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Radiative parameters of Eu^{3+} ions in CdSe nanocrystal containing silica matrices

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Abstract

Optical absorption and emission spectra of Eu^{3+}/CdSe nanocrystallites and Eu^{3+} in sol–gel silica glass samples are being carried out. From the measured intensities of various absorption bands and applying thermal correction, the three Judd–Ofelt parameters Ω_2, Ω_4 and Ω_6 are evaluated for these glasses. From this theory, various radiative properties like transition probability A, branching ratio β, the radiative lifetime τ_R, absorption cross-section σ_a and the emission cross-section σ^E for various levels of these glasses are determined.

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1. Introduction

Sol–gel silica glasses are considered as very good materials for hosting rare-earth ions along with semiconductor nanocrystals (quantum dots) as they allow incorporation at low temperatures with predetermined concentration and size [1]. Sol–gel method is useful in the preparation of quantum dots-doped gel glasses with relatively high particle concentrations, small particle diameter and uniform size distribution [2]. The spectral intensities of the trivalent lanthanide ions can be fine tuned by an appropriate choice of the medium in which the ion is embedded [3]. Optical transitions of rare-earth ions, which are confined within the 4f level structure, have got crucial applications in optoelectronic technology [4]. Electron–electron and

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spin–orbit interactions dominate the electronic structure of the rare-earth ions. Lanthanide ions have a fairly unique property of sharp spectral lines (4f–4f) in the solid phase [5,6]. Eu^{3+} is an excellent indicator of the site symmetry and chemical bonding in glasses since Eu^{3+} ions incorporated in low-symmetry sites exhibit enhanced f–f transition probabilities [7]. Knowledge of the local structure of the rare-earth in hosts is valuable in optical devices like upconversion laser and laser induced holographic gratings [8]. The development of new luminescent materials with complex composition is of interest for understanding the electronic excitation and relaxation phenomena with participation of two and more active centers.

2. Experimental details

Europium-doped and CdSe/Eu^{3+}-codoped silica glasses were prepared by the sol–gel process with tetraethyl orthosilicate (TEOS) as a precursor and cadmium acetate, selenic acid and europium nitrate in the presence of water and ethanol. We introduced Eu^{3+} ions into precursor sols within the framework of the modified sol–gel technique based on the catalytic hydrolysis of silicon-organic compounds with subsequent polycondensation of R–Si–O fragments. CdSe nanocrystallites were prepared from cadmium acetate and selenic acid by their decomposition reaction and incorporated into the SiO_2-matrix through annealing. Measured volumes of 1 M HCl were added as a catalyst. The mixture (sol) is poured into polypropylene containers, which is sealed and kept to form stiff gel. Eu^{3+}(3 wt%) CdSe(7 wt%) [sample A]- and Eu^{3+}(3 wt%) [sample B]-doped silica samples were prepared. Variation in the annealing conditions resulted in stabilization of final products and provided a high mechanical strength of materials. The absorption spectrum is recorded using a spectrophotometer (Shimadzu-UVPC 2401). The excitation and luminescence spectra were taken using a spectrophotofluorimeter (Shimadzu-RFPC 5301) for samples heated to 500 °C. All measurements were done at room temperature (~300 K).

3. Theoretical analysis

The theory of atomic spectra allows identification of definite J levels of $4f^6$ in the Eu^{3+} ion. A convenient way of representing the intensity of an absorption band is to measure the oscillator strength of the transition, which is found to be proportional to the area under the absorption line shapes. Oscillator strength (f) can be expressed in terms of molar extinction coefficient (ε), and energy of the transition in wave number (v) by the relation [9]:

$$f_{\exp} = 4.32 \times 10^{-9} \int \varepsilon(v)\,\mathrm{d}v. \tag{1}$$

The absorption properties of rare-earth ions are best distinguished in the context of the Judd–Ofelt theory [10,11]. In essence the 4f→4f transitions of a rare-earth ion can be described as a simple linear combination of the so-called J–O parameters $\Omega_\lambda(\lambda = 2, 4, 6)$. The coefficients of each linear combination of Ω_λ are independent of the host and are determined by the fundamental nature of the 4f wave functions and the particular transitions at hand.

According to the J–O theory

$$f_{\mathrm{ed}} = \frac{v}{(2\mathrm{J}+1)}\left[\frac{8\pi^2 mc}{3h}\frac{(n^2+2)^2}{9n}\right] \times \sum_{\lambda=2,4,6} \Omega_\lambda \langle \psi \mathrm{J}||U^\lambda||\psi' \mathrm{J}'\rangle^2, \tag{2}$$

where $(2J+1)$ is the degeneracy of the ground state, v is the mean energy of the $|\psi J\rangle \rightarrow |\psi' J'\rangle$ transition, U^λ is a unit tensor operator of rank λ and Ω_λ's are known as J–O intensity parameters. For Eu^{3+} ion the ground term $^7F_0$ is very close to the next excited $^7F_1$ level and, therefore, both levels are populated at room temperature and absorption takes place from both the levels to the excited states. The fractional thermal population C_J/C_0 of any excited level $^{2S+1}L_J$ is given by

$$C_J/C_0 = \left[\frac{g_J}{g_0}\right] \exp\left((-E_J - E_0)/kT\right),$$

where C_0, g_0 and E_0 refer to the population, degeneracy and energy respectively, of the ground state and the subscript 'J' refers to the excited state. The experimental oscillator strengths must