Ce³⁺ ion-doped α-NaYF₄ single crystal for UV laser

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A Ce³⁺ ion-doped α-NaYF₄ single crystal of high quality is grown successfully by an improved flux Bridgman method under the conditions of taking the chemical raw composition of NaF:KF:YF₃:CeF₃ in the molar ratio of 30:18:48:4, where the KF is shown to be an effective assistant flux. The x ray diffraction, absorption spectra, excitation spectra, and emission spectra of the Ce³⁺-doped α-NaYF₄ single crystal are measured to investigate the phase and optical properties of the single crystals. The absorption spectrum of the Ce³⁺:α-NaYF₄ shows a strong band that peaks at the wavelength of 300 nm. The emission spectrum of the Ce³⁺:α-NaYF₄ emits an intense ultraviolet (UV) band at the wavelength of 332 nm under the excitation of 300 nm light. Two separated luminous bands of 330 and 350 nm, which correspond to the transitions $5d \to {}^2F_{5/2}$ and $5d \to {}^2F_{7/2}$, can be obtained by Gauss fitting. The strong emission intensity at the UV band and the excellent optical transmission in the range of UV wavelengths indicate that Ce³⁺:α-NaYF₄ single crystals can be considered as a promising material for UV lasers.

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In recent decades, the development of ultraviolet (UV) solid-state lasers has attracted great interest for their advantages of stable physical and chemical properties, narrow fluorspar spectral lines, strong absorption band, and high fluorescence quantum efficiency. UV lasers based on solid-state materials have many practical applications, such as medical procedures, semiconductor processing, optical communications and remote sensing, and so on. Although various kinds of lasers and tunable color center lasers have been investigated as UV sources, their applications are still restricted because many of them only operate at low temperatures and some of their materials deteriorate[1,2].

Rare earth ion-doped solid-state materials are mainly considered for devices due to the abundant energy levels of rare earth ions and the super properties of some of their matrixes. The Ce³⁺ ion is one of the most important active ions applied to UV lasers because of the transition $5d \to 4f$ around 325 nm[3]. The optical spectra and UV lasers based on Ce³⁺ ion-doped single crystals, glasses, and glass ceramics have already been studied[3–7].

Besides the rare earth ion dopant, the host material also plays an important role in the doping concentration, luminescence efficiency, thermal stability, etc. In the reported Ce³⁺ ion-doped materials, fluoride single crystals such as LiYF₄ were mostly mentioned due to their low phonon energy, good chemical and thermal stability, high transparency at UV wavelengths, and high luminous efficiency[3,8].

NaYF₄ crystals, such as the cubic α-NaYF₄ and the hexagonal β-NaYF₄, have been widely studied for their application as excellent host for up-conversion[2] because of their low maximum phonon energy, which is about 360 cm⁻¹. More recently, α-NaYF₄ bulk single crystals doped with Ho³⁺/Yb³⁺[9], Tb³⁺/Eu³⁺[10], and Tm³⁺[11] were successfully grown in our laboratory by an improved flux Bridgman method. The transmittance in the UV wavelength and the Raman spectra of an α-NaYF₄ single crystal have already recorded[9–11]. Compared with LiYF₄ single crystals, the α-NaYF₄ has a lower-value maximum phonon energy, about 390 cm⁻¹, and a higher transparency in the UV range[2,8]. The excellent properties of α-NaYF₄ single crystals in thermal, mechanical, chemical, and optical behaviors are beneficial for its application in UV lasers to obtain a high luminous efficiency and high stability. However, there have been few reports for Ce³⁺ ion-doped α-NaYF₄ bulk single crystals for UV lasers because of the difficulty of the crystal growth. In this Letter, the Ce³⁺ was incorporated in an α-NaYF₄ single crystal. The concentration of Ce³⁺ in the α-NaYF₄ single crystal was measured, and the optical performance of the obtained single crystal was explored to get a better-quality UV emission.

The Ce³⁺ doped α-NaYF₄ single crystal was grown by a vertical Bridgman method using KF as the flux in a NaY-YF₃ system. The raw materials were commercially available powders of high purity NaF (99.99%), KF (99.99%), YF₃ (99.99%), and CeF₃ (99.99%). The moisture and the some oxygen impurities in the fluoride powders could be removed completely using the high-temperature hydrofluorinating method, by which the powders were sintered with anhydrous HF at 750°C for 8 h. The molar ratio of the powders was NaF:KF:YF₃:CeF₃ = 30:18:48:4.

Then, the mixture of those materials was ground about an hour in a mortar. The growth orientation was along the a-axis by using an oriented seed crystal. The temperature gradient cross-solid-liquid interface was 70–90°C/cm; the growth process was carried on by lowering the crucible at a rate of ~0.6 mm/h. The detailed process of crystal growth is described elsewhere[9,10]. The obtained crystal shows high transparency. However, a white region of several centimeters in length which is main KF, CeF_3, and some deviating components excluded from the melt exists at the top of the boule, corresponding to the final portion of the melt to freeze. The as-grown crystal was cut into pieces and well polished. The inset of Fig. 1 shows a polished piece of crystal. An fxamination using a polarizing microscope showed that the single crystal part is free from macroscopic defects.

The Ce^{3+} concentration in the α-$NaYF_4$ single crystal was measured by an inductive coupled plasma (ICP) atomic emission spectrometer (PerkinElmer Inc., Optima 3000) and was about 0.788×10^{20} ions/cm³. The phase composition of the as-obtained crystals was recorded by x ray diffraction (XRD) using an XD-98X diffractometer (XD-3, Beijing). The scan was performed in the 2θ range from 10°–90° with a scanning step size of 0.02° and a 6 s swept time. A Cary 5000 UV/VIS/NIR spectrophotometer (Agilent Co., America) recorded the absorption spectra ranging from 200 to 600 nm. The optical properties of the α-$NaYF_4$ single crystal doped with Ce^{3+} ions were characterized by excitation spectra and photoluminescence spectra measured using an F-4500 spectrophotometer (Hitachi high-technologies Co., Tokyo, Japan). All the above measurements were carried out at room temperature, and the samples were under the same conditions to get comparable results.

The phase compositions of the as-prepared sample were analyzed by powder XRD. Figure 1(a) shows the XRD patterns of the α-$NaYF_4$:Ce^{3+} sample. Figure 1(b) shows the XRD patterns of card JCPD 77-2042[10,11]. It confirms that the transparent crystal obtained is an α-$NaYF_4$ single crystal and that KF was excluded from the final part of the
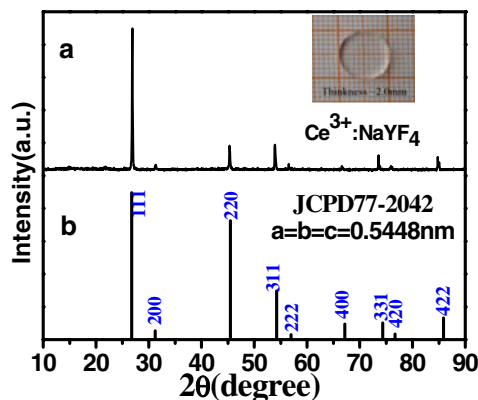
boule. Notably, compared with card JCPD 77-2042, the peak positions and intensity pattern matched well. It also confirms that the current Ce^{3+} ion doping level and introduction of K^+ ions do not bring any meaningful changes to the single crystal structure. As is well known, an α-$NaYF_4$ single crystal has a fluorite structure (CaF_2), in which Na^+ and Y^{3+} ions are randomly distributed in the cation sites, which are situated in the cubic center, and its lattice constants could be calculated from the XRD pattern data as the following lattice parameters[12]: $a_L = b_L = c_L = 0.5510$ nm for the lower part of the single crystal corresponding to the initial stage of crystal growth, and $a_U = b_U = c_U = 0.5562$ nm for the upper part of the single crystal corresponding to the final stage of crystal growth, which are close to the standard parameters as shown in Fig. 1 ($a = b = c = 0.5470$ nm).

The absorption spectra of Ce^{3+}-doped α-$NaYF_4$ single crystals are shown in Fig. 2. It is obvious that the Ce^{3+}:α-$NaYF_4$ single crystals have only one intense absorption peak located at 300 nm. The absorption peak represents the absorption transition of Ce^{3+} ion in an α-$NaYF_4$ single crystal from the ground state to the excitation state, viz, the $4d \rightarrow 5f$ electronic transition. In contrast, the single crystal doped with Ce^{3+} grown by the Czochralski method shows the absorption peak at 297 nm[3]. They are almost similar. Figures 3(a) and 3(b) display the excitation spectrum of the Ce^{3+}-doped α-$NaYF_4$ single crystal by measuring the emission at 332 nm and the emission spectrum for the Ce^{3+}-doped α-$NaYF_4$ single crystal under excitation at 300 nm wavelengths. It can be noted from Figs. 3(a) and 3(b) that there exists an excitation band at ~300 nm and an strong, sharp UV emission band at the wavelength of 332 nm.

It is known that the stable state of the rare-earth Ce^{3+} ion has a $4f^1$ configuration and the excited state has a $5d^1$ configuration[13–15]. The $4f$ configuration is in the $5s$ configuration and $5p$ configuration. Thus, interference from the surrounding plasma electric field is small, and its energy level splitting obeys the spin orbit. The $4f^1$ configuration splits into two levels with $^2F_{7/2}$ and
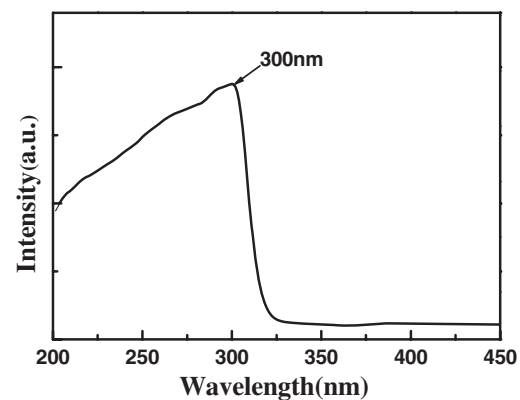

Fig. 1. XRD pattern of (a) Ce^{3+}:α-$NaYF_4$ crystal and (b) literature data of the corresponding bulk materials with crystal structure for α-$NaFY_4$ (JCPDS 77-2042).

Fig. 2. UV absorption spectra of the α-$NaYF_4$:Ce^{3+} single crystal.
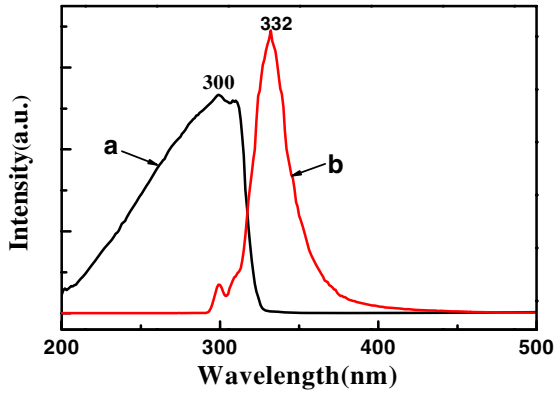
Fig. 3. Excitation spectra of the α-NaYF$_4$:Ce^{3+} single crystal (curve a) and the emission spectra of the α-NaYF$_4$:Ce^{3+} single crystal (curve b).
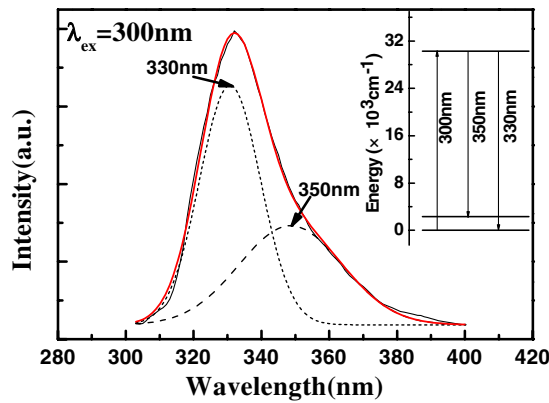

Fig. 4. Fitted results of luminescence spectra of Ce^{3+} ion-doped α-NaYF$_4$ single crystal excited by 300 nm wavelength. The inset is the energy level of a Ce^{3+} ion.

$^2F_{5/2}$ for the spin-orbit (LS) coupling. The first excited state of Ce^{3+} ions is the $5d$ configuration; because the $5d$ configuration is more sensitive to the environment, the strong electro-acoustic coupling divides the $5d$ configuration into five configurations at room temperature. Because the $5f \rightarrow 4d$ electronic transition is allowed, the wavelength of 332 nm belongs to the electric dipole transition of the $5f \rightarrow 4d$ electronic transition and it can be seen as consisting of two broadbands. All luminescence spectra can be fitted by two Gaussian functions corresponding to the luminescence transitions from the lowest $5d$ state to the $^2F_{5/2}$ and $^2F_{7/2}$ levels of the $4f$ state[3]. Figure 4 shows fitted results of the luminescence of Ce^{3+}:α-NaYF$_4$ by two Gaussian functions corresponding to the emission spectrum of the excitation wavelength of 300 nm. The fitted results indicate that the centers of the $5d \rightarrow {}^2F_{5/2}$ and $5d \rightarrow {}^2F_{7/2}$ luminescence transitions are at 330 and 350 nm, respectively. The splitting energy of about 2000 cm^{-1} between the $^2F_{7/2}$ and $^2F_{5/2}$ levels can be reflected from the two emission peaks. Table 1 shows the fitted results of the luminescence spectra of the Ce^{3+}:NaYF$_4$ single crystal.

Table 1. Fitted Results of Emission Spectra of the Ce^{3+}:α-NaYF4 Single Crystal Excited by 300 nm Wavelength

	Peak wavelength	
Excitation source	Peak: $5d \rightarrow {}^2F_{5/2}$	Peak: $5d \rightarrow {}^2F_{7/2}$
300 nm	330 nm	350 nm
	30303 cm^{-1}	28571 cm^{-1}

In conclusion, the Ce^{3+} ion can be incorporated into an α-NaYF$_4$ single crystal by a modified flux Bridgman method. When excited by the wavelength of 300 nm light, the emission spectra of the α-NaYF$_4$ single crystals doped with Ce^{3+} ions can emit an intense beam of UV at the wavelength of 332 nm, which is composed of 330 and 335 nm broadbands and which is due to the electric-dipole transition of the $5f \rightarrow 4d$ electronic transition. The strong emission band at UV wavelengths and the super chemical-physical properties indicate that the Ce^{3+} ion-doped α-NaYF$_4$ single crystal has potential applications in UV lasers.

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