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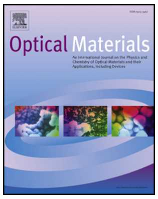

Spectroscopic investigation of Er^{3+} doped BaF_2 single crystal

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ABSTRACT

We report on the spectroscopic investigation of Er^{3+} doped BaF_2 single crystals. High-quality crystals have been gown by the Bridgman-Stockbarger pulling technique. The room temperature absorption, excitation, emission and fluorescence decay spectra of the luminescent Er^{3+} ions inserted in BaF_2 fluoride single crystals have been investigated. Using the Judd-Ofelt (JO) theory, the intensity parameters of Er^{3+} ions have been calculated to be $\Omega_2 = 0.949 \times 10^{-20}\ cm^2$, $\Omega_4 = 0.975 \times 10^{-20}\ cm^2$ and $\Omega_6 = 1.258 \times 10^{-20}\ cm^2$. These parameters were then used to calculate the radiative transition probabilities ($A_{JJ'}$), branching ratios ($\beta_{JJ'}$) and radiative lifetimes (τ_{rad}) of the main laser emitting levels of Er^{3+} ions. The obtained spectroscopic properties are compared to those of Er^{3+} 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 Erbium green emission. The emission spectrum is mainly dominated by the green emission alongside a weak red emission. 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.

1. Introduction

Nowadays, crystalline lasers play a special role in modern laser physics and nonlinear optics. The amplifying medium is generally an inorganic material doped with luminescent elements. Such medium is used as single crystals, glasses, glass ceramics or optical fibers. The most materials studied are doped with rare earth ions (RE) which constitute the optically active centers by considering the 4f–4f transitions. Among all solid-state laser materials, the fluorides have the advantageous to be transparent in a large electromagnetic domain and they have low maximum phonon frequency leading to a large number of potential emitting levels by limiting the non radiative emissions since they gave rise to laser emissions at different wavelengths of the optical spectrum. In this context, MF_2 difluoride crystals (M = Alkaline earth element, Cd or Pb) with fluorite structure are of great interest as material for photonics, in general, and specially in solid state laser. BaF_2 is an alkali earth fluoride and a great deal of attention is attributed to its optical properties [1–3]. These optical properties are related to the structural and electronic properties of BaF_2 such as a very large band gap. Much work has been devoted to the search of new laser host materials. Barium fluoride BaF_2 doped with rare earth ions TR^{3+} occupies a wide range of applications such as lasers [4], optical communications [5]. In the research, BaF_2 doped with RE^{3+} is known as an excellent scintillator [6] for the detection of X-rays or high energy particles. A such fluoride material have a relatively low phonon energy and a large optical transparency over a wide wavelength range from ultraviolet (UV) to far infrared (FIR) from 0.2 to 14.0 μm and is used to make optical components, such as windows for infrared spectroscopy. On another hand, rare earth ions like Er^{3+} are considered as luminescence centers in crystals as well as in glasses [7–10]. A great interest is paid to erbium due to its emission band at 1.53 μm for optical transmission (erbium-doped fiber amplifier), eye-safe light detecting and in the visible region (blue-green) for data storage. The emission of erbium Er^{3+} in the visible range can be obtained by up-conversion process. The laser performance of Er^{3+} has been observed in glass fibers [11] and crystals [12]. Indeed, fluorides offer an advantage more than the oxides because

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the lifetime of the electronic states is longer in these systems, this comes from the low energy phonon of this hosts leading to a small non-radiative transition.

In this paper, we report the spectral properties of Er^{3+} ions doped BaF_2 crystal. Absorption, excitation, emission and fluorescence decay spectra are recorded at room temperature. The Judd-Ofelt (JO) analysis was applied using the absorption spectra recorded at room temperature in order to deduce the emission transition probabilities, branching ratios and radiative lifetimes.

2. Physical properties of BaF_2 crystals

The barium difluoride (BaF_2) crystallizes in the fluorite structure and has the Fm3m space group with four unit formula per unit cell [13]. Its lattice constant is 6.20 Å. It has a melting point temperature of 1360–1480 °C [14]. The transmission range of BaF_2 is 0.2–14 µm, due to its large bandwidth of 11 eV [15]. During the synthesis of BaF_2: Er^{3+}crystal, the Er^{3+} ion substitutes the Ba^{2+} divalent ion, short-range charging compensation will then be possible. For the site tetragonal (C_{4v}), charge compensation is provided by a fluorine ion F^- in interstitial position in the center of the nearest neighbor cube to ensure the electrical neutrality of the crystal. The phonon energy is 319 cm^{-1} [16]. Such value remains low compared with oxides, which leads to high radiative transitions in these materials. The optical and physical properties of BaF_2 make it versatile optical material. The whole of these properties and others are summarized in Table 1.

3. Crystal growth and X-ray ray characterization

Er^{3+}: BaF_2 is grown by the use of Bridgman-Stockbarger pulling technique. The crucible that contains the powder mixture is placed in a vacuum furnace in fluorine atmosphere. The BaF_2 initial powder is purified several times using repeated growth of single crystals. The erbium ion is introduced in the form of erbium trifluoride (ErF_3) after the purification step. The pulled crystals have a diameter of more than 8 mm and they are 20–30 mm in length. Fig. 1 shows a part of the pulled cylindrical crystal and a sample obtained from a cut slice. Since it has a cubic structure, we have cut the samples in a direction perpendicular to the cylinder axis. The samples were checked in polarized light and have been found to be free of macles and crackles. They could easily be cut into laser bulk single crystals with high optical quality. The crystal structure was checked by X-ray diffraction (XRD) pattern (Fig. 2) using a Philips X'Pert Pro diffractometer. The XRD diffractogram of Fig. 2 shows a set of diffraction lines. The diffraction peaks are ascribed to the cubic structure according to the file (JCPDS 04–0452). The fitted value of lattice parameter is 6.23 Å which is in agreement with those obtained in the literature [13].

Table 1
Physical characteristics of BaF_2 crystal.

Properties		Ref.
Crystal structure	Cubic	[13]
Space group	Fm3m	[13]
Lattice parameter	6.2 Å	[13]
Number of unit formula	4	[13]
Symmetry site	C_{4v}	[14]
Melting temperature	1386 °C	[15]
Refractive index	1.475	[13]
Energy gap	11 eV	[17]
Phonon energy	319 cm^{-1}	[16]
Thermal conductivity	11.72 $W m^{-1} K^{-1}$	[16]
Thermal expansion coefficient	18.1 10^{-6}/K	[15]
Density	4.9 g/cm^3	[17]

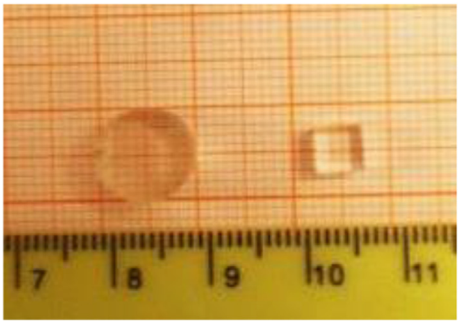

Fig. 1. A polished sample of Er^{3+}: BaF_2 crystal.

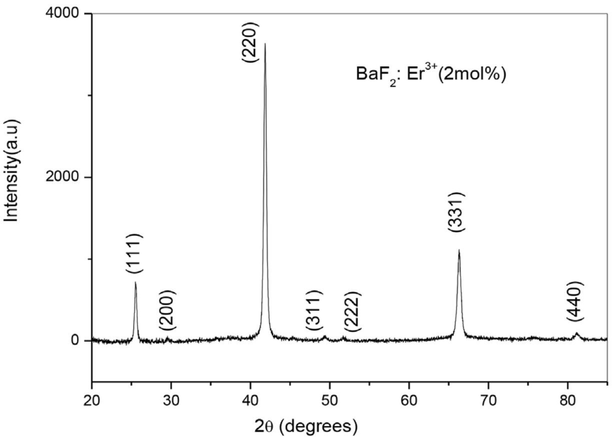

Fig. 2. X-Ray diffraction pattern of barium fluoride sample BaF_2: Er^{3+}(2% mol.).

4. Judd–Ofelt (JO) formalism

The absorption lines of trivalent rare-earth ions (RE) in a crystalline host are due to intra-configurational f–f transitions. JO model [18,19] has been employed to describe the absorption and photoluminescence properties of RE in many ion-host combinations [20]. Fitting procedure of the experimental absorption oscillator strengths to the theoretical ones allows evaluating the phenomenological JO parameters Ω_2, Ω_4, Ω_6, which can be used to calculate other important parameters, as radiative transition probabilities, radiative lifetimes and branching ratios. In the framework of the Judd–Ofelt theory, we need the average wavelength of each absorption band which is often given by the following formula:

$$\bar{\lambda} = \frac{\int_{J\to J'} \lambda DO(\lambda)d\lambda}{\int_{J\to J'} DO(\lambda)d\lambda} \tag{1}$$

The measured line strengths $S_{JJ'}^{mes}$ of the chosen bands are determined using the following expression:

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

Where J and J′ represent the total angular momentum quantum numbers of the initial and final levels, respectively, n is the refractive index of the material, h is Planck's constant, c is the vacuum light celerity, ε_0 is the vacuum permittivity, e is the electron charge, $\bar{\lambda}$ is the average wavelength of the J→J′ absorption transition. The magnetic dipolar line strength is:

$$S_{JJ'}^{MD} = \left(\frac{h}{4\pi mc}\right)^2 |\langle 4f^N\alpha[L,S]J||\vec{L} + 2\vec{S}||4f^N\alpha'[L',S']J'\rangle|^2 \tag{3}$$