Luminescence properties of $GaBO_3 : Bi^{3+}$

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Abstract

The luminescence properties of $GaBO_3 : Bi^{3+}$ have been studied. In contrast to other borates with calcite structure, $GaBO_3 : Bi^{3+}$ shows a very efficient UV emission and a blue Stokes-shifted emission caused by an annihilation of the impurity-trapped excitons. The former is attributed to single Bi^{3+} ions in S_6 sites, whereas the latter is related to bismuth defect centers which arise due to difference in the size of the Ga^{3+} and Bi^{3+} ions (0.645 Å versus 1.02 Å).

Keywords: Gallium; Borate; Bismuth; Luminescence; Stokes shift; Electronic structure

1. Introduction

It is well known that luminescence properties of Bi^{3+} depend strongly on the host lattice. Some time ago Wolfert et al. [1] reported on the luminescence of Bi^{3+} in $ScBO_3$ and $LuBO_3$. These compounds have the calcite structure in which the cations are coordinated by six oxygen atoms to form undistorted octahedra. The site symmetry for the cation is S_6. The borate groups $(BO_3)^{3-}$ are isolated in the crystal structure. It was found the Stokes shift of the Bi^{3+} emission in these borates is very small and at low temperatures the excitation and emission spectra show extended vibrational structure. At low temperatures the emission is due to the forbidden $^3P_0 \rightarrow {}^1S_0$ transition. At higher temperatures the $^3P_1$ level becomes populated and emission is observed from this level. Recently the authors [2] have reported on the luminescence properties of Bi^{3+} in $InBO_3$ which has

the same calcite structure. The emission spectrum of $InBO_3 : Bi^{3+}$ consists of a broad band with a maximum at about 3.10 eV. The Stokes shift of this emission is about 1.25 eV. This value is much larger than those (0.23–0.25 eV) found for Bi^{3+} emission in other borates with calcite structure. In view of the large Stokes shift and band width, the $InBO_3 : Bi^{3+}$ emission was considered as "anomalous". This phenomenon has been ascribed to photoionization of the impurity ion followed by formation of an exciton-like state. This implies that, in contrast to $ScBO_3$ and $LuBO_3$, the excited states of the Bi^{3+} ion in $InBO_3$ are situated in the conduction band. By analogy to the recent experimental results for Eu^{2+} and Yb^{2+} in some fluorides [3,4], the anomalous emission of $InBO_3 : Bi^{3+}$ was interpreted by Blasse et al. [2] in terms of radiative decay of an impurity-trapped exciton, which is composed of an impurity-trapped hole and an electron bound to it. The luminescence properties of $In_{1-x}Lu_xBO_3 : Bi^{3+}$ solid solutions have been studied in our laboratory [5]. For the compounds with $0 < x < 0.30$ we observed coexistence

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of a luminescence band due to $^3P_{0,1} \rightarrow {}^1S_0$ transitions in the impurity ions and a broad Stokes-shifted band arising from impurity-trapped excitons.

It seemed interesting to ascertain how the Bi^{3+} behaves in isostructural $GaBO_3$. By studying this system, we hoped to understand the relationship between the electronic structure of the crystals and their luminescent properties. We note also that mixed crystals of $Ga_{1-x}Fe_xBO_3$ with various composition ratio attract attention because of their interesting physical properties [6]. These crystals can be grown from the melt of B_2O_3–Bi_2O_3 [7]. In this case the presence of traces of bismuth in these materials seems rather probable.

The lattice parameters of MBO_3 (M = Ga, Sc, In, Lu), together with ionic radii of the cations are collected in Table 1. From the table it is seen that lattice parameters of $GaBO_3$ are small compared to those of other borates. Note that the In atom has valence electrons of $(5s^2 5p^1)$ and Ga of $(4s^2 4p^1)$, so that corresponding borates are isoelectronic.

2. Experimental

Powdered samples of $Ga_{1-x}Bi_xBO_3$ $(0.001 \leq x \leq 0.01)$ obtained by means of the multistage firing $(T = 600$–$850°C)$ of the furnace charge containing Ga_2O_3, Bi_2O_3, and the boron-containing component (H_3BO_3) were the objects of investigation. In the first step the powdered samples of $Ga_{2(1-x)}Bi_{2x}O_3$ were prepared. After that the oxides were mixed with hydroboric acid, and fired in air at a temperature of about 700°C for 30–50 h. In the preparation of these mixtures excess of boric acid (200%) was added to compensate for possible volatization during heating. The fired mixtures were ground in agate mortar and

given a second heat-treatment at 700–850°C for 30 h. The resulting products had a white color. All samples were checked by X-ray diffraction using Cu $K\alpha$ radiation.

Luminescence measurements were carried out on spectrofluorimeters SDL-1 and SDL-2 equipped with the photon counting system. Xenon lamp and a YAG:Nd laser ($\lambda_{exc} = 266$ nm, $\tau_{exc} = 8$–15 ns) were used as the excitation sources. The temperature of measurements was 80–300 K. Diffuse reflectance spectra were recorded at room temperature using a Perkin-Elmer Lambda-9 spectrometer.

3. Results and discussion

In contrast to $MBO_3 : Bi^{3+}$ (M = Sc, In, Lu), two emission bands and two excitation bands are observed for the $GaBO_3 : Bi^{3+}$. At room temperature, $GaBO_3 : Bi^{3+}$ shows a very intense emission band peaking at 290 nm (4.275 eV) and a blue emission band with a maximum at 423 nm (2.93 eV). The excitation spectra of these bands are quite different, but the excitation maximum is practically at the same position. In Table 2 the positions of excitation and emission bands of $GaBO_3 : Bi^{3+}$ are given. As can be seen the UV emission is characterized by small Stokes shift, whereas the Stokes shift of the blue emission is about 1.51 eV. This value is close to but larger than that of "anomalous" emission of $InBO_3 : Bi^{3+}$.

The emission and excitation spectra of $GaBO_3 : Bi^{3+}$ at 80 K are given in Fig. 1. The UV emission band at 80 K shows extended vibrational structure. The first line is at 286.9 nm and has low intensity. Since there is resemblance with the emission spectra of $MBO_3 : Bi^{3+}$ (M = Sc, Lu) at liquid

Table 1
Crystal data for calcite-type borates (MBO_3)

M	Electron. configuration	Host cation radius (Å)	Cell parameters			Ref.
			a (Å)	c (Å)	c/a	
Ga	$3d^{10}4s^2 4p^1$	0.645	4.568	14.182	3.11	[8]
Sc	$3d^1 4s^2$	0.745	4.759	15.321	3.22	[9,10]
In	$4d^{10}5s^2 5p^1$	0.800	4.823	15.456	3.21	[9,10]
Lu	$4f^{14}5d^1 6s^2$	0.861	4.915	16.211	3.30	[8,9]

Table 2
Comparison of the luminescence properties of $MBO_3:Bi^{3+}$ at 300 K

M	Excitation E_{max} (eV)	Emission, E_{max} (eV)	Stokes shift (eV)	Ref.
Ga	4.49	4.28	0.21	this work
	4.44	2.93	1.51	
Sc	4.37	4.14	0.23	[1]
In	4.35	3.10	1.25	[2]
Lu	4.32	4.07	0.25	[1,5]

helium temperature [1], one can expect that this line is the zero-phonon line. The excitation spectrum of this emission band has a clear doublet structure with maxima at 285 and 275 nm. The decay time of this emission amounts to 470 μs at 80 K and drops rapidly with increasing temperature.

Comparison with literature data indicates that the excitation band corresponds to the $^1S_0 \rightarrow {}^3P_1$ transition in Bi^{3+} ions. The two components of the $^1S_0 \rightarrow {}^3P_1$ excitation band are caused by the crystal–field splitting of the $^3P_1$ excited state. It is evident that UV-part of the room temperature emission spectrum corresponds to the $^3P_1 \rightarrow {}^1S_0$ transition in isolated Bi^{3+} centers. As mentioned above, at relatively low temperatures vibrational structure is observed in the emission spectrum (Fig. 1). In this case the zero-phonon line and UV-emission band seem to be mainly the emission from $^3P_0$ state of Bi^{3+} ions. The main
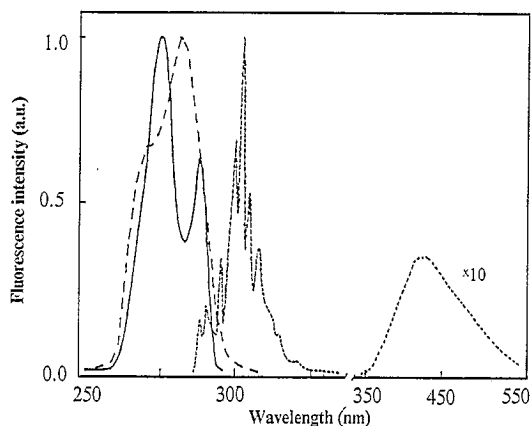

Fig. 1. Emission spectrum (dotted line) of $GaBO_3:Bi^{3+}$ at 80 K for 274 nm excitation. Comparison of normalized excitation spectra of UV emission band (solid line) and blue emission band (dashed line) at 80 K.

reason for this assignment is a relatively long decay time of this emission. Comparison with data for bismuth luminescence in $ScBO_3$ and $LuBO_3$ (Table 2) has led us to assign the UV emission to single Bi^{3+} ions in S_6 sites.

The emission state responsible for the blue emission is of quite different nature than that of the Bi^{3+} ion in S_6 site, owing to their different spectroscopic characteristics. The relative intensity of the blue band depends on some preparative conditions. For example, it somewhat increases with increasing temperature of the heat-treatment. At 80 K the decay time of the emission is 3.4 μs. It decreases with increasing temperature and amounts to 0.5 μs at 300 K. Our interpretation of this emission is based on the following facts:

(i) the observed luminescence is not found in nominally pure $GaBO_3$,

(ii) Bi^{3+}-rich phases (BiB_3O_6, $Bi_3B_5O_{12}$) do not show any emission at room temperature [11],

(iii) the characteristics of the blue emission (value of Stokes shift, decay time at room temperature) are similar to those reported for impurity-trapped exciton emission in $InBO_3:Bi^{3+}$ [2] and $Gd_3Ga_5O_{12}:Bi^{3+}$ [12].

In view of the large Stokes shift and long decay time at room temperature, the emission band at 423 nm is attributed to the decay of an impurity-trapped exciton into the ground state of Bi^{3+} ion.

Let us consider the electronic structure of the borates with calcite structure. It is known that the interaction between boron and oxygen atoms within the borate groups is stronger than the interaction between the borate groups and cations. The valence-band electronic structure of MBO_3 (M = Sc, Lu) is determined by the $(BO_3)^{3-}$-isolated groups [13]. The top of the valence band arises from the 2p oxygen states. Transitions from these states to vacant 2s and 2p levels of boron lead to strong absorption in the vacuum ultraviolet region (6.2–10 eV) [13,14]. It is evident that the bottom of the conduction band of MBO_3 arises either from corresponding states of metal or 2s, 2p boron states. The electronegativity value of scandium (lutetium) is essentially lower than that of gallium. This difference leads to removal of Sc^{3+} (Lu^{3+}) states from the top of the valence band. As a consequence, the optical absorption edge of $GaBO_3$ is at about 5.2 eV, while in the case of
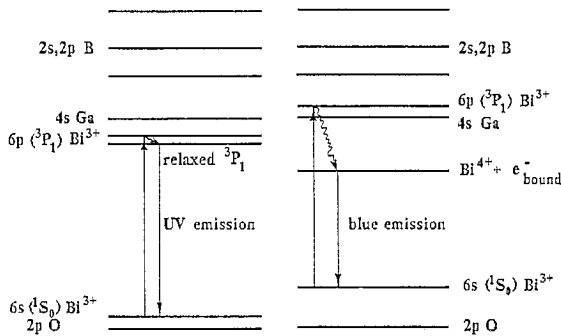
Fig. 2. Schematic diagram to describe the luminescence behavior of $GaBO_3:Bi^{3+}$. Radiative and nonradiative processes are shown by arrows. See also text.

$ScBO_3$ $(LuBO_3)$ it is at larger energy (≈ 6.5 eV). Most probably the 4s and 3d states of scandium lie higher than the bottom of the conduction band of $ScBO_3$.

A simplified diagram to explain the origin of the UV and blue emissions is shown in Fig. 2. Since the excitation spectra of the emission bands are quite different, one can conclude that the excitation occurs in two different bismuth centers. The excitation bands can be assigned to $6s \rightarrow 6p$ transitions. As can be seen from Fig. 2 the $^3P_1$ excited state of a single Bi^{3+} ion in S_6 site is situated in the forbidden gap, so that only emission due to the $^3P_{0,1} \rightarrow {}^1S_0$ transitions in Bi^{3+} ion is observed. The $^3P_1$ excited state of the other absorption bismuth center lies in the conduction band and an impurity-trapped exciton state $(Bi^{4+} + e^-_{bound})$ is the lowest excited state of the system. Under the optical excitation of the $^1S_0 \rightarrow {}^3P_1$ transition this state may be populated via ionization of the impurity ion followed by a relaxation from the $(Bi^{4+} + e^-_{free})$ state, or a direct relaxation from the $^3P_1$ state. The radiative decay of an impurity-trapped exciton into the ground state of Bi^{3+} ion results in the blue emission of $GaBO_3:Bi^{3+}$.

Finally, in spite of the fact that in calcite structure only one crystallographic site is available for the trivalent cation, two bismuth centers are observed for $GaBO_3$. Most probably it is a consequence of the difference in size of the Ga^{3+} and Bi^{3+} ions (0.645 Å versus 1.02 Å). Due to the small space available for the Bi^{3+} ion in $GaBO_3$ the crystal lattice is deformed in the vicinity of the Bi^{3+} impurities, so that the neighboring atoms can be shifted from exact symmetry position, i.e. substitution of Bi^{3+} for Ga^{3+} may result in a reconstruction of impurity center. It is clear that the possibility of this process depends on the sample-preparation conditions. This information may be useful for optimization of the synthesis method for $Ga_{1-x}Fe_xBO_3$ mixed crystals.

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