**Photoluminescence and evolution of polar order in Eu:BaZr_{x}Ti_{1-x}O_{3} ceramics**

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**INTRODUCTION**

BaTiO_{3}-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 thermostats.

BaTiO_{3} can be considered as the prototype of ferroelectric oxides with perovskite structure. Phase transitions and properties of BaTiO_{3} can be strongly modified by formation of solid solutions. BaZr_{x}Ti_{1-x}O_{3} (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 ≥ 0.25) and finally paraelectric non polar state for neat BaZrO_{3}. The trivalent europium ion (Eu^{3+}) 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, Eu^{3+} 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 Eu^{3+} as active centre.

**EXPERIMENTAL**

Dense ceramics (relative density: 96-99 %) with composition Eu_{x}Ba_{1-x}Zr_{x}Ti_{1-x}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 Eu^{3+} incorporation at the Ba site. The dielectric permittivity of the samples was measured from -150 to 150 °C and at 10^{-10} Hz to determine reference values of the phase transition temperatures. Room temperature photoluminescence experiments have been carried out with an Horiba Fluorolog 3 spectrophotometer 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 Pelletier cooled CCD detector (Horiba Synapse) using a backscattering acquisition geometry and a 450 W Xe arc lamp as the excitation source.

**RESULTS AND DISCUSSION**

**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 4D_{0} → 2F_{5} (J = 0, 1, 2, 4) bands typical of Eu^{3+} 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 characterized by a low Zr^{4+} content. The temperatures corresponding to the phase transitions, determined from permittivity measurements, are indicated by black horizontal lines.

In the classical ferroelectric regime (y = 0 - 0.15) three different regions can be observed:

1. Below -10 °C, the spectra do not show significant variations. It is worth noting that the bands J = 4 have an anomalously high intensity.
2. Between 0 and 20/30 °C, the intensity of the J = 1 transition rapidly increases while that of the J = 4 transition decreases with exception of the y = 0. With further increasing temperature, the intensity of the J = 2 bands gets progressively higher.
3. Above 100 °C the band J = 2 becomes dominant and a couple of very broad shoulders appear between 630 and 650 nm.

The sample with relaxor behaviour (y = 0.30) shows only two distinct regions with cross-over in the range -20 to 0 °C.

The paraelectric ceramines (BaZrO_{3}, y = 1) shows more conventional PL spectra dominated by the J = 1 transition and similar to those of many oxides.

**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. With decreasing temperature, two ferro/ferro transitions are observed: tetragonal to orthorhombic (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 ≥ 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.

**CONCLUSIONS**

- The remarkable variation of the PL spectra with temperature in Eu_{x}Ba_{1-x}Zr_{x}Ti_{1-x}O_{3} ceramics is clearly related to the existence of a ferroelectric polar order, either of long- or short-range type.
- When y = 0 (BaTiO_{3}), the variation of band intensity well correlates with the T/C and O/T phase transitions whereas the R/O transition has no influence on the intensity of the 4D_{0} → 2F_{5} bands.
- With increasing y (0.05, 0.15), the temperature (T_{F}) corresponding to the fastest variation of R_{i} with T remains constant whereas the O/T phase transition temperature increases. This means that a variation of the local symmetry around Eu^{3+} occurs before the macroscopic phase transition takes place or, differently, that two different sites contribute to PL with a cross-over of their relative importance at T_{F}.
- 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.
- In contrast, the composition y = 1 (BaZrO_{3}) show no significant variations of bands relative intensity with temperature.