 wt% of  $\text{CeO}_2$ .

The spectral dependence of the reflectance of the crystalline and amorphized powder was taken in the total-reflection mode, using a Cary 5G instrument.

PL was measured using a U1000 Jobin–Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon-counting system. The 488.0 nm exciting wavelength of an argon-ion laser was used, with the laser's maximum output power kept within 200 mW. All the measurements were taken at room temperature.

The transmission electron microscopy (TEM) images of the powders was made in a Philips CM 200.

Quantum mechanical calculations were carried out within the framework of the Density Functional

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