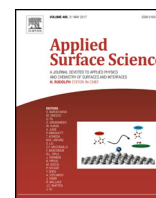




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Full Length Article

# Discrimination of polar order extent in BaZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> epitaxial thin films by Raman spectroscopy

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## ABSTRACT

Raman spectroscopy studies of BaZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> (BZT) epitaxial thin films are presented over the entire compositional range ( $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1$ ). The analysis of the results has allowed the elaboration of the phase diagram of the BZT thin films in which three types of ferroelectric behaviour were distinguished based on the polar order extent: long range conventional ferroelectricity for  $x \leq 0.2$ , relaxor behaviour for  $0.3 \leq x \leq 0.7$  and weak polar interaction for  $0.8 \leq x \leq 0.9$ . In order to verify the validity of this phase diagram, Raman spectra of the films were also performed over a wide temperature range (from 97 K to 497 K). The results reveal that the presence or absence of a temperature dependent structural transition correlates with the polar order extent and, thus, the ferroelectric behaviour of BZT.

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## 1. Introduction

BaZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> is among the most widely investigated perovskite systems due to the possibility to tailor its ferroelectric properties by controlling the composition. This solid solution of ferroelectric BaTiO<sub>3</sub> and paraelectric BaZrO<sub>3</sub> yields different behaviors such as relaxor ferroelectric and polar-cluster behaviour [1]. The dynamic coupling between BaTiO<sub>3</sub> polar nanoregions and BaZrO<sub>3</sub> nonpolar ones is thought to be behind such a rich variety of properties. Ferroelectric Ti-rich regions in BZT are expected to be separated by non-polar Zr-rich regions [2–4] leading to an inhomogeneous cationic distribution and mechanical stress [5]. The size and volume fraction of the polar nanoregions in BZT is controlled by the Zr molar fraction, opening an interesting route to a better understanding of the relaxor phenomenon. On the other hand, there are evidences [2,3,6–8] that BZT presents some singularities as compared to canonical relaxors. However, these short-range compositional variations are elusive to detect and this topic is thus rarely addressed.

In a previous work [9] we have reported the growth of 100 nm thick BaZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> epitaxial thin films on (001)SrTiO<sub>3</sub> by pulsed laser deposition (PLD) sweeping the entire compositional range

between BaTiO<sub>3</sub> and BaZrO<sub>3</sub> in increments of 0.1 in  $x$ . X-ray diffraction showed that their crystal structure was fully relaxed in a single cube-on-cube domain configuration with an average unit cell size proportional to the Zr molar fraction. This suggested a proper intermixing of Zr<sup>4+</sup> and Ti<sup>4+</sup> into an average BZT lattice.

In this paper we report a Raman spectroscopy study of BZT thin films in order to provide knowledge about their short and medium range structural order. So far as we know it is the first time that such study is done for this material obtained in thin film form. The method to identify the polar order extent in BZT bulk ceramics recently introduced by Buscaglia et al. [10] for some compositions is extended here to our BZT thin films which have been obtained in the entire compositional range. Moreover, Raman spectra of the films were performed at different temperatures with the purpose of detecting any structural change in the films.

## 2. Experimental

The BZT thin films were grown on (001) SrTiO<sub>3</sub> (STO) substrates by PLD using a KrF excimer laser (Lambda Physik 210i) with a fluence of 2.0 J/cm<sup>2</sup> and a repetition rate of 5 Hz [9]. Stoichiometric targets of BaZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> sweeping the entire composition range between BTO and BZO in increments of 0.1 in  $x$  were used (*i.e.*  $x = 0, 0.1 \dots 1$ ). The substrate temperature and oxygen pressure were set to 700 °C and 0.3 mbar respectively; the substrate-to-target distance was 5 cm. After deposition, the samples were cooled down to

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room temperature under an O<sub>2</sub> rich atmosphere to minimize oxygen desorption. The thickness of the films presented here is 100 nm as verified by low angle X-ray reflectometry. Atomic concentrations were measured by wavelength dispersive spectroscopy (WDS).

Raman scattering measurements were performed with a micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR800), equipped with a notch filter and a Peltier cooled multichannel CCD detector, using as excitation an UV radiation source (He–Cd laser, 325 nm) in back-scattering configuration. The ultraviolet laser was used instead of a conventional visible one because the high optical transparency along with the low thickness of the BZT films resulted in a very weak Raman signal from the layer with predominance of the signal from the substrate. Additionally, excitation with ultraviolet light, with photon energy higher than the bandgap energy of the material, maximizes the optical absorption and the subsequent excitation of the Raman active modes coming from the layer.

However, the minimum detectable wavenumber using the UV laser source is around 290 cm<sup>-1</sup> so the study of lower energy modes could not be carried out. The laser light was focused onto a surface area of about 6 μm of diameter yielding an irradiance below 1.5 W/mm<sup>2</sup> to prevent the sample from being heated. Raman activity measurements at different sample temperatures between 97 K and 497 K with increments of 20 K were performed by means of a Linkam heating-cooling module.

### 3. Results and discussion

The Raman spectra of the BZT films at room temperature are shown in Fig. 1 [9]. The modes present in the spectrum of the  $x = 0$  (BaTiO<sub>3</sub>) film agree with those of the P4 mm tetragonal ferroelectric

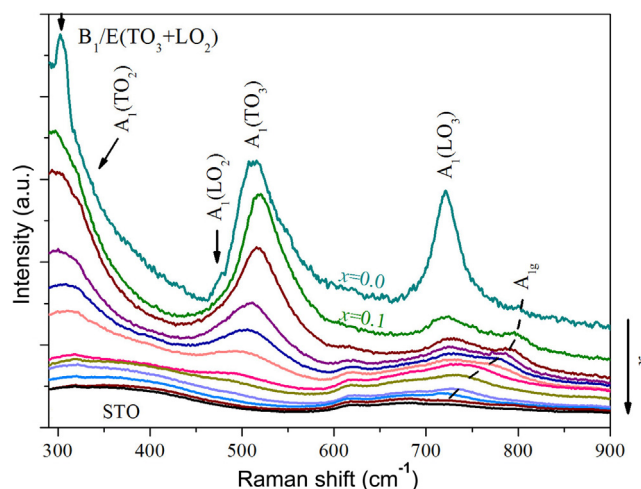


Fig. 1. Raman spectra of the BZT samples and of the STO substrate (in black).

phase [11,12], in accordance with the XRD results [9]. The coexistence of the A<sub>1</sub>(TO<sub>3</sub>) and the A<sub>1</sub>(LO<sub>3</sub>) (stretching Ti–O into TiO<sub>6</sub> octahedra) vibrational modes indicates the simultaneous presence of *c* and *a* oriented domains [13] where the polar axis is perpendicular and parallel to the plane of the layer, respectively. The Raman spectra changes substantially with the partial substitution of Ti<sup>4+</sup> by Zr<sup>4+</sup>. The evolution of the spectra with the composition shows no separation of the BaTiO<sub>3</sub> and BaZrO<sub>3</sub> modes but a gradual change of the vibration modes of BaTiO<sub>3</sub> (*i.e.* monomodal behaviour). The increase in both structural and compositional intrinsic disorder [10]

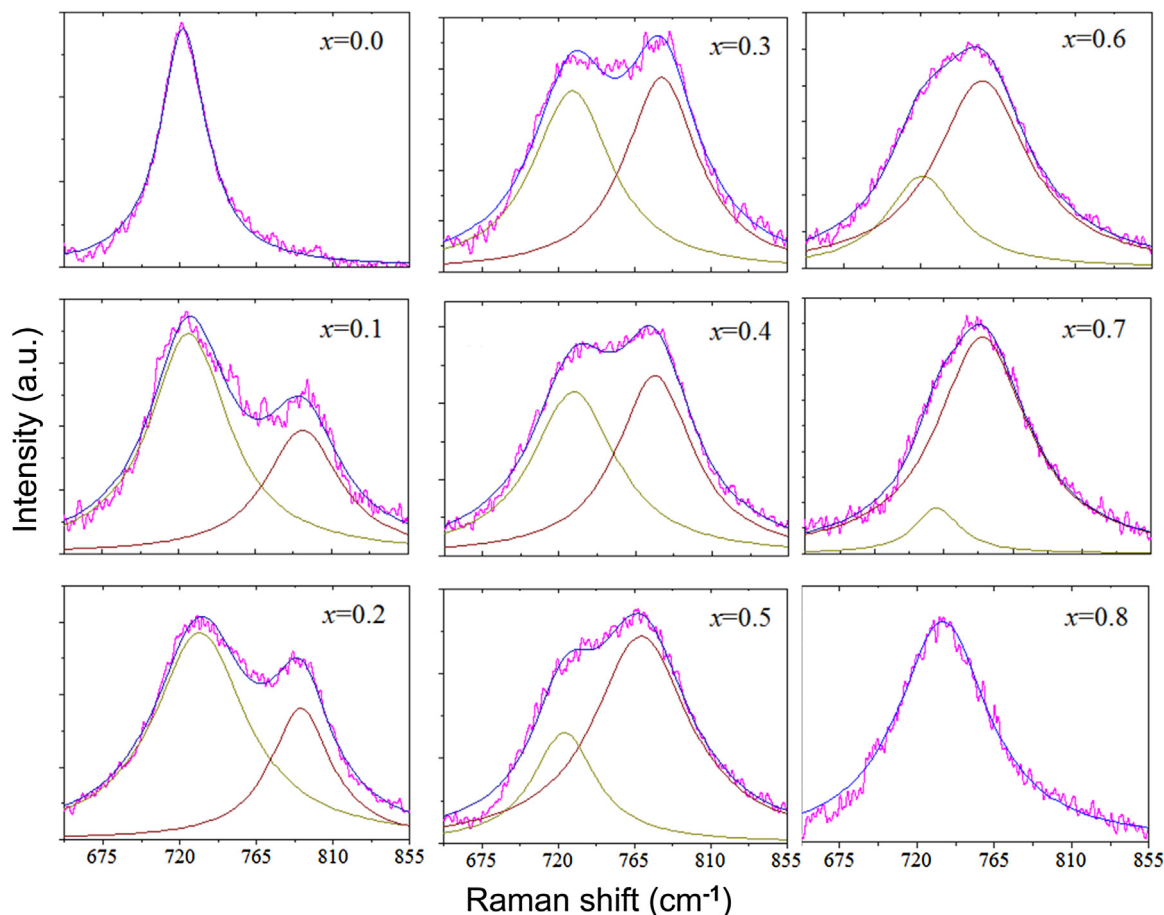


Fig. 2. Decomposition of the Raman spectra of the BZT samples into A<sub>1</sub>(LO<sub>3</sub>) (—) and A<sub>1g</sub> (—) modes (— experiment, — fit).

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