

## SPECTROSCOPIC STUDIES OF Ho<sup>3+</sup>-DOPED SrF<sub>2</sub> CRYSTAL OR GREEN AND RED LASER APPLICATIONS

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*Spectroscopic studies of Ho<sup>3+</sup>-doped SrF<sub>2</sub> crystals were performed regarding applications in solid-state lasers. The crystal structure of the Ho:SrF<sub>2</sub> crystal was investigated using single-crystal X-ray diffraction. SrF<sub>2</sub> exists as a cubic structure with an Fm3m space group. A Raman shift of 288 cm<sup>-1</sup> was observed for the Ho:SrF<sub>2</sub> single crystal. SrF<sub>2</sub> hosts with low-frequency vibrational modes are suitable for reducing nonradiative emissions while maximizing radiative emissions. The absorption spectrum was recorded in the visible region from 400 to 800 nm, yielding absorption lines at 416, 450, 468, 473, 484, 536, 638, and 643 nm. The fluorescence spectrum recorded at an excitation wavelength of 450 nm shows two emission bands at 546 and 656 nm, which correspond to green and red emission, respectively. The intensity parameters  $\Omega_\lambda$  ( $\lambda = 2, 4, \text{ and } 6$ ) were estimated using the Judd–Ofelt theory. For Ho:SrF<sub>2</sub> single crystal, the calculated  $\Omega_\lambda$  are  $\Omega_2 = 0.14 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_4 = 3.14 \times 10^{-20} \text{ cm}^2$ , and  $\Omega_6 = 3.74 \times 10^{-20} \text{ cm}^2$ . The radiative transition probabilities, radiative lifetimes, and branching ratios  $\beta_R$  for Ho:SrF<sub>2</sub> were determined using the Judd–Ofelt parameters. The  $^5S_2 + ^5F_4 \rightarrow ^5I_8$  transition is more effective for population-building processes because of its lifetime (0.26 ms) and higher branching ratios (~82.86%). Ho:SrF<sub>2</sub> is, therefore, a promising solid-state laser crystal for green and red spectral regions.*

**Keywords:** single crystal, phonon, absorption, emission, fluorescence, solid-state laser, oscillator strength, Judd–Ofelt theory, transition probabilities, radiative lifetime, branching ratios.

**Introduction.** Lasers operating in the visible spectrum region are extensively used in laser spectroscopy, nonlinear optics, and coherent control equipment. It has been observed experimentally that rare-earth (RE) group elements provide an efficient gain medium for solid-state lasers in the visible range. RE ions are transparent when doped into crystals, glasses, and fibers, with sharp optical transitions. However, the crystal environment produces a broadening of the emission lines. In previous studies, Er<sup>3+</sup> [1, 2], Tm<sup>3+</sup> [3], Dy<sup>3+</sup> [4, 5], Sm<sup>3+</sup> [6], Tb<sup>3+</sup> [7], and Ho<sup>3+</sup> [8] have shown laser operation in the visible region. Compared to all RE ions, the holmium ion (Ho<sup>3+</sup>) is well recognized because of its multiple metastable levels. They can exhibit laser emission from the visible to infrared spectral regions [8, 9]. Large population inversion can be achieved at relatively long-lived  $^5I_7$  levels of Ho<sup>3+</sup> ions [10] and has shown an emission of approximately 2  $\mu\text{m}$  from the  $^5I_7$  to  $^5I_8$  transition. Therefore, this laser wavelength is safe for the eyes and is used in the medical treatment of the eyes. During the transition from  $^5F_4, ^5S_2$  to  $^5I_8$ , a green-wavelength emission at 545 nm has been observed [11]. A red-wavelength emission at 663 nm is recorded for the transition from  $^5F_5$  to  $^5I_8$  [12, 13]. The host material, SrF<sub>2</sub>, affects the spectroscopic transitions of Ho<sup>3+</sup> because of the phonon modes of the host. In rare-earth-doped materials, the emission quantum efficiency is dependent on the phonon energy of the host matrix; hence, the selection of the host material is crucial for the exploration of luminescence features. The SrF<sub>2</sub> crystal has a prominent vibrational mode at 282 cm<sup>-1</sup> [14]; furthermore, the low-phonon energy host is favorable for Ho<sup>3+</sup> ions since a few of the energy levels in Ho<sup>3+</sup> have an energy gap of approximately 1000 cm<sup>-1</sup>. Nonradiative emissions can be reduced and radiative emissions can be increased in a host material with low phonon energy [15]; thus, it is crucial to select a host material with low lattice vibrational modes. However, crystal field splitting due to the host atoms may be observed. In the present work, a SrF<sub>2</sub> single crystal is selected as the host material for Ho<sup>3+</sup> ions. The crystal structure of Ho: SrF<sub>2</sub> is confirmed using single-crystal X-ray diffraction (XRD). SrF<sub>2</sub> is a member of the fluoride MF<sub>2</sub> family (M = Ca, Sr, and Ba). The structures of these fluorides are fluorite-like, with symmetry O<sub>h</sub><sup>5</sup> and space group Fm3m.

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Our crystal (SrF<sub>2</sub>) has a cubic crystal structure with a lattice constant of 5.7928 Å. The absorption spectra were measured from 400 to 800 nm and absorption peaks were observed at 416, 450, 468, 473, 484, 536, 638, and 643 nm. The emission spectrum was recorded at an excitation wavelength of 450 nm. Two emission bands corresponding to the green and red wavelength regions were observed at 546 nm and 656 nm, respectively. Furthermore, we calculated the Judd–Ofelt (J–O) intensity parameters  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$  from the room temperature absorption spectra using the J–O theory. The radiative transition probabilities ( $A_R$ ), branching ratios ( $\beta_R$ ), and radiative lifetimes ( $\tau_R$ ) of various excited states of the Ho<sup>3+</sup> ion in the SrF<sub>2</sub> single crystal were calculated based on the obtained J–O intensity parameters.

**Experimental.** The X-ray diffraction (XRD) pattern was recorded using a Supernova, a single source, at an offset Hypix 3000 diffractometer. Monochromatic MoK<sub>α</sub> was used as an X-ray source with  $\lambda = 0.71073$  Å. Raman spectroscopy is used to study the vibrational modes of the SrF<sub>2</sub> host lattice, which has a cubic lattice. Raman spectra were recorded using a Raman spectrophotometer (WITEC alpha 300 Ri). A diode laser with a wavelength of 785 nm was used as an excitation source. LAMBDA 750 UV-Vis NIR Spectrophotometer (Perkin Elmer) was used to record the UV-visible spectrum in the visible spectral wavelength range of 400 to 800 nm. LS 55 (Perkin Elmer) fluorescence spectrometer was used to record the emission spectrum at an excitation wavelength of 450 nm.

**Results and Discussion.** The structure of the Ho:SrF<sub>2</sub> crystal is determined by single crystal XRD using monochromatic MoK<sub>α</sub>, having  $\lambda = 0.71073$  Å. During the data collection, the crystals were maintained at 293 K. The data collection spans a  $2\theta$  range from 12.20 to 52.52°. The structure was solved using intrinsic phasing in the ShelXT structural solving program [16]. The olex2.refine refinement program was used to refine the XRD data [17]. In olex2.refine, refinement was performed using Gauss–Newton minimization [18]. The Ho:SrF<sub>2</sub> crystal was confirmed as having cubic symmetry, and the unit cell parameters obtained are  $a = 5.7928(3)$  Å,  $b = 5.7928(3)$  Å, and  $c = 5.7928(3)$  Å. It has a space group of *Fm3m* and a volume of 194.386 Å<sup>3</sup>. The VESTA program was used to model the SrF<sub>2</sub> unit cell. The lattice parameters and atomic position coordinates were found by refining the XRD data, which can be seen in Fig. 1. The coordination number of the Sr ions obtained is 8 and that of the fluorine ion is 4. Sr<sup>2+</sup> is connected to eight equivalent F<sup>1-</sup> atoms in a body-centered cubic shape. The length of all Sr–F bonds is 2.5084 Å. The bonding of F<sup>1-</sup> to four equivalent Sr<sup>2+</sup> atoms creates an FSr<sub>4</sub> tetrahedron. The fractional atomic coordinates, equivalent isotropic displacement parameters, and atomic occupancies are listed in Table 1. Table 2 lists the unit cell dimensions, additive crystallographic data, and refinement results. The XRD results for the single crystals agree well with the reported values and thus confirm the structure of the Ho:SrF<sub>2</sub> crystal [14].

Analysis of the Raman spectrum determines the lattice vibrational mode of the SrF<sub>2</sub> host matrix. A diode laser source with 785 nm excitation was used to record Raman spectra. Three atoms in the primitive cubic cell of SrF<sub>2</sub> generate nine fundamental vibrational modes. These modes are defined as  $\Gamma_9 = 2F_{1u} + F_{2g}$ , which is the irreducible representation (at  $k = 0$ ) of the symmetry group O<sub>h</sub><sup>5</sup> [19].  $F_{2g}$  is a triply degenerate optical mode. There are two types of  $F_{1u}$  representations: triply degenerate and zero-acoustical mode [20]. The other is doubly degenerate and represents the transverse optical mode and the nondegenerate longitudinal optical mode. All  $F_{1u}$  representations are IR-active and Raman-inactive, in contrast to the  $F_{2g}$  representation, which is Raman-active and IR-inactive [14]. This vibrational mode ( $F_{2g}$ ) of undoped SrF<sub>2</sub> is Raman-active, with  $\omega$  at 282 cm<sup>-1</sup> [14]. In this mode, the F<sup>1-</sup> anions moved closer to each other along the crystallographic axes, a phenomenon related to the excited fluorine sublattice of SrF<sub>2</sub>. The Raman spectra of the Ho<sup>3+</sup>-doped SrF<sub>2</sub> are shown in Fig. 2. A Raman shift with a phonon frequency of 288 cm<sup>-1</sup> is observed for Ho-doped SrF<sub>2</sub>. The Raman shift towards a higher wavenumber in Ho:SrF<sub>2</sub> may be due to the change in the chemical environment around the F<sup>1-</sup> ion when Ho is doped in the SrF<sub>2</sub> host matrix. Thus, the low-energy vibrational mode of SrF<sub>2</sub> makes it suitable for Ho-doped lasers. It is well understood that a system with relatively low phonon energies can boost radiative emissions while reducing nonradiative emissions [15]. This is because lower phonon energy reduces nonradiative transitions, which increases the fluorescence intensity.

Absorption spectra were obtained in the 400–800 nm wavelength range, as shown in Fig. 3. The  $4f-4f$  transition of Ho<sup>3+</sup> accounted for the observed absorption lines in the visible region. The absorption lines were observed at 416, 450, 468, 473, 484, 536, 638, and 643 nm. Table 3 compares the observed absorption wavelengths with previously published absorption spectra [8, 21]. Among all the observed peaks, the absorption transition from <sup>5</sup>I<sub>8</sub> to <sup>5</sup>G<sub>6</sub> is very sensitive to the surrounding environment of the Ho<sup>3+</sup> ions. Transitions <sup>5</sup>I<sub>8</sub> to <sup>5</sup>G<sub>6</sub> follow the selection rules  $\Delta J \leq 2$ ,  $\Delta L \leq 2$ , and  $\Delta S = 0$  [22]. The transition from <sup>5</sup>I<sub>8</sub> to <sup>5</sup>G<sub>5</sub> corresponds to violet light absorption, and <sup>5</sup>I<sub>8</sub> to <sup>5</sup>F<sub>1</sub>, <sup>5</sup>G<sub>6</sub>, <sup>3</sup>K<sub>8</sub>, <sup>5</sup>F<sub>2</sub>, and <sup>5</sup>F<sub>3</sub> corresponds to blue light absorption peaks. The transitions from <sup>5</sup>I<sub>8</sub> to <sup>5</sup>S<sub>2</sub>, <sup>5</sup>F<sub>4</sub>, and <sup>5</sup>I<sub>8</sub> to <sup>5</sup>F<sub>5</sub> show green and red lights, respectively. The intensity of the absorption line is calculated as a function of oscillator strength  $f_{\text{exp}}$  using the expression [23, 24]:

$$f_{\text{exp}} = 4.32 \times 10^{-9} \int \varepsilon(\nu) d(\nu), \quad (1)$$

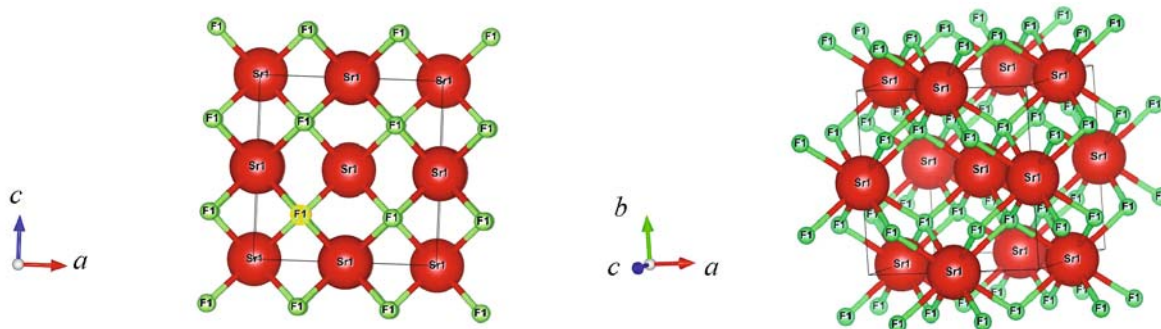


Fig. 1. Unit cell of sample SrF<sub>2</sub> as modeled by VESTA.

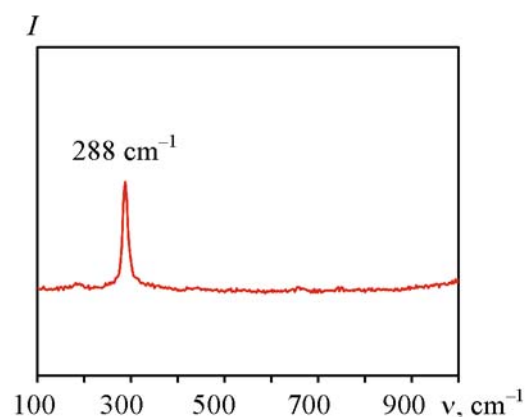


Fig. 2. Raman spectrum of Ho:SrF<sub>2</sub>.

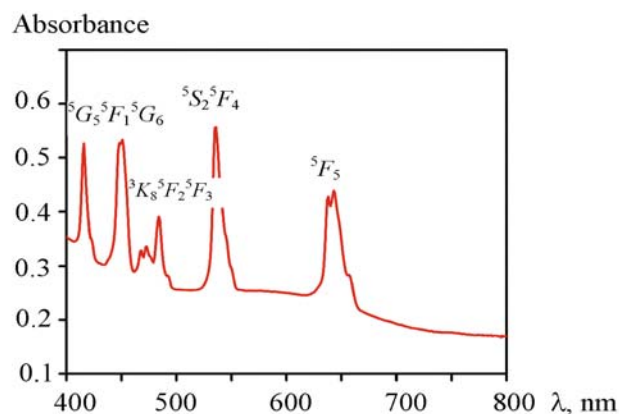


Fig. 3. Absorption spectrum of Ho:SrF<sub>2</sub> showing absorption transitions of Ho<sup>3+</sup> ion.

TABLE 1. Fractional Atomic Coordinates ( $\times 10^{-4}$ ) Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) and Atomic Occupancy for Ho-SrF<sub>2</sub>. U(eq) Is Defined as 1/3 of the Trace of the Orthogonalised UIJ Tensor

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)	Occupancy
Sr1	5000	5000	5000	10.9(7)	0.999840
F1	2500	2500	2500	14.1(18)	1.000080

where  $\varepsilon(\nu)$  is the molar extinction coefficient at wavenumber ( $\nu$ ,  $\text{cm}^{-1}$ ). As can be observed from Table 4, the transitions  $^5I_8 \rightarrow ^5S_2$ , and  $^5F_4$  have the highest oscillator strengths ( $5.50 \times 10^{-6}$ ), whereas the transitions  $^5I_8 \rightarrow ^3K_8$  have the lowest oscillator strengths ( $1.23 \times 10^{-6}$ ). Oscillator strength ( $f_{\text{cal}}$ ) can also be determined for an induced electric-dipole transition from the ground state  $\Psi J$  to an excited state  $\Psi J'$  using the J-O theory. The electric dipole transition between  $4f^n$  states of rare earth ions has an oscillator strength per the J-O theory and is calculated using the following formula [25]:

$$f_{\text{cal}} = \nu / (2J + 1) \left[ \left( \frac{8\pi^2 mc (n^2 + 2)^2}{27nh} \right) \sum_{\lambda=2,4,6} \Omega_{\lambda} \left| \langle \Psi J | U^{\lambda} | \Psi J' \rangle \right|^2 \right], \quad (2)$$

where  $\nu$  is the wavenumber of the transition,  $n$  is the refractive index of the material,  $J$  is the total angular momentum of the ground state, and  $J'$  is the total angular momentum of the excited state,  $\Omega_{\lambda}$  ( $\lambda = 2, 4, \text{ and } 6$ ) are the J-O intensity

TABLE 2. Crystal Data and Structure Refinement for Ho:SrF<sub>2</sub>

Identification code	Ho–SrF <sub>2</sub>
Empirical formula	F <sub>2.67</sub> Sr <sub>1.33</sub>
Formula weight	167.47
Temperature, K	293
Crystal system	cubic
Space group	<i>Fm3m</i>
<i>a</i> , Å	5.7928(3)
<i>b</i> , Å	5.7928(3)
<i>c</i> , Å	5.7928(3)
$\alpha$ , °	90
$\beta$ , °	90
$\gamma$ , °	90
Volume, Å <sup>3</sup>	194.386(17)
<i>Z</i>	3
$\rho_{\text{calc}}$ , g/cm <sup>3</sup>	4.2916
$\mu$ , mm <sup>-1</sup>	27.368
<i>F</i> (000)	218.1
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection, °	12.2 to 52.52
Index ranges	$-7 \leq h \leq 7, -7 \leq k \leq 5, -7 \leq l \leq 6$
Reflections collected	445
Independent reflections	22 [Rint = 0.1070, Rsigma = 0.0261]
Data/restraints/parameters	22/0/2
Goodness-of-fit on F <sup>2</sup>	1.023
Final <i>R</i> indices [ $I \geq 2\sigma(I)$ ]	R1 = 0.0226, wR2 = 0.0510
Final <i>R</i> indices [all data]	R1=0.0226, wR2=0.0510
Largest diff. peak/hole/e, Å <sup>-3</sup>	0.43/−0.65

parameters, and  $U^\lambda = |\langle \Psi J | U^\lambda | \Psi J' \rangle|^2$  are the doubly reduced matrix elements of the unit tensor operator. The  $f_{\text{exp}}$  and  $f_{\text{cal}}$  values were matched well for each transition, as shown in Table 4. In a previous study, Carnal et al. provided host-independent doubly reduced matrix elements for Ho<sup>3+</sup> ions [26]. For each spectral transition, one can compare Eqs. (1) and (2) and then use the least-squares fitting method to obtain the  $\Omega_\lambda$  values. These three intensity characteristics are the causes of the range of transition intensities. The calculated values for the J–O intensity parameters are  $\Omega_2 = 0.14 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_4 = 3.14 \times 10^{-20} \text{ cm}^2$ , and  $\Omega_6 = 3.74 \times 10^{-20} \text{ cm}^2$ . It is important to note that the  $\Omega_2$  value for the crystal is low and follows the order  $\Omega_2 < \Omega_4 < \Omega_6$ .  $\Omega_2$  is affected by ligand field covalence, structural change, and asymmetry around the RE<sup>3+</sup> site, whereas  $\Omega_4$  and  $\Omega_6$  measure the rigidity of the host medium [27–29]. The low value of  $\Omega_2$  and the trend of  $\Omega_2 < \Omega_4 < \Omega_6$  for Ho<sup>3+</sup> ions in SrF<sub>2</sub> suggest that the surrounding Ho<sup>3+</sup> site is comparatively highly symmetric, whereas the Ho–F bond is less covalent.

The observed ground-state absorption spectrum was utilized to estimate the excitation wavelength for the emission spectrum using the reciprocity approach [23, 24]. The emission spectra of Ho:SrF<sub>2</sub> were recorded at an excitation wavelength

TABLE 3. Comparison of Absorption Spectrum ( $\lambda$ , nm) of Ho-doped SrF<sub>2</sub> with [8] and [21]

Transition from $^5I_8$ to	Observed absorption wavelength, nm	Absorption wavelength [8], nm	Absorption wavelength [21], nm
$^5G_5$	416	418	–
$^5F_1, ^5G_6$	450	448	449.9, 452.9
$^3K_8$	468	–	468
$^5F_2$	473	–	473
$^5F_3$	484	485	484.5, 486
$^5S_2, ^5F_4$	536	537	537.3, 535.2
$^5F_5$	638, 643	642	–

 TABLE 4. Reduced Matrix Elements,  $f_{\text{exp}}$  and  $f_{\text{cal}}$  of Ho:SrF<sub>2</sub> Crystal

Transition from $^5I_8$ to	Wavenumber, $\text{cm}^{-1}$	$U^2$	$U^4$	$U^6$	$f_{\text{exp}}, 10^{-6}$	$f_{\text{cal}}, 10^{-6}$
$^5G_5$	24,038	0	0.5338	0.0002	3.80	3.30
$^5F_1, ^5G_6$	22,223	1.5201	0.841	0.1411	5.36	5.36
$^3K_8$	22,295	0.0208	0.0334	0.1578	1.23	1.26
$^5F_2$	21,141	0	0	0.1921	1.25	1.24
$^5F_3$	20,652	0	0	0.346	2.66	2.18
$^5S_2, ^5F_4$	18,613	0	0.2392	0.7071	5.50	5.16
$^5F_5$	15,532	0	0.425	0.5687	3.81	4.38

of 450 nm, as shown in Fig. 4a. Green and red lights emissions occur with blue-light pumping. Ho<sup>3+</sup> ions were initially stimulated from the ground state  $^5I_8$  to the excited state  $^5G_6$ , as depicted in Fig. 4b. Following this, because of the closely spaced higher energy levels, both radiative and nonradiative relaxations occurred. The excited electrons at the  $^5G_6$  level populate the  $^5S_2$ ,  $^5F_4$ , and  $^5F_5$  levels via nonradiative relaxation. The emission spectrum exhibits two emission lines at 546 nm (green) and 656 nm (red). The emission line at 546 nm correlates with the transition from  $^5S_2$  to  $^5F_4$  to  $^5I_8$ , whereas the emission line at 656 nm is related to the transition from  $^5F_5$  to  $^5I_8$ . The emission peaks of  $^5S_2$ ,  $^5F_4$ ,  $^5I_8$ ,  $^5I_8$ ,  $^5S_2$ , and  $^5F_4$  match each other, that is, their wavelengths lie between 525 and 553 nm. The  $^5F_5$  to  $^5I_8$  emission band matches the absorption band  $^5I_8$  to  $^5F_5$ , that is, their wavelengths lie between 624 and 664 nm, which is an evidence of the resonance energy-transfer mechanism [8]. According to the emission spectra, the intensities of the  $^5S_2$ ,  $^5F_4$ , and  $^5I_8$  transitions are greater than those of the  $^5F_5$  and  $^5I_8$  transitions. This variation in intensity can be attributed to different multiphonon relaxation modes. The rate of multiphonon relaxation increases as the energy difference between the excited state and the lower-lying state narrows [25]. The excited states  $^5S_2$  and  $^5F_4$  have an energy gap of approximately 2900  $\text{cm}^{-1}$  from their lower-lying energy levels [20], while the energy gap from the lower-lying level to the  $^5F_5$  excited state is approximately 1704  $\text{cm}^{-1}$  [8]. As a result, compared with the  $^5F_5$  to  $^5I_8$  transition, the  $^5S_2$  to  $^5F_4$  to  $^5I_8$  transition gains more populated excited states and less multiphonon relaxation; thus, green light emission is more intense than red light. The emission lines confirm that the Ho:SrF<sub>2</sub> crystal is a potent candidate as a laser medium in green and red light.

The spontaneous emission probability  $A_R$  ( $A_{jj'}$ ), fluorescence branching ratio  $\beta_R$ , and radiative lifetime  $\tau_R$  are calculated using the J–O intensity parameters using the following formulas [30]:

$$A_R = \frac{64\pi^4 \nu^3 e^2 n (n^2 + 2)^2}{27h(2J + 1)} \sum_{\lambda=2,4,6} \Omega_\lambda \left| \langle \Psi J | U^\lambda | \Psi J' \rangle \right|^2, \quad (3)$$

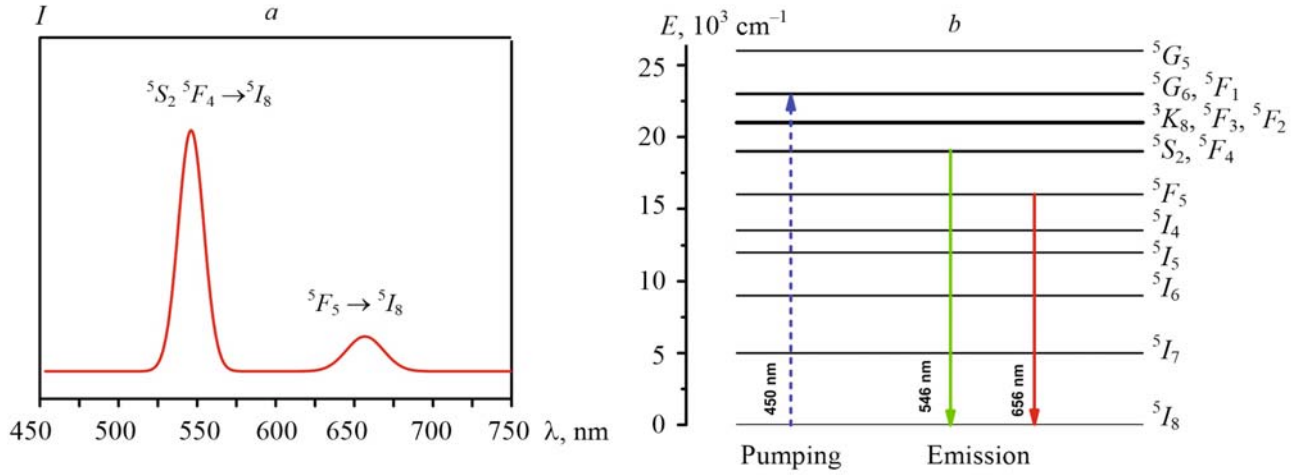


Fig. 4. (a) Fluorescence spectrum and (b) Schematic diagram of emission spectrum of Ho:SrF<sub>2</sub>.

TABLE 5. The Predicted Radiative Transition Probability  $A_R$ , Total Radiative Transition Probability  $A_T$ , Calculated Branching Ratio  $\beta_R$  and Radiative Lifetime  $\tau_R$  of the Energy Levels of Ho<sup>3+</sup> Ion in Ho-doped SrF<sub>2</sub> Crystal [34]

Transition	$\nu$ , cm <sup>-1</sup>	Matrix elements			$A_R$ , s <sup>-1</sup>	$A_T$ , s <sup>-1</sup>	$\beta_R$ , %	$\tau_R$ , ms
		$U^2$	$U^4$	$U^6$				
${}^5S_2 + {}^5F_4 \rightarrow {}^5I_8$	18.315	0.0000	0.2421	0.7087	3135.89	3784.60	82.86	0.26
${}^5I_7$	13,499	0.0000	0.1960	0.0322	272.54		7.20	
${}^5I_6$	9919	0.0011	0.2576	0.1721	213.29		5.63	
${}^5I_5$	7493	0.0016	0.1327	0.4651	136.36		3.60	
${}^5I_4$	5429	0.0002	0.0237	0.2585	25.03		0.66	
${}^5F_5$	3066	0.2001	0.0919	0.0075	1.49		0.04	
${}^5F_5 \rightarrow {}^5I_8$	15.244	0.0000	0.4241	0.5698	1508.73	1978.24	76.27	0.50
${}^5I_7$	10.433	0.0190	0.3318	0.4346	373.07		18.86	
${}^5I_6$	6853	0.0112	0.1242	0.4960	88.92		4.49	
${}^5I_5$	4427	0.0068	0.0279	0.1637	7.47		0.38	
${}^5I_4$	2363	0.0001	0.0060	0.0040	0.05		$0.25 \times 10^{-2}$	

$$\beta_R = \frac{A_{JJ'}}{\sum_{J'} A_{JJ'}} \quad (4)$$

$$\tau_R = \frac{1}{\sum_{J'} A_{JJ'}} \quad (5)$$

Using Eqs. (3)–(5), the calculated values of the emission transition parameters like emission probability  $A_R$ , fluorescence branching ratio  $\beta_R$ , and radiative lifetime  $\tau_R$  are tabulated in Table 5. The transition probability is the highest for the  ${}^5S_2 + {}^5F_4 \rightarrow {}^5I_8$  transition. The term "lifetime" refers to the period after which the population level has decreased to 36.8% of the initial population. The  ${}^5S_2 + {}^5F_4 \rightarrow {}^5I_8$  transition is the most effective for lasing, owing to its lifetime of 0.26 ms. The computed branching ratios of 82.86% and 76.27% for the  ${}^5S_2 + {}^5F_4 \rightarrow {}^5I_8$  and  ${}^5F_5 \rightarrow {}^5I_8$  transitions, respectively, are in good

agreement with [31–33]. Emission transitions with larger magnitudes of  $\beta_R$  are better suited for laser action, as  $\beta_R$  denotes a more effective transition for laser action. Consequently, a transition with a fluorescence branching ratio greater than 50% is appropriate for lasing [8]. Thus, green and red emissions can be obtained as laser transitions in Ho:SrF<sub>2</sub>.

**Conclusions.** In the present work, the Ho-doped SrF<sub>2</sub> crystal was investigated as a gain medium for solid-state lasers in the visible spectral band. The crystal structure of the Ho:SrF<sub>2</sub> crystal was confirmed using single-crystal XRD. Olex2 software was used to solve the structure by utilizing intrinsic phasing with the ShelXT structure solution tool. The olex2 refine software was used to refine the XRD data using Gauss–Newton minimization. SrF<sub>2</sub> has a cubic structure with a lattice constant  $a = 5.7928$  Å. A lattice vibrational mode of 288 cm<sup>-1</sup> is observed in the Ho:SrF<sub>2</sub> single crystal via Raman spectroscopy, which is a suitable environment for fluorescence intensity by limiting nonradiative transitions. The UV-visible absorption spectrum was recorded in the 400–800 nm region and different absorption lines were observed at wavelengths of 416, 450, 468, 473, 484, 536, 638, and 643 nm. The emission spectrum was studied using fluorescence spectroscopy at an excitation wavelength of 450 nm. Two emission bands were observed: one at 546 nm corresponds to the green-light region, and the second at 656 nm corresponds to the red-light region. The intensity parameters  $\Omega_\lambda$  ( $\lambda = 2, 4, 6$ ) were estimated using Judd–Ofelt's theory. The low  $\Omega_2$  value in the Ho:SrF<sub>2</sub> single crystal suggests low covalence of Ho<sup>3+</sup>–F<sup>-</sup> bonds and high ligand field symmetry around Ho<sup>3+</sup> ion sites. The radiative properties of various excited levels were predicted using the measured Judd–Ofelt's intensity values. The <sup>5</sup>S<sub>2</sub> + <sup>5</sup>F<sub>4</sub> → <sup>5</sup>I<sub>8</sub> transition has a shorter lifespan (0.26 ms) and a higher branching ratio (82.86%), making it more suitable for lasing. Thus, Ho:SrF<sub>2</sub> can be a promising crystal as a laser in the green and red spectral regions.

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## REFERENCES

1. T. Danger, J. Koetke, R. Brede, E. Heumann, G. Huber, and B. H. T. Chai, *Appl. Phys.*, **76**, 1413–1422 (1994).
2. F. Moglia, S. Müller, T. Calmano, and G. Huber, *5th EPS-QEOD Europhoton Conf. 2012*, Stockholm, Sweden, **25** (2012).
3. B. P. Scott, F. Zhao, R. S. F. Chang, and N. Djeu, *Opt. Lett.*, **18**, 113–115 (1993).
4. S. R. Bowman, S. O'Connor, and N. J. Condon, *Opt. Express*, **20**, 12906–12911 (2012).
5. P. W. Metz, F. Moglia, F. Reichert, S. Müller, D.-T. Marzahl, N.-O. Hansen, C. Kränkel, and G. Huber, *Conf. on Lasers and Electro-Optics (CLEO/Europe — EQEC) 2013*, Munich, Germany, paper: CA-2.5 (2013).
6. B. N. Kazakov, M. S. Orlov, M. V. Petrov, A. L. Stolov, and A. M. Tkachuk, *Opt. Spectrosc.*, **47**, 676 (1979).
7. H. Jensen, D. Castleberry, D. Gabbe, and A. Linz, *IEEE J. Quantum Electron.*, **9**, 665 (1973).
8. P. Rekha Rani, M. Venkateswarlu, Sk. Mahamuda, K. Swapna, Nisha Deopa, and A. S. Rao, *J. Alloys Compd.*, **787**, 503–518 (2019).
9. Wenqian Cao, Feifei Huang, Tao Wang, Renguang Ye, Ruoshan Lei, Ying Tian, Junjie Zhang, and Shining Xu, *Opt. Mater.*, **75**, 695–698 (2018).
10. M. Kochanowicz, J. Zmojda, P. Miluski, A. Baranowski, M. Leich, A. Schwuchow, M. Jeager, M. Kuwik, J. Pisarska, W. A. Pisarski, and D. Dorosz, *Opt. Mater. Express*, **9**, 1450–1458 (2019).
11. E. Chicklis, C. Naiman, L. Esterowitz, and R. Allen, *IEEE J. Quantum Electron.*, **13**, 893–895 (1977).
12. J. Y. Allain, M. Monerie, and H. Poignant, *Electron. Lett.*, **26**, 261–263 (1990).
13. David S. Funk and J. G. Eden, *IEEE J. Quantum Electron.*, **37**, 980–992 (2001).
14. A. A. Kaminski, L. Bahaty, P. Becker, H. J. Eichler, and H. Rhee, *Laser Phys. Lett.*, **4**, 668–673 (2007).
15. Bingrui Li, Xin Zhao, Edwin Yue Bun Pun, and Hai Lin, *Opt. Laser Technol.*, **107**, 8–14 (2018).
16. G. M. Sheldrick, *Acta Cryst. A*, **71**, 3–8 (2015).
17. L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *Acta Cryst. A*, **71**, 59–75 (2015).
18. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Cryst.*, **42**, No. 2, 339–341 (2009).
19. R. L. Rousseau, R. P. Baumann, and S. P. S. Porto, *J. Raman Spectrosc.*, **10**, No. 1, 253 (1981).
20. G. A. Kourouklis, E. Anastassakis, *Phys. Rev. B*, **34**, 1233 (1986).
21. F. Reichert, F. Moglia, P. W. Metz, A. Arcangeli, D.-T. Marzahl, S. Veronesi, D. Parisi, M. Fechner, M. Tonelli, and G. Huber, *Opt. Mater. Express*, **5**, 88–101 (2014).

22. D. Rajesh, M. Dhamodhara Naidu, Y. C. Ratnakaram, and A. Balakrishna, *J. Lumin.*, **29**, No. 7, 854–860 (2014).
23. B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).
24. G. S. Ofelt, *J. Chem. Phys.*, **37**, 511–520 (1962).
25. R. D. Peacock, *Structure & Bonding*, **22**, 83 (1975).
26. W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49**, 4412 (1968).
27. S. Tanabe, T. Ohayagi, N. Soga, and T. Hanada, *Phys. Rev. B*, **46**, 3305 (1992).
28. H. Ebendorff-Heidepriem, D. Ehrt, M. Bettinelli, and A. Speghini, *J. Non-Cryst. Solids*, **240**, 66 (1998).
29. H. Takebe, Y. Nageno, and K. Morinaga, *J. Am. Ceram. Soc.*, **78**, 61 (1995).
30. B. M. Walsh, P. B. Norman, and D. B. Baldassare, *J. Appl. Phys.*, **83**, 2772 (1998)
31. V. D. Rodríguez, J. Del Castillo, A. C. Yanes, J. Méndez-Ramos, M. Torres, and J. Peraza, *Opt. Mater.*, **29**, 1159 (2007).
32. J. Peng, H. Xia, P. Wang, H. Hu, L. Tang, Y. Zhang, H. Wang, and B. Zhang, *J. Mater. Sci. Technol.*, **30**, 910 (2014).
33. R. S. Quimby, N. J. Condon, S. P. O'Connor, and S. R. Bowman, *Opt. Mater.*, **34**, 1603 (2012).
34. H. M. Ha, T. T. Q. Hoa, L. V. Vu, and N. N. Long, *J. Mater. Sci.: Mater. Electron.*, **29**, 1607–1613 (2018).