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Optical high-resolution spectroscopic study of Tm^{3+} crystal-field levels in $LiLuF_4$

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Abstract: We report on the first high-resolution study of $LiLuF_4$:Tm^{3+}. The accurate energy level scheme of Tm^{3+} in the $LiLuF_4$ matrix was obtained for the $^3H_{6,5,4}$, $^3F_{4,3,2}$, and $^1G_4$ multiplets. It was shown that electric-dipole transitions dominate for all the studied multiplets except the $^3H_5$ one.

Keywords: Fourier-transform spectroscopy; Tm^{3+} crystal-field levels; $LiLuF_4$; rare earths

$LiYF_4$ crystals doped with rare earth (RE) ions have proved themselves to be laser systems[1]. Optical spectroscopic study has allowed obtaining energy levels schemes of various RE ions in this matrix[1–3].

Lithium-yttrium and lithium-lutecium double fluorides $LiRF_4$ (R=Y or Lu) have a scheelite ($CaWO_4$) structure with the space group C_{4h}^6. Dopant RE^{3+} ions substitute for isovalent R^{3+} and occupy a single S_4-symmetry position. The crystal field (CF) levels of a RE^{3+} ion with even number of electrons (like Tm^{3+}) are described by non-degenerate Γ_1 and Γ_2 irreducible representations and by doubly degenerate Γ_{34} one.

Recently, a novel $LiLuF_4$:Tm^{3+} laser has been made and investigated[4]. However, as far as we know, the data on the scheme of CF levels of the Tm^{3+} ion in this host are rare. In this work, we presented energy levels for the $4f^{12}$ configuration of Tm^{3+} in $LiLuF_4$ as a result of a high-resolution spectroscopic investigation of $LiLuF_4$:Tm^{3+} single crystals.

1 Experimental

In this study, we used samples of weakly doped $LiLuF_4$:Tm^{3+} single crystals. They were grown by the Bridgman-Stockbarger method, as described in Ref.[5]. The thulium concentration was 0.1at.%. All samples were oriented by X-ray diffraction method and cut along or perpendicularly to the crystallographic *c*-axis. Polarized high-resolution (up to 0.005 cm^{-1}) absorption spectra were measured in a broad spectral (5000–23000 cm^{-1}) and temperature (3.5–300 K) ranges using a Fourier spectrometer BRUKER IFS 125 and a Si diode or a liquid nitrogen cooled InSb detectors. For low-temperature measurements we used a closed-cycle cryostat Cryomech ST 403.

2 Results and discussion

To obtain CF level scheme of the Tm^{3+} ion in $LiLuF_4$, we analyzed the polarized spectra of $LiLuF_4$:Tm^{3+} registered at two different temperatures: 4 and 70 K. The experimental data showed that the spectra in the α-$(\vec{k} \parallel \vec{c}; \vec{E}, \vec{H} \perp \vec{c})$ and σ-$(\vec{k}, \vec{E} \perp \vec{c}; \vec{H} \parallel \vec{c})$ polarizations are the same for all investigated multiplets, with the exception of the $^3H_5$ one. Therefore, electric-dipole transitions dominate for a majority of the multiplets, as it follows from the selection rules for the S_4 site symmetry (Table 1). All three polarizations, α, σ, and π $(\vec{k} \perp \vec{c}, \vec{E} \parallel \vec{c}, \vec{H} \perp \vec{c};)$, differ for the $^3H_5$ multiplet, manifestating that both electric-dipole and magnetic-dipole transitions are active. This fact is in good agreement with the selection rules for magnetic-dipole transitions in a free Tm^{3+} ion. Only transitions from the ground state of the $^3H_6$ multiplet to the $^3H_5$ one are allowed (ΔJ=1).

There are two different ways to denote the first exited multiplet of the Tm^{3+} ion, namely, $^3F_4$ or $^3H_4$. This is because of the mixing of the $^3F_4$, $^3H_4$, and $^1G_4$ states by the spin-orbit interaction. In our work, we followed the $^3F_4$ notation of Jenssen[2]. The absorption spectrum of $LiLuF_4$:Tm^{3+} in the region of the $^3H_6 \rightarrow {}^3F_4$ transition is shown in Fig. 1. This multiplet splits into three Γ_1, two Γ_2, and two Γ_{34} levels. To identify spectral line, we used the following notations: CF levels of the ground $^3H_6$ multiplet are labeled I, II, III, etc, while those in each excited multiplets A, B, C, etc, in

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the sequence of increasing energies. Transitions from the ground state are only observed in the polarized low-temperatures spectra: three lines (5596.5, 5763.1 and 5976.0 cm^{-1}) for π-polarization and two lines (5762.8 and 5982.9 cm^{-1}) for σ-polarization. Therefore, using the selection rules of Table 1 we can claim that (1) the ground state has the Γ_2 symmetry, (2) the three levels of the $^3F_4$ multiplet observed in the π-polarized spectrum have the Γ_1 symmetry and the two levels observed in the σ-polarized spectrum have the Γ_{34} symmetry. The transitions from the ground state Γ_2 to the Γ_2 levels are allowed only as magnetic-dipole ones and are not observed in the spectra of the $^3F_4$ multiplet. To obtain the positions of these levels we used the spectra registered at 70 K. Some other lines appear in them. They are shifted to 32 and 60 cm^{-1} from the main lines and correspond to transitions from upper CF sublevels of the ground multiplet. First, this gives us information on two levels of the $^3H_6$ multiplet which are 32 and 60 cm^{-1} and have Γ_{34} and Γ_1 symmetries correspondingly (see Table 1 and Fig. 1). Second, we found the positions (5837.5 and 5972.0 cm^{-1}) of the Γ_2 levels of the $^3F_4$ multiplet. A complex line shape of the highest-energy transitions in this multiplet is due to the resonant enhancement of a vibronic transition[6] and will be discussed elsewhere.

Situation is more complicated in the case of the $^3H_5$ multiplet which splits into three Γ_1, two Γ_2, and three Γ_{34} levels. There are both electric-dipole and magnetic-dipole transitions in the spectra (see Fig. 2): five lines (8305.0, 8326.3, 8509.5, 8524.2, and 8544.0 cm^{-1}) are observed for π-polarization, five lines (8288.4, 8305.0, 8509.5, 8524.2, and 8538 cm^{-1}) for σ-polarization and four lines (8305.0, 8509.5, 8524.2, and 8538 cm^{-1}) for α-polarization. Using again the section rules and the spectra registered at 4 and 70 K we find out that 8326.3, 8524.2, and 8544.0 cm^{-1} lines correspond to the Γ_1 levels, 8305.0, 8509.5, and 8538 cm^{-1} lines are Γ_{34} levels. At last, very strong 8288.4 cm^{-1} line observed in σ-polarization corresponds to the Γ_2 level. We did not succeed in obtaining the position of the other Γ_2 level. Here it should be said that, first, the S_4 point group is a subgroup of the D_{2d} point group, and some transitions allowed in S_4 are strictly forbidden in D_{2d}. If the deviation of the actual arrangement of atoms (the S_4 symmetry) from the D_{2d} symmetry is small (which is the case for R^{3+} ions in $LiRF_4$), some lines in the optical spectra have weak relative intensity or are absent. Second, enhanced vibronics, like as in vicinity of 5982.9 cm^{-1} line (see Fig. 1), make the determination of weak transitions obscured.

In the same way we investigated the spectra of the other ($^3H_4$, $^3F_{3,2}$, and $^1G_4$) multiplets. Information on the CF levels of Tm^{3+} in $LiLuF_4$ is presented in Table 2. The obtained re-

Table 1 Section rules for optical transitions in the S_4 site symmetry (Notations $d_i(\mu_i)$, $i = x, y$, or z refer to the components of electric (magnetic) dipole moment)

S_4	Γ_1	Γ_2	Γ_{34}
Γ_1	$\mu_z(\sigma_m)$	$d_z(\pi_e)$	$d_{xy}, \mu_{xy}(\alpha_e, \sigma_e; \alpha_m, \pi_m)$
Γ_2	$d_z(\pi_e)$	$\mu_z(\sigma_m)$	$d_{xy}, \mu_{xy}(\alpha_e, \sigma_e; \alpha_m, \pi_m)$
Γ_{34}	$d_{xy}, \mu_{xy}(\alpha_e, \sigma_e; \alpha_m, \pi_m)$	$d_{xy}, \mu_{xy}(\alpha_e, \sigma_e; \alpha_m, \pi_m)$	$d_z, \mu_z(\pi_e, \sigma_m)$

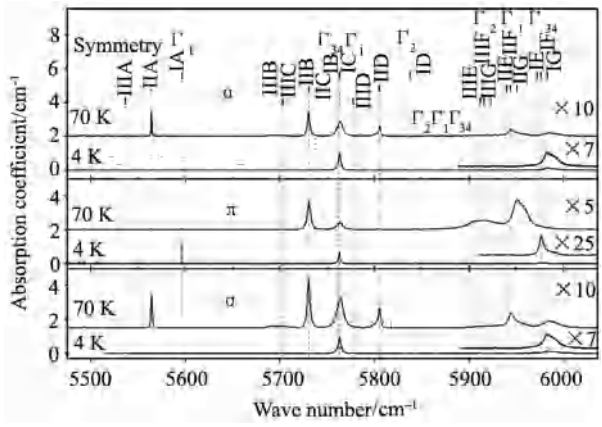

Fig. 1 Absorption spectra of $LiLuF_4$:Tm^{3+} in the region of the $^3H_6 \rightarrow {}^3F_4$ transition

Table 2 Experimental energy levels and their irreducible representations for Tm^{3+} in $LiLuF_4$

Multiplet	Γ	Energy/cm^{-1}	Multiplet	Γ	Energy/cm^{-1}
				2	12598.7
			$^3H_4$	1	12624.1
				34	12648.3
				1	12749.4
$^3H_6$	2	0	$3\Gamma_1+2\Gamma_2+2\Gamma_{34}$	1	–
	34	32.2		34	12842.7
$3\Gamma_1+4\Gamma_2+3\Gamma_{34}$	1	60.0		2	12896.3
				34	14525.1
			$^3F_3$	2	14547.3
				34	14602.7
				2	14605.0
			$\Gamma_1+2\Gamma_2+2\Gamma_{34}$	1	14612.7
	1	5596.5			
	34	5762.8		2	15099.5
$^3F_4$	1	5763.1	$^3F_2$	34	15208.8
	2	5837.5		2	--
$3\Gamma_1+2\Gamma_2+2\Gamma_{34}$	2	5972.0	$\Gamma_1+2\Gamma_2+\Gamma_{34}$	1	15208.8
	1	5976.0			
	34	5982.9			
	2	8288.4		1	20963.2
	34	8305.0		34	21190.3
$^3H_5$	1	8326.3	$^1G_4$	2	21280.5
	34	8509.5		1	21302.8
$3\Gamma_1+2\Gamma_2+$	1	8524.2		2	21514.0
$3\Gamma_{34}$	2	–	$3\Gamma_1+2\Gamma_2+2\Gamma_{34}$	34	21564.1
	34	8538.0		1	21564.1
	1	8544.0			

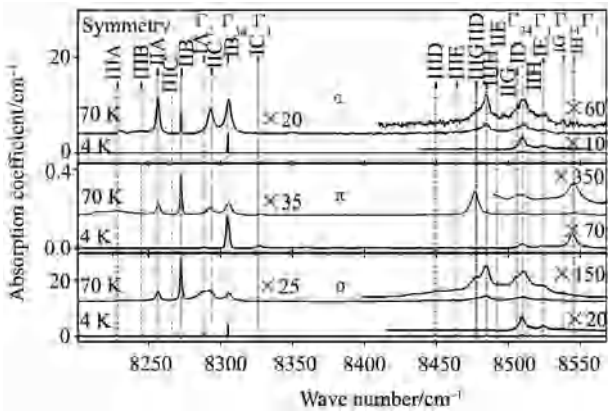

Fig. 2 Absorption spectra of $LiLuF_4$:Tm^{3+} in the region of the $^3H_6 \rightarrow {}^3H_5$ transition

sults are close to the data on CF levels of Tm^{3+} in the $LiYF_4$ host[7], which confirms the fact of similarity of the crystal structures, the crystal fields, and CF-parameters in both the compounds.

3 Conclusion

In this study, CF levels of Tm^{3+} in $LiLuF_4$ for infrared and visible range were established. The electric-dipole contribution dominated in the spectra of $LiLuF_4$:Tm^{3+}, with the exception of the $^3H_6 \rightarrow {}^3H_5$ transitions. The obtained information could be useful for future investigation of efficient laser action in Tm-doped $LiLuF_4$ solid-state lasers.

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