LUMINESCENCE CHARACTERISTICS OF Bi^{3+} -ACTIVATED OXIDES

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The value of the Stokes shift of the emission of Bi^{3+} -activated oxides can be related to the optical trap depth, i.e. the energy difference between the 3P_1 and the 3P_0 level. A useful interpretation of the luminescence properties of these materials seems to be possible starting from this point of view.

1. INTRODUCTION

THE LUMINESCENCE of Bi^{3+} -activated phosphors has been studied extensively from several points of view. In some investigations attention was focussed on the wide variation of the emission and excitation spectra [1, 2], in others on the occurrence of vibrational structure in these spectra [3–5] and, finally, in still others on the decay characteristics connected with the presence of an optical trap below the emitting 3P_1 level [6, 7]. Recently Moncorgé *et al.* [8] reported on the luminescence of $\text{LaPO}_4\text{—Bi}^{3+}$ which is exceptional due to the large Stokes shift and the small optical trap depth. These authors divide Bi^{3+} -activated phosphors in two groups, *viz.* those with “typical bismuth isolated centres” and those where the Bi^{3+} levels overlap with the host lattice levels [7, 8]. It is the purpose of this letter to reinterpret the results reported for $\text{LaPO}_4\text{—Bi}^{3+}$, to question the way in which Bi^{3+} -activated phosphors are subdivided and to relate the results of several types of investigations in this field. Further it is shown that there is a link with the numerous investigations performed on Tl^{+} -activated alkali halides (see, e.g. reference [9]).

2. THE LUMINESCENCE OF Bi^{3+} -ACTIVATED LaPO_4

In reference [8] the luminescence properties of $\text{LaPO}_4\text{—Bi}^{3+}$ have been reported. In contradiction with the greater part of other publications the measurements were extended far into the vacuum ultraviolet. The emission occurs in a broad band around 450 nm. The first excitation band is at 240 nm, so that the Stokes shift is very large. The authors conclude from this that the lowest-energy transition ($^1S_0 \rightarrow ^3P_1$) is not observed for $\text{LaPO}_4\text{—Bi}^{3+}$. In view of earlier work [1, 2] this conclusion is incorrect. The $^1S_0 \rightarrow ^3P_1$ transition of Bi^{3+} in oxides can be found in the spectral region up to 230 nm depending on the nephelauxetic ratio factor [2]. In phosphates this factor is low and, consequently, the $^1S_0 \rightarrow ^3P_1$ transition is situated at high energy. In $\text{YPO}_4\text{—Bi}^{3+}$ it has even been found at 230 nm [1, 2].

Table 1. Stokes shift and trap depth of some Bi^{3+} -activated oxidic phosphors

Phosphor	Stokes shift (eV)	Trap depth (eV)	Ref.
CaO—Bi	0.4	0.15	3
$\text{CaSb}_2\text{O}_6\text{—Bi}$	1.1	0.051	6, 10
BiOCl	1.2	~0.05	11, 12
$\text{La}_2\text{O}_3\text{—Bi}$	1.35	0.046	6, 13
$\text{La}_2\text{SO}_6\text{—Bi}$	1.4	0.047	14
$\text{Bi}_2\text{Al}_4\text{O}_9$	2.0	~0.003	15, 16
$\text{Bi}_3\text{Ge}_4\text{O}_{12}$	2.2	0.003	17
$\text{LaPO}_4\text{—Bi}$	2.4	0.002	8

The drastic increase of the luminescence decay time of $\text{LaPO}_4\text{—Bi}^{3+}$ below some 25 K is due to the optical trap (3P_0 level). The activation energy involved (0.002 eV according to [8]) is the energy difference between the lowest component of the 3P_1 level and the 3P_0 level (trap depth). What is special about $\text{LaPO}_4\text{—Bi}^{3+}$ is the large value of the Stokes shift (2.4 eV) and the low value of the optical trap depth. We will show now that these quantities must be related to each other in view of experimental data in the literature.

3. A RELATION BETWEEN STOKES SHIFT AND TRAP DEPTH

In Table 1 we have summarized a number of representative data on the luminescence of Bi^{3+} -activated phosphors. From this table we come to the following remarks.

(a) There seems to be a pronounced dependence of the optical trap depth on the value of the Stokes shift. This relation does not depend on the Bi^{3+} concentration, since the table contains Bi^{3+} compounds as well as Bi^{3+} -activated oxides. Especially the new values for $\text{LaPO}_4\text{—Bi}^{3+}$ [8] underline this fact. The relation between Stokes shift and trap depth is, therefore, a typical property of the Bi^{3+} ion. Small trap depths have sometimes been interpreted in an exciton model [17] but in our opinion there is no need for this.

(b) The subdivision of Bi^{3+} -activated phosphors in two groups mentioned above seems to us to be artificial. Since a regularly varying range of Stokes shifts has been reported, the same should be true for the trap depth, if suitable materials are studied: to the list of Table 1 we may add $\text{NaGdO}_2\text{--Bi}^{3+}$ (0.6 eV, 5), $\text{LiScO}_2\text{--Bi}^{3+}$ (0.9 eV, 5), $\text{LaBO}_3\text{--Bi}^{3+}$ (1.6 eV, 1) and $\text{YPO}_4\text{--Bi}^{3+}$ (1.75 eV, 1). Between brackets are given the Stokes shift and the reference. The group of phosphors with a Stokes shift of 0.5 eV or less are those showing extended vibrational structure in the absorption and emission spectra at lower temperatures. Examples are CaO--Bi^{3+} [3], $\text{NaScO}_2\text{--Bi}^{3+}$ [5], $\text{YAl}_3\text{B}_4\text{O}_{12}\text{--Bi}^{3+}$ [19] and $\text{Cs}_2\text{NaYCl}_6\text{--Bi}^{3+}$ [20].

(c) From Table 1 it seems to be clear that the value of the Stokes shift depends on the coordination number of the Bi^{3+} ion and the ionic radius of the ion for which Bi^{3+} is substituted (as a matter of fact these two factors are not completely independent). The smaller Stokes shifts are found for six coordination (CaO , NaScO_2 , $\text{YAl}_3\text{B}_4\text{O}_{12}$, CaSb_2O_6), the larger for higher coordinations (La_2O_3 : seven coordination and LaPO_4 : eight coordination).

(d) The present relation reminds of results obtained by Fukuda and coworkers [18]. In a study on Ti^{4+} -activated alkali halides they found that the optical trap depth can be related to the Q_3 (eg) interaction-mode coordinate. This suggests that for these materials we may expect a similar relation between Stokes shift and trap depth. The relation following from Table I is the more impressive if one considers the large variation of the Stokes shift for one and the same luminescent ion and the difference in site symmetry between the several phosphors.

We realize that other factors are also of importance in explaining the luminescence properties of Bi^{3+} -activated phosphors. One problem, for example is the question whether the Bi^{3+} emission is of the A_T and/or the A_X type like proposed for the Ti^{4+} -activated alkali halides ([9], see also [5]). The present results, however, suggest a systematic way to investigate the Bi^{3+} -activated phosphors further.

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