High-pressure Luminescence Study of GdOCl:Eu Phosphor

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The emission spectra of GdOCl:Eu have been measured at high pressures up to 10 GPa and at room temperature to examine the pressure effect on the energy levels of Eu^{3+} in the crystal. About 60 spectral lines have been measured at various pressures. These lines slowly shift to the red at rates $3\text{--}9\text{ cm}^{-1}/\text{GPa}$. On the basis of experimental data the pressure dependences of 24 Stark levels belonging to the ${}^5\text{D}_{0-2}$ and ${}^7\text{F}_{0-5}$ multiplets have been determined. By fitting experimental levels the crystal field parameters and free ion parameters have been found out. The crystal field strength parameter S , Slater integral F_2 and spin-orbit coupling parameter ζ decrease with pressurization in some degree. [High pressure luminescence, GdOCl:Eu, energy level, crystal field effect]

1. Introduction

The rare earth oxyhalides (REOX) constitute a versatile matrix system, widely isomorphous but displaying considerable changes in the coordination of the RE^{3+} ion. This versatility provides an excellent opportunity to study the variation of the crystal field (CF) effects along both the rare earth and the halide series. On the other hand, the Eu^{3+} ion gives a convenient approach to the study of the interaction between the central ions and their crystalline environment because of the particular features of its energy level scheme and the easier interpretation of its spectrum. Therefore Eu^{3+} activated rare earth oxyhalides have received a lot of scientific attention [1–3] and become an important object in the studying of the CF effects.

High pressure can continuously decrease the interatomic distance in crystals and is widely used in studying the physical and chemical properties of crystals. We had studied the luminescence properties of $\text{LaOCl}:\text{Eu}$, $\text{LaOBr}:\text{Eu}$ and $\text{GdOBr}:\text{Eu}$ under high pressure [4–6] in order to examine the effect of crystal field on the energy level scheme of the RE ions in continuous contraction of the interatomic distance. The details have been reported in our previous papers [4–6]. In these studies we observed some interesting phenomena. Firstly, the splitting of the two Stark levels of the ${}^7\text{F}_1$ multiplet decreases with increasing pressure. Secondly, the crystal field strength parameters S of these samples decrease in pressurization process although a decrease in the interatomic distance leads to an increase in interaction between atoms. And the free ion parameters F_k and ζ also decrease with the pressure increase.

In the present work, we studied the luminescence of GdOCl:Eu under high pressure in order to know if this sample has the above mentioned properties.

2. Experimental

The polycrystalline GdOCl:Eu sample used in this work was prepared by a solid state reaction between the corresponding rare earth oxides and ammonium chloride at high temperature. The nominal concentration of Eu in the sample is 5 mol. %. The sample was routinely checked by x-ray powder diffraction. The high pressure was generated with a gasketed diamond anvil cell and calibrated by the ruby fluorescence method. The well-known 4:1 methanol-ethanol mixture was used as pressure transmitting medium. The 465.8 nm line of an argon ion laser was used to pump the sample and a Spex-

1403 Raman Spectrometer to record the luminescence of the sample. The spectrum measured in the range from 21430 cm^{-1} to 13000 cm^{-1} nearly includes all the emissions from ${}^5\text{D}_{0-2} \rightarrow {}^7\text{F}_{0-5}$ transitions. About 60 spectral lines were recorded at room temperature and high pressures up to 10 GPa. Their assignment was carried out according to Hölsä's work [1].

3. Results and Discussion

The spectral lines measured in the pressure range of this work shift to the red with pressurization. The red shift rates are between $3\text{ cm}^{-1}/\text{GPa}$ and $9\text{ cm}^{-1}/\text{GPa}$. This phenomenon shows that the CF levels of the ${}^5\text{D}_{0-2}$ multiplets lower more rapidly than those of the ${}^7\text{F}_{0-5}$ multiplets. On the basis of the peak positions of the lines measured at various pressures the dependence of the CF levels on the pressure was determined and plotted in Fig. 1. From the figure it can be seen that all the levels slowly change with increasing pressure. This phenomenon represents the fact that 4f electrons shielded by $5\text{s}^25\text{p}^6$ electronic shell are insensitive to outside pressure effects. The two levels of ${}^7\text{F}_1$ close to each other with pressurization, as might be expected.

After knowing the change in CF levels, it is possible to study the effects of pressure on the interatomic and intra-atomic interactions for Eu^{3+} in GdOCl:Eu. As we know, for an RE^{3+} ion in a crystal the Hamiltonian H can be written as

$$H = H_f + H_c, \quad (1)$$

where H_f is the free ion Hamiltonian describing the interaction inside the RE^{3+} ion and H_c the CF Hamiltonian representing the interaction between the RE^{3+} ion and its crystalline environment. The Eu^{3+} ion in the GdOCl:Eu mainly occupies the site with C_{4v} symmetry and its H_c can be expressed as

$$H_c = B_0^2 C_0^2 + B_4^0 C_4^0 + B_4^4 (C_4^{-4} + C_4^4) + B_6^0 C_6^0 + B_6^4 (C_6^{-4} + C_6^4). \quad (2)$$

In the expression C_k^q are the tensor operators associated with spherical harmonics by

$$C_k^q = [4\pi/(2k+1)]^{1/2} \sum_i Y_i^q(\theta, \varphi) \quad (3)$$

Fig. 1. Effect of pressure on the levels of the ${}^7F_{1-4}$ and ${}^5D_{0-2}$ multiplets.

and B_q^t the CF parameters to be determined. There are 24 CF levels available to derive these CF parameters. In the calculation the 7F and 5D manifolds have been considered. In the constructing of the matrix of H_C the intermediate coupling wave functions and J-mixing were taken into account. By fitting the calculated levels to the observed ones the five CF parameters were obtained in the least squares calculation. The result is given in Table 1. The CF strength parameter and the rms deviation σ are also given in the same table. The strength parameter S , defined by Chang [7], can be derived from the B_q^t set:

$$S = \left\{ \frac{1}{3} \sum_k \frac{1}{2k+1} [(B_0^t)^2 + 2 \sum_{q>0} |B_q^t|^2] \right\}^{1/2}. \quad (4)$$

S is an invariant under arbitrary rotation of the crystal lattice and also a quantitative measure of the CF strength. From the table it can be seen that S decreases with increasing pressure, which is similar to the situation in $\text{LaOCl}:\text{Eu}$, $\text{LaOBr}:\text{Eu}$ and $\text{GdOBr}:\text{Eu}$ [4–6].

As we know pressure affects not only the interaction between the RE ion and its crystal environment, but also the interaction inside the RE ion. In the first approximation

$$H_f = \sum_k f^k F_k + \zeta \sum_i s_i \cdot l_i + [\alpha L(L+1) + \beta G(G_2) + \gamma G(G_4)], \quad (5)$$

where the first term stands for the 4f electron Coulomb repulsion, the second term represents the spin-orbit interaction and the last term expresses the configuration interaction. $F_k(k = 2, 4, 6)$ are the Slater parameters and f^k the corresponding coefficients. ζ is the spin-orbit coupling parameter, l_i and s_i are, respectively, the orbital and spin angular momentum of the i th 4f electron. α , β and γ are the configuration interaction parameters, L is the total orbital angular momentum, $G(G_2)$ and $G(R_7)$ are the eigenvalues of Casimir's operators for the Lie groups G_2 and R_7 . To minimize the number of free parameters, we express F_4 and F_6 with F_2 by fixing the ratios of $F_4/F_2 = 0.1484$ and $F_6/F_2 = 0.0161$. On the basis of the experimental values of the $^7F_{0-4}$ and $^5D_{0-2}$ multiplet barycenters, the values of F_2 and ζ at various pressures have been obtained in the least squares refining calculations and are plotted in Fig. 2. In the pressure range of the present work the values of F_2 and ζ decrease by 0.38% and 0.44%, respectively, which is similar to the situation in GdOBr : Eu [6].

Table 1 CF parameters, CF strength parameters and rms deviations (in cm^{-1}) at pressures (in GPa).

P	0	2	4	6	8	10
B_2^0	-946	-908	-858	-812	-786	-761
B_4^0	-685	-676	-668	-698	-738	-758
B_4^4	887	896	900	887	869	869
B_6^0	1039	1113	1111	1140	1221	1224
B_6^4	386	381	416	428	397	403
S	413	413	408	404	404	403
σ	11	12	11	11	11	12

Fig. 2. Dependences of the Slater parameter F_2 and the spin-orbit coupling parameter ζ .

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