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HYDROSTATIC PRESSURE EFFECT ON EMISSION SPECTRA AND CRYSTAL FIELD PARAMETERS FOR YAG : Tb^{3+}

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The emission spectra of Tb^{3+} ion activated yttrium aluminum garnet (YAG) were measured at room temperature in the pressure range of 1 bar to 82 kbar. The peaks of the $^5D_4 \rightarrow {}^7F_J$ transition exhibit a red shift at a rate not larger than $1\ cm^{-1}$/kbar. The pressure dependence of the energy levels are discussed, and that of the crystal field parameters are also calculated.

1. Introduction

Tb^{3+} ion activated YAG [illegible]

phere. In the used phosphor the Tb^{3+} concentration was 5 mol%.

[illegible]

Table I
The energy of $^5D_4 \rightarrow {}^7F_J$ transitions for YAG : Tb^{3+} at ambient pressure and their red shift rate (RSR) with increasing pressure

$^5D_4 \rightarrow$	Energy (cm^{-1})	RSR (cm^{-1}/kbar)	$^5D_4 \rightarrow$	Energy (cm^{-1})	RSR (cm^{-1}/kbar)
^7F_O	14665	0.28	$^7F_4$	17120	0.07
	14775	0.99		17167	0.08
$^7F_1$	14928	0.99		17203	0.09
	14937	0.84		17264	vs^a
	15046	1.00		17290	vs^a
$^7F_3$	15844	0.34	$^7F_5$	17983	0.51
	15872	0.16		18231	0.35
	15911	0.40		18252	0.34
	15939	0.33		18304	0.19
	16016	0.19		18328	0.20
	16117	0.30		18388	0.19
	16161	vs^a		18433	vs^a
	16237	vs^a		18479	0.26
$^7F_4$	16806	0.25	$^7F_6$	20092	0.30
	16882	0.29		20146	0.35
	16912	0.16		20326	vs^a
	17090	vs^a			

^{a} vs = very small

cause the number of spectral lines of Tb^{3+} is very large, we paid attention only to the lines which have relatively high intensities and have been identified under pressure. The experimental results show that the spectral lines of the $^5D_4 \rightarrow {}^7F_J$ transitions tend to shift to the red (fig. 1). The peak positions shift nearly linearly with pressure in the measured range. The red shift rates are from very small to 1 cm^{-1}/kbar. Some spectral lines and their red shift rates are listed in table I. The rates are calculated from a curve fitting of the experimental data. The luminescent intensities weaken with increasing pressure, but the $^5D_4 \rightarrow {}^7F_5$ transitions still predominate.

3. Discussion

The change of the spectra reflects directly the relevant energy levels. According to the spectra measured at different pressures we have estimated the energy levels listed in table II. The energy of the level ^7F_O is taken as the zero point of energy in our calculation. The assignment of the spectra is based on Koningstein's work [1].

From table II we can see that the shift rate of $^7F_1$ is small and that of $^7F_{3-6}$ is slightly larger. The different Stark levels within the same manifold change in a similar manner.

The crystal field analysis of the measured energy levels can extend our knowledge of the interaction between the luminescence center and the surrounding crystal lattice. The change of the crystal field parameters with pressure should show how the hydrostatic pressure affects the centers. For the reason given above, we have calculated the crystal field parameters for YAG : Tb^{3+} from the energy levels measured at different pressures. Tb^{3+} ions doped in YAG usually replace Y^{3+} ions with D$_2$ point site symmetry. In the static crystal field model, the Hamiltonian for equivalent 4f electrons at a site of D$_2$ symmetry has the familiar form:

$$H = H_0 + H_{\mathrm{cf}} ,$$

where H_0 is the free ion Hamiltonian and H_{cf} represents the effect of the crystalline environment, which is considered as a perturbation of H_0. H_{cf} can be written in the following way:

$$H_{\mathrm{cf}} = \sum_{kq} B_q^k C_q^{\ k} ,$$

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Table II
Observed energy levels at ambient pressure and their shift rate (SR) with increasing pressures for YAG : Tb^{3+}

Level	Energy (cm^{-1})	SR (cm^{-1}/kbar)	Level	Energy (cm^{-1})	SR (cm^{-1}/kbar)
$^7F_0$	0		$^7F_4$	−2528	−1.08
$^7F_1$	−260	−0.06	$^7F_5$	−3286	−0.61
	−272	0.01		−3506	−0.81
$^7F_3$	−1178	−0.78		−3528	−0.82
	−1207	−0.86		−3551	−0.80
	−1350	−0.93		−3709	−0.92
	−1484	−1.09		−3727	−1.01
$^7F_4$	−2187	−0.87		−3769	−0.94
	−2395	−0.80	$^7F_6$	−5439	−0.81
	−2473	−1.10		−5609	−1.09
	−2502	−1.05			

where $k = 2, 4, 6$ and $|q|$ is an even number not larger than k. C_q^k are the operators associated with the spherical harmonics by

$$C_q^k = [4\pi/(2k+1)]^{1/2} Y_q^k .$$

The coefficients B_q^k, the crystal field parameters are treated as empirical parameters whose magnitudes are adjusted to fit the experimental data. In evaluating the matrix elements, the general tensor operator method is adopted. In our calculation the intermediate coupling wavefunction obtained by Ofelt [3] is taken as a free ion eigenfunction. J-mixing is also considered. The Hamiltonian H_0 is diagonal in J and J_z. Since free ion calculations typically give rms errors of 40 cm^{-1} or more, the "free ion energies" of the crystal field levels have been treated as parameters, introducing one additional parameter for each J manifold. It is a proper approximation to consider the ^7F multiplet only, because the $^5D_4$ multiplet is more than 14 000 cm^{-1} above the $^7F_0$. The combined free-ion plus crystal field matrices were diagonalized on a computer. The energy level of the ^7F multiplet was calculated by diagonalizing one 49 × 49 matrix. The nine crystal field parameters and seven "free ion energies" were obtained by using an optimization method. Our calculating process is similar to that described by Cone and Faulhaber [4]. The crystal field parameters are listed in table III, from which it is found that the absolute values of the parameters tend to increase with pressure. The "free ion energies" of the crystal field energy levels are listed in table IV. Their absolute values also tend to increase with pressure. This phenomenon is probably caused by enhanced J-mixing. The J-mixing effect itself results from the crystal field.

Table III
Crystal field parameters B_q^k (in cm^{-1}) at different pressures

B_q^k	1 bar	30 kbar	45 kbar	60 kbar	75 kbar	82 kbar
B_0^2	−353	−361	−370	−363	−368	−366
B_2^2	222	254	266	292	299	298
B_0^4	−2531	−2585	−2613	−2639	−2676	−2694
B_2^4	438	429	426	445	458	475
B_4^4	1152	1194	1216	1229	1248	1259
B_0^6	753	790	807	821	831	843
B_2^6	−182	−208	−220	−231	−235	−230
B_4^6	1557	1598	1620	1642	1663	1678
B_6^6	22	23	26	31	37	40

Table IV
"Free ion energies" (in cm^{-1}) at different pressures

	1 bar	30 kbar	45 kbar	60 kbar	75 kbar	82 kbar
$^7F_0$	−154	−164	−170	−176	−182	−184
$^7F_1$	−521	−544	−555	−570	−580	−584
$^7F_2$	−697	−716	−725	−734	−743	−748
$^7F_3$	−1262	−1289	−1302	−1316	−1330	−1335
$^7F_4$	−2301	−2329	−2342	−2356	−2369	−2375
$^7F_5$	−3527	−3549	−3560	−3571	−3582	−3587
$^7F_6$	−5587	−5616	−5630	−5645	−5659	−5665

The fitted "free ion energies" are not, in general, the same as the centers of gravity of the manifolds. This situation is also due to the J-mixing. The total of 16 parameters we obtained can well reproduce the energy levels scheme of ^7F multiplet. $\Sigma_i \sigma_i^2$ nearly equals $150\,cm^{-1}$ for various pressure, σ_i is the difference between the calculated and observed energies, while the sum is over all 21 levels used. The maximum difference between the observed and calculated values is not larger than $7\,cm^{-1}$. In the present calculation,

$$rms = \left[\left(\sum_i \sigma_i^2\right)\Big/(N-M)\right]^{1/2} < 6\,cm^{-1} ,$$

where $N = 21$, the number of levels used, and $M = 16$, the number of the parameters introduced.

References

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