Invited lecture

Multisite luminescence of rare earth ions doped Y₄Al₂O₉ crystals

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Over the past several years there has been an ongoing research for trivalent rare-earth (RE³⁺) activated materials for optical amplifiers, lasers, phosphors and scintillators. Oxide crystals and nanocrystals from the Y₂O₃-Al₂O₃ binary system are one of the most studied groups of optical materials, owing to their various applications. The monoclinic Y₄Al₂O₉ (YAM) phase is the least studied one and only limited information is available on the spectroscopic properties of this system so far. YAM is more complicated than YAG and YAP crystals due to the existence of four distinct Y³⁺ sites which could be substituted by RE³⁺ ions [1]. Limited spectroscopic studies of RE³⁺ ions in YAM have confirmed multisite features of this host lattice [2–4].

In this study, we have considered RE³⁺ dopant ions as structural probes to investigate changes of the local environment and to resolve the multisites of rare earth ions in YAM host. This was based on high resolution absorption, excitation and emission spectra measurements and selectively excited fluorescence decays performed at low temperatures.

YAM samples, with Pr³⁺, Sm³⁺, Eu³⁺ and Yb³⁺ activator concentrations of 0.1, 1, 5 and 10 at.%, used in this study were grown by micro-pulling down (µ-PD) method in the Institute of Electronic Materials Technology (ITME) in Warsaw. Polycrystals in the form of rods 2–3 mm in diameter and several cm long were obtained.

Sm³⁺ and Eu³⁺ have been employed as a structural probe because of its hypersensitive transitions; $^5G_{7/2} \rightarrow ^7H_{5/2}$ and $^5D_0 \rightarrow ^7F_2$, respectively, which intensity can vary by orders of magnitude depending on the local environment. Also, important and unique feature of Eu³⁺ ions is the existence of $^7F_0 \leftrightarrow ^5D_0$ transitions connecting two non-degenerate levels that cannot be split by crystal-field effects. Thus, the number of lines related to this transition reflects the number of sites occupied by Eu³⁺ ions in the matrix. Anti-Stokes, up-conversion fluorescence originating from the $^3P_0$ state while exiting the $^3H_4 \rightarrow ^3D_2$ transition was observed in Pr³⁺:YAM. The participation of distinct sites to up-conversion emission was revealed for the first time. The dynamical behavior of the upconverted emission arising from four sites was studied and modeled via energy transfer process.

New results on the site preferences for impurity ions, number of ion sites, their relaxation dynamics and energy transfer between RE³⁺ ions in different sites are presented and discussed in a function of temperature and activator concentration.

Keywords: rare earth ions; photoluminescence; site-selective spectroscopy; energy transfer

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References