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HOST LATTICE DEPENDENCE OF THE Bi^{3+} LUMINESCENCE IN ORTHOBORATES $LnBO_3$

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The luminescence of Bi^{3+} in the host lattices $LnBO_3$ depends strongly on the nature of the Ln^{3+} ion. The Stokes shift increases from 0.22 eV for $ScBO_3$-Bi to 1.16 eV for $LaBO_3$-Bi.

1. INTRODUCTION

The luminescence of the $Bi^{3+}(6s^2)$ ion depends strongly on the nature of the host lattice. The emission can be varied from ultraviolet to red. In order to investigate this phenomenon further, we studied the luminescence of Bi^{3+} in host lattices $LnBO_3$(Ln = Sc, Lu, Y, Gd, La). In this manuscript we present our main results. A more extensive report will be submitted elsewhere[1]. The host lattices $LnBO_3$ can be characterized as follows:

Compound	$r_{Ln^{3+}}$ (Å)	Crystal structure	Coordination Ln^{3+}
$ScBO_3$	0.745	calcite	6
$LuBO_3$(hT)	0.861	calcite	6
$LuBO_3$(lT)	0.861	YBO_3	6, 6+6
YBO_3	0.900	YBO_3	6, 6+6
$GdBO_3$	0.938	YBO_3	6, 6+6
$LaBO_3$	1.20	aragonite	9

$LuBO_3$ shows two modifications. The YBO_3 structure is related to vaterite and shows two sites for Y. One is six coordinated, the other (indicated as 6+6) has six oxygen neighbours at shorter and six others at longer distance.

2. EXPERIMENTAL

The experimental procedures are described in ref. 1.

3. RESULTS

In the borates with calcite structure the Bi^{3+} ion shows efficient luminescence in the uv region. Fig. 1 shows the emission and excitation spectrum of the Bi^{3+} luminescence of $ScBO_3$-Bi. At low temperature vibrational structure appears.

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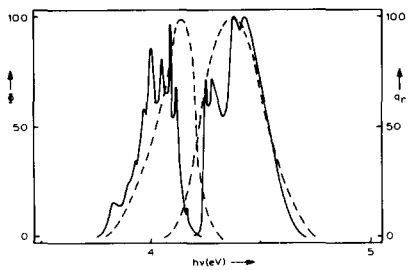

FIGURE 1

Emission and excitation spectrum of $ScBO_3$-Bi^{3+} at LHeT(——) and 300 K (---)

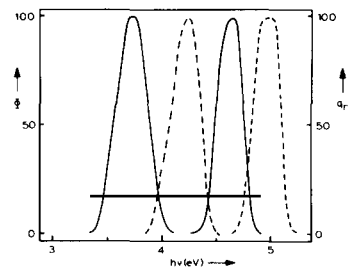

FIGURE 2

Emission and excitation bands of the two Bi^{3+} centres in YBO_3 at LHeT. 6-coordinated centre ---; (6+6)-coordinated centre ——

This shows that the parabolae offset in a configurational coordinate diagram is only small. From the decay times we derive τ ($^3P_0 \rightarrow {}^1S_0$) = 900 μs and $\Delta E(^3P_1 - {}^3P_0)$ = 0.15 eV.

Concentration quenching of the Bi^{3+} luminescence occurs at low values of the Bi^{3+} concentration, i.e. <0.5 % Bi^{3+}. This is due to efficient energy transfer between Bi^{3+} ions in the calcite structure. The critical distance for energy transfer (R_c) at LHeT is estimated from the spectral data to be 20 Å (ref. 2).

The results for the compositions with YBO_3 structure are more complicated. No Bi^{3+} emission is observed in $GdBO_3$-Bi. In this lattice the Bi^{3+} emission overlaps the Gd^{3+} $^8S \rightarrow {}^6P$ transitions. Efficient energy transfer from Bi^{3+} to Gd^{3+} occurs. Energy migration over the Gd^{3+} sublattice follows. The fate of the excited state depends on the temperature and on the presence of activators in the host lattice.

In YBO_3-Bi and $LuBo_3$-Bi(1T) two emission and excitation bands are observed. These corresponds to Bi^{3+} on the 6 coordinated site and to Bi^{3+} on the 6+6 coordinated site. The Stokes shift is larger than in the calcite structure. Energy transfer between both sites was observed. At LHeT the R_c value amounts to ∿ 48 Å for $LnBO_3$ (with complete spectral overlap) and ∿ 17 Å for YBO_3. Fig. 2 presents the relevant spectra for YBO_3-Bi.

In $LaBO_3$-Bi we observed also emission from two Bi^{3+} sites, although only one crystallographic site is present for La. The lower-energy emission increases with Bi^{3+} concentration and is, therefore, ascribed to Bi^{3+} pairs. Spectra are given in fig. 3. For both centres the Stokes shift is large. The higher-energy emission is ascribed to isolated Bi^{3+}. From the decay curves we find:

	$\tau(^3P_0 \rightarrow {}^1S_0)$	$\Delta E(^3P_1 - {}^3P_0)$
Bi^{3+} single	220 μs	0.055 eV
Bi^{3+} pair	110 μs	0.006 eV

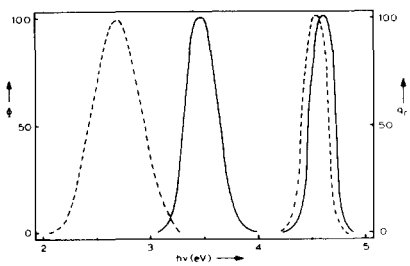

FIGURE 3
Emission and excitation spectra of $LaBO_3$-Bi^{3+} at LHeT

4. DISCUSSION

The luminescence of the Bi^{3+} ion in the systems $ScBO_3$, $LuBO_3$, YBO_3, $LaBO_3$ show a gradual variation which is best characterized by the increasing Stokes shift. This can be correlated immediately to the space available for the Bi^{3+} ion in the host lattice, which confirms earlier proposals[3].

REFERENCES

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