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INFLUENCE OF HIGH PRESSURE ON THE EMISSION SPECTRA AND CRYSTAL FIELD PARAMETERS FOR TbP_5O_{14}

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The emission spectra and the energy levels of Tb^{3+} for TbP_5O_{14} were measured at 81K up to 8 GPa. At various pressures between atm. and 8GPa, the crystal field parameters have been determined.

TbP_5O_{14} is an excellent fluorescent material, it has stimulated interest in its possible use in optical communication system. Recently, Tang Zhuoran[1] has realized the fine structure of energy level of TbP_5O_{14}. The crystal field (c.f) parameters with C_{2v}[2] and C_{4v}[3] point site symmetry of Tb^{3+} in TbP_5O_{14} at ambient pressure have been calculated respectively.

We measured the emission spectra of TbP_5O_{14} using a monochromator in the range of 12000--20000 cm^{-1} at fixed temperature (81K) and various pressures up to 8GPa. A gasketed diamond anvil cell was used to produce high pressure, with 4:1 methanol-ethanol mixture for the hydrostatic pressure medium. Pressure was calibrated using the well-known Ruby fluorescence technique. The liquid nitrogen was spounted continously into the diamond cell to keep the constant temperature (81K). Thin plates of samples approximately 100 μm in linear dimensions and 50 μm thickness were used. The fluorescence was excited by the 4880 Å line of an argon laser. With the exception of the $^5D_4(A_1)$-$^7F_5(B_2)$ transition, the observed 60 emission lines show red shift with increasing pressures. The energy levels corresponding to the spectra at various pressures are summarized in table 1. The assignment of the spectra was based on Tang's work[1]. From table 1 it can be seen that with increasing pressure the most energy levels close to the $^7F_0$, only a few levels are away from it. The shift rates of the ^7F_J are not larger than $10cm^{-1}$/GPa.

We have calculated the c.f. parameters for TbP_5O_{14} from the measured energy levels. In this calculation we consider the luminescent center Tb^{3+} occupying a site with distorted C_{4v} symmetry[4]. The hamiltonian for equivalent 4f electrons of Tb^{3+} can be written as a polynomical

$$H = H_0 + B_0^2 C_0^2 + B_0^4 C_0^4 + B_4^4 (C_{-4}^4 + C_4^4) + B_0^6 C_0^6 + B_4^6 (C_{-4}^6 + C_4^6)$$

where H_0 is the free ion Hamiltonian, the rest are the c.f. Hamiltonian, the tensor operators

$$C_q^k = \sum_i C_q^k (\theta_i, \varphi_i)$$

are related to the spherical harmonics Y_q^k by

$$C_q^k (\theta_i, \varphi_i) = (4\pi/(2k+1))^{\frac{1}{2}} Y_q^k (\theta_i, \varphi_i)$$

Our calculating process and the definition of the rms deviations σ is similar to that described by reference[5]. At different pressures, the sets of the c.f. parameters and the rms deviations are listed in Table 2, the "free ion energies" of the crystal field energy levels in Table 3. From table 2 it can be seen that the absolute values of the c.f. parameters tend to increase with pressure. It implies that the c.f. tends to strenthen and therefore the split-

Table 1 The observed energy levels (in cm^{-1}) at different pressure for TbP_5O_{14}

		atm.	2GPa	4GPa	6GPa	8GPa
$^5D_4$	E	14812	14789	14780	14770	14761
	A_1	14753	14748	14744	14743	14742
	A_2	14741	14734	14729	14724	14719
	A_1	14722	14721	14713	14706	14698
	E	14708	14703	14697	14692	14686
	B_1	14698	14689	14684	14680	14675
	B_2	14694	14682	14672	14667	14657
$^7F_0$	A_1	0	0	0	0	0
$^7F_1$	E	-263	-255	-247	-237	-229
$^7F_2$	E	-573	-561	-550	-539	-528
	B_1	-594	-589	-584	-577	-572
	A_1	-739	-722	-705	-688	-671
	B_2	-842	-841	-840	-838	-831
$^7F_3$	A_2	-1364	-1364	-1364	-1360	-1360
	E	-1401	-1400	-1398	-1397	-1395
	E	-1425	-1425	-1425	-1423	-1423
	B_1	-1479	-1476	-1473	-1470	-1467
	B_2	-1500	-1506	-1511	-1515	-1521
$^7F_4$	A_1	-2221	-2218	-2214	-2208	-2202
	A_2	-2272	-2267	-2262	-2255	-2251
	E	-2315	-2315	-2309	-2301	-2296
	A_1	-2345	-2356	-2353	-2350	-2347
	B_2	-2388	-2376	-2366	-2354	-2344
	E	-2468	-2475	-2477	-2472	-2474
F_5	B_1	-3602	-3595	-3578	-3565	-3553
	E	-3614	-3602	-3591	-3576	-3564
	A_2	-3673	-3664	-3656	-3648	-3640
	A_1	-3698	-3699	-3701	-3704	-3706
	B_2	-3723	-3729	-3735	-3738	-3745
	E	-3740	-3743	-3748	-3752	-3761

ting of each ^7F_J multiplet increases with pressure. The increasing of σ with pressure is probably caused by the increased deviation from C_{4v} site symmetry for the Tb^{3+}.

Table 2. Crystal field parameters B_q^k and rms deviations (in cm^{-1}) at various pressures

	atm.	2GPa	4GPa	6GPa	8GPa
B_0^2	-771	-816	-866	-986	-1062
B_0^4	-856	-861	-751	-702	-603
B_4^4	578	598	628	664	685
B_0^6	843	902	1022	924	1031
B_4^6	76	100	78	150	144
σ	17	19	21	22	24

Table 3. "Free ion energies" (in cm^{-1}) at different pressures

	atm.	2GPa	4GPa	6GPa	8GPa
$^7F_0$	-50	-56	-63	-79	-103
$^7F_1$	-242	-233	-224	-213	-205
$^7F_2$	-687	-678	-668	-658	-647
$^7F_3$	-1431	-1432	-1434	-1434	-1438
$^7F_4$	-2364	-2363	-2360	-2349	-2345
$^7F_5$	-3636	-3630	-3625	-3617	-3612
$^7F_6$	-5704	-5699	-5697	-5677	-5671

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