

## **BaZrO<sub>3</sub>:Yb NANOPHOSPHOR FOR EFFICIENT UP-CONVERSION LIGHT EMISSION**

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**Abstract**—Strong visible green upconversion emission in nanocrystalline BaZrO<sub>3</sub>:Yb<sup>3+</sup> powder, obtained by a hydrothermal process at 100°C, is reported. The unconverted emission has a quadratic dependence on the pump intensity with a lifetime around half that of the NIR lifetime. Results suggest cooperative upconversion as the mechanism responsible for the green fluorescence. This efficient Yb<sup>3+</sup>-based cooperative up-conversion process allows the development of novel emitting materials in the ultraviolet to visible (UV-VIS) range.

### **1. INTRODUCTION**

Frequency up-conversion phenomena in trivalent Rare-Earth (RE) ions, hosted in a number of matrixes, have been widely investigated in the past two decades, due to their potential use as visible-wavelength luminescent materials [1–11]. Indeed, Yb<sup>3+</sup>-based up-conversion phosphors are thought for applications ranging from biotechnology [1,2] to high power lasers [3–5]. Since inexpensive near-infrared (NIR) pump sources, such as solid-state lasers and semiconductor laser diodes, are readily available nowadays, all kinds of NIR-to-visible up-conversion emissions and various energy-transfer processes based on the use of Yb<sup>3+</sup> have been investigated [6–9]. Recently, detailed reviews involving Yb<sup>3+</sup> as the base of up-conversion processes in solids have been published by Auzel [10]

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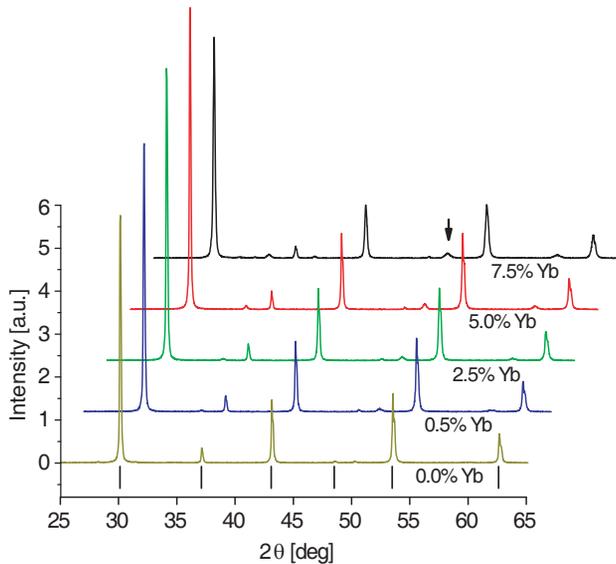
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and Gudel et al. [11]. More specifically, improved functionality related to  $\text{Yb}^{3+}$  in a nanosized host appears to be a promising area of research [12,13]. Particularly active is the search of new host materials with small multiphonon decay rates and good structural and chemical stability over a wide range of temperatures and corrosive environments. Perovskite materials have attracted vast attention due to their excellent optical, electrical, chemical properties and capability of hosting functional ions of various sizes [14–16]. In particular, oxides such as  $\text{YAlO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{LiNbO}_3$ , and fluorides such as  $\text{KMgF}_3$  and  $\text{NaYF}_4$  have found important applications in visible-emitting phosphors when hosting Er and Yb ions [11, 17–20]. Oxides are quite resistant to corrosive environments and have good optical properties. However, most perovskites present phase transformations that lead to anisotropies in their refraction index, which causes non-linear optical phenomena such as second harmonic generation. For some high-energy upconversion applications, this represents a limiting factor, since the upconversion-generated heat can induce anisotropies, thus limiting the effective range of pumping power.

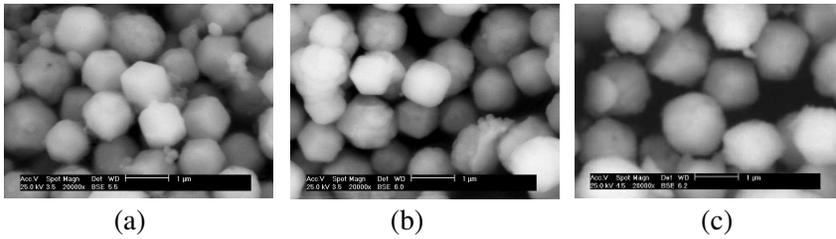
Barium zirconate ( $\text{BaZrO}_3$ ) is a very promising refractory structural material with a very high melting point ( $2920^\circ\text{C}$ ) and low chemical reactivity with corrosive compounds like the ones used in the fabrication of high temperature superconductors. Among the cubic oxide perovskites,  $\text{BaZrO}_3$  (BZO) is the only one that does not follow phase transitions over the range from 1600 K down to 4 K [21]. Recently, columnar inclusions of BZO nanocrystallites were found to enhance the transport currents in YBCO superconductors [22]. Additionally, BZO has attracted attention as a promising candidate for protonic electrolytes in fuel cell applications [16]. Here, we report the NIR and visible (VIS) emission properties of nanocrystallites of  $\text{Yb}^{3+}$ -doped BZO (BZO:Yb), as powders synthesized by simple hydrothermal method. The strong green upconversion luminescence of BZO:Yb makes it a feasible candidate for visible light generation via upconversion processes and, therefore, suitable for biological labeling under NIR excitation [1, 2].

BZO powders, both as-prepared and doped with  $\text{Yb}^{3+}$  0.1, 0.5, 1.0, 2.5, 5.0, and 7.5 mol% ions, were synthesized by a hydrothermal process [23]. All chemicals were analytical grade reagents from Sigma-Aldrich (USA) and used as received. In a typical procedure,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , and  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  with the corresponding mole ratio of cations are completely dissolved in a 0.02 M CTAB ethanol-water solution (20 vol% ethanol) under vigorous stirring for 1 h at RT. Then, sodium hydroxide (0.5 M) was added and stirred again for 1 h at RT. The hydrothermal reactions were carried out in a Teflon autoclave

(500 mL) at 1000°C for 24 h. The precipitate was then washed with distilled water and dried in an oven at 1000°C for 15 h. This was further annealed at 1000°C for 14 h in air to remove organic materials and to enhance crystallinity. X-ray diffraction (XRD) patterns of as-prepared and annealed samples were obtained in a Siemens D-500 equipment equipped with a Cu tube with  $K\alpha$  radiation at 1.5405 Å, scanning in the 25° to 75°  $2\theta$  range at 0.02° steps and a sweep time of 8 s. SEM images were obtained in a XL30 JEOL equipment. The photoluminescence characterization and lifetime measurements were performed using two NIR excitation pump sources: 10 ns pulsed tunable Optical Parametric Oscillator (MOPO from Spectra Physics) pumped by the third harmonic of Nd: YAG pulsed laser and a 967 nm laser diode LDD-9A (from ATC semiconductor devices). The fluorescence emission was analyzed with an Acton Pro 500i monochromator and a R5509-73 Hamamatsu PMT connected to a SR830-DSP lock-in amplifier. Lifetimes were measured with a 500 MHz Lecroy oscilloscope. All photoluminescence measurements were performed at RT, and for VIS emissions a low band pass filter (cut off at 700 nm) was placed before the monochromator to prevent spurious excitation and its harmonics reaching the detector.



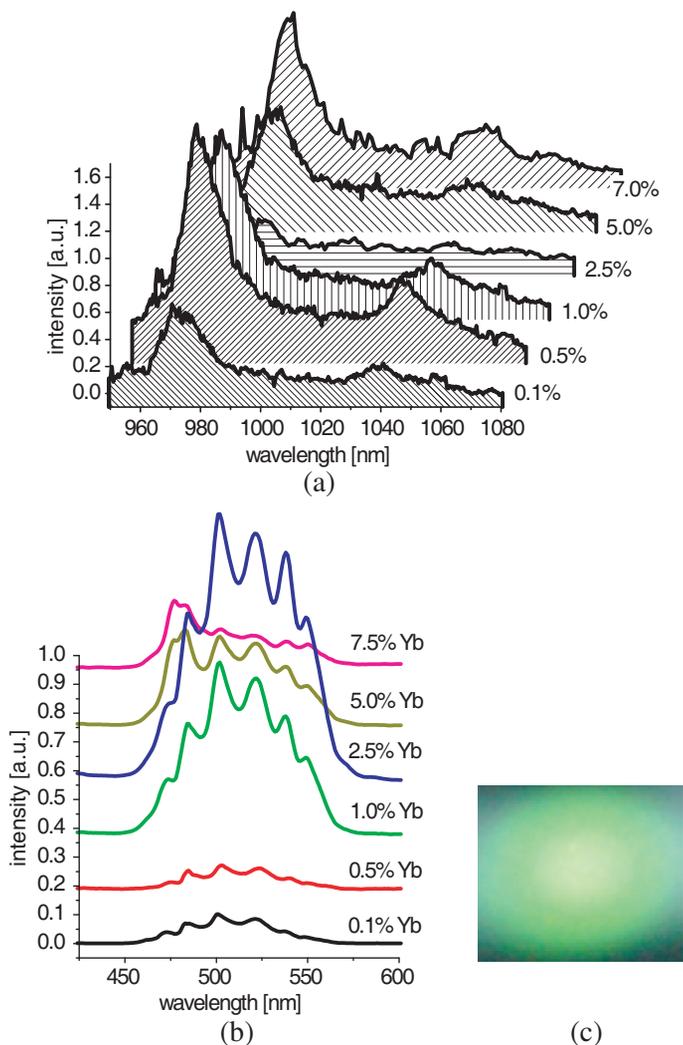
**Figure 1.** X-ray diffraction patterns of the as-synthesized BaZrO<sub>3</sub> (100°C) and Yb<sup>3+</sup> doped BaZrO<sub>3</sub> annealed at 1000°C. Vertical bars at the bottom correspond to the JCPDS 6-0399 standard cubic perovskite BaZrO<sub>3</sub>.



**Figure 2.** SEM micrographs of (a) undoped, (b) 1.0 and (c) 2.5 mol%  $\text{Yb}^{3+}$  samples annealed at  $1000^{\circ}\text{C}$ .

The XRD patterns of annealed BZO:Yb samples and undoped BZO (as-prepared) sample are shown in Figure 1. These patterns agree with JCPD-6-0399 standard for pure cubic perovskite  $\text{BaZrO}_3$ , with a lattice constant of  $4.18^{\circ}\text{A}$ . As the  $\text{Yb}^{3+}$  concentration increases, the degree of crystallinity increases, as revealed by the increase in intensity of the  $[1\ 1\ 0]$  reflection. When compared with undoped as-prepared BZO (at  $100^{\circ}\text{C}$ ) no measurable differences can be observed. This confirms the high structural stability of the cubic phase of BZO, up to a  $1000^{\circ}\text{C}$ , and with doping concentrations as high as 2.5 mol%  $\text{Yb}^{3+}$ . The presence of additional reflections in the pattern for the 5.0 and 7.5 mol%  $\text{Yb}^{3+}$  samples (arrow) suggests segregation of other crystalline phases. Scherrer's equation gives crystallite sizes between 54 and 93 nm. Figure 2 shows typical SEM micrographs of undoped, 1.0 and 2.5 mol%  $\text{Yb}^{3+}$  samples annealed at  $1000^{\circ}$ . The observed morphologies correspond to well disperse secondary particles (i.e., aggregates) of around 750 nm, composed, in turn, by nanosized crystallites. For doping concentrations of 1.0 mol%  $\text{Yb}^{3+}$  and lower, the aggregates show well defined faceted morphologies, whereas for higher concentrations the morphology starts to switch to a spherical form. That is in agreement with the fact that segregation for high dopant concentration takes place and suggests that the segregation might be taking place at concentrations as low as 2.5 mol%  $\text{Yb}^{3+}$ .

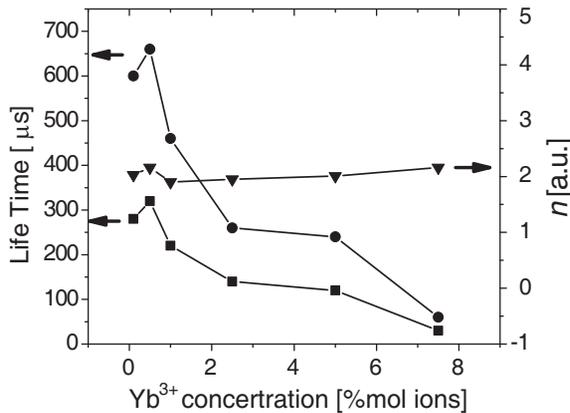
The NIR emission spectra of all BZO:Yb $^{3+}$  samples under excitation at 920 nm is shown in Figure 3(a). The spectra consist of two bands around 973 and 1032 nm, associated with the transition  $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ . Besides the NIR emission, strong blue-green emission was observed (Figure 3(c)). The VIS spectra between 450 nm and 580 nm (Figure 3(b)) correspond nearly to the half-wavelength range of the NIR emission from single  $\text{Yb}^{3+}$  ions. The best VIS emission corresponds to the 2.5 mol%  $\text{Yb}^{3+}$  sample, whereas the best NIR emission corresponds to the 0.5 mol%  $\text{Yb}^{3+}$  sample. The band at 502 nm almost corresponds to double energy of the infrared emission



**Figure 3.** (a) NIR and (b) VIS emission spectra under 920 nm excitation of  $\text{Yb}^{3+}$  doped  $\text{BaZrO}_3$ . (c) Strong blue-green visible emission of 2.5 mol%  $\text{Yb}^{3+}$  doped  $\text{BaZrO}_3$  under 920 nm excitation.

peak of 973 nm. The rest of the VIS peaks correspond to  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  impurities emissions. Figure 4 shows the measured lifetimes of both 973 nm (circles) and 502 nm (squares) emission peaks. For all  $\text{Yb}^{3+}$  concentrations the visible lifetimes are almost half of the NIR lifetimes, suggesting that the emission at 502 nm is due to a cooperative up-conversion process among  $\text{Yb}^{3+}$  pair ions. This

behavior is similar to the report by Cannibano et al. for  $\text{Yb}^{3+}$  doped YAG, GGG and KBM hosts [24]. The relationship  $I_{upc} = kI_{pump}^n$  between the upconverted intensity emission  $I_{upc}$  and pump intensity  $I_{pump}$  is broadly used to estimate the number of absorbed photons,  $n$ , required to produce an upconverted emission photon. The corresponding values of  $n$  for each  $\text{Yb}^{3+}$  concentration are plotted in Figure 4 (triangles). It is remarkable that  $n$  is almost constant with a value around 2. That supports the assumption that the up-conversion emission is a two-photon process due to the simultaneous de-excitation of two excited  $\text{Yb}^{3+}$  ions. Therefore, the green emission is due to a cooperative process among  $\text{Yb}^{3+}$  pairs. The observed visible luminescence (Figures 3(b) and 3(c)) is not completely originated by the cooperative emission between  $\text{Yb}^{3+}$  ions because of the presence of undesirable rare earth ions impurities in the precursor materials. The most likely impurities are erbium and thulium. Thus, the emissions in the visible range could also result from energy transfer processes from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  and/or  $\text{Tm}^{3+}$ . Such emissions can even mask the cooperative luminescence, provided that the impurity concentrations are high enough: See curves for 5.0 and 7.5 mol%  $\text{Yb}^{3+}$  in Figure 3(b). It is worth noticing that such impurities do not show detectable emission when excited directly in the UV-VIS range. Thus, it is likely that their emissions are basically due to energy transfer from the  $\text{Yb}^{3+}$  ions. The emissions peaks at 522 nm, 538 nm and 550 nm (Figure 3(b)) are characteristic of the  ${}^2H_{11/2} + {}^4S_{3/2} \rightarrow {}^4I_{15/2}$  transition



**Figure 4.** Dependence on  $\text{Yb}^{3+}$  concentration of the NIR and VIS emission life times, and dependence on the  $\text{Yb}^{3+}$  concentration for the number of NIR photons  $n$  needed to produce a VIS photon.

of  $\text{Er}^{3+}$  ion, due to the energy transfer from  $\text{Yb}^{3+}$  [6]. Thulium emission peaks at 474 nm and 484 nm, corresponding to the transition  $^1G_4 \rightarrow ^3H_6$ , are also observed. Because the presence of  $\text{Tm}^{3+}$  and  $\text{Er}^{3+}$  impurities was not detected neither by absorption nor direct excitation, their concentration must be of the order of traces. Thus, the noticeable strong emission intensity at such low concentrations suggests very efficient energy transfer processes involving traces of  $\text{Tm}^{3+}$  and  $\text{Er}^{3+}$  ions having the  $\text{Yb}^{3+}$  ions as sensitizers.

That the observed reduction of both NIR and VIS life times as  $\text{Yb}^{3+}$  concentration increases (Figure 4) indicates the presence of quenching processes not related with the emission of the Er and Tm impurities, since their respective emissions are being quenched, as well. In Figures 3(a) and 3(b), it can be observed that both NIR and VIS emission bands are drastically reduced for concentrations above 2.5 mol%  $\text{Yb}^{3+}$  ions. With the increase of  $\text{Yb}^{3+}$  concentration, the separation between Yb-Yb pairs is reduced, promoting their interaction and thus enhancing the cooperative up-conversion emission at 502 nm, which on time reduces the NIR emission and promotes ET from  $\text{Yb}^{3+}$  pairs to  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$ , being the net result a reduction of both NIR and VIS emissions. Thus, the dominant effect is the  $\text{Yb}^{3+}$  pair interaction. It is presumed that if the  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions concentrations are increased to nominal ones, then efficient ET process between  $\text{Yb}^{3+}$  and these ions could lead to strong emission in the blue ( $\text{Tm}^{3+}$ ), green and red ( $\text{Er}^{3+}$ ) regions. This would open the possibilities of BZO as a good phosphor for biolabeling applications [1, 2, 25, 26].

## 2. CONCLUSION

In conclusion, we have shown that  $\text{Yb}^{3+}$  doped  $\text{BaZrO}_3$  as a up-conversion phosphor. BZO has very good structural and morphological characteristics and is stable in a wide range of annealing temperature and dopant concentrations.  $\text{Yb}^{3+}$  cooperative processes in BZO could be the base for new rare earth and transition metal doped phosphors for photonic applications in the VIS range under NIR excitation.

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