JOURNAL OF SOLID STATE CHEMISTRY 75, 201–204 (1988)

Luminescence of Bi^{3+} in the Metaphosphates LnP_3O_9 (Ln = Sc, Lu, Y, Gd, La)

E. W. J. L. OOMEN AND G. BLASSE

Physical Laboratory, University of Utrecht, P.O. Box 80 000,
3508 TA Utrecht, The Netherlands

Received November 18, 1987

The luminescence of the Bi^{3+} ion ($6s^2$) is studied in the metaphosphates LnP_3O_9 (Ln = Sc, Lu, Y, Gd, La). For Ln = Sc, Lu, Y, Gd the metaphosphates have a monoclinic structure with four slightly different sites for the trivalent cations. For Ln = Sc, Lu, Y the Stokes shift of the Bi^{3+} luminescence increased with increasing radius of the host lattice cation. Concentration quenching of the Bi^{3+} luminescence is observed. In the case of GdP_3O_9-Bi^{3+} the excitation energy is transferred to the Gd^{3+} ions. LaP_3O_9 adopts an orthorhombic structure with only one site available for the trivalent cations. The different coordination of the Bi^{3+} ion leads to a large increase of the Stokes shift of the Bi^{3+} luminescence.

Introduction

The rare earth metaphosphates LnP_3O_9 can adopt two different crystal structures, depending on the radius of the trivalent cations. The metaphosphates with large rare earth ions (La^{3+}–Nd^{3+}) have an orthorhombic structure while those with small rare earth ions (Sm^{3+}–Lu^{3+}, Y^{3+}, Sc^{3+}) have a monoclinic structure (*1*). The orthorhombic structure offers one crystallographic site for the trivalent cation which is coordinated by eight oxygen ions (*2*). In the monoclinic structure four slightly different crystallographic sites are available for the trivalent cation which is always coordinated by six oxygen ions (*3*).

Recently, we reported on the luminescence of the $5s^2$ ion Sb^{3+} in LnP_3O_9 (Ln = Sc, Lu, Y, Gd, La) (*4*). The luminescence of Sb^{3+} in monoclinic-structured metaphosphates (Ln = Sc, Lu, Y, Gd) was strongly influenced by the Jahn–Teller effect, leading to a double-minimum potential energy surface of the ^3P relaxed excited state of Sb^{3+} in YP_3O_9. The difference between the luminescence properties of Sb^{3+} on the four different sites increased for decreasing radius of the host lattice cation. For LaP_3O_9-Sb^{3+}, which has the orthorhombic crystal structure, the influence of the Jahn–Teller effect was found to be much smaller.

Here we report on an extension of these investigations to the luminescence of the $6s^2$ ion Bi^{3+} in LnP_3O_9.

Experimental

The samples were prepared as described in (*4*). The dopant ion is added as Bi_2O_3

0022-4596/88 $3.00

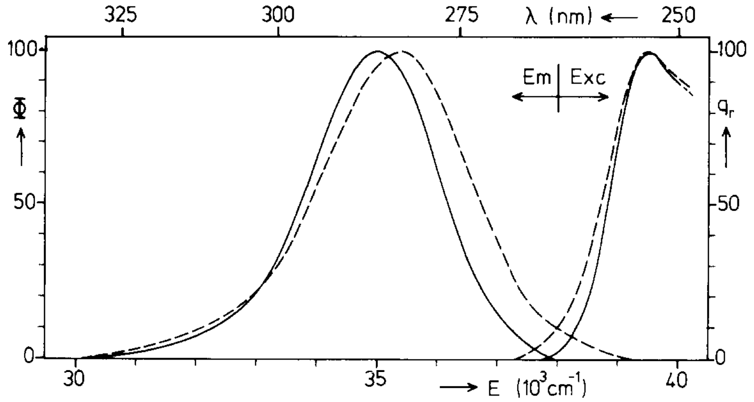

FIG. 1. Emission and excitation spectra of the luminescence of Bi^{3+} in ScP_3O_9 at $T = 6$ K (—) and 115 K (---). Φ denotes the radiant power per constant energy interval in arbitrary units; q_r gives the relative quantum output in arbitrary units. All spectra are normalized.

(Merck, p.a.). Luminescence spectra were recorded using a Perkin–Elmer MPF-44B spectrofluorometer equipped with an Oxford Instruments CF 204 liquid helium flow cryostat.

Results and Discussion

Figure 1 displays the emission and excitation spectra of the luminescence of ScP_3O_9-Bi^{3+} at $T = 6$ and 115 K. Due to instrumental limitations the excitation band cannot be determined accurately. The same emission band was found for any excitation wavelength. The broad emission and excitation bands will be superpositions of the bands arising from the four slightly different Bi^{3+} centers in ScP_3O_9. Obviously, the difference between these centers is small because the bands of the different centers overlap each other almost completely. This is in line with the results of Sb^{3+} in LnP_3O_9 (*4*) and Eu^{3+} in GdP_3O_9 (*5*).

The excitation band is assigned to the $^1S_0 \rightarrow {}^3P_1$ transition. The emission band is ascribed to the $^3P_1 \rightarrow {}^1S_0$ transition or, at low temperatures, to the $^3P_0 \rightarrow {}^1S_0$ transition. The Stokes shift amounts to 4500 cm^{-1} at $T = 6$ K.

Temperature quenching of the Bi^{3+} luminescence starts at 90 K for a sample with a weighted-in amount of 1 mole% Bi while for a sample with a weighted-in amount of 0.05 mole% Bi no quenching is observed up to 300 K. This is explained by concentration quenching of the Bi^{3+} luminescence. Due to the small Stokes shift the emission and excitation bands of the Bi^{3+} ion have a spectral overlap. For increasing temperature the spectral overlap will increase due to broadening of the bands. If the Bi^{3+} concentration exceeds the critical concentration for energy migration among the Bi^{3+} ions (which is related to the spectral overlap), energy migration occurs and the excitation energy will be transferred to quenching centers. This has, for example, also been observed in the case of Bi^{3+} in $LnBO_3$ (Ln = Sc, Lu) (*6*) and the $5s^2$ ions Sb^{3+} in $Cs_2NaSbCl_6$ (*7*) and Te^{4+} in Cs_2TeCl_6 (*8*). From Dexter's formula (*9, 10*) it can be calculated, using a value of 10^{-16} eV cm^2 for the absorption cross section (*10*) and the experimental spectral overlap of 0.25 eV^{-1} at 90 K, that R_c, the critical distance for transfer, is about 26 Å. This value results with Eq. 5 of Ref. (*10*) in a critical concentration of $x_c = 0.02$. This is the same order

TABLE I

SPECIAL DATA ON THE Bi^{3+} LUMINESCENCE IN LnP_3O_9 (Ln = Sc, Lu, Y, Gd, La) AT 4.2 K

Composition	Excitation maximum	Emission maximum	Stokes shift
ScP_3O_9-Bi^{3+}	~39,500	35,000	4,500
LuP_3O_9-Bi^{3+}	~41,500	34,600	6,900
YP_3O_9-Bi^{3+}	~41,500	34,100	7,400
GdP_3O_9-Bi^{3+}	~41,500	—	—
LaP_3O_9-Bi^{3+}	~42,500	21,900	20,600

Note. All values are in cm^{-1}.

of magnitude as the weighted-in amounts of Bi^{3+} suggest.

The luminescence of Bi^{3+} in LuP_3O_9 and YP_3O_9 is very similar to that of ScP_3O_9-Bi^{3+}. The emission and excitation spectra consist of one broadband and concentration quenching is observed. The maxima of the excitation and emission bands, as well as the Stokes shifts, are gathered in Table I. The Stokes shift increases for increasing radius of the host lattice cation (*11*). This is generally observed for s^2 ions in inorganic host lattices and has been ascribed to the tendency of s^2 ions to occupy an "off-center" position in the ground state (*12, 13*).

GdP_3O_9-Bi^{3+} reveals no Bi^{3+} emission after excitation at 250 nm. The emission spectrum consists of two sharp lines, a strong one at 32,000 cm^{-1} (312 nm) and a weaker one at 31,000 cm^{-1} (322 nm). These lines are due to Gd^{3+} luminescence ($^6P \rightarrow {}^8S$) from which we conclude that energy transfer from Bi^{3+} to Gd^{3+} occurs. The Bi^{3+} emission is estimated to be a broadband around 33,500 cm^{-1} (Table I) which overlaps the Gd^{3+} $^8S \rightarrow {}^6P$ absorption lines well, so that energy transfer from Bi^{3+} to Gd^{3+} is expected. The same has been observed for, e.g., GdB_3O_6-Bi^{3+} (*14*). However, for application as a commercial phosphor GdP_3O_9-Bi^{3+} codoped with any activator ion is unsuitable, because it has been observed that energy migration does not occur within the Gd^{3+} sublattice (*15*).

LaP_3O_9-Bi^{3+}, finally, has a much larger Stokes shift than the other compositions discussed here. A comparable Stokes shift has also been reported for $LaPO_4$-Bi^{3+} (*16*) and for some concentrated Bi^{3+} compounds like $Bi_2Ge_3O_9$, $Bi_4Ge_3O_{12}$, and $Bi_2Al_4O_9$ (*12*). Temperature quenching starts at 130 K which is a direct consequence of this large Stokes shift (concentration quenching is not possible due to the lack of any spectral overlap). The large Stokes shift of the emission of LaP_3O_9-Bi^{3+} compared to that of LnP_3O_9-Bi^{3+} (Ln = Sc, Lu, Y) may not only be due to the larger host cation radius, but also to the structural difference.

In conclusion, the Bi^{3+} luminescence in metaphosphates LnP_3O_9 (Ln = Sc, Lu, Y, Gd, La) varies strongly with the choice of Ln and can be explained using existing models.

Acknowledgment

The authors are indebted to E. Molenbroek and K. J. van de Berg for performing part of the experimental work.

References

1. P. P. MELNIKOV, P. H. KOMUSSAROVA, AND T. A. LYMYSOVA, *Izv. Akad. Nauk. SSSR, Neorg. Mater.* **17,** 2110 (1981).

2. H. Y. P. HONG, *Acta Crystallogr. Sect. B* **30,** 468 (1974).

3. H. Y. P. HONG, *Acta Crystallogr. Sect. B* **30,** 1857 (1974).

4. E. W. J. L. OOMEN, R. C. M. PEETERS, W. M. A. SMIT, AND G. BLASSE, *J. Solid State Chem.*, in press.

5. M. BUIJS AND G. BLASSE, *J. Luminescence*, in press.

6. A. WOLFERT, E. W. J. L. OOMEN, AND G. BLASSE, *J. Solid State Chem.* **59,** 280 (1985).

7. E. W. J. L. OOMEN, W. M. A. SMIT, AND G. BLASSE, *Chem. Phys. Lett.* **138,** 23 (1987).

8. G. BLASSE, G. J. DIRKSEN, AND W. ABRIEL, *Chem. Phys. Lett.* **136,** 460 (1987).

9. D. L. DEXTER, *J. Chem. Phys.* **21,** 836 (1953).
10. G. BLASSE, *Philips Res. Rep.* **24,** 131 (1969).
11. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr. Sect. B* **25,** 925 (1969).
12. C. W. M. TIMMERMANS AND G. BLASSE, *J. Solid State Chem.* **52,** 222 (1984).
13. W. M. A. SMIT AND E. W. J. L. OOMEN, "Fall Meeting of the Electrochemical Society, San Diego, 1986, Extended Abstracts," Vol. 86-2, No. 699 (1986).
14. A. J. DE VRIES AND G. BLASSE, *J. Phys.* **46,** 109 (1985).
15. H. S. KILIAAN, F. P. VAN HERWIJNEN, AND G. BLASSE, *J. Solid State Chem.*, in press.
16. R. MONCORGÉ, G. BOULON, AND J. DENIS, *J. Phys. C* **12,** 1165 (1979).