Synthesis and photoluminescent proprieties of barium zirconate doped with Eu$^{3+}$

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Abstract – We report in this work a microwave–hydrothermal route providing synthesis of Eu$^{3+}$ doped BaZrO$_3$ (BZ) micro-sized. The powders of Eu$^{3+}$ doped BaZrO$_3$ (BZ:Eu$^{3+}$) were characterized by powder X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), Fourier transform Raman spectroscopy (FT-Raman) and photoluminescence (PL). The emission spectrum line shape exhibits transitions from the excited $^5D_0$ state to $^7F_J$ ($J = 1, 2, 3, 4$) levels of the Eu$^{3+}$ ion and transitions from probably the existence of the local of disorder in the network of both ZrO$_6$ octahedral and dodecahedral (BaO$_{12}$) clusters.

In this work, microcrystalline BZ doped with 0.1, 0.2, 0.4 mol % Eu$^{3+}$ and BZ-pure were synthesized by microwave assisted hydrothermal (HTMW) method. BaZrO$_3$ is a cubic oxide perovskite and the perovskite-type oxides have shown interesting results in use as host materials for rare earth luminescence$^{[1]}$, these microsize polyhedral crystals are functionalized by introducing rare earth ions into the crystal lattice, which endows the microcrystals luminescent properties and provides new opportunities for BaZrO$_3$ ceramics applications.

Various methods have been employed to synthesize metal zirconates and Komarmeni et al.$^{[2]}$ has introduced the microwave assisted hydrothermal (HTMW) method for synthesis of several electro ceramic powders. The HTMW method use low temperature and fast reacting than the others methods.

The XRD of all synthesized sample shows phase-pure cubic perovskite BaZrO$_3$ (JCPDS 06-0399). The behavior of the Eu$^{3+}$ lattice modifier was followed in a long-range order by XRD, while (FT-Raman) spectroscopy was used to analyze the short-range order. The room temperature Raman spectra show BZ cubic phase with smallest incrustations of $m$-ZrO$_6$, $t$-ZrO$_6$ and BaCO$_3$. The (FE-SEM) images of the products are similar in shape and size. Room temperature photoluminescence (PL) spectra (Fig. 1) of the synthesized BaZrO$_3$ crystals with different doping concentrations are investigate with the excited wavelength at 350.7 nm. The thin and intense red emission peak around 612 nm is due to the $^5D_0 \rightarrow ^7F_2$ transition expected from the Judd–Ofelt selection rules. In these spectra the presence of the bands at 591, 651 and 698 nm were also observed, which are respectively attributed to the $^5D_0 \rightarrow ^7F_J$ ($J = 1, 3$ and $4$) transitions of the Eu$^{3+}$. The spectra of all samples show blue-green emission peak and blue emission peak, both peak are related with broad and strong peaks. Significantly, the bands differ only in their intensities that vary with the dopant concentrations. These broad intense luminescence bands of the PL spectra is observed, hence the charge transference in the ZrO$_6$ octahedral and dodecahedral (BaO$_{12}$) clusters. The clusters may be responsible for the PL behavior resulting from the structural order–disorder in the BZ lattice. However, the increase or decrease of the number of clusters affects the structural order in the system, reducing or increasing the PL intensity. We related the PL emission in the BZ:Eu$^{3+}$ lattice as a consequence of its structural evolution in terms of the structural order–disorder.

Figure 1: a) Room temperature photoluminescence spectrum of samples synthesized at 140º for 40 minutes with a) BZ-pure. b) BZ-Eu$^{3+}$ 1.0 % mol. c) BZ-Eu$^{3+}$ 2.0 % mol. d) BZ-Eu$^{3+}$ 4.0 % mol.

References