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Asymmetry ratio as a parameter of Eu³-local environment in phosphors

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Abstract: Study of the local environment of certain ion is quite a complex problem. Due to the unique luminescent properties, Eu^{3+} ions can be used as a structural probe. In this paper, effect of doping concentration, excitation wavelength and excitation mechanism on asymmetry ratio was systematically studied using $Y_3Al_5O_{12}:Eu^{3+}$, $YVO_4:Eu^{3+}$ and $Y_2O_3:Eu^{3+}$ nanophosphors. The asymmetry ratio gives information about the local surrounding and environmental changes around the Eu^{3+} ions. Asymmetry ratios of $YAG:Eu^{3+}$ and $YVO_4:Eu^{3+}$ nanopowders were calculated using standard technique and the obtained average values were found to be 0.75 and 8.2, respectively. However, it was found that standard method of asymmetry ratio calculation is suitable only for samples where all Eu^{3+} ions occupy one site. The "multisite model" of asymmetry ratio calculation was developed and used for $Y_2O_3:Eu^{3+}$ nanocrystalline powders. Average value of asymmetry ratio for Eu^{3+} ions occupied "normal" sites is 6.0 and for Eu^{3+} ions occupied "defect" sites is 2.3.

Keywords: Eu³⁺; Oxide powders; Luminescence; Asymmetry ratio; Structural probe; Rare earths

1. Introduction

Last decades luminescent materials have attracted intensive interest due to their technological importance and scientific application. Materials doped with rare earth ions have unique physical and chemical properties, which make them critically important in optical amplifiers, fluorescent lamps, cathode ray tubes, medical imaging, pigments, and phosphor screens [1–7].

Among all the lanthanide ions, the europium ion is one of the most widely used in spectroscopic studies. Eu³⁺ combines an intense visible (red) luminescence with a relatively easiness in interpreting the spectrum. The relative intensities and the splitting of the peaks in the spectra are indications for the site symmetry of the luminescent europium ions.

It is well-known that emission spectra of Eu³⁺ doped phosphors consist of intra-configurational (f–f) transitions [8–10]. Generally, most of the f–f transitions of the trivalent lanthanides are insignificantly affected by the environment. However, a few transitions are sensitive to the environment and become more intense. They are called hypersensitive transitions. The magnetic dipole transitions (${}^5D_0 - {}^7F_1$) are insensitive to the site symmetry, because they are parity-allowed. But the forced electric dipole transition ${}^5D_0 - {}^7F_2$ with $\Delta J = 2$ is hypersensitive, and the intensity

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