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Luminescence properties of Eu^{3+} doped CdF_2 single crystals

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This paper reports the photoluminescence properties of Eu^{3+} doped CdF_2 single crystals. The pulled crystals were prepared by use of the Bridgman technique from a vacuum furnace in fluoride atmosphere. Absorption, excitation and emission spectra of the crystal doped with three Eu^{3+} concentrations (0.02%, 0.1% and 0.6% mol.) were recorded at room temperature. The emission spectra exhibit a strong yellow and red emissions in the spectral range 550–720 nm which are assigned to $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 4) transitions and a weak infrared emission around 816 nm corresponding to $^5D_0 \rightarrow {}^7F_6$ transition. The magnetic dipole emission ($^5D_0 \rightarrow {}^7F_1$) is the most intense for each Eu^{3+} concentration.

The Judd-Ofelt intensity parameters Ω_2, Ω_4, Ω_6 for 4f-4f transitions of Eu^{3+} ions were computed from the emission spectra using the $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 4, 6) transitions. Via these phenomenological intensity parameters, the spontaneous emission probabilities, branching ratios, radiative lifetimes, quantum efficiencies and emission cross-sections for the main Eu^{3+} emitting levels are evaluated.

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1. Introduction

In recent years, rare earths (RE) doped host matrix have been studied extensively due to their potential applications in green technology. They have an important role in the development of optical systems, cathode ray tubes, clean energy, postings 3D, infrared radiation detection, color display, medical applications, sensors, optical data storage, plasma display panels (PDP), optoelectronic devices, biological fluorescence labeling, laser technology, luminescent paints and inks for security [1–5]. They have been reported in various fields due to the electronic and optical characters arising from the 4f electrons of lanthanide adding to the stability of chemical and physical properties of inorganic host matrices [6,7]. Among many solid-hosts materials studied so far, MF_2 difluoride crystals (M = Alkaline earth element, Cd or Pb) with fluorite type structure are of great interest as material for photonics. This choice refers to the low phonon frequency of such materials leading to a large number of potential emitting levels by limiting the non-radiative emissions.

CdF_2 crystals occupy a specific place among MF_2 crystals. They are transparent in the UV, visible and near infrared (NIR) electromagnetic domain. CdF_2 is used as a main constituent of many fluoride glasses, material for laser, infrared detectors and medium for optical information processing systems [8–10]. In addition, we are particularly interested in the Europium ions because they exhibit an intense red emission and also narrow transitions in the absorption and luminescence spectra leading to the possible use as probe of the local environment. Furthermore, lasers based on the red emission of europium could also be an attractive choice for a medical application since NIR radiation can penetrate biological tissues such as human skin [4]. Also, the UV excitation of ^5D_J Europium levels generates yellow, red as well as green emission leading to white light greatly required in many applications.

The Judd-Ofelt (JO) theory has long been considered to be one of the most successful theories in estimating the magnitude of the forced electric dipole transitions of rare earth ions. The standard JO analysis is applied to the room temperature absorption intensities of RE^{3+} to determine the Ω_t optical intensity parameters extremely depending on the rare earth ion and its local environment. The accurate values of these parameters are necessary to characterize the spectroscopic and laser properties of host matrix.

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In connection with previously, from the emission spectrum the JO technique was also developed to obtain the Ω_t parameters [11–15]. The radiative transition probabilities between the energy levels of the $4f^n$ configuration of the Eu^{3+} ions are then determined with the radiative lifetimes and branching ratios.

The purpose of the present work is to investigate the optical properties of Eu^{3+} ions doped CdF_2 single crystal. To perform these studies, the results of luminescence and lifetime measurements were analyzed. The JO intensities parameters were investigated using the data taken from luminescence spectra which allowed evaluating of the transition probabilities, radiative lifetimes and, as a final result, emission cross section and the quantum efficiency of the Eu^{3+} emission in CdF_2 single crystal.

2. Material characteristics and experimental procedure

The fluorides with divalent metals, i.e. MF_2 compounds (M = Ca, Sr, Ba, Pb, Cd), crystallise in a face centred cubic structure having the fluorite type (CaF_2) and belonging to Fm3m space group with four unit formula per unit cell (4 M^{2+}cations and 8 F^- anions) [16,17]. Also, CdF_2 is characterized by the smallest lattice parameter among the MF_2 compounds (5.388 Å) as well as its melting point of 1100 °C [18–21]. The trivalent Europium ion (Eu^{3+}) substitutes the divalent Cadmium ion (Cd^{2+}) requiring a charge compensation with interstitial F^- ion. Since the maximum phonon energy (384 cm^{-1}) [22] is quite low relative to those of oxides, this leads to a limitation of the non-radiative transitions in such materials.

Eu^{3+} ions doped CdF_2 single crystals with 0.02, 0.1 and 0.6% nominal concentrations are grown by use of the Bridgman technique from a vacuum furnace in fluorine atmosphere. After the purification step, Eu^{3+} ions were introduced in the form of trifluoride powder (EuF_3). For optical measurements, the samples are polished to flat and parallel faces with 3.0 mm of thickness. The experimental synthesis diagram is depicted on Fig. 1.

Absorption spectra at room temperature (RT) were recorded using Cary 500 spectrophotometer (Fig. 2). Excitation, photoluminescence and decay spectra under UV excitation were on performed on Perkin Elmer LS-50B spectrofluorimeter. In order to have a well-resolved emission spectrum, we have used an home-made spectrometer after direct excitation using a tunable pulsed source β-BaB_2O_4-OPO pumped by the second harmonic of a Q-switched Nd:YAG laser. The fluorescence signal was dispersed through a 0.25 m ORIEL monochromator and detected using an Hamamatsu photomultiplier tube in the visible region.

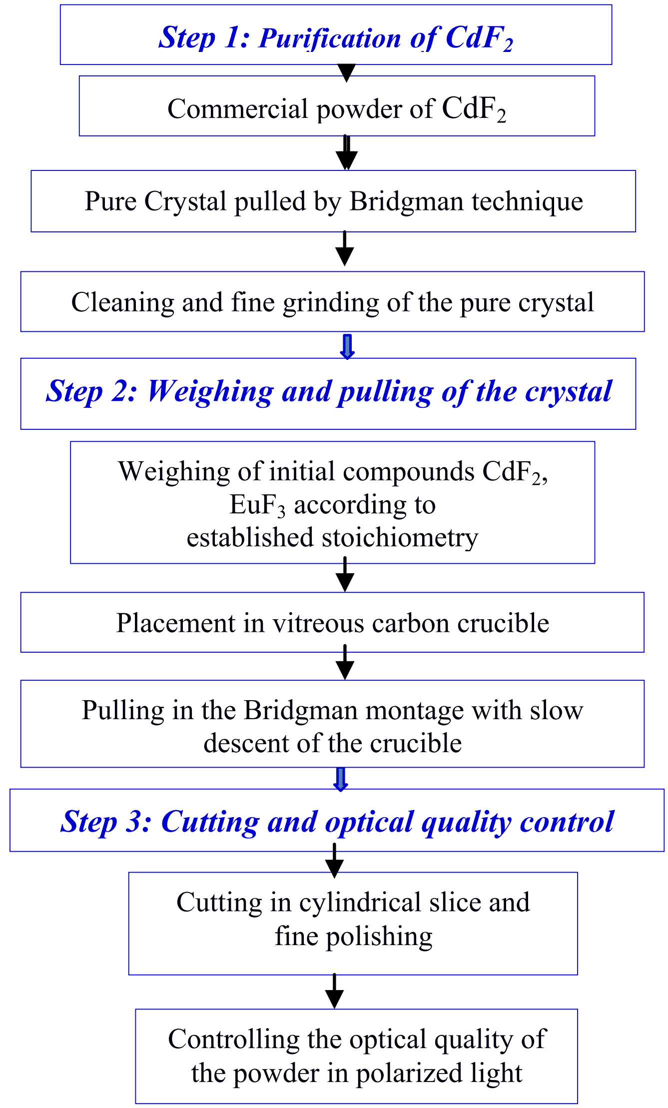

Fig. 1. Schematic synthesis diagram of CdF_2: Eu^{3+} single crystal.

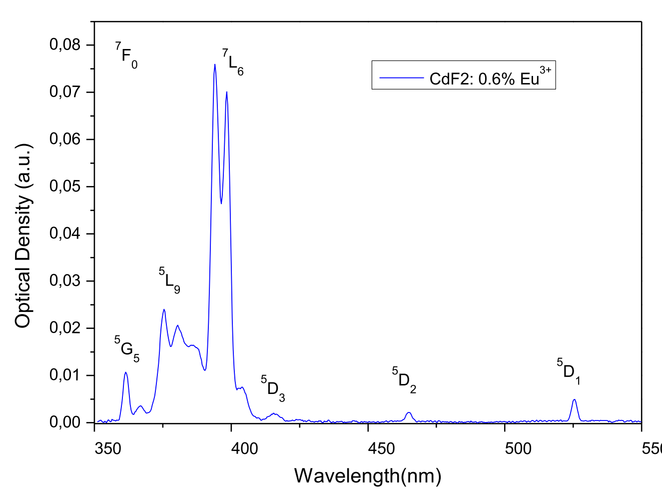

Fig. 2. Room temperature absorption spectrum of CdF_2: Eu^{3+} (0.6 mol.%) single crystal in visible range.

3. Judd–Ofelt theory

The Judd-Ofelt (JO) theory is widely used to calculate 4f transition intensities of rare-earth ions in various material hosts. Its application requires the computation of three parameters, Ω_2, Ω_4 and Ω_6, by a fitting procedure of experimental data usually obtained from absorption or emission spectra. These parameters give significant information on the local structure and the bond in the vicinity of the rare earth ions. The parameter Ω_2 is more sensitive to the local environment of the RE^{3+} ions and is often related with the asymmetry of the local crystal field and the valency of RE^{3+}ligand bond while Ω_6 is a measure of the covalence in the network. The JO intensity parameters are then used to determine the radiative transition probabilities depending on the particular rare earth ion and its local environment, accurate values of these parameters are necessary to characterize the spectroscopic and laser properties of Eu^{3+} doped CdF_2.

In this study, the emission spectrum was involved to calculate the three JO intensity parameters from the ratio of the intensity of