The optical properties of Eu^{3+} embedded in the rare earth borogermanate matrix: REBGeO$_5$

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Abstract. The luminescent properties of the trivalent europium ion in two borogermanate matrices, LaBGeO$_5$ (trigonal) and GdBGeO$_5$ (monoclinic), have been analysed. The energy level schemes of the 24 and 20 ^{7}F$_J$ ($J5 = 0$–4) electronic levels are well reproduced with 14 (LaBGeO$_5$) and 9 (GdBGeO$_5$) crystal field parameters (CFPs) according to the local point site symmetry occupied by the rare earth element in the matrix.

1. Introduction

Two crystallographic varieties of the REBGeO$_5$ system are found. For the larger rare earth ions, RE = La, Pr and Nd (low-temperature phase) a trigonal phase having the stillwellite (CeBSiO$_5$) structural type can be obtained [1–6, 8]. For the smaller ones, i.e. Nd (high-temperature phase) Er and Y, a monoclinic phase exists, with the datolite structural type [5, 7]. For other rare earths (Tm, Yb, Lu) this stoichiometry probably does not exit, and even GdBGeO$_5$ is difficult to obtain free of pyrogermanate Gd$_2$Ge$_2$O$_7$. Verwey *et al* [9] studied the luminescence processes in the crystalline and glass modifications of Eu^{3+}-doped REBGeO$_5$-type compositions at 300 K, whereas Lysanova *et al* [6] published the luminescence spectra of GdBGeO$_5$:Eu^{3+} at room temperature and Kaminskii recently studied LaBGeO$_5$:Nd^{3+} [10]. The interest of these compounds is their potential use as an effective self-frequency-doubling mini-laser. It is thus important to study their optical properties in order classify these compounds among the laser matrices and derive the knowledge of the wavefunctions, which are necessary to interpret the excited states dynamics in that system.

2. Experimental details

Polycrystalline samples of REBGeO$_5$:2% Eu^{3+} were synthesized by solid state reactions between high-purity RE$_2$O$_3$ (or Pr$_6$O$_{11}$), H$_3$BO$_3$ and GeO$_2$ as starting materials. The stoichiometric mixture is ground and progressively heated in a platinum crucible at 850 °C over 24 hours. The resulting compound is ground again and heated for a further 24 hours at 1100 °C. In order to avoid the formation of the pyrogermanate phase RE$_2$Ge$_2$O$_7$, especially in the case at the end of the rare earth series, some preparation was carried out with a small

excess of H_3BO_3 ($\sim$25% per mole). The samples were checked by the x-ray diffraction technique. For the trigonal lanthanum compound a single phase was obtained, but for the monoclinic gadolinium compound an impurity phase was detected which is identified as the pyrogermanate.
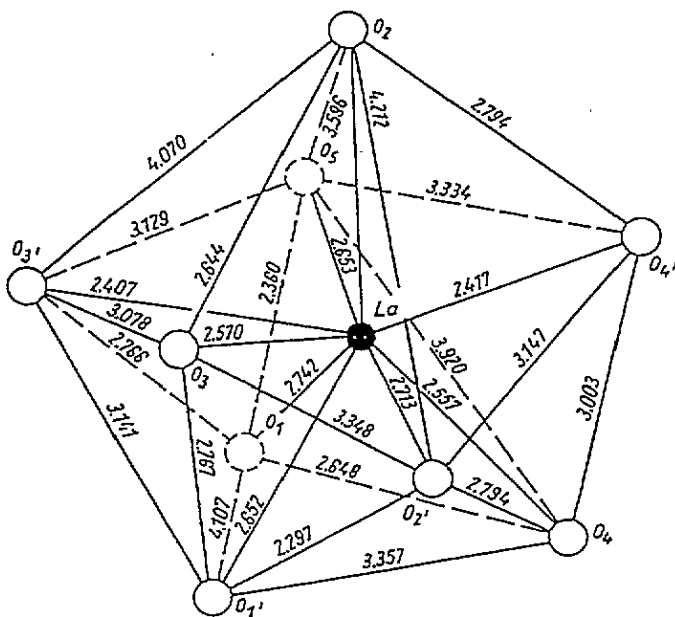

Figure 1. The geometry of LaO_9 polyhedron in $LaBGeO_5$ trigonal phase. Interatomic distances are given in 10^{-1} nm (from [8]).

The 457.9 nm blue line of a 5 W argon ion laser was used to excite the $^5D_2$ level of Eu^{3+} in $REBGeO_5$ matrix, allowing the classical emitting and/or quenching cascade $^5D_2 \rightarrow \; ^5D_1 \rightarrow \; ^5D_0$. Selectively excited emission of the $^5D_0$ level of Eu^{3+} was performed also by using a continuous wave rhodamine-6G dye laser pumped by an argon ion laser. Non-polarized fluorescence spectra were recorded at 77 K in the 520–750 nm wavelength range through a 1 m Jarrell–Ash monochromator equipped with a Hamamatsu R374 photomultiplier. The spectral resolution is then better than 1 cm^{-1}.

3. Crystal structure

For the rare earth borogermanates series with the general formula $REBGeO_5$, two different crystallographic modifications have been found [5,6]. For RE = La, Pr (Nd low-temperature phase) the compounds crystallize in the structure type of stillwellite, space group $C_3^2-P3_1$ (No 144), [3,4,8]. In that phase the single point symmetry site of the rare earth ion is very low, C_1. The rare earth ion is ninefold coordinated as shown in figure 1 (from [8]). The variety with RE = Nd–Er, Y crystallizes in the datolite-type structure, $CaBSiO_4(OH)$. The unit cell symmetry is monoclinic with $P2_1/a$ (No 14) as space group. The rare earth ion is surrounded by eight oxygen atoms forming a distorted cube [7]. According to the crystallographic structure, the point site symmetry of the rare earth ion can be C_i or C_1.
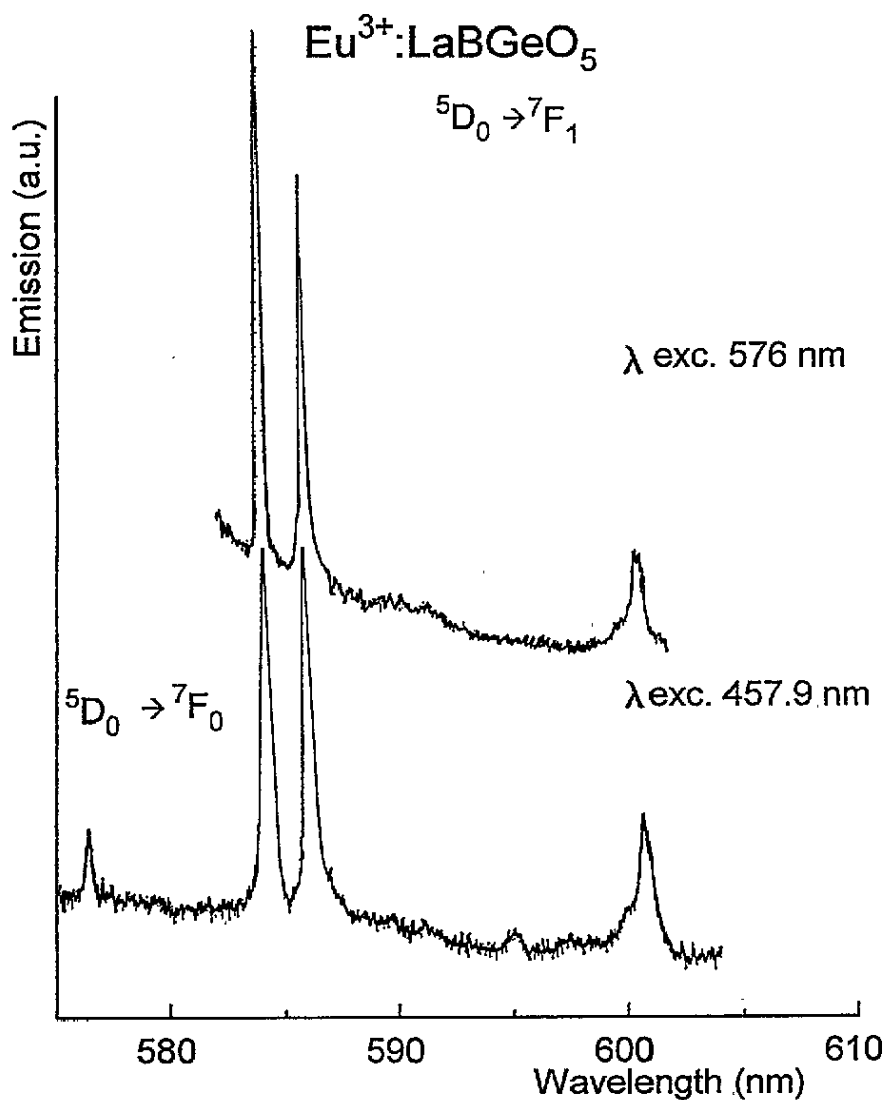
Figure 2. A part of fluorescence spectra of LaBGeO$_5$:Eu^{3+} at 77 K.

The analysis of the luminescence properties of the Eu^{3+} in the monoclinic borogermanate modification confirms this feature, although we can suspect the symmetry to be close to a higher one (with a ternary axis). Both rare earth borogermanate modifications contain BO$_4$ and GeO$_4$ tetrahedra in an ordered arrangement.

4. Results and discussion

The two compounds studied fluoresce reasonably well. Under 457.9 nm argon ion laser excitation at 300 and 77 K, the radiative deexcitation between $^5D_2$, $^5D_1$ and $^5D_0$ levels occurs and almost all emission observed arises from the $^5D_0$ level. This efficient quenching
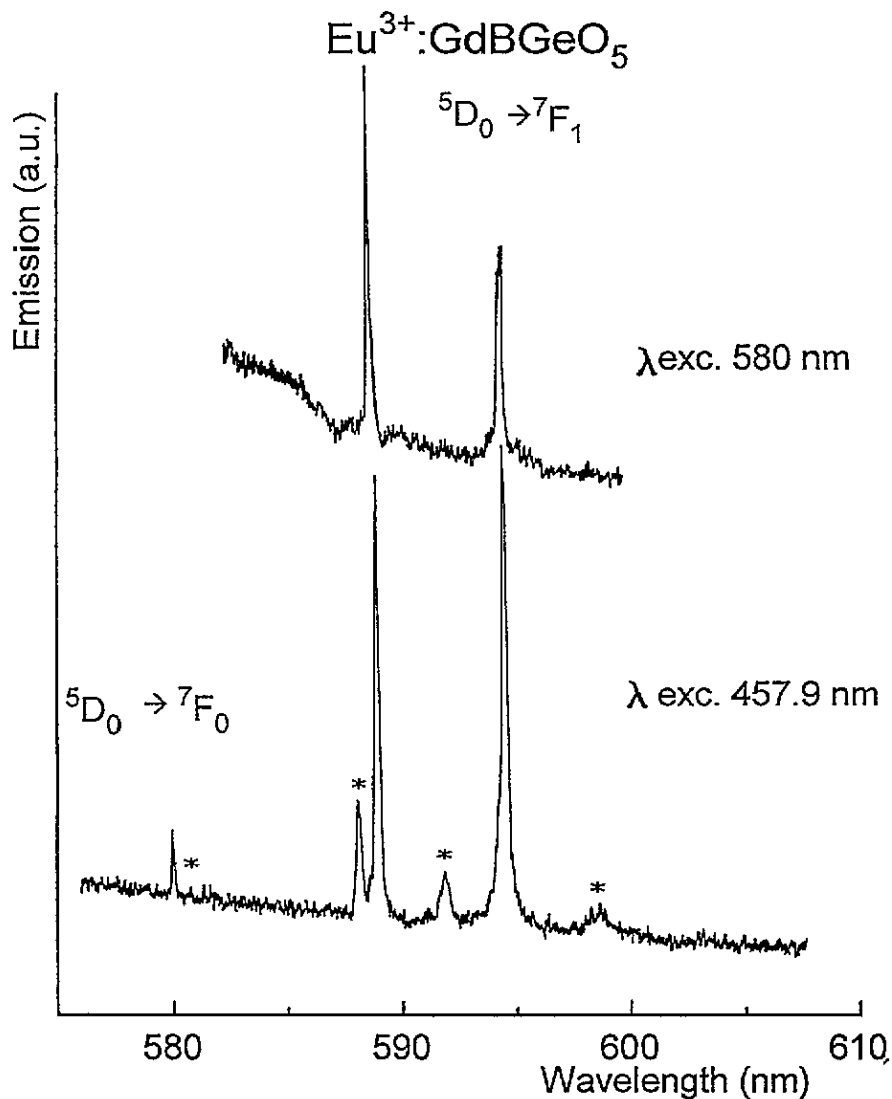
Figure 3. A part of fluorescence spectra of $GdBGeO_5:Eu^{3+}$ at 77 K; the $Gd_2Ge_2O_7$ phase is also observed (*).

is favoured by multiphonon relaxation of the excitation energy which considers the lattice phonons of highest energy (~ 800 cm-1 for the GeO_4 group [5]). The $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ electronic transitions are of similar intensity in both compounds, but the more intense spectra are obtained for the trigonal phase. The $^5D_0 \rightarrow {}^7F_0$ transition is observed, and is seen to be single and not very intense (figure 2 and figure 3). By applying both group theory and electric dipole transition selection rules, this feature is only compatible with C_n, C_{nv}, or C_s point symmetries for the rare earth ion [11]. By using selective dye laser excitation, only the fluorescence from the $^5D_0$ level is recorded, permitting the construction of the partial energy level scheme for the ^7F_J ($J = 0$–4) ground multiplet.

4.1. The trigonal phase

The analysis of other transitions shows that the degeneracy of the J levels is completely lifted for the trigonal phase which does not permit a point site symmetry higher than C_2. In fact, the real symmetry is C_1 according to and in agreement with the crystallographic data. The crystal field splitting of the $^7F_1$ level is one of the largest of the europium compounds. The exceptions are oxyapatites $Ca_{10-x}Eu_x(PO_4)_6O_{1+x/2}$ [12] and oxides with the byxbite structure (S_6 site) [13]. The overall splitting is 476 cm^{-1} (about 650 cm^{-1} for oxyapatites) and the position of the $^5D_0$ level is relatively high, situated at 17 350 cm^{-1} and 17 510 cm^{-1} for oxyapatites, and about 17 300 cm^{-1} for oxide). This indicates a large absolute value for the crystal field parameters of rank 2. The rather complete energy level scheme permits a simulation in a C_2 symmetry, considered as an approximation of the C_1 real symmetry.

Table 1. Experimental and calculated crystal field energy levels of the Eu^{3+} ion in two REBGeO5 modifications at 77 K. All values in units of cm^{-1}.

$^{2S+1}L_J$ level	LaBGeO5		GdBGeO5	
	E (exp.)	E (calc.)	E (exp.)	E (calc.)
$^7F_0$	0	0	0	0
$^7F_1$	242	239	262	262
	293	299	427	424
	718	715	430	432
$^7F_2$	867	859	914	914
	900	890	942	941
	1145	1153	1070	1075
	1264	1275	1092	1092
	1359	1354	1205	1206
$^7F_3$	1781	1792	—	1813
	1804	1805	1908	1905
	1966	1975	1931	1930
	1992	2007	—	1953
	2044	2038	1966	1968
	2079	2070	—	1984
	2161	2136	1989	1989
$^7F_4$	2748	2734	—	2737
	—	2855	2750	2750
	2936	2931	2782	2781
	2954	2954	2866	2865
	2986	2992	—	2895
	3032	3028	2977	2978
	3065	3071	3031	3028
	3108	3121	3058	3058
	3208	3206	—	3188
$^5D_0$	17350	—	17244	—

4.2. The monoclinic phase

We observed three and five Stark levels for $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions respectively. This suggests a low point symmetry like in the trigonal phase. In fact, four weak transitions are observed for $^5D_0 \rightarrow {}^7F_3$ (from seven allowed) and six (from nine) for $^5D_0 \rightarrow {}^7F_4$ transitions. Moreover, the two upper Stark levels of $^7F_1$ are separated by only

3 cm^{-1}, whereas several $^5D_0 \rightarrow {}^7F_2$ components are also close together. This fact suggests that the point symmetry is close to a higher one, probably with a ternary axis (C_3 or C_{3v}). In their analysis of the same compound Verwey *et al* [9] observed two and three lines for the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, which is probably due to low resolution of the apparatus and measurements at 300 K. Practically the assumed crystal field symmetry will be C_{2v}. The overall splitting of the $^7F_1$ level is much smaller (168 cm^{-1}) than for the trigonal phase and the $^5D_0$ energy position at 17 244 cm^{-1} is lower than in the trigonal phase.

Table 2. The phenomenological B_q^k (S_1^k) crystal field parameter values for the Eu^{3+} ion in two REBGeO$_5$ modifications. All values are in units of cm^{-1}.

	LaBGeO$_5$ C$_2$	GdBGeO$_5$ C$_{2v}$
B_0^2	−434	−621
B_2^2	891	−38
B_0^4	968	−321
B_2^4	−606	−1263
S_2^4	570	—
B_4^4	436	−854
S_4^4	−306	—
B_0^6	75	−929
B_2^6	−372	−51
S_2^6	−736	—
B_4^6	70	−160
S_4^6	349	—
B_6^6	−331	−39
S_6^6	−169	—
Levels	24	20
RMS	11.8	2.4

4.3. Simulation of the energy level schemes

The europium trivalent ion ($4f^6$ configuration) is very convenient for the crystal field calculation. The ground ^7F term is almost isolated from the rest of the configuration, the first excited level, $^5D_0$, being situated at about 12 000 cm^{-1} above $^7F_6$. That means that the ^7F_J wavefunctions are almost pure in ^7F states. The crystal field calculation can be performed accurately on a very reduced 49×49 basis of the ^7F_J multiplet [14].

The crystal field potential is written as follows

$$H_{cf} = \sum_{kq} B_q^k \left[C_q^k + (-1)^q C_{-q}^k \right] + i S_q^k \left[C_q^k - (-1)^q C_{-q}^k \right].$$

The number of non-zero CFPs depends on the symmetry: 27 for the C_1 symmetry, nine for C_{2v}, and 15 for C_2. (14 when S_2^2 is set to zero by an appropriate choice of the reference axis). The experimental and calculated energy level schemes of Eu^{3+} in two borogermanate crystallographic modifications are gathered together in table 1 [15]. The two sets of CFPs reproduce the observed fluorescence data i.e. 24 observed from 25 expected $^7F_{0-4}$ levels of LaBGeO$_5$: Eu^{3+} with RMS of 11.8 cm^{-1} and a residue of 2078.4 cm^{-1} on one hand, and 20 $^7F_{0-4}$ levels of GdBGeO$_5$: Eu^{3+} with RMS of 2.4 cm^{-1} and a residue of 56.9 cm^{-1} on the other hand (table 2). The last result confirms the assumption for a point symmetry close to an higher one.

References

[1] McAndrew J and Scott T R 1955 *Nature* **176** 509
[2] Gay P 1956 *Miner. Mag.* **31** 465
[3] Voronkov A A and Pyatenko Yu A 1967 *Crystallography* **12** 214
[4] Callegari A, Giuseppetti G, Mazzi F and Tadini C 1992 *Neuef Jahnbuch für Mineralogie Monatshefte (Germany)* 49
[5] Rulmont A and Tarte P 1988 *J. Solid State Chem.* **75** 244
[6] Lysanova G V, Dzhurinskii B F and Komova M G 1989 *Izv. Akad. Nauk SSSR Ser. Neorg. Mater.* **25** 632
[7] Belokonova E L, Mill B V, Butashin A V and Kaminski A A 1991 *Izv. Akad. Nauk. SSSR Ser. Neorg. Mater.* **27** 556
[8] Kaminski A A, Mill B V, Belokoneva E L and Butashin A V 1990 *Izv. Akad. Nauk. SSSR Ser. Neorg. Mater.* **26** 1105
[9] Verwey J W M, Van der Voort D, Dirksen G J and Blasse G 1990 *J. Solid State Chem.* **89** 106
[10] Kaminski A A, Bagaev S N, Butashin A V and Mill B V 1993 *Izv. Akad. Nauk. SSSR Ser. Neorg. Mater.* **29** 545
[11] Blasse G and Bril A 1966 *Philips Res. Rep.* **21** 368
[12] Piriou B, Fahmi D, Dexpert-Ghys J, Taitai A and Lacout J L 1987 *J. Lumin.* **39** 97
[13] Antic-Fidancev E, Aride J, Lemaitre-Blaise M, Porcher P and Taibi M 1992 *J. Alloys Compounds* **188** 242
[14] Porcher P and Caro P 1976 *J. Chem. Phys.* **65** 89
[15] Porcher P 1989 *Computer Routine REEL for Simulation of the nd^N and nf^N Configurations* unpublished