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HIGH PRESSURE EFFECT ON LUMINESCENCE AND CRYSTAL FIELD IN Y_2O_2S:Eu

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The emission spectra of Y_2O_2S:Eu were measured at pressures up to 16GPa. The levels at different pressures were estimated. The dependence of crystal field parameters on pressure was calculated.

The Y_2O_2S:Eu as a red phosphor has been of considerable interest both theoretically and technologically. Many authors have widely and deeply studied it in recent years (1,2). In this paper we report the pressure effect on its luminescence and crystal field. High pressure is a powerful means reducing interatomic distance, it changes interaction between the central ion and its crystalline environment. Being a better model, the dependence of crystal field parameters on pressure properly reflects this change of the interaction.

In our experiment a diamond anvil cell was used to generate hydrostatic or quasihydrostatic pressure up to 16 GPa. The pressure medium is the mixture of methanol and ethanol. The pressure was determined on the basis of the ruby fluorescence scale. The luminescence was excited by 4579 A° line of Ar^+ laser and recorded with a Spex- 1403 monochrometer. All the measurements were carried out at room temperature. About 50 spectral lines were received at different pressures. They belong to $^5D_{0,1,2} \rightarrow {}^7F_{0-4}$ transitions. All of them tend to red-shift with different rates less than 9 cm^{-1}/GPa. According to the frequences of these lines the positions of related levels were determined at various pressures. The results are listed in Table 1. The $^7F_0$ is taken as the initial point of energy. From the table we can find that the energies of ^5D manifold rapidly decrease with increasing pressure, but the energies of ^7F manifold change up and down with pressure. In general the levels of ^7F manifold change slowly.

Table 1. Position of levels at various pressure (cm^{-1})

level		atm.	2.5GPa	5GPa	7.5GPa	10GPa
$^7F_1$	E	351	352	353	354	356
	A	387	383	378	374	370
$^7F_2$	A	917	914	910	907	904
	E	946	941	935	930	924
	E	1192	1195	1199	1202	1206
$^7F_3$	E	1867	1867	1866	1866	1865
	A	1882	1880	1878	1876	1874
	A	1921	1924	1926	1928	1930
	E	1929	1929	1929	1929	1929
$^7F_4$	A	2596	2591	2585	2580	2574
	E	2803	2801	2799	2797	2794
	A	2828	2858	2858	2859	2859
	E	2969	2971	2974	2976	2978
	E	3003	3006	3009	3012	3015
	A	3023	3026	3029	3032	3035
$^5D_0$	A	17155	17141	17127	17113	17098
$^5D_1$	E	18907	18893	18879	18864	18850
	A	18915	18899	18883	18867	18851
$^5D_2$	E	21330	21313	21295	21278	21260
	E	21395	21379	21362	21346	21329
	A	21408	21392	21376	21360	21344

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In Y_2O_2S the point symmetery of Y^{3+} site is C_{3v}. The Eu^{3+} mainly replaces the Y^{3+} in Y_2O_2S:Eu. The Hamiltonian of Eu^{3+} can be written as $H=H_0+H_{cf}$. H_0 is the free ion Hamiltonian and H_{cf} represents the effects of crystalline environment on the Eu^{3+} ion. In this case

$$H_{cf} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_3^4 (C_{-3}^4 - C_3^4)$$

$$+ B_0^6 C_0^6 + B_3^6 (C_{-3}^6 - C_3^6) + B_6^6(C_{-6}^6+C_6^6)$$

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

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

The coeficients B_q^k, the crystal field parameters, can be obtained by fitting the experimental data with an optimization method. In order to calculate the matrix elements of H_{cf}, the usual tensor operator technique was adopted.

In the calculation the intermediate wave function was used and the J-maxing caused by H_{cf} was also considered. Our calculating procedure is similar to that described by Cone and Faulhaber[4]. The calculation results are shown in Table 2 and Table 3. The rms deviations are not larger than $7cm^{-1}$, they are estimated on basis of wybounrne's work[3]. It is very interesting that $|B^k|$ increase if k or q=3n, where n is an integer; otherwise they will decrease.

Table 2. Crystal fied parameters at pressure, (cm^{-1})

B_q^k	atm.	2.5GPa	5GPa	7.5GPa	10GPa
B_0^2	83	71	56	43	29
B_0^4	1100	1080	1066	1040	1023
B_3^4	882	924	968	1010	1054
B_0^6	325	341	358	373	382
B_3^6	-378	-387	-396	-403	-413
B_6^6	524	526	532	538	546

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

	atm.	2.5GPa	5GPa	7.5GPa	10GPa
$^7F_0$	24	25	27	28	29
$^7F_1$	395	395	396	397	399
$^7F_2$	1075	1074	1075	1075	1075
$^7F_3$	1923	1924	1924	1925	1926
$^7F_4$	2893	2893	2893	2894	2894

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