

Sol-gel synthesis of monophasic Ba₂SiO₄:Eu(III) red phosphor for optical devices.

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The research in phosphor-based white LEDs has been increasing due to their suitable properties, such as energy saving, high stability, long life time and no mercury pollution¹. In this context, silicate compounds have been investigated because of their stability, and relative easy preparation². For instance, Ba₂SiO₄ (orthorhombic crystal system, *Pmcn* space group) doped with Eu³⁺ ions can be used as a red phosphor in white LEDs. Thus, the objective of this work was to improve luminescence properties of Ba₂SiO₄:Eu³⁺ obtained via sol-gel route by modifying synthesis conditions in order to produce samples without the spurious basic carbonate phase and therefore, minimizing non radiative losses. Ba₂SiO₄:Eu(III)5ch% was synthesized from barium and europium acetates, acetic acid and TEOS, yielding a gel phase that was preheated at 120 °C forming a xerogel, which was calcinated at 1100 °C varying the calcination conditions listed in Table 1. Then, the concentration of the dopant was isoelectronically varied from 1-5 %.

Table 1. Calcination conditions for Ba₂SiO₄:Eu³⁺ (5%)

Sample	Pre calcination	Calcination	Time	Atmosphere
1	X	1100 °C	2 h	Circulating air
2	X	1100 °C	3 h	Circulating air
3	X	1100 °C	4 h	Circulating air
4	X	1100 °C	2 h	CO
5	450 °C / 2 h	1100 °C	2 h	Circulating air

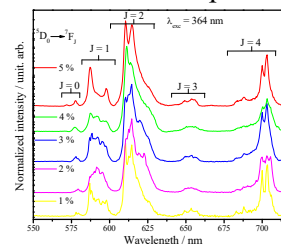


Fig. 1. Emission spectra under 393 nm.

XRD data confirmed the formation of Ba₂SiO₄ phase and the presence of BaCO₃ spurious one for all obtained phosphors prepared according to Table 1 data, except sample 5, which showed silicate single-phase XRD profile. In addition, sample 5 exhibited the highest relative emission intensity. Therefore, sample 5 synthesis condition was chosen for the preparation of monophasic Ba₂SiO₄:Eu³⁺ (1 to 5%) phosphors with high crystallinity. Moreover, FTIR data suggest that the Eu³⁺ is occupying Ba²⁺ sites with CN 9 or 10. SEM images, for instance, show an aggregate structure for all samples, presenting on the surface nanowires assigned to the preferential growth of nanocrystals. The band gap values estimated from diffuse reflectance data vary from 4.62 to 4.75 eV for doped samples and 5.28 for non-doped one. Phosphors luminescence spectra, Fig. 1, show the expected Eu³⁺ transitions and the presence of a single ⁵D₀→⁷F₀ one indicating that the Eu³⁺ is occupying at least one site with no center of inversion. Sample doped with 4% showed the highest relative emission intensity, indicating that the luminescence is suppressed by concentration effect at higher concentrations. Therefore, the sol-gel route was successfully applied to prepare monophasic Ba₂SiO₄:Eu³⁺ red phosphors with potential application to be used in white LED designing.

¹Wang, Z.; Guo, S.; Li, Q.; Zhang, X.; Li, T.; Li, P.; Yang, Z.; Guo, Q. *Physica B*, **2013**, 411, 110.

²Pires, A. M.; Davolos, M. R. *J. Lumin.* **1997**, 244, 72–74.

³Han, J.K.; Hannah, M.E.; Piquette, A.; Talbot, J.B.; McKittrick J. *J. Am. Ceram. Soc.*, **2013**, 96, 1526.

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