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Optical properties of Er^{3+}-Yb^{3+} codoped CdF_2 single crystals

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ABSTRACT

Er^{3+} (1%), Yb^{3+} (4%): CdF_2 single crystals with good optical quality are grown by the standard Bridgman method. Absorption, excitation, fluorescence and upconversion spectra are carried out at room temperature. The standard Judd–Ofelt (JO) model is applied to absorption intensities of Er^{3+} to obtain the three phenomenological intensity parameters by the least square fit procedure. The values obtained are in accordance with those of other fluoride hosts with good root mean square fitting. These JO intensity parameters are then applied to determine the radiative transition probabilities ($A_{JJ'}$), radiative lifetimes (τ_{rad}) and branching ratios ($\beta_{JJ'}$) of Er^{3+} transitions. Green excitation spectrum shows that the Er^{3+} ions doped CdF_2 is preferably excited by $^4I_{15/2} \rightarrow {}^4G_{11/2}$ (375 nm). The obtained Stokes fluorescence spectrum is characterized by an intense green emission and weak red emission for which we have measured the fluorescence lifetime, the cross-section emission, the gain and the radiative quantum efficiency. Under 980 nm laser excitation, intense red and green upconversion emissions induced by efficient energy transfer between Yb^{3+} and Er^{3+} ions were achieved in the investigated matrix via a proposed upconversion process. The spectroscopic data indicate that the studied host may offer visible and infrared laser emission.

1. Introduction

Optical devices continue to grow from one year to another. This requires developing new materials that have more interesting luminescent, mechanical and thermal properties. During the last two decades, special attention has been made to materials having low phonon energies, such fluorides and chlorides to reveal more luminescence. The most materials studied are doped with various luminescent rare earth ions. They are found to be good amplifying mediums in laser technology and they have many applications in the vast field of optics characterized by the emergence of new lighting technologies and display panels in addition to the optical components. Erbium-doped materials have generated a lot of interest for many years due to their excellent luminescence properties as long as they offer near-infrared and visible luminescence. On the other hand, when codoped with Ytterbium, such materials are used as NIR-to-visible upconverters with good efficiencies.

Difluoride crystals MF_2 (M is an alkaline earth element, Cd or Pb) with fluorite type structure are of great interest for Erbium doping the time they have already given laser emissions [1–4]. They have large rare earth ion admittance and large electromagnetic domain transparency which extends from near UV to middle infrared.

In this direction, we are interested to study the spectroscopic properties of the MF_2 binary crystals and MF_2-$M'F_2$ pseudo-binary solid solutions, where M or M′ is an alkaline-earth element (Ca, Ba, Sr) or cadmium (Cd) doped with trivalent rare earth ions (Eu^{3+}, Tb^{3+}, Ho^{3+}, Er^{3+}, mainly).

In the current study, we limited this investigation to cadmium difluoride (CdF_2) single crystals codoped with Er^{3+} and Yb^{3+} ions. Erbium acts as an activator while ytterbium is a sensitizer. After obtaining the pulled crystals, we present measurements of absorption, emission and fluorescence dynamics at room temperature of the visible transitions. We have also employed the Judd–Ofelt (JO) formalism, by use of the absorption spectra recorded at room temperature, in order to establish the spectroscopic properties of all of the radiative transitions that can take place. Finally, upconversion emission spectra exciting at 980 nm have been measured highlighting the red and green emissions.

2. Experimental procedure

2.1. Sample preparation

The CdF_2 single crystals codoped with Er^{3+} (1.0 mol. %) and Yb^{3+} (4.0 mol. %) are grown by use of standard Bridgman pulling technique from a vacuum furnace in fluorine atmosphere. The CdF_2 powder, which came from Merck, is purified by repeated

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growth of simple crystals. After the purification step, the rare earth doping ions (i.e. Er^{3+} and Yb^{3+}) are introduced as trifluoride powders with the proposed concentrations. The cylindrical pulled crystals are about 8 mm in diameter and 25–35 mm in length. Using a diamond polishing paper, they are polished in flat and parallel faces for optical measurements. They are quite transparent at nicked eye.

2.2. Optical characterization

The room temperature absorption spectra are performed using a Cary 500 spectro-photometer working in the spectroscopic domain 175–3300 nm. As CdF_2 is anisotropic crystal, the absorption spectra are obtained without the birefringent polarizer of the used spectrophotometer. The absorption spectra were obtained with a resolution of 1 nm in the infrared range and with 0.4 nm in the UV-visible range.

The luminescence properties are studied by photoluminescence (PL) measurements, conducted on a Perkin Elmer LS 50B spectrometer using a Xe lamp as the excitation light source at room temperature. The discharge lamp is equivalent to 20 kW for 8 μs duration. The detector electronics are controlled so that delay and gate time can be varied to measure fluorescence between source pulses. The apparatus used can cover a broad spectral range extending from 200 to 900 nm. The upconversion spectra were performed under excitation at 980 nm with a cw Ti: Sapphire laser (Coherent 890) pumped by an argon laser (Spectra Physics 2000). All graphs are treated with Origin graphical software.

3. Results and discussion

3.1. Absorption measurements and Judd-Ofelt analysis

The absorption spectrum of CdF_2 co-doped with Er^{3+} and Yb^{3+} ions are recorded at room temperature in the spectral range from 300 to 1800 nm (Fig. 1). All bands are attributed to 4f-4f transitions of Er^{3+} and Yb^{3+}. In the infrared region of the spectrum (Fig. 1a), we observe three bands at 800, 980 and 1450 nm. The second band, showing a high optical density, corresponds to an absorption overlap between the two transitions ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ (from Yb^{3+} ions) and ${}^4I_{15/2} \rightarrow {}^5I_{11/2}$ (from Er^{3+} ions). The UV-Visible domain of the absorption spectrum consists of several well resolved lines attributed to the transition from the ground level ${}^4I_{15/2}$ to all successive near UV and visible multiplets of Er^{3+} ions as mentioned in Fig. 1 b. The location and assignments of these absorption bands have been done according to Carnall et al. [5] and all related works. In order to exploit the absorption spectra by means of the Judd-Ofelt theory, it is wise to avoid the continuous good background for each absorption band of the spectrum and from there calculate the average wavelength of each transition according to the following formula:

$$\bar{\lambda} = \frac{\int\limits_{J\rightarrow J'} \lambda DO(\lambda) d\lambda}{\int\limits_{J\rightarrow J'} DO(\lambda) d\lambda} \tag{1}$$

From the measured averaged wavelengths and the integrated absorption cross-sections, we determine the transition strengths of the main transitions as follows:

$$S^{mes}_{JJ'} = \left(\frac{9n}{(n^2+2)^2}\right)\left(\frac{3hc\varepsilon_0}{2\pi^2 e^2}\right)\frac{1}{\bar{\lambda}}(2J+1)\int \sigma_{ads}(\lambda)d\lambda \tag{2}$$

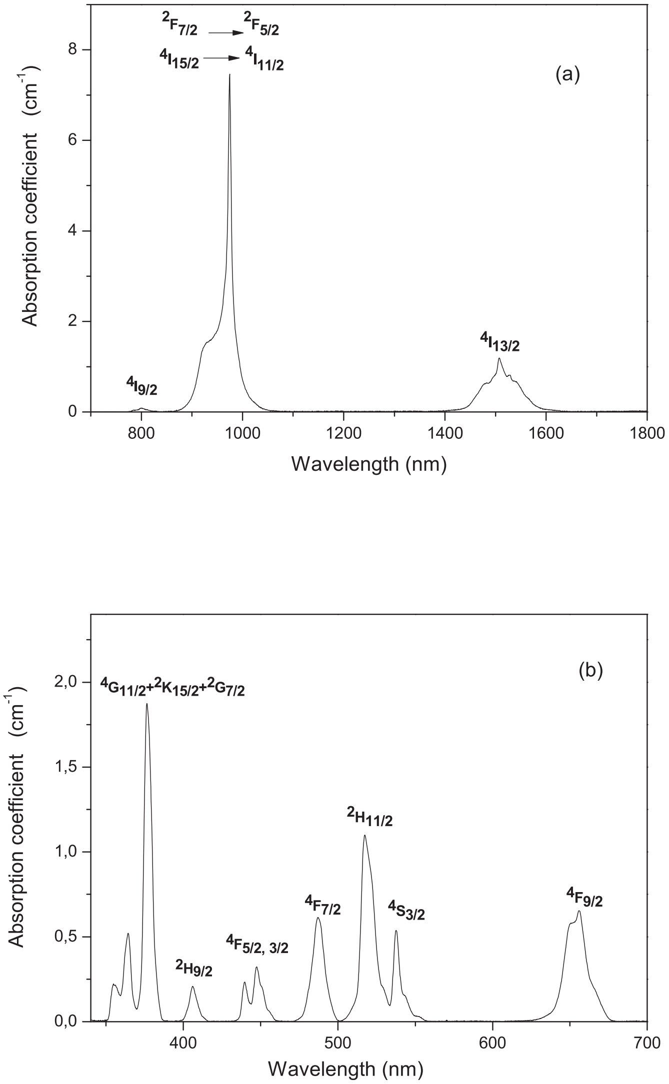

Fig. 1. Room temperature absorption spectrum of CdF_2: Er^{3+}(1 mol.%), Yb^{3+}(4 mol.%) single crystal. (a) UV–visible range and (b) near infrared range.

The corresponding line strengths of electrical dipole (ED) transition transitions is given by the formula:

$$S^{DEmes}_{JJ'} = S^{mes}_{JJ'} - \left(\frac{9n^2}{(n^2+2)^2}\right)\cdot S^{DM}_{JJ'} \tag{3}$$

We have chosen six absorption bands. The values of the corresponding measured absorption line strengths S_{em} are tabulated in Table 1.

In JO approach, the line strength of electric dipole transition is written by the equation:

$$S^{DEmes}_{JJ'} = \sum_{t=2,4,6} \Omega_t \left| \left\langle 4F^n \alpha[L,S]J \middle| U^{(t)} \middle| 4F^n \alpha\left[L',S'\right]J' \right\rangle \right|^2 \tag{4}$$

where Ω_t (t = 2,4,6) are the JO intensity parameters, U(t) are the doubly reduced matrix elements of rank t between states characterized by the quantum numbers of (S, L, J) and(S′, L′, J′). The matrix elements depend only on the angular momentum of the Er^{3+} states and are independent of the host and can be found in Kaminskii [6]. The line strength of the magnetic dipole transition is: