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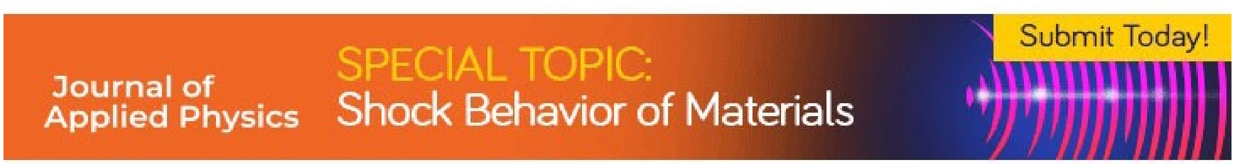

Luminescence, lifetime, and quantum yield studies of redispersible Eu^{3+}-doped $GdPO_4$ crystalline nanoneedles: Core-shell and concentration effects

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Crystalline nanoneedles of Eu^{3+}-doped $GdPO_4$ and Eu^{3+}-doped $GdPO_4$ covered with $GdPO_4$ shell (core shell) have been prepared at relatively low temperature of 150 °C in ethylene glycol medium. From luminescence study, asymmetric ratio of Eu^{3+} emission at 612 nm (electric dipole transition) to 592 nm (magnetic dipole transition) is found to be less than one. Maximum luminescence was observed from the nanoparticles with Eu^{3+} concentration of 5 at. %. For a fixed concentration of Eu^{3+} doping, there is an improvement in emission intensity for core-shell nanoparticles compared to that for core. This has been attributed to effective removal of surface inhomogeneities around Eu^{3+} ions present on the surface of core as well as the passivation of inevitable surface states, defects or capping ligand (ethylene glycol) of core nanoparticles by bonding to the shell. Lifetime for $^5D_0$ level of Eu^{3+} was found to increase three times for core-shell nanoparticles compared to that for core confirming the more Eu^{3+} ions with symmetry environment in core shell. For 5 at. % Eu^{3+}-doped $GdPO_4$, quantum yield of 19% is obtained. These nanoparticles are redispersible in water, ethanol, or chloroform and thus will be useful in biological labeling. The dispersed particles are incorporated in polymer-based films that will be useful in display devices.
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I. INTRODUCTION

Lanthanide ion doped inorganic materials are potential candidates for many applications such as lamp phosphors, optical amplifiers,[1,2] lasers,[3] and electroluminescent display devices.[4] Due to this reason extensive studies on nanoparticles doped with lanthanide ions have been reported.[5,6] Although the f-f transitions of lanthanide ions (Ln^{3+}) are forbidden in nature, the crystal field surrounding the dopant ions relaxes the selection rule so that the luminescence is observed.[7] Since $4f^n$ electrons of Ln^{3+} are shielded by outer shell (5s and 5p), $4f^n$ electrons interact weakly with any external environment. As a result, absorption and emission spectra of lanthanide (III) ions appear as sharp narrow bands, whose positions are weakly dependent on the environment or crystal field to provide important information about the crystallography and position of lanthanide ions in such structures.[8]

Recently, nanoparticles made of lanthanide oxides have been investigated as emerging materials for fluorescent labeling.[9,10] In this aspect, Y_2O_3, Lu_2O_3, and Gd_2O_3 are potential host materials, which can make solid solutions with lanthanide ion activators (Eu^{3+}, Dy^{3+}, and Tb^{3+}) at any concentration with or without change in crystal structure because Y^{3+}, Lu^{3+}, and Gd^{3+} have ionic radii, which are similar to Ln^{3+} ($Ln^{3+}=Eu^{3+}$, Dy^{3+}, and Tb^{3+}). They have wide band gaps ~5–6 eV compared to other hosts such as SnO_2 (3.6 eV), TiO_2 (3.2 eV), and ZnO (3.3 eV).[11–14]

Different methods such as hydrothermal synthesis,[15–19] coprecipitation technique,[20–22] etc., have been reported for preparation of RE^{3+}-doped lanthanide phosphate nanoparticles. Dexpert-Ghys *et al.*[23] prepared $LaPO_4$ at high temperature 1300 °C. High temperature treatment on lanthanide-doped nanoparticles results in lanthanide ion clustering leading to phase separation and nanoparticle sintering, which leads to a decrease in the luminescence efficiency due to self-quenching and poor photocatalytic activity. Kornowski and co-workers[20,21] synthesized $LaPO_4:Eu^{3+}$ and $LaPO_4:Tb^{3+}$ nanocrystals including nanowires (NWs) for the first time at 200 °C. These authors used a lengthy process involving many reagents, which might lead to incorporation of unwanted substances. Lehmann *et al.*[22] have also prepared $LaPO_4:Eu^{3+}$ core and core-shell nanoparticles at high temperature. One of the ways to prevent the agglomeration of the lanthanide-doped nanoparticles is to cap the nanoparticles by suitable ligand. If a suitable ligand is used then these nanoparticles can be made dispersible in solvents such as water, ethanol, or chloroform, which will enhance their multifunctional applications.

Moreover, there has been a growing interest in energy transfer in gadolinium compounds, which provide opportuni-

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uted to the removal of surface inhomogeneities around Eu^{3+} as well as the passivation of inevitable surface states, defects, or capping ligand (ethylene glycol) of the core nanoparticles by bonding to the $GdPO_4$ shell. Eu^{3+}-doped $GdPO_4$ nanoparticles can be dispersed in water, ethanol, chloroform, and such nanoparticles will be useful in biological labeling and are incorporated in polymer films that will be useful for display devices.

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