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Luminescence of Eu^{3+} Ion as a Structural Probe in High Temperature Phase Transformations in Lutetium Orthoborates*

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The rare earth (RE) borates offer an interesting possibility to monitor the polymorphic relationships of compounds with the same composition as a function of the ionic radius of the RE host cation and the temperature of preparation. The reaction between the RE oxides and B_2O_3 (or boric acid, H_3BO_3) leads to the formation of borates having usually the composition of the RE_2O_3:B_2O_3 ratio 1:3, 1:1 or 3:1 [1]. Other compounds with different RE_2O_3:B_2O_3 ratios have been synthesized, as well. In addition, the borate compounds exhibit polymorphism depending on the temperature and pressure during preparation. This is typical of the RE orthoborates corresponding to the empirical formula $REBO_3$ [2].

In this investigation the optical luminescence of the Eu^{3+} ion is used as a structural probe in order to resolve the structure–spectra relationships in lutetium orthoborates. The Eu^{3+} ion luminescence is a well known probe in a study of both glasses showing structural disorder and crystalline substances of high symmetry. The luminescence properties of the Bi^{3+} doped RE orthoborates have been quantitatively described by Wolfert *et al.* [3], whereas the Eu^{3+} doped $GdBO_3$ and $LaBO_3$ have been mentioned only in a preliminary manner [4].

Experimental

Preparation of the $LuBO_3$:Eu^{3+} Powders

The polycrystalline $LuBO_3$:Eu^{3+} samples were obtained by the direct reaction between the lutetium oxide and boric acid (H_3BO_3) in 1:2 molar ratio in air using an excess of boric acid. The vaterite type modification was obtained by heating for 1 h at 670 K and for 2 + 3 hours at 1120 K. Above 1270 K the calcite type form of $LuBO_3$ was obtained. In order to ensure the completeness of the phase transformation the samples were heated at 1470 K for 2 h. The vaterite sample contained some unreacted Lu_2O_3 as well as the calcite form according to X-ray powder diffraction analysis. For luminescence measurements the $LuBO_3$ samples were doped with the Eu^{3+} ion (nominally 1.5 mol% of the total RE amount).

Optical Measurements

The luminescence of the $LuBO_3$:Eu^{3+} powder samples were excited either by a conventional UV lamp, the blue line (458.6 nm) of an argon ion laser or a rhodamine dye laser. A 200 W mercury lamp with a wide band filter provided a global excitation source passing radiation of around 250 nm, corresponding to the charge-transfer absorption band of the Eu^{3+} ion.

The blue line of a Spectra Physics 164 continuous wave argon ion laser at 458.6 nm was used to excite the $^5D_2$ level of the Eu^{3+} ion. In addition, a Spectra Physics 375/376 continuous wave rhodamine 6G dye laser (line width 0.7 cm^{-1}) pumped by an argon ion laser was used to excite selectively on the lowest excited ^5D level, $^5D_0$, near 580 nm.

The luminescence was recorded both at ambient and liquid nitrogen temperatures. The emission was dispersed by a 1-m Jarrell–Ash monochromator and detected by a Hamamatsu R374 photomultiplier. The resolution of the equipment was better than 1.0 cm^{-1}. The wavelength range between 400 and 750 nm was scanned.

Crystal Structure of $LuBO_3$

The RE orthoborates, $REBO_3$, have been known to possess the three polymorphic forms of $CaCO_3$: aragonite, vaterite and calcite [2]. There exists, however, no individual $REBO_3$ with all three polymorphs. The lighter rare earths (from La to Nd) possess the aragonite type structure [2] and the heavier lanthanoids have the vaterite structure [5]. Only the smallest RE ions, *i.e.* lutetium and scandium, are known to exhibit the calcite structure [6–8].

The vaterite type structure of $LuBO_3$ crystallizes in the rhombohedral crystal system with $P6_3/mmc$ ($Z = 2$) as the space group [5]. The rare earth ions occupy two crystallographically non-equivalent sites in the ratio 2:1 [5, 9, 10]. The former RE cation is octahedrally coordinated and the latter is 12-coordinated to oxygens. For the 12-coordinated site, six oxygens are at a shorter distance from the RE cation while the remaining six are farther away. The point symmetry of both the RE sites should be rather high, D_3 [3].

The crystals of the calcite type $LuBO_3$ are trigonal with $R3c$ ($Z = 6$) as the space group [11]. The calcite type contains the RE ions in a single site in six-fold coordination to oxygens. The point symmetry of the RE site is S_6.

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Results and Discussion

Vaterite Type $LuBO_3$:Eu^{3+}

The vaterite type $LuBO_3$:Eu^{3+} shows red luminescence between 580 and 750 nm under both UV and argon ion laser excitation (Fig. 1). The groups of sharp lines can be easily attributed to the $^5D_0 \rightarrow {}^7F_{0-4}$ transitions of the Eu^{3+} ion. The emission from the higher excited ^5D_J ($J = 1-4$) levels is quenched by efficient multiphonon de-excitation processes associated with the lattice vibrations. The vibronic coupling to the $^5D_0$ level seems to be rather strong since vibronic sidebands can be observed in the emission spectrum.

Due to the absence of inversion symmetry in the Lu site (D_3 point symmetry) electric dipole (e.d.) transitions to the $^7F_2$ and $^7F_4$ levels are observed between 610 and 623 nm and 686 and 710 nm, respectively. The magnetic dipole (m.d.) transition, $^5D_0 \rightarrow {}^7F_1$, is, however, clearly stronger than the e.d. transitions. The high energy of the charge transfer states has been concluded to favour m.d. transitions [12]. The free ion selection rule for e.d. transitions, $\Delta J = 2$, 4 or 6 (for an initial state of $J = 0$), is obeyed quite rigorously since the intensities of the 'forbidden' transition to the $^7F_3$ level are weak. The presence of this transition originates from the mixing of the $^7F_3$ wave functions with those of $^7F_{2,4,6}$ [13].

The $^5D_0 \rightarrow {}^7F_0$ transition has significant intensity in $LuBO_3$:Eu^{3+}. This transition is allowed as an e.d. induced transition for the C_s, C_n and C_{nv} site symmetries by the presence of the linear odd rank c.f. term A_0^1 [14]. Accordingly, it must be concluded that the Eu^{3+} ion occupies a site of lower than D_3 symmetry.

TABLE I. Energies of the $^5D_0 \rightarrow {}^7F_{0-4}$ Transitions Observed in the Emission Spectrum of the Vaterite Type $LuBO_3$:Eu^{3+} under Dye Laser Excitation on the $^7F_0 \rightarrow {}^5D_0$ Transition[a]

Transition	Energy	Transition	Energy
$^5D_0 \rightarrow {}^7F_0$	17220	$^5D_0 \rightarrow {}^7F_3$	15420
			15357
$^5D_0 \rightarrow {}^7F_1$	16887		15325
	16872		15273
	16854		15229
$^5D_0 \rightarrow {}^7F_2$	16410	$^5D_0 \rightarrow {}^7F_4$	14446
	16390		14325
	16377		14226
	16340		14163
	16329		14125
	16003 (vibr.)		14038
	15983 (vibr.)		
	15954 (vibr.)		

[a] All values in cm^{-1} units.

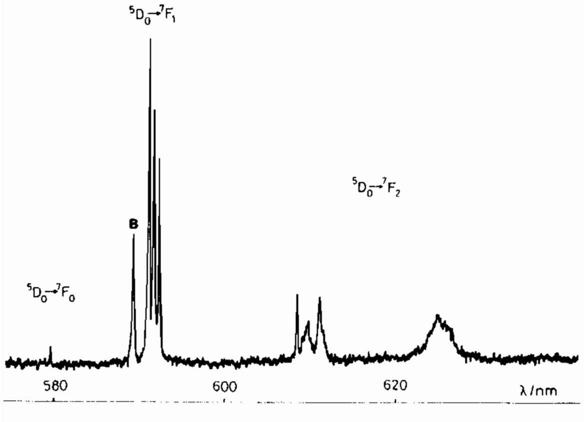

Fig. 1. Part of the argon laser excited luminescence spectrum of the vaterite type $LuBO_3$:Eu^{3+} at 77 K.

The dye laser excitation on the $^7F_0 \rightarrow {}^5D_0$ transition yielded the UV luminescence spectra with the exception of a single peak at 590.3 nm (marked by B in Fig. 1). The spectrum revealed the complete lifting of the $2J + 1$ degeneracy of the ^7F_J ($J = 1-4$) levels by the c.f. effect (Table I). The absence of selection rules and the presence of the $^5D_0 \rightarrow {}^7F_0$ transition excludes the D_3 symmetry. The single peak at 590.3 nm ($^5D_0 \rightarrow {}^7F_1$ transition) with no e.d. transitions indicates that the Eu^{3+} ion occupies another site of higher than D_3 symmetry. The optical data are in partial agreement with the structural data of Newnham *et al.* [7] where it was concluded that the thulium atoms in $TmBO_3$ occupy two sites with D_{3d} (inversion symmetry) and T point symmetries. The lowering of the tetrahedral point symmetry might be accomplished by, e.g., slight distortions in the coordination within the BO_3 groups.

The c.f. splittings of the ^7F_J ($J = 1-4$) levels are small, e.g. only 30 cm^{-1} for the $^7F_1$ level, indicating very weak c.f. effect on the ^7F_J energy level scheme.

Calcite Type $LuBO_3$:Eu^{3+}

The emission spectrum of the calcite type $LuBO_3$:Eu^{3+} contains only two lines at 589.7 and 595.7 nm (Fig. 2). These two lines can be attributed to the $^5D_0 \rightarrow {}^7F_1$ m.d. transition. The absence of the electric dipole transitions, *i.e.* the $^5D_0 \rightarrow {}^7F_{0,2,4}$ transitions, is in excellent agreement with the S_6 symmetry of the Lu site with inversion symmetry. The absence of the $^5D_0 \rightarrow {}^7F_3$ transitions indicates their e.d. origin. The absence of the vibronically induced transitions associated with the $^5D_0 \rightarrow {}^7F_{0,2}$ transitions should be noted, too.

The splitting of the $^7F_1$ level (168 cm^{-1}) in the calcite type $LuBO_3$ gives a high value of the B_0^2 parameter. It should be concluded that the c.f. effect in the calcite type $LuBO_3$:Eu^{3+} is significantly stronger than in the vaterite type.

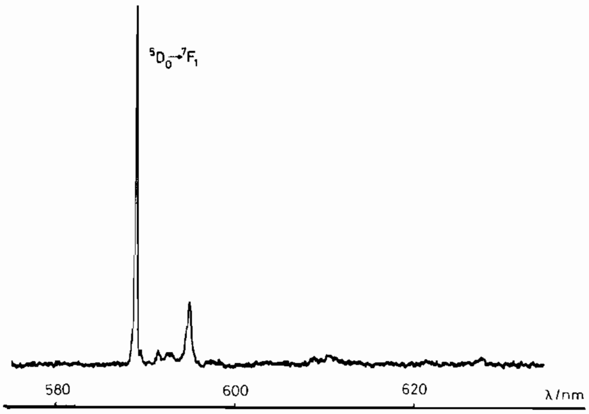

Fig. 2. Part of the argon ion laser excited luminescence spectrum of the calcite type $LuBO_3:Eu^{3+}$ at 77 K.

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