

On the Quenching of Bi³⁺ Luminescence in the Pyrochlore Gd₂GaSbO₇

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The luminescence of Bi³⁺ in the pyrochlore Gd₂GaSbO₇ is evaluated in the 15 to 300 K temperature range. The rapid thermal quenching of Bi³⁺ luminescence, despite the small Stokes shift, is postulated to involve a photoionization process arising from the interaction between the Bi³⁺ ³P_{0,1} excited states and the host lattice conduction band. The blue emission of the host lattice is attributed to the octahedral gallate groups of Gd₂GaSbO₇. The Bi³⁺ luminescence in Gd₂GaSbO₇, La₂Zr₂O₇ (pyrochlore structure), Y₂O₃ (fluorite structure), and materials with the perovskite structure are compared to gain insight into structure-photoionization issues. © 1999 Academic Press

INTRODUCTION

The spectroscopy of the Bi³⁺ ion has been investigated extensively in a variety of host lattices (1). The ground state of the free ion is ¹S₀ whereas the *nsnp* excited states gives rise to the triplet levels [³P₀, ³P₁, ³P₂] and the ¹P₁ singlet state. The ¹S₀ → ³P₁ transition (A-band) is allowed as a result of spin-orbit coupling whereas the ¹S₀ → ³P₂ transition (B-band) is forbidden but can be induced by coupling with unsymmetrical lattice vibrational modes. The ¹S₀ → ¹P₁ transition (C-band) is an allowed transition while the ¹S₀ → ³P₀ transition is strongly forbidden. Another transition appearing in the optical spectra of the Bi³⁺ ions is the so-called D-band. It is assumed that the D-bands are due to charge transfer transitions although an earlier view ascribed the bands to a perturbed exciton (2).

In certain host lattice ions with *ns*² ground state yield an emission spectrum which is uncharacteristic of the *ns*² ion incorporated. A photoionization process involving the excited states of the *ns*² ion and the host lattice conduction band has been proposed to account for the uncharacteristic luminescence. The photoionization step proceeds with the luminescent center in the excited state injecting an electron in the host lattice conduction band. This results in the formation of an impurity trapped exciton-like state with the hole localized on the luminescent center and the electron delocalized on the surrounding cations (3). The decay of this

bound exciton may be radiative or nonradiative. An illustrative example is the luminescence of Pb²⁺ in CdCl₂ where emission in the ultraviolet and in the visible spectral regions is observed. The ultraviolet band constitutes the Pb²⁺ ion emission from the localized excited states whereas the visible band is a result of the photoionization process due to the close proximity of the excited Pb²⁺ ³P_{0,1} states with the conduction band of the CdCl₂ host lattice (4). The luminescence from the impurity bound exciton state is also observed in the luminescence of Pb²⁺ in materials with the PbFCl structure and in alkaline earth carbonates, where it has been attributed to emission from the so-called D-state (5, 6).

Adverse effect on the *ns*² ion emission efficiency is anticipated in the event of the impurity trapped exciton state decaying nonradiatively (or with low efficiency) to the ground state. The low quantum efficiency of Bi³⁺ luminescence in Y₂O₃ is postulated to involve such a process (7). More significant in relation to our evaluations of the Bi³⁺ luminescence in Gd₂SbGaO₇ is the observation that ions with *nd*¹⁰*ns*⁰ electronic configuration (such as Ga³⁺, In³⁺, and Sb⁵⁺), in certain instances, have a profound influence on the *ns*² ion luminescence. For example, the In³⁺ ion with 4*d*¹⁰5*s*⁰ electronic configuration induces a new luminescent center in Bi³⁺ activated YPO₄ whereas the presence of this ion in Y₂O₃, La₂O₃, and LaOCl quenches the Bi³⁺ luminescence (8). In stark contrast to these results is the efficient and characteristic Bi³⁺ ³P_{0,1} → ¹S₀ emission in the perovskite LaInO₃, which suggests an independence of the Bi³⁺ excited states and the 4*d*¹⁰5*s*⁰ wavefunction of the In³⁺ ions (9).

The purpose of this work is to determine the influence, if any, of the Ga³⁺ (3*d*¹⁰4*s*⁰) and Sb⁵⁺ (4*d*¹⁰5*s*⁰) ions on the Bi³⁺ luminescence in the pyrochlore Gd₂GaSbO₇ (10). The cubic pyrochlore structure of the oxide A₂B₂O₇ (space group *Fd3m*) can be considered to be derived from the fluorite structure by removing one-eighth of the anions so that the composition can be written as A₂B₂O₇V_a, where V_a is the anion vacancy (11). The large A cations are eight-coordinated with hexagonal bipyramidal geometry. The site

exhibits two short and six longer bonds so that the coordination can be described as (2 + 6). The small *B* cations are in octahedral coordination.

EXPERIMENTAL

Samples with the general composition (Gd_{1-x}Bi_x)₂GaSbO₇ were synthesized by heating blends of the starting materials, Gd₂O₃, Ga₂O₃, Sb₂O₃ (5 mole% excess), Bi₂O₃, at 600 (2 h), 1300 (5 h), and 1350°C (5 h) in a covered crucible. The samples were rehomogenized between each heating step. X-ray diffraction indicated single phase formation. Luminescence measurements were done as previously described (12).

RESULTS AND DISCUSSION

1. Luminescence of Gd₂GaSbO₇

First, the host lattice excitation and emission spectrum in a sample with composition (Gd_{0.995}Bi_{0.005})₂GaSbO₇ is discussed. The excitation spectrum consists of two broad bands centered at 275 and 315 nm, respectively (Fig. 1a). The broad band emission centered at 450 nm (Fig. 1b) is independent of the excitation wavelength. The excitation band at 275 nm coincides with a strong absorption in the room temperature diffuse reflectance spectrum of the pure Gd₂GaSbO₇ material. The weaker 315-nm excitation band was not detected in the room temperature diffuse reflectance spectrum of the pure material. A lattice defect center arising from stoichiometry deviation or anionic disorder, to which the pyrochlore lattice is particularly prone, could be responsible for this center. For example, the different site of Eu³⁺

in Eu₂Ti₂O₇ can be accounted for by the anionic disorder between the 8(*a*) and 8(*b*) sites of the pyrochlore unit cell (13).

The observation of Gd³⁺ excitation lines (⁸S_{7/2} → ⁶P_J) in the excitation spectrum of the host lattice emission indicates Gd³⁺ to host lattice energy transfer. Excitation of the host lattice at 275 nm also excites the Gd³⁺ ions through the ⁸S_{7/2} → ⁶P_J transition which accounts for the Gd³⁺ ⁶P_{7/2} emission at 310 nm (Fig. 1b).

The low room temperature efficiency of the host lattice luminescence is probably due to thermally induced quenching. Interestingly, with increasing temperature the high energy band in the excitation spectrum quenches more rapidly than the low energy band; at room temperature only the low energy band with very weak intensity is observed in the excitation spectrum. The difference between the thermal quenching behavior of the two excitation bands may also reflect their different origins, as previously postulated.

The luminescence of ions with *nd*¹⁰*ns*¹⁰ electronic configuration has been known for decades (14). Interpretation of the Gd₂GaSbO₇ optical spectra is complicated by the presence of two ions with the aforementioned electronic configuration (Ga³⁺ and Sb⁵⁺). However, the pertinent literature data on the luminescence of antimonates and gallates suggests assigning the blue emission of Gd₂GaSbO₇ to octahedrally coordinated gallate groups. The luminescence of β-Ga₂O₃, for example, consists of two broad bands centered at 470 and 520 nm, respectively (15). It is assumed that the blue emission occurs when an electron from a V_o^x or Ga_i^x center recombines with a trapped hole. A similar origin for the blue emission of Gd₂GaSbO₇ is conceivable. Also, the excitation and emission bands of pure BaGa₁₂O₁₉ (with octahedral gallate groups) are centered at 250 and 440 nm, respectively (16).

The pyrochlore Ca₂Sb₂O₆F displays broad excitation and emission bands centered at 260 and 588 nm, respectively (17). The yellow emission is attributed to the Sb⁵⁺ ions of the host lattice. Comparable luminescence of octahedral Sb⁵⁺ groups in the weberites NaGdSb₂O₇ (18) and Ca₂Sb₂O₇ (14) are observed. This suggests emission in the yellow spectral region when the Sb⁵⁺ ions occur in an octahedral coordinated. However, several antimonates are known to emit in the blue spectral region, but their luminescence is particularly excited by very short wavelength ultraviolet radiation (14). In view of these observations the blue emission of Gd₂GaSbO₇ is assigned to the octahedral gallate groups.

2. Luminescence of (Gd_{0.995}Bi_{0.005})₂GaSbO₇

We now proceed to examine the Bi³⁺ luminescence in the composition (Gd_{0.995}Bi_{0.005})₂GaSbO₇. The ³P_{0,1} → ¹S₀ and the ¹S₀ → ³P₁ optical transitions on the Bi³⁺ ion are responsible for the emission and excitation bands centered

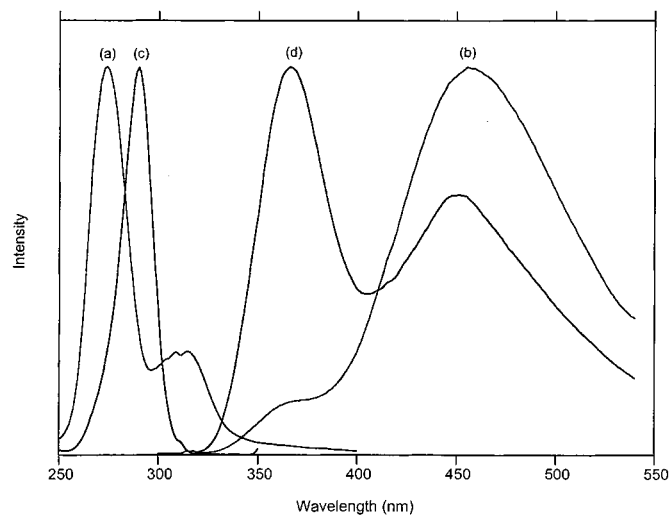


FIG. 1. Excitation and emission spectra of (Gd_{0.995}Bi_{0.005})₂GaSbO₇ at *T* = 15 K: (a) host lattice excitation spectrum ($\lambda_{em} = 450$ nm); (b) host lattice emission spectrum ($\lambda_{ex} = 275$ nm); (c) excitation spectrum for Bi³⁺ emission ($\lambda_{em} = 370$ nm); (d) emission spectrum for Bi³⁺ excitation ($\lambda_{ex} = 290$ nm).

at 370 (Fig. 1d) and 290 nm (Fig. 1c), respectively. It is straightforward to see from Figs. 1a and 1c that Bi^{3+} excitation at 290 nm will additionally excite the host lattice. Therefore the emission spectrum for $\lambda_{\text{ex}} = 290$ nm additionally contains the host lattice emission (Fig. 1d). The presence of $\text{Gd}^{3+} \ ^8S_{7/2} \rightarrow \ ^6P_{7/2}$ transition in the excitation spectrum for Bi^{3+} emission indicates Gd^{3+} to Bi^{3+} energy transfer. This is expected in view of the spectral overlap between the Bi^{3+} excitation band and Gd^{3+} emission line at 311 nm. The temperature dependence of the integrated Bi^{3+} emission intensity is shown in Fig. 2. Despite the small Stokes shift (about 7450 cm^{-1}) the luminescence of Bi^{3+} rapidly quenches with increasing temperature.

We now perform some comparisons between the optical properties of materials in the pyrochlore family with materials in the perovskite family to gain understanding of structure-luminescence issues. Table 1 summarizes the comparison of the optical data on the relevant materials. We specifically note that the Stokes shift of Bi^{3+} luminescence in all materials, including LaInO_3 with $nd^{10}ns^0$ ion (In^{3+}), are comparable. Optical data exist in the archival literature that suggests that the Stokes shift in materials which favor interaction of the Bi^{3+} excited states with $nd^{10}ns^0$ states is often greater than about $10,000 \text{ cm}^{-1}$ (19). This is certainly not the case with the materials listed in Table 1. Therefore, the luminescence of $\text{Gd}_2\text{GaSbO}_7$: Bi^{3+} suggests an independence of Bi^{3+} and $\text{Ga}^{3+}/\text{Sb}^{5+}$ states (see Table 1).

In Table 1 we would like to draw attention to the comparatively larger Stokes shift of the Bi^{3+} luminescence in materials with the pyrochlore structure. The perovskite LaInO_3 has the orthorhombic GdFeO_3 type structure where the *A*-site ions (La^{3+} , Gd^{3+}), as in the pyrochlore structure, are eight coordinated (20). The larger Stokes shift

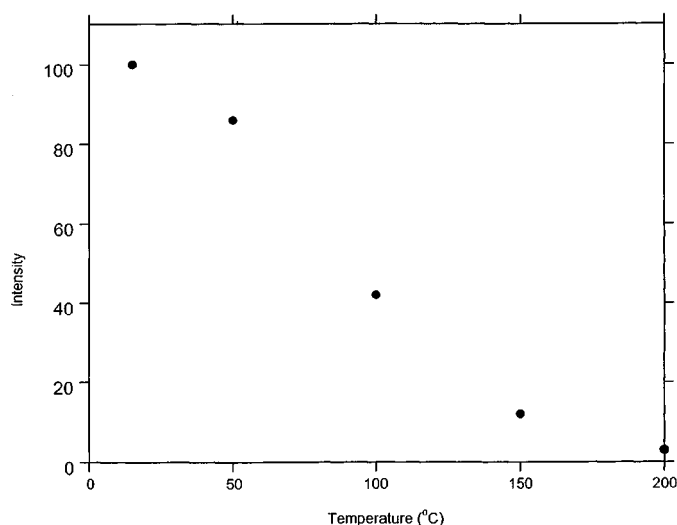


FIG. 2. Temperature dependence of the Bi^{3+} emission intensity in $(\text{Gd}_{0.995}\text{Bi}_{0.005})_2\text{GaSbO}_7$.

TABLE 1
Optical Data on Bi^{3+} Luminescence ($^1S_0 \leftrightarrow ^3P_{0,1}$ Transitions) in the Pyrochlores $\text{Gd}_2\text{GaSbO}_7$, $\text{La}_2\text{Zr}_2\text{O}_7$, and Some Compounds with the Perovskite Structure

Compound	Excitation maxima ($\times 10^{-3} \text{ cm}^{-1}$)	Emission maxima ($\times 10^{-3} \text{ cm}^{-1}$)	Stokes shift ($\times 10^{-3} \text{ cm}^{-1}$)	Ref.
$\text{Gd}_2\text{GaSbO}_7^a$	34.5	27.0	7.5	This work
LaAlO_3^b	35.1	26.6	8.5	(9)
LaInO_3^c	29.4	23.8	6.0	(9)
$\text{La}_2\text{Zr}_2\text{O}_7^a$	34.5	25.9	8.6	(23)

^a $T = 15$ K.

^b $T = 300$ K.

^c $T = 4.2$ K.

and the higher energy position of the $\text{Bi}^{3+} \ ^1S_0 \rightarrow \ ^3P_1$ excitation transition in $\text{Gd}_2\text{GaSbO}_7$ relative to LaInO_3 suggests the dominance of s^2 ion effect in the pyrochlore structure (4). The larger Stokes shift in the pyrochlore structure may be related to the asymmetric coordination of the *A*-site ion (2 + 6 coordination). However, the GdFeO_3 structure also offers an asymmetric coordination for the Bi^{3+} ion so that the difference in the Stokes shift may not be explained in terms of coordination characteristics.

It is conceivable that the Stokes shift is determined by the variance in the network rigidity between the pyrochlore and perovskite structures. The mode of BO_6 octahedra linkage leads to B–O–B angles close to 180° in the ideal perovskite structure whereas this angle deviates considerably from 180° in the pyrochlore structure. Further, the *B*-site symmetry in the pyrochlore structure is $\bar{3}$. Consequently the B–O–B angles within the octahedral BO_6 groups are not constrained to being 90° . In fact, the octahedron is distorted and is actually a trigonal antiprism. It is therefore feasible that the cubic network of the perovskite structure reinforces the network rigidity yielding a smaller Stokes shift of the Bi^{3+} luminescence in LaInO_3 relative to $\text{Gd}_2\text{GaSbO}_7$. The higher Stokes shift in the case of LaAlO_3 (rhombedrally distorted perovskite) may be attributed to the higher coordination number (12) for the La^{3+} ions (s^2 ion effect) (9).

The relatively small Stokes shift of the Bi^{3+} luminescence in $\text{Gd}_2\text{GaSbO}_7$ suggests localized luminescence and insignificant interaction with the host lattice $nd^{10}ns^0$ cations. The rapid intensity quenching with increasing temperature is, however, inconsistent with the expectation of efficient luminescence resulting from the small Stokes shift of luminescence. It is also at variance with the efficient luminescence of Bi^{3+} in LaInO_3 despite their similar Stokes shifts (see Table 1). The spectral overlap between the Bi^{3+} excitation and emission band in $\text{Gd}_2\text{GaSbO}_7$ is small, so it is unlikely that the strong temperature dependence is due to energy transfer from Bi^{3+} ions to host lattice quenching

sites. A part of the thermal quenching may be attributed to the thermal induced band broadening of the host lattice excitation band that results in less efficient excitation of the Bi³⁺ ion with increasing temperature. This thermal broadening is, however, not adequate to explain the total quenching of the Bi³⁺ luminescence in Gd₂GaSbO₇ at room temperature.

A viable explanation for luminescence quenching involves energy transfer from Bi³⁺ to the host lattice. The spectral overlap between Bi³⁺ emission and the low energy excitation band of the host lattice center is evident from Figs. 1a and 1d. Hence, radiative or nonradiative energy transfer from Bi³⁺ to this center may be responsible for the quenching of Bi³⁺ luminescence.

An alternative explanation for the thermal quenching of Bi³⁺ luminescence in Gd₂GaSbO₇ involves the photoionization process. After absorption of the exciting photon, the Bi³⁺ ion photoionizes and ejects an electron into the conduction band. Consequently two channels for relaxation following optical excitation are the ³P_{0,1} → ¹S₀ radiative decay and the ionization process. The former process dominates at low temperatures whereas the thermally assisted ionization process becomes more efficient at higher temperatures. In the ionization process the lower energy impurity trapped exciton state receives energy from the localized Bi³⁺ ³P_{0,1} excited states. The decay of the impurity trapped exciton state is radiationless since optical transitions representative of this state are not observed. Therefore, thermal quenching of the Bi³⁺ luminescence in Gd₂GaSbO₇ can be explained by the thermal ionization process involving the localized (³P_{0,1}) and the exciton state. The high efficiency of this process is probably due to the close proximity of the Bi³⁺ ³P_{0,1} excited states with the host lattice extended states. The structure of the exciton-like state can be envisioned as follows. Since the pyrochlore structure may be viewed as an A₂O sublattice interpenetrating the BO₃ framework, the hole can be thought to reside on the (Gd, Bi)₂O' sublattice and the electron in the (GaSbO₃) framework (21).

The involvement of the D-state in the nonradiative process can also explain the temperature dependence of the Bi³⁺ emission in Gd₂GaSbO₇. The bottom of the conduction band in materials constituted of ions with nd¹⁰ns⁰ electronic configuration is primarily constructed of the ns⁰ orbitals (22). Therefore the bottom of the Gd₂GaSbO₇ conduction band is composed of the Ga³⁺ (3s⁰)/Sb⁵⁺ (5s⁰) orbitals. Consequently, the D-state can be thought to arise from charge transfer transition between Bi³⁺ (6s²) and Ga³⁺ (3s⁰)/Sb⁵⁺ (5s⁰) orbitals. The thermally assisted relaxation of the localized Bi³⁺ ³P_{0,1} states into the D-state and the subsequent radiationless D → ¹S₀ decay thus accounts for the thermal quenching of Bi³⁺ luminescence. The different interpretations of the excited state as an impurity bound exciton or as a charge transfer state are due to our lack of understanding of the excited state composition (7).

3. Comparison of Gd₂GaSbO₇: Bi³⁺, La₂Zr₂O₇: Bi³⁺, and Y₂O₃: Bi³⁺

The involvement of the impurity trapped exciton state or D-state has also been proposed to account for the low efficiency of Bi³⁺ luminescence in Y₂O₃ (7). In the following we suggest a common entity in the crystal structures of Gd₂GaSbO₇ and Y₂O₃ that may be responsible for the high photoionization efficiency of luminescent centers in these materials. The fluorite derived structure of Y₂O₃ exhibits oxygen ions that are surrounded by four Y³⁺ in a tetrahedral arrangement. In the pyrochlore structure, the three tetrahedral interstice sites available for the anions are the 48(f) positions with two A and two B near neighbors, the 8(b) position having four B near neighbors (the site are unoccupied in the pyrochlore structure), and the 8(a) position with four A near neighbors. The close similarity in the tetrahedral network between the two structures may reflect a structural entity that promotes photoionization in these materials. We therefore suggest that the A₄O network in these materials promotes photoionization of the Bi³⁺ ion, which adversely influences its luminescence efficiency.

We further offer a comparative study of Bi³⁺ luminescence in the pyrochlores La₂Zr₂O₇ and Gd₂GaSbO₇. The luminescence of La₂Zr₂O₇: Bi³⁺ has been recently evaluated by Srivastava and Beers (23). The optical data for localized transitions (¹S₀ ↔ ³P_{0,1}) in the two systems are quite similar (Table 1). The larger Stokes shift in La₂Zr₂O₇ is due to larger ionic radii of La³⁺ which promote off-center positioning of the Bi³⁺ ion (s² ion effect) (1). In Bi³⁺ activated La₂Zr₂O₇ emission from the impurity trapped excitonic state is observed that clearly implies the interaction of Bi³⁺ ³P_{0,1} excited states with the bottom of the host lattice conduction band. At room temperature the efficiency of Bi³⁺ luminescence in La₂Zr₂O₇ is weak due to a thermal ionization process involving both the localized ³P_{0,1} and the excitonic states. A similar mechanism for the absence of Bi³⁺ luminescence in the pyrochlore Gd₂GaSbO₇ is concluded for this work.

CONCLUSION

The Bi³⁺ luminescence in the pyrochlore Gd₂GaSbO₇ is reported and discussed. The rationale for the strong thermal quenching of the Bi³⁺ luminescence is difficult to comprehend due to the presence of several luminescent centers in this host lattice. A viable mechanism for the quenching of the Bi³⁺ luminescence involves the impurity bound exciton state or the D-state. It is proposed that the nonradiative relaxation of the this state is responsible for the low quenching temperature of the Bi³⁺ luminescence in this material. We conclude that the nd¹⁰ ions (Ga³⁺, Sb⁵⁺) influence the quenching temperature of Bi³⁺ luminescence in Gd₂GaSbO₇.

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