Photoluminescence and evolution of polar order in Eu:BaZr , Ti_{1-x}O₃ ceramics UNIVERSITÀ DEGLI STUDI G. Bottaro,¹ G. Canu,² M. T. Buscaglia,² C. Costa,² O. Condurache,³ V. Preutu,³ L. Curecheriu,³ L. Mitoseriu,³ L. Armelao,^{1,4} V. Buscaglia² DI PADOVA ¹ICMATE-CNR and INSTM, Department of Chemical Sciences, University of Padova, Via F. Marzolo 1, 35131 Padova, Italy ² ICMATE-CNR, Via De Marini 6, 16149 Genoa, Italy ³Department of Physics, Alexandru Ioan Cuza University, 11 Blvd. Carol I, 700506 Iasi, Romania ⁴Department of Chemical Sciences, University of Padova, Via F. Marzolo 1, 35131 Padova, Italy *Corresponding Author: vincenzo.buscaglia@ge.icmate.cnr.it ALEXANDRU IOAN CUZA

INTRODUCTION

BaTiO₃-based ferroelectric ceramics show interesting properties such as high dielectric constant, low losses, high hydrostatic piezoelectric coefficient and PTCR effect. For these reasons, barium titanate is widely used in the electronic industry for manufacturing miniaturised multilayer ceramic capacitors, underwater transducers and self-regulating thermistors. BaTiO₃ can be considered as the prototype of ferroelectric oxides with perovskite structure. Phase transitions and properties of BaTiO₃ can be strongly modified by formation of solid solutions. BaZr_xTi_{1-x}O₃ (BZT) solid solution possesses the perovskite structure and shows a series of phase transitions and a progressive evolution of ferroelectric order from long-range order typical of classic ferroelectrics (x = 0-0.15), via a diffuse transition behaviour (x = 0.15-0.25), to short-range order typical of relaxors (x \ge 0.25) and finally paraelectric non polar state for neat BaZrO₃. The trivalent europium ion (Eu³⁺) is well known for its strong luminescence in the red spectral region. Even very small variations in the coordination sphere of europium ions induce major changes in the emission spectrum. Thanks to these features, Eu³⁺ is a unique and powerful local structural probe. In this framework, we used photoluminescence (PL) as a tool to investigate phase transitions and ferroelectric order in BZT ceramics using Eu³⁺ as active centre.

EXPERIMENTAL

RESULTS AND DISCUSSION

Dense ceramics (relative density: 96-99 %) with composition $Eu_{x}Ba_{1-x}Zr_{y}Ti_{1-y-x/4}O_{3}$ (x = 0.01, y = 0, 0.05, 0.15, 0.30, 0.50, 0.70 and 1) were prepared by the classical solid-state route and sintered at 1450-1500 °C.

The stoichiometry is formulated to promote Eu³⁺ incorporation at the Ba site. The dielectric permittivity of the samples was measured from -150 to 150 °C and at 10²-10⁶ Hz to determine reference values of the phase transition temperatures.

Room temperature photoluminescence experiments have been carried out with an Horiba Fluorolog 3 spectrofluorimeter equipped with double-grating monochromator in both the excitation and emission sides coupled to a R928P Hamamatsu photomultiplier and a 450 W Xe arc lamp as the excitation source. Temperature-dependent experiments (-100 °C < T < 140 °C) have been performed using the third stage of an Horiba T64000 triple spectrometer equipped with a Peltier cooled CCD detector (Horiba Synapse) using a backscattering acquisition geometry and a 450 W Xe arc lamp as the excitation source.

Dielectric permittivity

The permittivity provides the phase transition temperatures and some insight into the polar order as a function of composition. At y=0 the Curie temperature, corresponding to the cubic (C) paraelectric to the tetragonal (T) ferroelectric transition, is 125 °C.

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With decreasing temperature, two ferro/ferro transitions are observed: tetragonal to orthorhomic (O) at about 10 °C and orthorhombic to rhombohedral (R) at -70 °C. The transitions become progressively more diffuse with increasing y. At y = 0.15 only a very broad R/C transition with coexistence of different polymorphs is observed. When $y \ge 0.30$, a typical relaxor behaviour is observed and there is no longer a phase transition but only a dielectric relaxation peak, determined by the orientation of the polar nanoregions in a paraelectric matrix.



Photoluminescence

The study of PL spectra as function of the temperature, in the interval -100 to 140 °C, reveals strong variations of the shape and relative intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (J = 0, 1, 2, 4) bands typical of Eu³⁺ luminescence.

The degeneracy of each J multiplet can be fully removed in low symmetry sites thus originating a complex spectrum. Bands with J even correspond to electrical dipole transitions and are sensitive to local symmetry variations, especially the band J = 2. Detailed analysis of high resolution spectra revealed the existence of at least two spectroscopic sites. More complex behaviours have been evidenced in the sample characterised by a low Zr⁴⁺ content. The temperatures corresponding to the phase transitions, determined from permittivity measurements, are indicated by black horizontal lines.



- 1. Below \approx -10 °C, the spectra do not show significant variations. It is worth noting that the bands J = 4 have an anomalously high intensity.
- exception of ceramic y = 0. With further increasing temperature, the intensity of the J = 2 bands gets progressively higher.



> Significant intensity variations, but at lower temperature, are also observed for y ≥ 0.30 , suggesting a correlation with the existence of polar nanoregions in relaxors.

 \geq In contrast, the composition y = 1 (BaZrO₃) show no significant variations of bands relative intensity with temperature.