Journal of Engineering and Applied Sciences 1(4): 351-354, 2006

Spectroscopic Properties of Tm^{3+} Transitions in 5NaF.9YF3 Fluoride Host

Labbaci K and M. Diaf
Department of Physics, Badji Mokhtar University, Annaba,
B.P 12 Annaba 23000, Algeria

Abstract: Tm^{3+}:5NaF.9YF_3 crystal of good optical quality was grown by Czochralski method. Optical absorption measurements of Tm^{3+} in 5NaF.9YF_3 crystal have been investigated. The Judd-Ofelt (J-O) theory was applied to the absorption spectra of Tm^{3+}: 5NaF.9YF_3 to obtain three JO parameters $\Omega_{t=2,4,6}$. Values of the JO parameters were subsequently used to determine the radiative transition probabilities, the radiative lifetimes and the branching ratios. The calculated parameters show that Tm^{3+}: 5NaF.9YF_3 crystal possesses important spectroscopic and laser properties that are favorable for this material to become a potential candidate as an efficient laser system.

Key words: Crystal growth, czochralski method, fluoride crystals, rare-earth spectroscopy, judd-ofelt theory, radiative transition probabilities

INTRODUCTION

In the last few years, the search for new materials emitting in the eye-safe spectral range around 1.55 μm has aroused an increasing interest[1,2]. In this wavelength, the eye can support powers 10^6 times higher than those which they tolerate around 1.064 μ_m (laser YAG: Nd), the currently more developed. Many applications in various domains were carried out: Telemetry, dosage of pollutants in the atmosphere, telecommunications.

Currently, the fluorides attract much attention as a laser medium due to the fact that they generally present maximum phonon energies weaker than the oxides which make them possible to obtain high fluorescence quantum efficiency by limiting the non-radiative deexcitation probabilities. Moreover, the fluorides are significant host for the optically active trivalent rare earth ions because of the broad splitting of the crystal field and the high cross-sections of transition[3-5]. For this study, we chose a fluoride compound 5NaF-9YF_3 of the NaF-YF_3 system doped with Tm^{3+} ions which is very little studied as far as we know. Our choice of Thulium was dictated by the fact that it is a doping having interesting laser properties in the already studied fluoride hosts. It presented three efficient laser transitions in the near infrared around 1.5 μm ($^3H_4 \rightarrow {}^3F_4$), 1.8 μm ($^3F_4 \rightarrow {}^3H_6$) and 2.3 μm ($^3H_4 \rightarrow {}^3H_5$)[6]. To realize this study, a single-crystal of 5NaF-9YF3 doped with Tm^{3+} ions was synthesized by Czochralski pulling technique. The Judd-Ofelt analysis was then applied in order to determine the optical transition probabilities, the branching ratios and the radiative lifetimes of Tm^{3+} ion of which their knowledge is capital for the various laser studies.

Experimental

A. material: 5NaF.9YF_3 single crystals were prepared by Czochralski pulling technique from powders with 99.99% purity in the following proportions: 36 mol% NaF, 64 mol% YF_3 and 1 mol%TmF_3. The compound thus formed is presented under the chemical formula $Na_{0.36}Y_{0.64}F_{2.28}$[7-9]. This phase, stable at ambient temperature, is slightly disordered. The pulled crystal is of good optical quality. For spectroscopic measurements, the crystal was cleaved and polished in order to obtain a parallel face sample with 3 mm thickness. The 5NaF.9YF_3 has a cubic structure belonging to the space group Fm3m and lattice parameter of 5.503 Å[10-12]. The concentration of Tm^{3+} ions is 1.543_×_10^{20} cm^{-3}.

Absorption measurements: The absorption spectra of the 5NaF.9YF_3:1%Tm^{3+} sample were recorded using a Perkin-Elmer Lambda 9 spectrophotometer, double beam, in the spectral range 200-2000 nm. The spectral resolution was 0.2 nm for UV-Visible and 0.8 nm for Near Infrared region. A system of data acquisition (computer PC) is connected to the spectrometer using an electronic RS232 interface card, visualized during acquisition. The efficient integrated sections and the average wavelengths for all the transitions observed are calculated after the subtraction of a linear base line for each transition.

Corresponding Author: K. Labbaci, Department of Physics, Badji Mokhtar University, Annaba, B.P 12 Annaba 23000, Algeria

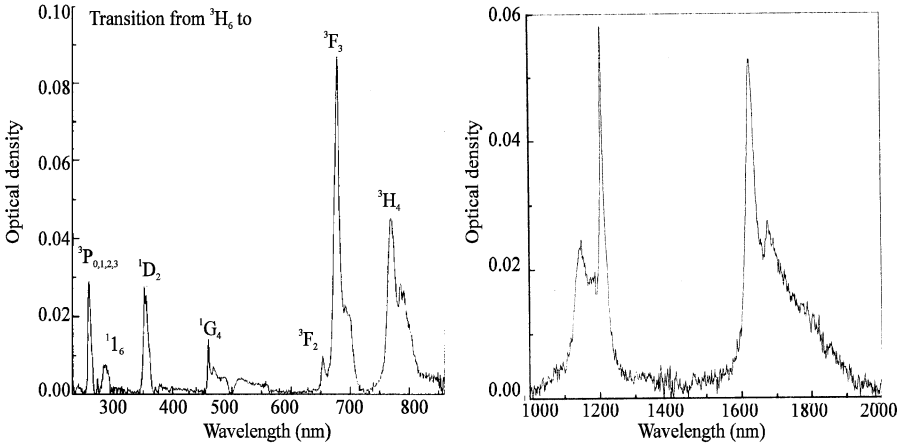

Fig. 1: Room temperature absorption spectrum of Tm^{3+} doped $5NaF.9YF_3$ a) from 320 to 860 nm. b) from 1000 to 2000 nm

RESULTS AND DISCUSSION

Many researchers have applied the Judd-Ofelt (J-O) theorical analysis[13,14] to determine the important spectroscopic and laser parameters of various hosts[15-21].

Its application requires the computation of three phenomenological parameters Ω_2, Ω_4 and Ω_6 by a fitting procedure of experimental data usually obtained from room temperature ground state absorption. Below, a brief summary of the J-O theory will be given, reporting only the important equations required to determine the measured and calculated line strengths, the J-O parameters, the radiative emission probabilities and the branching ratios.

In this study, we applied J-O analysis of Tm^{3+} ions doped $5NaF.9YF_3$ crystals. For this reasons, eleven absorption bands identified around 241; 260; 273; 286; 356; 485, 648, 678, 786, 1177 and 1713 nm (Fig. 1a, 1b) were used in the fitting procedure. These observed bands are attributed to the excitation from $^3H_6$ ground state to the $^3P_2$, $^3P_1$, $^3P_0$, $^1I_6$, $^1D_2$, $^1G_4$, $^3F_2$, $^3F_3$, $^3H_4$, $^3H_5$ and $^3F_4$ excited state, respectively.

In Judd–Ofelt approach, the measured electric dipole transition strengths S_{ed}^{meas} of the chosen transition (J→ J') are determined using the following expression:

$$(S_{JJ'}^{DE})^{meas} = \frac{9.n}{(n^2+2)^2}\left[\frac{3.h.c.(2.J+1).\varepsilon_0}{2.\pi^2.e^2.\bar{\lambda}}.\frac{\ln 10}{N.L}\int_{J\to J'} DO(\lambda).d\lambda - n.S_{JJ'}^{DM}\right] \quad (1)$$

Where J and J' represent the total angular momentum quantum numbers of the initial and final levels, respectively, n the refractive index of the material, h the Planck constant, c the vacuum light, ε_0 the vacuum permittivity, e the electron charge, λ is the mean wavelength of the J → J' absorption transition, N the Tm^{3+} concentration, L the thickness of the sample, DO(λ) the measured optical density and $S^{DM}_{J,J'}$ is the magnetic dipolar line strengths.

In the case of Tm^{3+}, only the $^3H_6 \rightarrow {}^3H_5$ transition has a magnetic dipolar component[22]: $Sdm(^3H_6 \rightarrow {}^3H_5) = 0.39 \times 10^{-20}\,cm^2$.

The three J-O intensity parameters Ω_2, Ω_4 and Ω_6 can be then calculated by solving the over determined set of equation given by the following equation:

$$\left(S_{JJ'}^{DE}\right)^{cal} = \sum_{t=2,4,6}\sqrt{\Omega_t\left|\left\langle\left\|U^{(t)}\right\|\right\rangle\right|^2} \quad (2)$$

Where $\left|\left\langle\left\|U^{(t)}\right\|\right\rangle\right|^2$ are the squared reduced matrix elements of rank t (t=2,4,6) between the two multiplets characterized by the quantum number (S,L,J) and (S',L',J'). The matrix elements $U^{(t)}$ used in the present study were tabulated by Spector[23] for the Tm^{3+} ions. However, when two absorption transitions are overlapped as in the case of the doublet ($^3F_2$,$^3F_3$), the squared matrix element was taken to be the sum of the corresponding squared matrix elements.

Thus, a series of calculation was carried out while varying the number of transitions used in the fitting procedure. The accuracy of fitting of each calculation was evaluated from the root mean-square (rms) deviation

between measured and calculated line strengths of the transitions.

Table 1: Caluclated scal line strength for measureed tranisitions

Transition from $^3H_6$	Average energies (cm^{-1})	Transition strengths: S^{meas} ($\times10^{-20}$ cm^2)	Transition strengths: S^{cal} ($\times10^{-20}$ cm^2)	Residuals ($\times10^{-20}$ cm^2)
$^3F_4$	5838	1.967	1.956	0.011
$^3H_5$	8496	0.943	1.021	0.078
$^3H_4$	12723	1.211	1.219	0.008
$^3F_3$	14749	1.206	0.970	0.236
$^3F_2$	15432	0.054	0.274	0.220
$^1G_4$	20619	0.242	0.151	0.091
$^1D_2$	28090	0.46	0.176	0.284
$^1I_6$	34965	0.177	0.053	0.124
$^3P_0$	36630	0.015	0.08	0.065
$^3P_1$	38462	0.416	0.131	0.285
$^3P_2$	41494	0.047	0.091	0.044

Table 2: Calculated radiative parameters of Tm^{3+} ions in $5NaF.9YF_3$ single crystal

Transition	Average wavelength (nm)	Average energy (cm^{-1})	A^{rad} (s^{-1})	τ_{rad} (ms)	β(%)	σ_a (10^{-20} cm^2)
$^3F_4 \rightarrow {}^3H_6$	1713	5838	88.63	11.28	100	0.286
$^3H_5 \rightarrow {}^3H_6$ ^{3}	1177	8496	169.33	5.86	99.3	0.338
F_4	3762	2659	1.25		0.7	
$^3H_4 \rightarrow {}^3H_6$	786	12723	568.3	1.58	89.8	0.259
$^3F_4$	1452	6885	56.02		8.9	
$^3H_5$	2366	4227	8.20		1.3	
$^3F_3 \rightarrow {}^3H_6$	678	14749	936.59	0.88	82.2	0.500
$^3F_4$	1122	8912	76.57		6.7	
$^3H_5$	1600	6253	124.41		10.9	
$^3H_4$	4934	2027	1.74		0.2	
$^3F_2 \rightarrow {}^3H_6$	648	15432	417.12	1.23	51	0.040
$^3F_4$	1042	9594	290.96		35.7	
$^3H_5$	1442	6936	98.31		12	
$^3H_4$	3691	2709	7.72		0.9	
$^3F_3$	14645	683	0.03		0.9	
$^1G_4 \rightarrow {}^3H_6$	485	20619	303.06	1.175	35.6	0.087
$^3F_4$	677	14781	68.33		8.0	
$^3H_5$	826	12122	356.91		41.9	
$^3H_4$	1271	7896	102.51		12.0	
$^3F_3$	1708	5869	17.77		2.1	
$^3F_2$	1885	5186	2.50		0.3	
$^1D_2 \rightarrow {}^3H_6$	356	28090	1777.39	0.095	16.9	0.159
$^3F_4$	449	22252	7013.15		66.9	
$^3H_5$	510	19594	55.67		0.5	
$^3H_4$	650	15367	815.57		7.8	
$^3F_3$	748	13341	485.12		4.6	
$^3F_2$	781	12658	247.65		2.4	
$^1G_4$	1332	7471	94.35		0.9	

$$rms = \sqrt{\frac{\sum((S^{DE}_{JJ'})^{cal} - (S^{DE}_{JJ'})^{meas})^2}{q-3}} \qquad (3)$$

Where q is the number of spectral bands analyzed and 3 reflects the number of fitting parameters. The best Judd-Ofelt parameters obtained for Tm^{3+} ions in $5NaF.9YF_3$ single crystal are: $\Omega_2 = 2.677$, $\Omega_4 = 0.252$ and $\Omega_6 = 1.059$ with rms = 0.076 (in 10^{-20} cm^2 units). The spectroscopic quality factor $\chi = \frac{\Omega_4}{\Omega_6}$ introduced by Kaminskii[11], for the Tm^{3+}: $5NaF.9YF_3$ host was found to be 0.238 which fall within the range of 0.22-1.5 for Nd^{3+} in different hosts[24]. The calculated S^{cal} line strengths for all measured transitions were then deduced and are given in Table 1.

The J-O parameters are determined from the fitting procedure and they are used to calculate other transitions properties between ground and excited states of the Tm^{3+} ion.

The radiative transitions probabilities $A_{JJ'}$ for emission from emitting levels [LS(J)] is given by[25]:

$$A^{rad}_{JJ'} = \frac{64\pi^3 e^2}{3h\bar{\lambda}^3(2J+1)}\left[\frac{n(n^2+2)^2}{9}S^{ED} + n^3 S^{MD}\right] \qquad (4)$$

Where the electric dipole line strengths (S^{DE}) are calculated from equation 2 while the magnetic dipole line strengths used in this study are reported by Spector[23]. Then, the radiative lifetime τ for an excited state (J) is calculated by:

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

Where the summation of $A_{JJ'}$ terms is over all lower energy levels. The branching ratio β_R is given by the equation:

$$\beta_R = \frac{A_{JJ'}}{\sum_{J'} A_{JJ'}} \quad (6)$$

The calculated transition probabilities and corresponding radiative lifetimes were then deduced and are given in Table 2. The values found are of the same order of magnitude as those found for other fluoride hosts[26,27]. From Table 2, the principal laser transitions $^3F_4$, $^3H_5$ and $^3H_4 \rightarrow {}^3H_6$ presented radiative lifetimes equal to 11.28, 5.907, 1.574 ms respectively, with high branching ratio ($\beta_R \rangle$ 80%) which predicts a laser emission around 1.8 μm and 800 nm.

CONCLUSION

Tm^{3+} doped $5NaF.9YF_3$ single crystals have been grown by Czochralski pulling technique. The Judd-Ofelt (JO) theory was applied to the thulium room temperature absorption spectra to obtain the three JO parameters: $\Omega_2 = 2.677 \times 10^{-20}$ cm^2, $\Omega_4 = 0.252 \times 10^{-20}$ cm^2 and $\Omega_6 = 1.059 \times 10^{-20}$ cm^2. These parameters Ω_t (t = 2, 4, 6) were in accordance with those calculated for other fluoride hosts. In addition, the quality factor $\chi = 0.238$ which is almost the same as the value determined in Nd^{3+} laser host. The radiative transition probabilities, radiative lifetimes and branching ratios of the principal intermanifold transitions of Tm^{3+} were calculated. The absorption cross-section at 800 nm was $\sigma_{abs} = 0.5\times10^{-20}$cm^2, which allow an efficient optical pump at this wavelengths. In comparison with other laser crystals, the calculated parameters show that Tm^{3+}:$5NaF.9YF_3$ crystal satisfies the fundamental spectral condition for laser emission.

ACKNOWLEDGMENT

The spectroscopic measurements were carried out at the C.I.R.I.L Labotatory of ENSI Caen (France). We would like to express our sincere thanks to the M.I.L group for their fruitful collaboration.

REFERENCES

1. Sliney, D. and M. Wolbarsht, 1980. Plenum press, New York, pp: 145.
2. Borel, C. and B. Viana, 1995. Ann. Chim. Fr., pp: 20-227.
3. Brunetaud,. J.M., 1998. Optique et photonique, pp: 3-53.
4. Kincade, K., 1995. Laser Focus, Aout: pp: 34.
5. Barnes, N.P., 1995. Laser Focus World, Avril, pp: 87.
6. Chai, B., J. Lefaucheur, A. Pham, G. Lutts and J. Nichols, 1993. Proceeding SPIE, pp: 1863-131.
7. Krivandina, E.A., A.A. Bystrova, B.P. Sobolev, A.F. Konstantinova, I.T. Ulukhanov, T.M. Glushkova, D.F. Kiselev, M.M. Firsova and A.P. Shtyrkova, 1992. Sov. Phys. Crysttalr, pp: 37-825.
8. Pontonnier, L.S.A., M.T. Roux and J. Solid, 1987. Stat. Chem., pp: 69-10.
9. Chou, H., P. Albers, A. Cassanho and H.P. Jenssen, 1989. MIT laboratory, pp: 322.
10. Thoma, R.E., G.M. Hebert, H. Insley and F.C. Weaver, 1963. Inorganic Chemistry, pp: 2-1005.
11. Kaminskii, A.A., 1996. Crystalline Laser: Physical Processes and Operating Schemes. (CRC Press, Boca Raton).
12. Ivanova, S.E., A.M. Tkachuk, M.F. Joubert, Y. Guyot and S. Guy, 2000. Optics and spectroscopy, 89: 535-548.
13. Judd, B.R., 1962. Phys. Rev., pp: 127-750.
14. Ofelt, G.S., 1962. J. Chem. Phys., pp: 37-511.
15. Krupke, W.F., 1971. IEEE J. Quantum Electron, pp: 7-153.
16. Krupke, W.F., 1974. IEEE J. Quantum Electron, pp: 10-450.
17. Weber, M.J. and T.E. Varitimos, 1971. J. Appl. Phys., pp: 42-4996
18. Beach, R., M.D. Shinn, L. Davis, R.W. Solarz and W.F. Krupke, 1990. IEEE J. Quantum Electron, pp: 26-1405.
19. Sardar, D.K., R.C. Velarde-Montecinos and S. Vizcarra, 1993. Phys. Status Solidi A., pp: 136-555.
20. Diaf, M., A. Braud, C. Labbe, J.L. Doualan, S. Girard, J. Margerie, R. Moncorge and M. Thuau, 1999. Can. J. Phys., 77: 1-5.
21. Dulick, M., G.E. Faulkner, N.J. Cockroft and D.C. Ngriyen, 1991. J. Lumin., 48: 49-517.
22. Carnall, W.T., P.R. Fields and K. Rajnak, 1968. J. Chem. Phys, 49: 4412-4423 .
23. Spector, N., R. Reisfeld and L. Boehm, Chem. Phys. Letters, 49: 49-53.
24. Powell, R.C., 1998. Phys. Solid. Stat. Laser Materials, Springer, New York, pp: 315.
25. Carnall, W.T. 1979. Handbook on the Physics and Chimistry of Rare Earths. 3: 171-208 .
26. Li, C., Y. Guyot, C. Linares, R. Mongorge and M.F. Joubert, 1994. In Advanced Solid-State lasers, Ed. By A. Pinto and T.Y. Fan (OSA, Washington, D.C., pp: 91.
27. Razumova, I.K., A.M. Tkachuk, D.I. Mironov and A.A. Nikitichev, 1996. Optics and Spectroscopy, pp: 81-205.