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Spectroscopic properties of Ho³⁺-doped PbF₂ single crystal for 2 μm lasers

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ABSTRACT

A Ho:PbF₂ crystal was grown successfully by the conventional technique modified Bridgman method. Based on the Judd–Ofelt theory, the spectral parameters of Ho³⁺ were studied in detail by using the absorption spectrum of the as-grown crystal. Moreover, the emission probabilities, branching ratio, and radiative lifetime for the as grown crystal were also calculated. The stimulated emission cross-sections of the $^5I_7 \rightarrow {}^5I_8$ transition were calculated by using the Fuchtbauer–Ladenburg (FL) method. The fluorescence lifetime of the $^5I_7$ manifold was measured with a value of 13.6 ms. We propose that the Ho:PbF₂ crystal may be a promising material for 2 μm laser applications.

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1. Introduction

Solid-state lasers operating around 2 μm regions have attracted much attention in recent years due to their wide applications in atmospheric monitoring, medical surgery, remote sensing, coherent lidar, scientific research, and the generation of longer wavelengths via nonlinear optics [1–7]. It is well know that Ho³⁺ is a natural candidate for ~2 μm lasers owing to the $^5I_7 \rightarrow {}^5I_8$ transition [8–10]. However, the ~2 μm laser operation cannot be obtained efficiently due to the lack of commercialized laser diodes (LD) corresponding to the intrinsic absorption of Ho³⁺ ions. Co-doping of Tm³⁺ ion as a sensitizer to Ho³⁺ ion has been used as a feasible alternative through energy transfer from Tm³⁺:³F₄ to Ho³⁺:⁵I₇ [11]. Nevertheless, the co-doping of Tm³⁺ ion would introduce a series of undesirable energy transfer processes, resulting in the increase of threshold and decrease of storage efficiency. Moreover, the Ho/Tm co-doped crystals are also subjected to upconversion process, which leads to increased thermal heat loads [12]. Fortunately, the development of high power Tm-based crystalline and fiber lasers operating at around 1.9 μm turn out to be attractive sources for resonantly pumped singly doped Ho lasers, which possess higher quantum efficiency and lower thermal generation [13]. In particular, a Q-switched Ho:YLF laser operating at 2051.3 nm with a pulse energy of 550 mJ has been demonstrated [14].

The ideal host material for mid-IR (MIR) lasers is expected to possess low phonon energy, which is beneficial for suppressing multiphonon de-excitation processes. Compared with oxide crystals, fluorides are more attractive to achieve high-energy Q-switched operation, as they possess several advantages: (i) lower phonon energy suppressing nonradiative relaxation between adjacent energy levels; (ii) longer fluorescence lifetime improving energy storage [15,16]. In our previous work [17], we have focused our scientific program on a new potential gain medium Ho:PbF₂ crystal for efficient laser operation, which has been proved with low phonon energy of 257 cm⁻¹, good 2.8 μm MIR emission performances, and low absorption coefficient in typical H₂O absorption band at 3 μm, and potential interest for laser applications. However, to our knowledge, there is no work has been carried out on the spectroscopic properties of this crystal in sufficient detail, especially in the wavelength of ~2 μm. Therefore, it is necessary to have a systematical investigation on the optical characterization of Ho:PbF₂, which may contribute to roundly characterize this crystal.

In this work, the grown and the spectroscopic properties of Ho:PbF₂ crystal was studied. The spectral parameters were calculated using absorption spectra based on the Judd–Ofelt (J–O) theory [18,19]. Moreover, the emission probabilities, fluorescence branching ratio, and radiative lifetime were also analyzed.

2. Experimental procedure

The Ho (2 mol.%):PbF₂ crystal was grown by the conventional technique modified Bridgman method under non-vacuum

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conditions. The raw materials used for the crystal growth were PbF_2 (99.99%) and HoF_3 (99.99%) powders. The constituent fluorides were weighted and mixed, followed by heating for 3 h at 180 °C in dried CF_4 atmosphere for dehydration treatment, and then loaded into a 30 mm-diameter platinum crucible for crystal growth. In order to avoid the oxidation, a chemical (rubber or carbon powder) was added to the top of the raw material. so as to exhaust the air sealed in the crucible during the crystal growth. At the same time, to avoid volatilization of the melt, the assembled crucible was sealed immediately. The furnace chamber used for crystal growth consists of three zones, including to the high-temperature zone, the gradient zone, and the low-temperature zone. Firstly, the melt was heated at 960 °C for 8 h in the crucible in the high-temperature zone. Then the growth process was driven by lowering the crucible at a rate of 0.5 mm/h in the gradient zone, which had a temperature gradient of around 35–40 °C/cm. At last, the as grown crystal was cooled to room temperature at the rate of 30 °C/cm–40 °C/h. The concentration and segregation coefficient of Ho^{3+} ion in the PbF_2 crystal has been provided in our previous work [17] with a value of 2.2×10^{20} ions/cm^3, and 1.15, respectively.

Crystal structure identification was under taken on a D/max2550 X-ray diffraction (XRD) using Cu Kα radiation. The absorption spectra of Ho:PbF_2 crystal in the range of 300–2200 nm were recorded by a JASCO V-570 UV/VIS spectrophotometer at room temperature. The fluorescence spectra and fluorescence decay curve under excitation of 637 nm were obtained with Edinburg Instruments FLS920 and FSP920 spectrophotometers, under excitation with an 8 ns pulse of an optical parametric oscillator. All the measurements were taken at room temperature.

3. Results and discussion

The Ho:PbF_2 crystal with dimension of $\varnothing30 \times 60$ mm^3 was successfully grown. The crystal is free from Cracks, bubbles and inclusions. The XRD patterns of the Ho:PbF_2 crystal and the standard pattern of PbF_2 (JCPDS 06-0251), are shown in Fig. 1. The diffraction peaks are strong and no second phase diffraction peak is found, indicating that the impurities do not change the essential structure of PbF_2.

The absorption spectra of Ho:PbF_2 crystal in the 300–2200 nm spectral range is shown in Fig. 2. The absorption peaks correspond

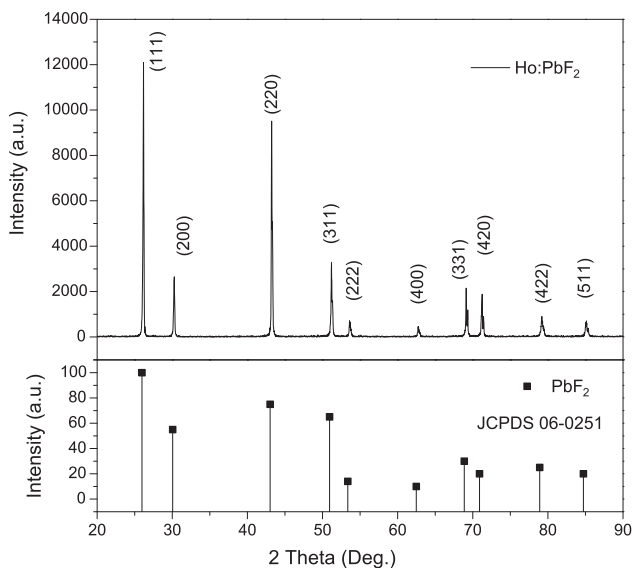to the transitions from the ground state $^5I_8$ to the excited states, which are marked in Fig. 2. The absorption cross-section was calculated using

$$\sigma_{abs} = \frac{OD(\lambda)}{L \cdot \log e \cdot N_0} \qquad (1)$$

where $OD(\lambda)$ is the absorption optical density, L is the thickness of the measured sample, and N_0 is the Ho^{3+} concentration in ions/cm^3. The peak absorption cross-section and the corresponding full width at half maximum (FWHM) for the main absorption bands are listed in Table 1. In particularly, the peak absorption cross-section at 1150 nm is 0.14 with FWHM of 61 nm. The peak absorption cross-section at 1150 nm is matched well with the emission wavelength of Yb-doped fiber lasers at 1147 nm [20].

In this work, the absorption spectra of Ho:PbF_2 crystal was used to calculate the J–O intensity parameters in details. After that, the spontaneous emission probabilities, radiative lifetime and fluorescence branching can also be obtained. A brief outline of the J–O analysis is given in the following.

On the basis of the J–O theory, the absorption line strength for electric-dipole (ED) transitions can be written as

$$S_{cal}(J \rightarrow J') = \sum_{t=2,4,6} \Omega_t \left| \langle S,L,J \| U^{(t)} \| S',L',J' \rangle \right|^2, \qquad (2)$$

where J and J' are the total angular momentum quantum numbers of the initial and final states, respectively, $\left| \langle S,L,J \| U^{(t)} \| S',L',J' \rangle \right|^2$ are the square of the matrix elements of the tensorial operator, which were calculated by Carnall et al. [21]. Ω_t (t = 2, 4, 6) parameters are the J–O intensity parameters. According to the intermediate coupling and the selection rules for magnetic dipole (MD) transitions in the lanthanides, only the $^5I_8 \rightarrow {}^5I_7$ transition in all observed
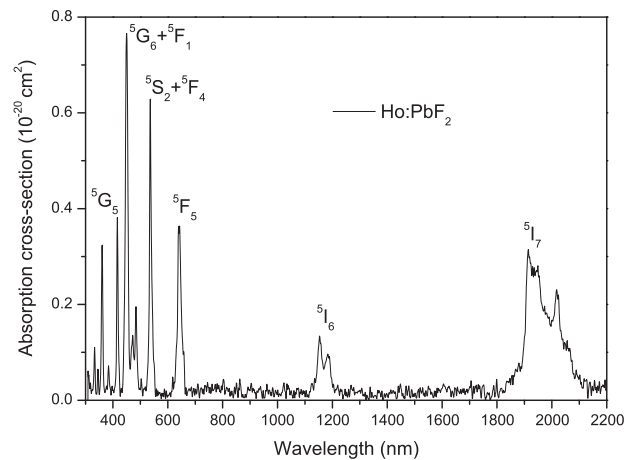
Fig. 2. The absorption cross-section of Ho:PbF_2 crystal.

Fig. 1. (a) XRD pattern of Ho:PbF_2 crystal and (b) XRD pattern of PbF_2 crystal (JCPDS 06-0251).

Table 1
Barycenter wavelengths, peak absorption cross-sections, and measured and calculated line strengths of Ho:PbF_2 crystal.

$^5I_8\rightarrow$	λ (nm)	FWHM (nm)	σ_{abs} (10^{-20} cm^2)	S_{mea} (10^{-20} cm^2)	S_{cal} (10^{-20} cm^2)
$^5I_7$	1914	64	0.31	1.72	1.92
$^5I_6$	1150	61	0.14	1.05	0.84
$^5F_5$	639	22	0.36	1.44	1.37
$^5S_2 + {}^5F_4$	536	10	0.63	1.58	1.47
$^5G_6 + {}^5F_1$	450	8	0.77	2.39	2.39
$^3G_5$	416	5	0.38	0.84	0.93
$^3K_7 + {}^5G_4$	361	5	0.32	0.17	0.14