



# Synthesis and study of spectroscopic properties of CdF<sub>2</sub> crystals codoped with luminescent rare earth ions (Ho<sup>3+</sup>/Yb<sup>3+</sup>)



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## ARTICLE INFO

### Article history:

Received 19 March 2014

Accepted 2 April 2014

Available online 13 April 2014

### Keywords:

CdF<sub>2</sub>

Holmium

Judd–Ofelt theory

Luminescence

Green emission

## ABSTRACT

In this paper, we report the optical analysis of Ho<sup>3+</sup> ions doped CdF<sub>2</sub> single crystals. The pulled crystals were prepared by use of the Bridgman technique from a vacuum furnace in fluoride atmosphere after purification of the starting materials. Absorption, excitation, emission and fluorescence decay spectra were recorded at room temperature. The Judd–Ofelt (JO) analysis was applied to obtain the three phenomenological intensity parameters ( $\Omega_t$ ,  $t = 2, 4, 6$ ) and the transition strengths. The JO intensity parameters  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$  for 4f–4f transitions of Ho<sup>3+</sup> ions were computed from the optical absorption spectra using UV, visible and near infrared transitions. These parameters were then used to calculate the radiative transition probabilities ( $A_{Jf}$ ), branching ratios ( $\beta_{Jf}$ ) and radiative lifetimes ( $\tau_{rad}$ ) of the main laser emitting levels of Ho<sup>3+</sup> ions. The obtained spectroscopic properties are compared to those of Ho<sup>3+</sup> transitions in other fluoride and oxide hosts. The excitation spectrum in the UV–Visible spectral range is very close to the absorption spectrum indicating that all observed absorption levels can excite the holmium green emission corresponding to  $^5F_4(^5S_2) \rightarrow ^5I_8$  transition. The emission spectrum is mainly dominated by the green emission alongside the blue and red emissions. For the main transitions, there is a good agreement between the emission spectrum and the spontaneous emission probabilities given by the JO analysis. Using the Fuchtbauer–Ladenburg method, the emission cross-section of the three main visible emission were determined in addition to other important laser parameters such radiative quantum efficiency and optical gain.

We discuss the mechanisms of energy transfer in a forthcoming publication.

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## 1. Introduction

Research in the field of inorganic materials doped with luminescent rare earth ions has steadily increased from one year to another. These materials have given rise to many optical applications in solid state lasers, lamp industry, color displays, etc. They have been used as single crystals, glasses or optical fibers. To increase their efficiency, these materials must have interesting mechanical and thermal properties, a rather broad range of transparency and rather threshold optical damage. During the last two decades, fluoride materials known to have low phonon energies, a good thermomechanical properties and a high chemical stability seem to meet these challenges. Moreover, among the rare earth ions extensively used as dopants, we find the Ho<sup>3+</sup> ion which has an interesting energy level scheme resulting in various transitions

in the infrared, visible and UV region. It shows laser action at different wavelengths from 550 nm to 3.9  $\mu$ m, in variety of glass and crystalline hosts and offers various up-conversion mechanisms [1–5]. Most of these studies have been concentrated on the eye-safe laser emission operating around 2  $\mu$ m and corresponding to the transition  $^5I_7 \rightarrow ^5I_8$ . Such transition possesses higher gain cross-sections, longer radiative lifetime and higher branching ratio. It generates a great interest in many fields especially in optical communications and medical instrumentation [6]. Besides of this, it is well known that Ho<sup>3+</sup> is an excellent candidate doped ions to produce visible emission from higher excited multiplets, i.e. 550 nm green emission (due to the  $^5F_4 + ^5S_2 \rightarrow ^5I_8$  transition) and red emission (due to the  $^5F_5 \rightarrow ^5I_8$  transition). Yb<sup>3+</sup> and Tm<sup>3+</sup> are often used as sensitizers for Ho<sup>3+</sup> because of the availability of high-power InGaAs laser diodes which easily excite the two ions [7–11].

For all these reasons, we have undertaken spectroscopic study of the Ho<sup>3+</sup> ions doping the fluoride matrix CdF<sub>2</sub>. In this paper, we fabricated Ho<sup>3+</sup>:CdF<sub>2</sub> transparent single crystals by using

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commercial powder. The prepared sample has been characterized by using the X-ray diffraction (XRD). This crystal possesses relatively low phonon energy resulting in a reduction of the multiphonon relaxation in favor of radiative transitions. We characterized the optical properties of  $\text{Ho}^{3+}$  ions using the theory of “forced” electric dipole transitions in rare-earth-doped materials developed by Judd [12] and Ofelt [13] exploiting the absorption spectra recorded at room temperature. The last part of this article deals with the excitation and the luminescence properties of  $\text{Ho}^{3+}$  ions. We focus on both green and red emissions which are useful for the development of visible solid state lasers.

## 2. Sample properties and preparation

The structural and physico-chemical characteristics of the studied sample were presented in our recent publication [14]. We merely mention here only the main properties. The  $\text{CdF}_2$  compound crystallises in a face centred cubic structure having the fluorite type and belonging to  $\text{Fm}\bar{3}\text{m}$  space group with four unit formula [15,16]. It has a lattice parameter of 5.388 Å [17,18]. The trivalent ions ( $\text{Ho}^{3+}$ ) substitute the divalent ions ( $\text{Cd}^{2+}$ ) which requires a charge compensation in the form of interstitial sites  $\text{F}_i^-$  thus changing the geometry and the formation of the active centre. The maximum phonon energy ( $384\text{ cm}^{-1}$ ) [19] is quite low relative to those of oxides.

The  $\text{CdF}_2$  single crystals are grown by use of the Bridgman technique from a vacuum furnace in fluorine atmosphere. The  $\text{CdF}_2$  commercial powder, coming from Merck, is purified by repeated growth of simple crystals. After the purification step, the holmium doping is introduced in the form of trifluoride powder ( $\text{HoF}_3$ ) with nominal concentration of 1%. The mixture is heated under vacuum for 2 h with progressive temperature increase until 400 °C. The pulled crystals have more than 8 mm in diameter and 10–25 mm in length. Checked in polarized light, they are exempted of makles and crackles. They could easily cut into laser bulk single crystals with high optical quality. The sample used for optical measurements was polished to flat and parallel faces with 3.0 mm thickness.

## 3. XRD and optical characterization protocol

We have used an X-ray powder diffractometer (Philips X'Pert Pro) to explore the nature and phase structure of the samples synthesized. The apparatus is used in Bragg–Brentano geometry with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54059\text{ \AA}$ ) operating at 45 kV and 40 mA. The X-ray diffraction (XRD) patterns were recorded in the range  $20^\circ \leq 2\theta \leq 90^\circ$ .

The absorption spectra were performed at room temperature using a Cary 500 spectrophotometer working in the spectroscopic domain 175–3300 nm. As  $\text{CdF}_2$  is an isotropic crystal, the absorption spectra were obtained without the birefringent polarizer of the used spectrophotometer. The luminescence properties were 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  $\mu\text{s}$  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.

## 4. Results and discussion

### 4.1. Phase characterization

The X-ray powder diffraction pattern of  $\text{Ho}^{3+}:\text{CdF}_2$  crystals is shown on Fig. 1. All of the observed peaks can be attributed to the cubic phase with the  $\text{Fm}\bar{3}\text{m}$  space group according to the ICSD file 75-0226. There is no diffraction peak corresponding to any impurity or allotropic phase. The fitted cell parameter was found equal to 5.3867 Å which is in a good agreement with that given in literature [20–22]. The holmium is introduced in low concentration, so its influence on the cell parameter of the host crystal is slight.

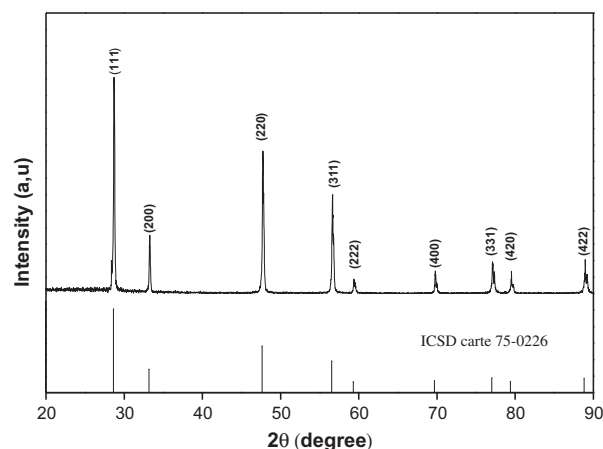


Fig. 1. XRD pattern of  $\text{CdF}_2:\text{Ho}^{3+}$  (1 mol.%),  $\text{Yb}^{3+}$  (1 mol.%).

### 4.2. Optical absorption spectra and Judd–Ofelt analysis

#### 4.2.1. Absorption properties

The absorption spectrum of  $\text{Ho}^{3+}:\text{CdF}_2$  recorded at room temperature in the spectral range from 300 to 2400 nm is shown in Fig. 2. The absorption bands are attributed to  $4f-4f$  transitions of  $\text{Ho}^{3+}$  from the ground state  $^5\text{I}_8$  to the different excited states. The spectrum consists of two net and separate parts composed of well resolved peaks. In the infrared part of the spectrum, we observe two bands at 1146 and 1924 nm corresponding to  $^5\text{I}_8 \rightarrow ^5\text{I}_6$  and  $^5\text{I}_8 \rightarrow ^5\text{I}_7$  transitions respectively (Fig. 2a). The bands  $^5\text{I}_4$  and  $^5\text{I}_5$

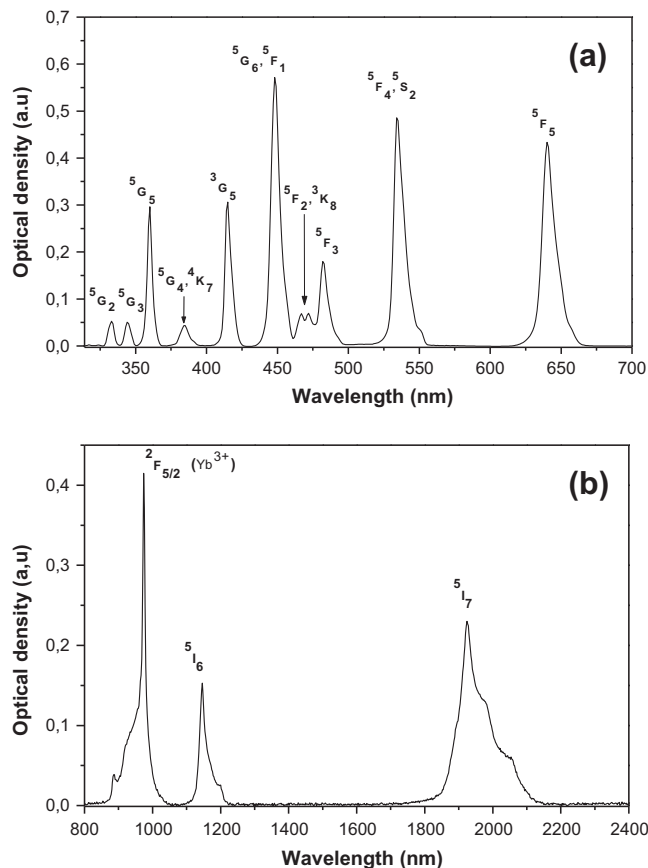


Fig. 2. Room temperature absorption spectrum of  $\text{CdF}_2:\text{Ho}^{3+}$  (1 mol.%),  $\text{Yb}^{3+}$  (1 mol.%) single crystals. (a) UV–visible range and (b) near infrared range.

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