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# Luminescence of $Bi^{3+}$ in Gallate Garnets

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The luminescence of $Bi^{3+}$ in the garnet structure is described for the first time. It consists of a broad emission band with a maximum at 480 nm. There is a strong analogy with $La_2O_3$:Bi. Time-resolved spectra are also reported. They yield information on the feeding process of the luminescent centers in the gallate garnet.

## Introduction

There has been a strong interest in rare earth aluminate and gallate garnets through the years, because they are interesting host lattices for luminescent ions.[1,2] Such materials have promise for several applications, like lighting,[3] lasers,[1,2] and computed tomography.[4-6] Powders, crystals, as well as ceramic samples have been studied.

In view of the potential of garnet ceramics in computed tomography,[4,6] we have studied several gallate garnets, like $Gd_3Ga_5O_{12}$. One of the dopants was $Cr^{3+}$. Our results agree with data in the literature, viz., $Cr^{3+}$ gives an efficient $^4T_2 \rightarrow {}^4A_2$ broad-band emission at room temperature. Replacing Gd by Y results in an increase of the sharp-line $^2E \rightarrow {}^4A_2$ emission of $Cr^{3+}$.

Another potential dopant is $Bi^{3+}$. As far as we are aware, the luminescence of $Bi^{3+}$ in the garnet structure is not known. In this paper the $Bi^{3+}$ luminescence in the garnet system $(Y,Gd)_3Ga_5O_{12}$ is reported.

## Experimental Section

Samples were prepared as described in ref 5. Using a final firing temperature of 1400 °C yields ceramic tablets which have 60% of the theoretical density. Firing at 1650 °C in $O_2$ yields dense and, depending on the dopant, transparant samples. X-ray diffraction showed these to be single-phase garnets.

The bismuth dopant presents a special problem due to the high volatility at the sintering temperatures applied. Addition of $Bi_2O_3$ powder appeared to be helpful. Samples appeared to be single-phase up to 6.7 mol % bismuth for gadolinium. According to chemical analysis after sintering this sample contains only 2.7 mol % bismuth. The lattice parameter of this sample was the same as for the undoped sample within the accuracy of the measurements. The bismuth-doped samples are characterized by a bluish luminescence.

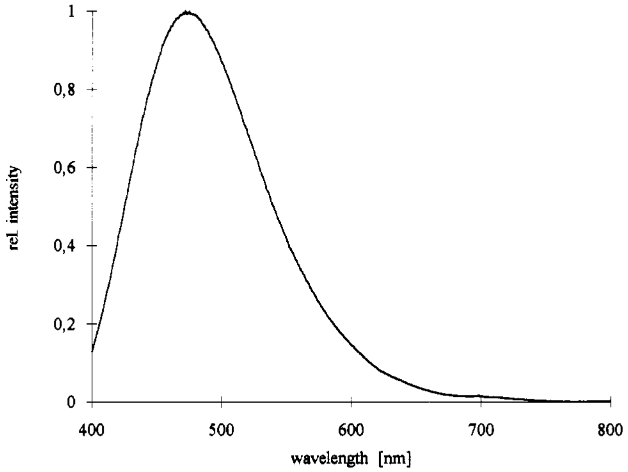

**Figure 1.** Emission spectrum of $Gd_3Ga_5O_{12}$:$Bi^{3+}$, $\lambda_{ex} = 297$ nm, 300 K.

Optical measurements were performed at room temperature using a Shimadzu RF-5001PC spectrofluorometer equipped with a 150-W Xe lamp and a Hamamatsu X-ray tube (55 kV, 35 mA). Time-resolved emission spectra were measured using pulsed excitation with an ArF excimer laser ($\lambda = 193.3$ nm). The pulse half-width is about 30 ns.[7]

## Results

Samples with composition $(Y,Gd)_3Ga_5O_{12}$:$Bi^{3+}$ show an intense bluish photoluminescence at room temperature. The emission spectrum is independent of the Y/Gd ratio and consists of a broad band with a maximum at 480 nm. This is shown in Figure 1 for $Gd_3Ga_5O_{12}$:$Bi^{3+}$. The corresponding excitation spectra depend slightly on the Y/Gd ratio (see Figure 2). They consist of two bands. In the case of $Gd_3Ga_5O_{12}$:$Bi^{3+}$ their maxima are 310 and 270 nm. The introduction of yttrium for gadolinium shifts these maxima to shorter wavelength, resulting in the values 305 and 260 nm for $Y_3Ga_5O_{12}$:$Bi^{3+}$. The Stokes shift of the emission is therefore about 11 000 $cm^{-1}$.

Comparison with the reflection spectrum of $Gd_3Ga_5O_{12}$[8] shows that the shorter-wavelength excitation band cor-

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(1) See, for example: Nie, W.; Monteil, A.; Boulon, G. In *Advances in Nonradiative Processes in Solids*; Di Bartolo, B., Ed.; Plenum Press: New York, 1991; p 425.

(2) Brenier, A.; Boulon, G.; Pedrini, C.; Madej, C. *J. Appl. Phys.* **1992,** *71,* 6062.

(3) Smets, B., p 353 in ref 1.

(4) Tsoukala, V. G.; Greskovich, C. D. European Patent Application, 0467044 A2, May 1991.

(5) Blasse, G.; Grabmaier, B. C.; Ostertag, M. *J. Alloys Compd.* **1993,** *200,* 17.

(6) Greskovich, C. D.; Cusano, D.; Hoffman, D.; Riedner, R. J. *Am. Ceram. Soc. Bull.* **1992,** *71,* 1120.

(7) Bayer, E. *Lambda Highlights* **1992,** *36/37,* 4.

(8) Lammers, M. J. J.; Severin, J. W.; Blasse, G. *J. Electrochem. Soc.* **1987,** *134,* 2356.

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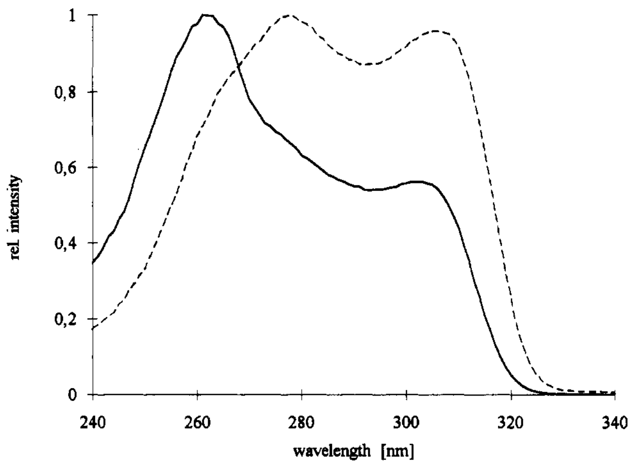

**Figure 2.** Excitation spectra of the luminescence of $Y_3Ga_5O_{12}$:$Bi^{3+}$ (—) and $Gd_3Ga_5O_{12}$:$Bi^{3+}$ (- - -), $\lambda_{em}$ = 473 nm, 300 K.

responds to host lattice excitation. The longer-wavelength excitation band and the emission band are due to the dopant $Bi^{3+}$.

The decay time of the emission under excimer-laser excitation amounts to (2.5 ± 0.5) μs, a characteristic value for $Bi^{3+}$.[9] The time-resolved emission spectra under excimer-laser excitation are given in Figure 3. Three emissions can be distinguished, viz., in the long-wavelength ultraviolet (maximum ≈ 360 nm), in the blue-green (maximum ≈ 480 nm), and in the deep-red (maximum ≈ 720 nm). They are due to the host lattice,[8] the $Bi^{3+}$ ion, and a $Cr^{3+}$ impurity,[2] respectively. Integration over time shows that the $Bi^{3+}$ emission dominates.

This is different for the emission spectrum under X-ray excitation (Figure 4), which shows a much larger amount of $Cr^{3+}$ emission. This shows that the surface layer of the ceramic samples contains relatively more bismuth, since the excimer laser excites the surface layer only. The X-ray excited emission spectrum shows also the rare-earth-metal impurity $Tb^{3+}$. Its emission originates from the lowest emitting level only ($^5D_4$). The $Tb^{3+}$ lines are at 490, 550, 590, and 620 nm.

## Discussion

The emission band with a maximum at 480 nm is clearly related to the presence of the dopant ion $Bi^{3+}$. The luminescence of $Bi^{3+}$ has been extensively studied in several hosts, but many unsolved questions remain.[10,11] At room temperature the emission is due to the $^3P_1 \rightarrow {}^1S_0$ transition, whereas the lowest absorption band is the $^1S_0 \rightarrow {}^3P_1$ transition. The spin-selection rule is considerably relaxed by the strong spin–orbit coupling in $Bi^{3+}$. It seems obvious to assign the 310-nm excitation band and the 480-nm emission band of $Gd_3Ga_5O_{12}$:$Bi^{3+}$ to the $^1S_0 \leftrightarrow {}^3P_1$ transitions.

The $Bi^{3+}$ ion in the garnet structure will replace the rare-earth-metal ion in view of its ionic size. Therefore it occupies an eight-coordinated site. The analogy between the luminescence of $Bi^{3+}$ in $Gd_3Ga_5O_{12}$ and $La_2O_3$ is striking: $La_2O_3$:$Bi^{3+}$ shows an emission at 470 nm with excitation bands at 310 and 250 nm.[9] In $La_2O_3$ the $Bi^{3+}$ ion is coordinated by seven oxygen ions. The absorption edge of undoped $Gd_3Ga_5O_{12}$ and $La_2O_3$ are also practically the same.

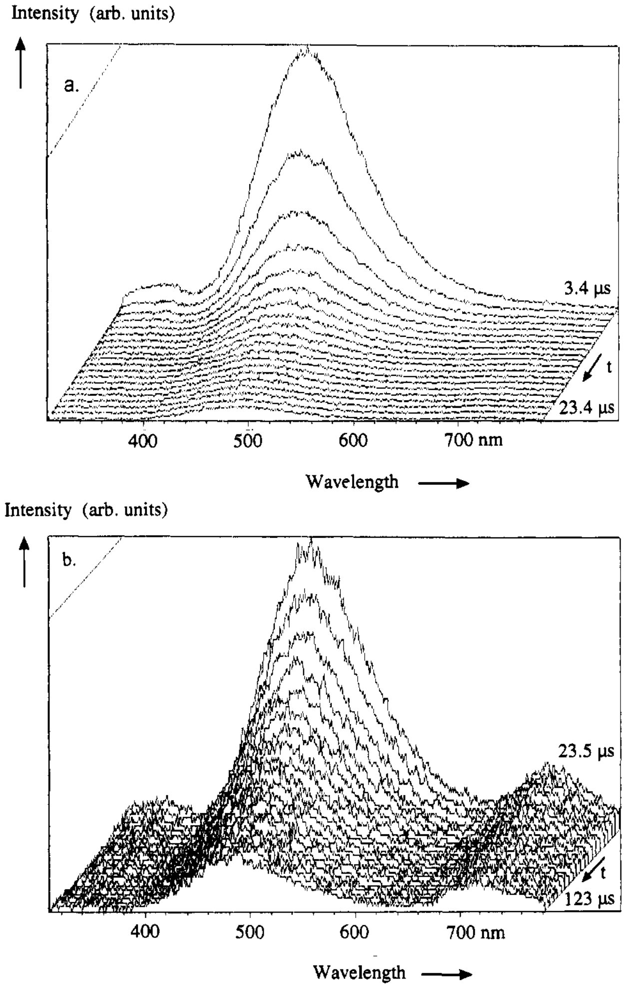

**Figure 3.** (a) Time-resolved emission spectra of $Gd_3Ga_5O_{12}$:$Bi^{3+}$, 3.4–23.4 μs after the excitation pulse of the excimer laser. (b) Time-resolved emission spectra of $Gd_3Ga_5O_{12}$:$Bi^{3+}$, 23.5–123.0 μs after the excitation pulse of the excimer laser.

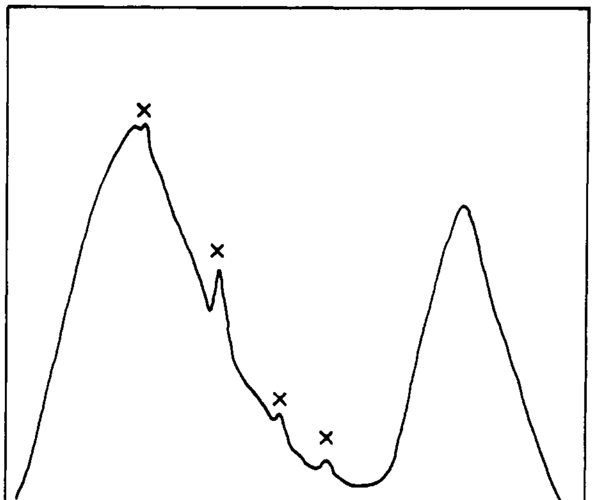

**Figure 4.** Emission spectrum of $Gd_3Ga_5O_{12}$:$Bi^{3+}$ under X-ray excitation at 300 K. The $Tb^{3+}$ emission lines are indicated by crosses.

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[9] Boulon, G. *J. Phys.* **1971**, *32*, 333.
[10] Blasse, G. *Prog. Solid State Chem.* **1988**, *18*, 79.
[11] Blasse, G. *Mater. Chem. Phys.* **1987**, *16*, 201.

**Table 1. Luminescence Data on Some $Bi^{3+}$-Activated Compounds**[a]

| composition | $\tau$ (300 K), $\mu$s | $Bi^{3+}$ coordination | optical bandgap host lattice, eV | ref |
|---|---|---|---|---|
| $Gd_3Ga_5O_{12}$:$Bi^{3+}$ | 2.5 | 8 | 5 | this work |
| $La_2O_3$:$Bi^{3+}$ | 0.3 | 7 | 5 | 9 |
| $YVO_4$:$Bi^{3+}$ | 5 | 8 | 3.5 | 9 |
| $LaBO_3$:$Bi^{3+}$ | <0.1 | 9 | ≈8 | 13 |

[a] The Stokes shifts of the emission are equal to within 1000 $cm^{-1}$.

It may be questioned whether the excited $^3P_1$ level is very close to or even in the conduction band in these two host lattices. In that case the excited state should be considered as an impurity-bound exciton in which the hole resides on the $Bi^{3+}$ ion and the electron occupies levels of the conduction band (i.e., mixed gallate–oxygen and mixed lanthanum–oxygen states). Such a description seems to be valid for $Bi^{3+}$ in $YVO_4$.[12] Due to a decreasing spin–orbit coupling (nephelauxetic effect) the decay time of the $Bi^{3+}$ luminescence is expected to become longer, and the exciton model becomes more appropriate because the excited state is more extended.

The data given in Table 1 seem to confirm this description. The smaller the optical bandgap $E_g$ of the host is, the longer the decay time at room temperature. Obviously the exciton model is a better description for $Gd_3Ga_5O_{12}$:$Bi^{3+}$ than for $La_2O_3$:$Bi^{3+}$. This can simply be due to a slightly lower position of the energy levels of $Bi^{3+}$ in the forbidden zone of $La_2O_3$. In spite of these results, the exact nature of the excited state remains an open questions.

Let us now turn to the host-lattice-excited emission spectra (Figure 3). The X-ray excited spectrum shows the presence of $Tb^{3+}$ (impurity in the starting $Gd_2O_3$ on a ppm level) and $Cr^{3+}$ (impurity in $Ga_2O_3$ and/or the synthesis environment) in addition to the $Bi^{3+}$ emission. Since the bismuth concentration is orders of magnitude larger than those of the impurities, Figure 4 shows that especially $Cr^{3+}$ captures the created electrons and holes very efficiently.

The time-resolved emission spectra (Figure 3) show immediately (i.e., 3.4 $\mu$s) after the excitation pulse host lattice emission and $Bi^{3+}$ emission. This host lattice emission agrees with literature data[8] and can be ascribed to octahedral gallate charge-transfer luminescence.[14] Since the decay time of $Cr^{3+}$ in $Gd_3Ga_5O_{12}$ is about 150 $\mu$s (ref 4 and this work), it is not observed at this time.

A long time after the pulse (≈100 $\mu$s) the $Bi^{3+}$ emission has to be considered as afterglow, but the $Cr^{3+}$ emission is still prompt. Following a model presented earlier,[5] these data are interpreted as follows: The X-ray excitation yields electrons and holes. A small part of these recombine on the octahedral gallate groups; at 4.2 K this is the dominating (self-trapped exciton) emission.[8] A dominant part recombines at the $Bi^{3+}$ dopant. Within 3 $\mu$s after the pulse the excited state of the dopant has captured this part. The $Cr^{3+}$ ions capture a hole which recombines with an electron.[5]

Afterglow is due to the presence of electron traps (oxygen vacancies[5]). This suggests that the $Bi^{3+}$ ion captures a hole which recombines later with an electron. This fits with the model proposed for the excited level of $Bi^{3+}$. If this level is close to or in the conduction band, electron trapping is not very probable. The considerable amount of afterglow in these samples is detrimental for application in computed tomography. $Gd_3Ga_5O_{12}$:$Tb^{3+}$, an efficient green X-ray phosphor, can for the same reason not be applied in X-ray imaging.[8]

In conclusion, the $Bi^{3+}$ ion in gallate garnets shows an efficient broad-band emission with a maximum at 480 nm. The $Bi^{3+}$ ion in gallate garnets captures holes.

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(12) Blasse, G. *Struct. Bonding* **1991**, *76*, 153.

(13) Wolfert, A.; Oomen, E. W. J. L.; Blasse, G. *J. Solid State Chem.* **1985**, *59*, 280.

(14) Dirksen, G. J.; Hoffman, A. N. J. M.; Bout van de, T. P.; Laudy, M. P. G.; Blasse, G. *J. Mater. Chem.* **1991**, *1*, 1001.