

The nature of Bi³⁺ luminescence in garnet hosts

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Abstract

The room temperature photoluminescence and excitation spectra of Bi³⁺ in the (Y,Gd)₃(Al,Ga)₅O₁₂ garnets is reported and analyzed. The luminescence spectra of these materials under ¹S₀ → ³P₁ Bi³⁺ excitation consist of two bands in the UV and the visible spectral regions. The UV emission band is attributed to the ³P_{0,1} → ¹S₀ emission of isolated Bi³⁺ ions and is observed for the first time in garnet host lattices. Previous reports of Bi³⁺ luminescence in (Y,Gd)₃Ga₅O₁₂ garnets only reported the visible emission and attributed this emission to an impurity trapped exciton, implying a strong interaction between the host lattice conduction band and the Bi³⁺ excited states. We disagree with this interpretation of the visible emission band. Our results show a strong dependence of the visible band intensity on the Bi³⁺ concentration and lead us to conclude that this emission is related to Bi³⁺ pairs and/or clusters in the garnet host lattice. There does not appear to be any interaction between the host lattice conduction band and the ³P_{0,1} excited states of Bi³⁺.

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1. Introduction

The spectroscopy of Bi³⁺ ions, with the 6s² electronic configuration, has been investigated extensively for potential phosphors or scintillation detectors as well as a spectroscopic probe for covalency [1,2]. The ground state of the free ion is ¹S₀ while the 6s6p excited states give rise to triplet levels (³P₀, ³P₁, ³P₂) and the ¹P₁ singlet state. The lowest energy ¹S₀ → ³P₀ transition is strongly forbidden, but the ¹S₀ → ³P₁ transition (A-band) and the ¹S₀ → ³P₂ transition (B-band) become more allowed due to spin–orbit coupling and coupling to asymmetrical phonon modes, respectively. The ¹S₀ → ¹P₁ transition (C-band) is an allowed electric dipole transition. Typically at room temperature, emission is observed from the ³P₁ → ¹S₀ transition, although at low temperatures the highly forbidden ³P₀ → ¹S₀ emission is also observed [3]. In addition to the intrinsic 6s² → 6s6p Bi³⁺ optical transitions, another optical transition (D-band) can appear in the emission spectra of Bi³⁺. The D-bands are presumed to be ligand to metal charge transfer transitions, although alternate views have ascribed these

bands to impurity trapped excitons [4–6]. D-band emission can occur when there can be significant coupling between the Bi³⁺ excited states (³P_{0,1}) and the electronic states of nd¹⁰/nd⁰ ions (such as Ga³⁺, In³⁺, V⁵⁺ and Sb⁵⁺) [5,6]. This coupling between the excited states of Bi³⁺ and the electronic states of nd¹⁰/nd⁰ host lattice ions can also be described using photoionization, implying a strong interaction between the excited states of Bi³⁺ and the host lattice conduction band [5,6].

One system where D-band emission has been reported is the Bi³⁺ doped garnets, (Y,Gd)₃Ga₅O₁₂, where Bi³⁺ replaces Y³⁺/Gd³⁺ on the eight-coordinated dodecahedral site. Ilmer et al. [7] studied the room temperature luminescence of sintered ceramic plates of Bi³⁺ doped (Y,Gd)₃-Ga₅O₁₂ at room temperature and observed a blue–green emission with a larger Stokes shift (~12,000 cm⁻¹) and longer decay time (~2.5 μs) compared to the typical Bi³⁺ ³P₁ → ¹S₀ optical transition. The combination of larger Stokes shift and longer decay time led Ilmer et al. to assign the Bi³⁺ luminescence in garnets to an impurity trapped exciton. Their results, therefore, implied the existence of a strong interaction between Bi³⁺ localized states (³P_{0,1}) and the extended conduction band states of the gallate garnets.

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It is relatively straightforward to alter the band gap of garnet hosts via chemical substitutions into the $\{C\}_3\{A\}_2\{D\}_3O_{12}$ garnet structure, where the $\{C\}$ cations are 8-coordinated in dodecahedra, the $\{A\}$ cations are 6-coordinated in octahedra, and the $\{D\}$ cations are 4-coordinated in tetrahedra. Therefore, we intended to examine the luminescence of the Bi^{3+} ion in several garnet compositions to study the effects of composition on the competition between $Bi^{3+} {}^3P_{0,1} \rightarrow {}^1S_0$ and “D-state” relaxation, as has been done in the pyrochlore family of materials [6,8,9]. However, there are significant differences between our measurements of Bi^{3+} luminescence in the garnets and those of Ilmer et al. In the gallate garnets, there are *two* broad emission bands when exciting into the $Bi^{3+} {}^1S_0 \rightarrow {}^3P_1$ absorption band: a visible band (VIS) similar to the one reported by Ilmer et al. [7] and a higher energy ultraviolet band (UV). The UV band is assigned to characteristic ${}^3P_{0,1} \rightarrow {}^1S_0$ Bi^{3+} emission. To the best of our knowledge, this has not been previously reported in garnets. In addition, we disagree with the interpretation of the VIS emission as an impurity trapped exciton by Ilmer et al. There is a strong Bi^{3+} concentration dependence for the relative strength of the VIS bands, making it reasonable to assign the luminescence of the VIS band to Bi^{3+} pairs or clusters similar to other Bi^{3+} doped host lattices [9–12]. We therefore conclude that the luminescence of Bi^{3+} in these garnets does not involve any interactions between $Bi^{3+} {}^3P_1$ states and the host lattice conduction band.

2. Experimental

Powder samples are made by typical solid-state synthesis methods using stoichiometric mixtures of high purity, elemental oxide precursors, except in the case of garnets with Ga^{3+} , where a slight excess of Ga_2O_3 is added to account for evaporation at high temperature. Samples are fired at ~ 1400 °C in air and are single-phase garnets as determined

by powder X-ray diffraction. The compositions that are reported in this paper are nominal compositions and most likely have lower Bi^{3+} concentrations due to the high vapor pressure of Bi_2O_3 under typical synthesis conditions. Emission and excitation spectra are taken on pressed powder pellets using a SPEX Fluorolog 2 spectrometer with corrections for Xe lamp intensity and instrument response. Since our spectrometer emission correction factors are less accurate for $\lambda_{em} < 310$ nm, some specific emission spectra will be reported as uncorrected spectra. Unless specifically mentioned, all luminescence measurements are made at room temperature.

3. Results and discussion

The luminescence behavior of the Bi^{3+} ion was examined in the garnets, $(Lu_{0.99}Bi_{0.01})_3Al_5O_{12}$ (LuAG:Bi), $(Y_{0.99}Bi_{0.01})_3Al_5O_{12}$ (YAG:Bi), and $(Y_{0.99}Bi_{0.01})_3Ga_5O_{12}$ (YGG:Bi). The room temperature emission ($\lambda_{ex} = 270$ nm) and excitation spectra ($\lambda_{em} = 330$ nm) and the position of the emission and excitation bands for these samples are given in Fig. 1 and Table 1, respectively. The emission spectra in these samples consist primarily of a dominant band in the ultraviolet. There is a weak visible emission band in YGG:Bi similar to previous reports [7], but its intensity is much weaker in comparison to the UV emission band (Fig. 2).

We first focus on the nature of the UV excitation and emission bands in these garnet materials. Considering the similarity between our excitation spectra and previously published excitation and absorption spectra for Bi^{3+} in garnets [7,13], it is straightforward to assign the broad UV excitation band in these samples to the $Bi^{3+} {}^1S_0 \rightarrow {}^3P_1$ absorption transition. The energy position of this transition is sensitive to the covalency of the $Bi^{3+}-O^{2-}$ bond (nephelauxetic effect) [2]: increasing covalency shifts this transition to lower energy. The position of the ${}^1S_0 \rightarrow {}^3P_1$

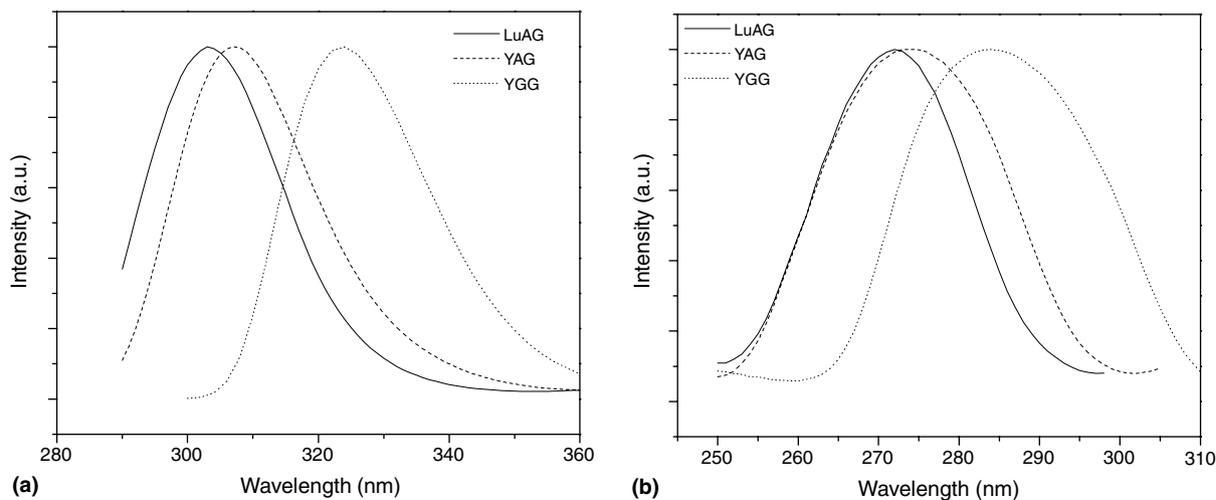


Fig. 1. (a) Emission ($\lambda_{ex} = 270$ nm) and (b) excitation ($\lambda_{em} = 335$ nm) spectra for $Lu_3Al_5O_{12}$ (LuAG), $Y_3Al_5O_{12}$ (YAG), and $Y_3Ga_5O_{12}$ with a nominal Bi^{3+} doping of 1%. The emission spectra in this figure are not corrected for detector and instrument response.

Table 1
Excitation and emission for Bi³⁺ luminescence in garnets and other host lattices with 8-coordination

Host	Coordination/ionic radii (Å)	¹ S ₀ → ³ P ₁ excitation (cm ⁻¹)	³ P _{0,1} → ¹ S ₀ emission (cm ⁻¹)	Stokes shift (cm ⁻¹)	Reference
<i>Garnets</i>					
LuAG	8/1.11	36,800	33,000	3800	This work
YAG	8/1.155	36,500	32,600	3900	This work
YGG	8/1.155	35,200	31250	3950	This work
<i>Perovskites</i>					
CaHfO ₃	8+4/1.26	32,500	26,200	6300	Unpublished
CaZrO ₃	8+4/1.26	32,000	25,600	6400	Unpublished
<i>Pyrochlores</i>					
Y ₂ Sn ₂ O ₇	8/1.155	35,700	30,100	5600	[9]
La ₂ Zr ₂ O ₇	8/1.32	34,500	25,900	8600	[6]
<i>Cs₃CoCl₅</i>					
Sr ₂ GdAlO ₅	8/1.20	33,100	22,100	11,000	Unpublished
Sr ₂ GdGaO ₅	8/1.20	32,000	21,200	10,800	Unpublished

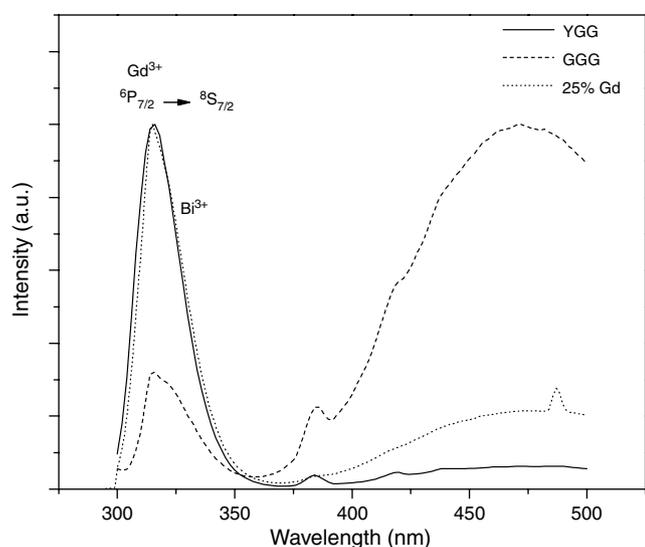


Fig. 2. Emission spectra ($\lambda_{\text{ex}} = 280$ nm) for $(\text{Y}_{0.99}\text{Bi}_{0.01})_3\text{Ga}_5\text{O}_{12}$ (YGG), $(\text{Y}_{0.74}\text{Gd}_{0.25}\text{Bi}_{0.01})_3\text{Ga}_5\text{O}_{12}$ (YGGG), and $(\text{Gd}_{0.99}\text{Bi}_{0.01})_3\text{Ga}_5\text{O}_{12}$ (GGG). In this figure, the emission intensities of the YGG:Bi and YGGG:Bi were scaled for the UV band maximum to show the change in the visible band emission intensity when Gd³⁺ is substituted for Y³⁺.

absorption band for the garnets is at higher energy versus other hosts where Bi³⁺ is in eight coordination (Table 1), indicating that the Bi³⁺–O²⁻ bond is less covalent in the garnets compared to these other hosts. Comparing the various garnets, the position of the A-band is at slightly higher energy in LuAG:Bi vs. YAG:Bi, indicating a more covalent Bi³⁺–O²⁻ bond in YAG:Bi. This difference in the Bi³⁺–O²⁻ covalency can be explained by associating the crystal-dependent ligand (O²⁻) polarizability with the host lattice cation radii. In the garnets, each O²⁻ anion is surrounded by two {C} dodecahedral cations, one [A] octahedral cation, and one (D) tetrahedral cation. The anion polarizability towards Bi³⁺ depends on the surroundings of the anion and decreases when the lattice contains small and highly charged ions. The effective O²⁻ polarizability towards

Bi³⁺ ions is therefore expected to be higher in YAG:Bi relative to LuAG:Bi, since the larger Y³⁺ ions ($r^{\text{VIII}}(\text{Y}^{3+}) = 1.155$ Å vs. $r^{\text{VIII}}(\text{Lu}^{3+}) = 1.11$ Å [14]) will not be able to attract O²⁻ electron density as well as the smaller Lu³⁺ ions. This leads to a more covalent Bi³⁺–O²⁻ bond via inductive effects and a lower energy ¹S₀ → ³P₁ transition as observed experimentally (Fig. 1/ Table 1). The A-band is at lower energy in YGG:Bi vs. YAG:Bi (Fig. 1) also indicating higher covalency of the Bi³⁺–O²⁻ bond in YGG:Bi. Considering inductive effects, this means that the (AlO₄)⁵⁻/[AlO₆]⁹⁻ network in YAG is more covalent relative to the (GaO₄)⁵⁻/[GaO₆]⁹⁻ network in YGG as expected given the relative size of Al³⁺ and Ga³⁺. Similar inductive effects on the Bi³⁺ luminescence have also been observed in the LaBO₃ (B = Al³⁺, In³⁺, Ga³⁺) perovskites [15,16].

The UV emission band is initially harder to characterize due to possible intrinsic emission from the garnet host lattice [17,18]. For example, in undoped YAG ceramics and single crystals, there are broad UV emission bands peaking from 300 to 370 nm, depending upon the grain size of the YAG sample [17]. However, the excitation spectra for these bands begin at $\lambda_{\text{ex}} < 250$ nm, and the undoped YAG emission bands are much broader than the UV emission bands (FWHM ~100 nm vs. 30 nm) in the YAG:Bi sample. Consequently, the UV emission band in YAG:Bi and LuAG:Bi is correlated to Bi³⁺ doping and is assigned to the characteristic Bi³⁺ ³P_{0,1} → ¹S₀ emission transition, not intrinsic host lattice emission. Similarly, Ga³⁺ based garnets have host lattice emission in the ultraviolet (~360 nm) when excited in the host lattice absorption edge ($\lambda < 300$ nm) [18]; this emission from octahedral [GaO₆]⁹⁻ groups is quenched at $T > 150$ K. Again, the UV excitation and emission bands of our YGG:Bi samples are different when compared to undoped YGG, and YGG:Bi has minimal luminescence quenching up to room temperature. Therefore, the emission band in YGG:Bi is also correlated to the presence of Bi³⁺ and is assigned to the characteristic Bi³⁺ ³P_{0,1} → ¹S₀ emission transition. To the best of our

knowledge, this is the first observation of characteristic $\text{Bi}^{3+} \ ^3\text{P}_{0,1} \rightarrow \ ^1\text{S}_0$ luminescence in garnet host lattices.

The Stokes shift of the intrinsic Bi^{3+} luminescence, increases slightly in the sequence $\text{LuAG:Bi} > \text{YAG:Bi} > \text{YGG:Bi}$ (Table 1). Correspondingly, the amount of space available for an activator ion (calculated from the average {C}–O bond length) also increases in the sequence, LuAG (2.330 Å) $>$ YAG (2.368 Å) $>$ YGG (2.383 Å) [19]. The correlation between the amount of space available in the host lattice and the Stokes shift is frequently observed in the luminescence of ions with ns^2 electronic configuration [12,20,21] and lends further credence to the assignment of the UV emission band to the $\ ^3\text{P}_{0,1} \rightarrow \ ^1\text{S}_0$ transition. It is postulated that when Bi^{3+} occupies a relatively large site, the lone pair of $6s^2$ electrons in the Bi^{3+} ground state favors an off-center or asymmetric coordination. In the $6s6p$ excited state, Bi^{3+} relaxes to the center of the polyhedra, leading to a significant rearrangement to a more symmetrical coordination and a large Stokes shift [21]. The difference in the Stokes shift between YAG:Bi and YGG:Bi suggests that the Stokes shift is not solely dependent on the ionic radii of the host lattice cations but depends on the {Y–O} bond lengths within the garnet hosts. In addition, Bi^{3+} emission in the garnets has a relatively small Stokes shift compared to other host lattices with 8-coordination (Table 1). Ions occupying the garnet {C} site are coordinated to eight O^{2-} anions that form an almost perfect dodecahedron. The relatively small Stokes shift for Bi^{3+} in garnets can be attributed to the fact that the dodecahedral coordination provides a more isotropic coordination for the Bi^{3+} ion reducing the contribution to the Stokes shift by the lone pair of $6s^2$ ions. This also points to a weak interaction between the Bi^{3+} ion and the host lattice.

Efficient $\text{Bi}^{3+} \rightarrow \text{Gd}^{3+}$ energy transfer is expected in the garnets, as in GdBO_3 [12] or GdB_3O_6 [22], since the UV Bi^{3+} emission band shows considerable spectral overlap with the $\text{Gd}^{3+} \ ^8\text{S}_{7/2} \rightarrow \ ^6\text{P}_{7/2}$ excitation transition at ~ 315 nm. Consequently, doping YAG:Bi or YGG:Bi with Gd^{3+} leads to Gd^{3+} emission at 315 nm ($\ ^6\text{P}_{7/2} \rightarrow \ ^8\text{S}_{7/2}$) under $\text{Bi}^{3+} \ ^1\text{S}_0 \rightarrow \ ^3\text{P}_1$ excitation (Fig. 2). This sharp emission line is superimposed on the broad $\text{Bi}^{3+} \ ^3\text{P}_{0,1} \rightarrow \ ^1\text{S}_0$ emission band, and the relative intensity of the Gd^{3+} emission increases with Gd^{3+} concentration, as expected. In the case of the Ga^{3+} garnets, the shift of the excitation band to lower energy increases the probability of $\text{Gd}^{3+} \rightarrow \text{Bi}^{3+}$ energy back transfer since the low energy tail of the Bi^{3+} excitation band overlaps with the $\text{Gd}^{3+} \ ^8\text{S}_{7/2} \rightarrow \ ^6\text{P}_{7/2}$ emission transition at 315 nm.

Adding Gd^{3+} to YGG:Bi also leads to a stronger visible emission band similar to the one observed by Ilmer et al. [7] (Fig. 2). It is evident that the visible band emission increases with Gd^{3+} concentration; the strongest visible emission is observed for $(\text{Gd}_{0.99}\text{Bi}_{0.01})_3\text{Ga}_5\text{O}_{12}$ (GGG:Bi). Similar results are also observed when Gd^{3+} is added to the Al^{3+} garnets. We now focus our attention on this visible (VIS) emission band. The excitation spectrum of the

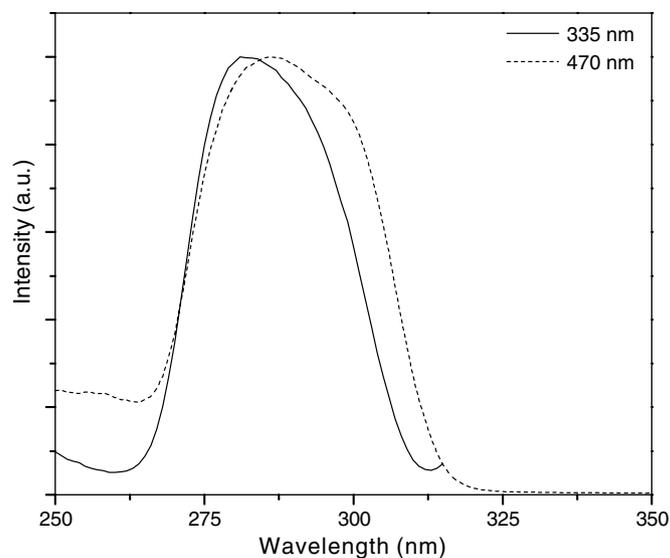


Fig. 3. Excitation spectra for UV emission band ($\lambda_{em} = 335$ nm) and VIS emission band ($\lambda_{em} = 470$ nm) of $(\text{Y}_{0.74}\text{Gd}_{0.25}\text{Bi}_{0.01})_3\text{Ga}_5\text{O}_{12}$.

VIS band in $(\text{Y}_{0.74}\text{Gd}_{0.25}\text{Bi}_{0.01})_3\text{Ga}_5\text{O}_{12}$ (YGGG:Bi), while similar to the UV band, is clearly shifted to lower energy and broadened (Fig. 3). The difference between the excitation spectra of the VIS and UV bands indicates that the VIS band is due to a different center in these materials. The relationship between Gd^{3+} concentration and the emission intensity of the VIS center can then be understood by realizing that the excitation spectrum of the VIS band center (Fig. 3) has considerable spectral overlap with the $\text{Gd}^{3+} \ ^8\text{S}_{7/2} \rightarrow \ ^6\text{P}_{7/2}$ excitation transition at 315 nm. Therefore, there is a high probability for $\text{Gd}^{3+} \rightarrow$ (VIS center) energy transfer. Consequently, after excitation at 270 nm into the $\text{Bi}^{3+} \ ^1\text{S}_0 \rightarrow \ ^3\text{P}_1$ transition, $\text{Bi}^{3+} \rightarrow \text{Gd}^{3+}$ energy transfer occurs, and excited Gd^{3+} ions then transfer their energy to the VIS center. The Gd^{3+} acts as an intermediate in transferring the energy between Bi^{3+} ions and the VIS emitting center. Obviously, increasing the Gd^{3+} concentration will increase the probability of both $\text{Bi}^{3+}(\text{UV}) \rightarrow \text{Gd}^{3+}$ energy transfer and Gd^{3+} – Gd^{3+} energy migration (the critical concentration for energy migration over the Gd^{3+} sub-lattice in garnets is ~ 0.50 [23]). Energy migration along the Gd^{3+} sub-lattice will increase VIS center emission since the VIS center can trap the migrating energy. Hence, the increase in the intensity of the VIS emitting center under 270 nm excitation with increasing Gd^{3+} concentration in $(\text{Y}_{1-x}\text{Gd}_x)_3\text{Ga}_5\text{O}_{12}:\text{Bi}^{3+}$ can be explained by the energy transfer process of $\text{Bi}^{3+}(\text{UV}) \rightarrow (\text{Gd}^{3+})_n \rightarrow \text{VIS}$ center.

We next address the nature of the VIS center in these garnets. These centers could be similar to visible emitting centers in unactivated gallium based garnets. At low temperatures, undoped YGG and GGG have broad emission bands centered around 420 nm and 470 nm, respectively [18] that can be excited by photons with sub-bandgap energy. These bands are attributed to the recombination of electron (donor) and holes (acceptor) on deep host lattice defect centers. However, these visible emission bands

are strongly quenched at $T > 150$ K. In contrast, the VIS emission from YGG:Bi and GGG:Bi is not quenched at room temperature. In addition, the peak wavelengths of the VIS emission bands in YGG:Bi and GGG:Bi are practically identical unlike in undoped YGG and GGG. Most importantly, the intensity of the visible emission band is strongly correlated to Bi^{3+} concentration (Fig. 4). In YGG:Bi and GGG:Bi, the intensity of the VIS center is strongly related to the Bi^{3+} concentration. At low nominal Bi^{3+} concentrations (0.1%), the broad VIS emission band is strongly reduced. The sharp visible emission lines superimposed on the broad VIS emission in Fig. 4b come from Tb^{3+} impurities in the Gd_2O_3 starting material that trap energy migrating along the Gd^{3+} sub-lattice (Fig. 4b). At higher Bi^{3+} concentrations (1%), the VIS emission band becomes dominant over both the ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ Gd^{3+} and ${}^3\text{P}_{0,1} \rightarrow {}^1\text{S}_0$ Bi^{3+} emission transitions. All of these results indicate that the VIS band is associated with the presence of Bi^{3+} ions in the host lattice, not from a host lattice defect emission.

Ilmer et al. have proposed that this VIS band is the emission from an impurity trapped exciton. It is possible to have both ${}^3\text{P}_{0,1} \rightarrow {}^1\text{S}_0$ and impurity trapped exciton emission in ns^2 luminescence as in $\text{LaOBr}:\text{Bi}^{3+}$ [4], $\text{La}_2\text{Zr}_2\text{O}_7:\text{Bi}^{3+}$ [6], or $\text{CdCl}_2:\text{Pb}^{2+}$ [24]. However, it is unlikely that the VIS emission band is due to an impurity trapped exciton. First, the intensity of the UV and VIS emission is virtually independent of temperature from 20 to 300 K with no intensity exchange between the UV emission and the VIS emission band. This differs from previous reports for ns^2 impurity trapped excitons [4,6,24], where there is an enhancement of the visible exciton emission band at higher temperatures. Second, an impurity-trapped exciton model cannot explain the dependence of the UV/VIS emission intensity ratio with Gd^{3+} concentration (Fig. 2). The behavior of the impurity trapped excitonic state in YGG:Bi

and GGG:Bi should be similar due to the similar host lattice bandgap and ionic radii of Y^{3+} and Gd^{3+} . Finally, as described above, the UV/VIS emission intensity ratio has a strong dependence on the Bi^{3+} concentration (Fig. 4). The relative intensity of the ns^2 impurity-trapped exciton emission and the ${}^3\text{P}_{0,1} \rightarrow {}^1\text{S}_0$ emission should have virtually no dependence on Bi^{3+} concentration [6]. Therefore, we believe that the VIS emission band in gallium garnets is not due to an impurity trapped exciton as previously proposed [3].

Since the VIS emission band intensity is highly Bi^{3+} concentration dependent, it is reasonable to attribute this center to Bi^{3+} pairs or clusters in the host lattice. It has been suggested that ns^2 ions frequently enter the host lattice as pairs or clusters [9–12], and rare earth ion clusters have also been observed in garnets [25]. Bi^{3+} pair/cluster luminescence can also explain the lower energy position of the VIS excitation band (Fig. 3) compared to the UV excitation band. In these pairs/clusters, the 6s and 6p orbitals of neighboring Bi^{3+} ions will overlap with one another forming a band. This shifts the excitation and emission bands to lower energy. The Stokes shift of the visible emission band is $\sim 12,000$ cm^{-1} , considerably higher than the isolated Bi^{3+} ion with considerable broadening of the visible emission band. We postulate that this broadening is due to cooperative intercluster effects [9].

Finally, we note that the results of Ilmer et al. [7] can also be explained using Bi^{3+} pair/cluster luminescence. The actual Bi^{3+} doping levels in the (Y,Gd)GG sintered ceramics used in the experiments of Ilmer et al. was measured at 2.7 mol%, much higher than our nominal compositions. The relatively high Bi^{3+} concentration inevitably increases the concentration of pairs and clusters. $\text{Bi}^{3+} \rightarrow \text{Bi}^{3+}$ energy migration is also likely given the large spectral overlap between Bi^{3+} emission and excitation (Fig. 1). Combining this with the high probability for

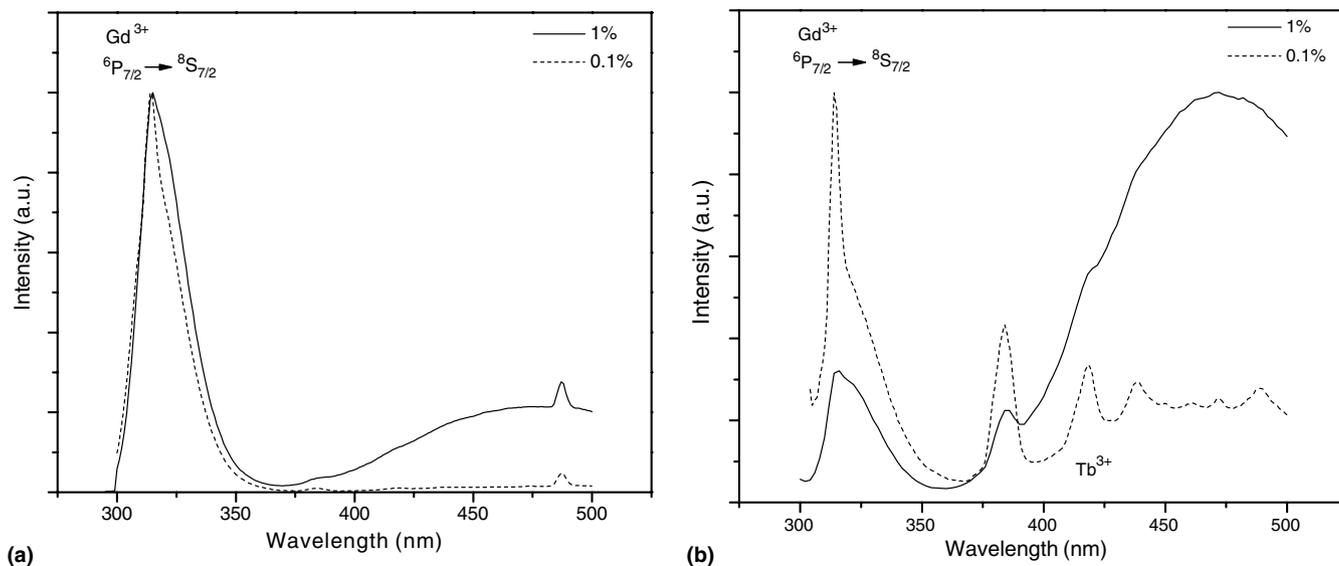


Fig. 4. Emission spectra ($\lambda_{\text{ex}} = 280$ nm) for (a) $(\text{Y}_{0.74}\text{Gd}_{0.25}\text{Bi}_{0.01})_3\text{Ga}_5\text{O}_{12}$ and $(\text{Y}_{0.749}\text{Gd}_{0.25}\text{Bi}_{0.001})_3\text{Ga}_5\text{O}_{12}$ and (b) $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ with Bi^{3+} levels of 0.1% and 1%.

$\text{Bi}^{3+} \rightarrow \text{Gd}^{3+}$ energy transfer and Gd^{3+} energy migration, it seems likely that Ilmer et al. did not observe the UV ${}^3\text{P}_{0,1} \rightarrow {}^1\text{S}_0$ emission in the garnets because of energy transfer from isolated Bi^{3+} ions to a relatively high concentration of Bi^{3+} pairs and clusters. The reasons for Bi^{3+} pair and cluster formation in garnet hosts are not clear and could be related to the synthesis conditions for these materials. These issues are not addressed in this paper.

4. Conclusions

In this paper, we have examined the luminescence of Bi^{3+} within various garnet host lattices. We observe typical ${}^1\text{S}_0 \rightarrow {}^3\text{P}_1$ Bi^{3+} excitation bands and correlate the position of these bands with host lattice composition. Comparison of the Bi^{3+} excitation bands in garnet hosts with other materials leads to the conclusion that the covalency of the $\text{Bi}^{3+}\text{-O}^{2-}$ bond is not especially large in garnet hosts. We also observe UV and visible (VIS) emission bands under ${}^1\text{S}_0 \rightarrow {}^3\text{P}_1$ excitation; the UV emission bands were not reported in the previous report on Bi^{3+} luminescence in garnets and are ascribed to the typical ${}^3\text{P}_{0,1} \rightarrow {}^1\text{S}_0$ emission transition for isolated Bi^{3+} ions. Efficient $\text{Bi}^{3+} \rightarrow \text{Gd}^{3+}$ energy transfer is also observed in these experiments. Finally, we observe a strong Bi^{3+} concentration dependence on the intensity of the VIS band, leading to an assignment of Bi^{3+} pairs and/or clusters emission for the VIS band, not impurity trapped exciton emission. We find no evidence for any interaction between the ${}^3\text{P}_{0,1}$ excited states of Bi^{3+} and the extended states of the garnet conduction band.

Note added in proof

During review of this paper, there have been reports regarding the UV emission of Bi^{3+} in garnet hosts (M. Nikl

et al., *J. Phys. Cond. Matter.* 17 (2005) 3367.) These authors came to the same basic conclusions for the assignment of the UV emission bands in single crystals of $\text{YGG}:\text{Bi}^{3+}$ as ${}^3\text{P}_{0,1} \rightarrow {}^1\text{S}_0$ emission.

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