

# Synthesis via sol-gel and energy transfer properties of a new $\text{Ba}_2\text{SiO}_4:\text{Eu}^{3+},\text{Tb}^{3+}$ blue, green and red phosphor for W-LED.

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The  $\text{Ba}_2\text{SiO}_4$  matrix can host  $\text{Tb}^{3+}$  as blue and green emitter and  $\text{Eu}^{3+}$  as the red one, so it could potentially be used in white LED due to its high structural, electrical and thermal stabilities.<sup>1</sup> Thus, the objective of this work was to produce by using an adapted sol-gel route  $\text{Ba}_2\text{SiO}_4:\text{Tb}^{3+},\text{Eu}^{3+}$  blue-green-red phosphors. All samples were synthesized from barium and europium acetates, terbium chloride, acetic acid and TEOS, yielding a gel phase that was preheated at 120 °C forming a xerogel, which was calcinated at 1100 °C upon CO reducing atmosphere. The  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  percentages were isoelectronically varied from 1 to 2 % and 0.01 to 1 %, respectively. XRD data confirmed that all phosphors have  $\text{Ba}_2\text{SiO}_4$  orthorhombic single phase (spatial group  $P_{mcn}$ ) with high crystallinity. In FTIR and Raman spectra detected vibrational modes related to orthorhombic silicate structure are in accordance with XRD data. Moreover FTIR data suggest that both  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions are occupying  $\text{Ba}^{2+}$  sites with CN 9 or 10. SEM shows that the particles are agglomerated spheroids with diameter near 300 nm. The band gap values estimated from diffuse reflectance data vary from 4.4 to 5.4 eV for doped samples and 5.75 eV for non-doped one. Fixing excitation at 240 nm both ions are excited through  $\text{Tb}^{3+} {}^7\text{F}_6 \rightarrow {}^4\text{F}_7/5\text{d}$  and  $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$  charge transfer transition. Green and blue emissions from  $\text{Tb}^{3+}$  ions and red emission from  $\text{Eu}^{3+}$  ions are observed, Fig.1.(a) being that sample codoped with 1% emitted nearest white. In the excitation spectra both  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  transitions are observed when the emission is fixed at the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$   $\text{Eu}^{3+}$  transition, Fig.1.(b). However, when the emission is fixed at the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$   $\text{Tb}^{3+}$  transition, Fig.1.(c), just the  $\text{Tb}^{3+}$  transitions are observed, except for the sample codoped with 1%. In this way, it is occurring energy transfer from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in any situation, but from  $\text{Eu}^{3+}$  to  $\text{Tb}^{3+}$  only at high concentrations of doping, when the distance between both ions are shorter. To investigate this energy transfer behavior, in Fig. 1.(d) it is plotted the linear fitting of  $\log(x)$  versus  $\log(I/x)$  according to the formula proposed by Dexter and Van Uiter.<sup>2</sup> The value of  $\theta = 6, 8, 10$ , corresponds to electric dipole–dipole, dipole–quadrupole or quadrupole–quadrupole interactions, respectively. As seen from Fig. 1.(d),  $\theta$  is approximately 6, indicating that the dipole–dipole interactions dominate the energy transfer mechanism among  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions. Therefore, the sol-gel route was successfully applied to prepare  $\text{Ba}_2\text{SiO}_4:\text{Tb}^{3+},\text{Eu}^{3+}$  phosphors, with blue-green-red emission. The produced phosphors show potential application to be used in LED designing.

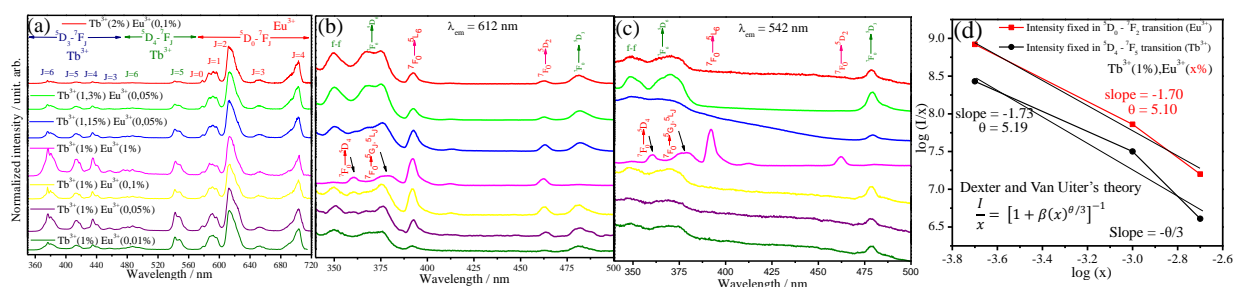


Fig. 1 (a) Emission spectra under 240 nm, (b) excitation spectra under 612 nm, (c) excitation spectra under 542 nm and (d) Linear fitting of  $\log(x)$  versus  $\log(I/x)$  to the series  $\text{Ba}_2\text{SiO}_4:\text{Tb}^{3+}(1\%),\text{Eu}^{3+}(x\%)$ ,  $x = 1, 0.1$  and  $0.05$  %.

<sup>1</sup> Pires, A. M.; Davolos, M. R. *J. Lumin.* **1997**, 244, 72.

<sup>2</sup> Van Uiter, L.G. *J. Electrochem. Soc.*, **1967**, 14, 1048.

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