

LUMINESCENCE OF THE Bi^{3+} ION IN COMPOUNDS LnOCl ($\text{Ln} = \text{La}, \text{Y}, \text{Gd}$)

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ABSTRACT

The luminescence spectra of LnOCl-Bi^{3+} ($\text{Ln} = \text{La}, \text{Y}, \text{Gd}$) are reported. In these compounds two luminescent centers are observed. In LaOCl-Bi^{3+} the luminescence is ascribed to isolated Bi^{3+} ions and to a second, BiOCl -rich, phase. In YOCl-Bi^{3+} and GdOCl-Bi^{3+} the luminescence is ascribed to Bi^{3+} pairs and also to a second, BiOCl -rich, phase. In GdOCl-Bi^{3+} energy transfer from Bi^{3+} to Gd^{3+} is observed.

Introduction

The luminescence properties of the Bi^{3+} ion in LnOCl -type host lattices are known for a long time. Despite the rather simple crystal structure, the luminescence of Bi^{3+} in these lattices appeared to be complicated. The crystal structure of these lanthanide oxychlorides is known to be isomorphous with PbFCl (1). The structure consists of lanthanide-oxygen layers separated by a layer of chloride ions. The trivalent ion is surrounded at one side by four oxygen ions and at the other side by five chloride ions, four of which are in a plane, whereas the fifth is situated on the fourfold axis. There is only one crystallographic site available for the trivalent ion. This site has C_{4v} symmetry.

Swindells (2) observed in LaOCl-Bi^{3+} two emission bands, a UV emission and a blue emission. Blasse and Bril (3) studied the luminescence of Bi^{3+} in LaOCl and YOCl . In YOCl-Bi^{3+} they observed two absorption bands which they ascribed to the $^1\text{S}_0-^3\text{P}_1$ and $^1\text{S}_0-^1\text{P}_1$ transitions. Excitation in the lower level, $^1\text{S}_0-^3\text{P}_1$, did not yield luminescence. These observations, together with the short decay times they measured, made them conclude that the emission originated from the $^1\text{P}_1$ level. Based on this assignment of the $^1\text{P}_1-^1\text{S}_0$ transition for the Bi^{3+} emission in YOCl , Simons (4) made assignments for the Bi^{3+} emission in LaOCl . The UV emission belonged to the $^1\text{P}_1-^1\text{S}_0$ transition and the blue emission to the $^3\text{P}_1-^1\text{S}_0$ transition.

Jacquier (5) studied also the luminescence of Bi^{3+} in LaOCl and YOCl . In both systems he observed several emission and excitation bands with different temperature dependencies. It was suggested that the main excitation in the two phosphors belonged to the same luminescent center. This center is responsible for two emissions: in LaOCl-Bi^{3+} a UV and a blue emission band and in YOCl-Bi^{3+} a broad blue emission band. The real nature of such a center could not be specified. Next to these emissions, he also observed the luminescence

of Bi^{3+} in La_2O_3 and Y_2O_3 in his spectra, which indicates the presence of impurities in the samples.

In this study we describe a reinvestigation of the luminescence properties of Bi^{3+} in lanthanide oxychlorides. In addition to the measurement of emission and excitation spectra we also performed decay time measurements as a function of temperature. For a better understanding of the luminescence of Bi^{3+} in the lanthanide oxychlorides with low concentration of Bi^{3+} , it appeared to be important to study these systems in relation to pure and doped BiOCl . It turns out that the greater part of the emissions described in the literature is not due to isolated Bi^{3+} centers in the oxychlorides.

Experimental

Sample preparation.

The samples were prepared in several ways. LaOCl-Bi^{3+} was prepared by dissolving La_2O_3 (Highways International, 99.99 %) and Bi_2O_3 (Baker) in HCl , evaporating to dryness and firing in air at 800 °C for 5 hours. LaOCl-Bi^{3+} was also prepared by a solid-state reaction. La_2O_3 and Bi_2O_3 were fired in air twice, 6 hours at 700 °C and after grinding 6 hours at 1000 °C. This oxide was converted into oxychloride by the reaction with NH_4Cl (Baker). An excess of ammonium chloride (about 30 %) was used. Because the reaction takes place at low temperatures (6,7), the mixture was fired at 300 °C for one hour. After this the temperature was raised to 800 °C to remove the excess of ammonium chloride and to convert possibly formed LaCl_3 into LaOCl .

GdOCl-Bi^{3+} could also be prepared this way. Because the decomposition of GdOCl starts already at a temperature of about 750 °C (6), the final step of the synthesis took place at a temperature of 500 °C. In the case of YbOCl-Bi^{3+} it was necessary to perform the last firing in moist air, also at a temperature of 500 °C (8,9). BiOCl was prepared by dissolving Bi_2O_3 in HCl , evaporating to dryness and firing in air for two hours at 600 °C. BiOCl was also prepared by the solid-state reaction between Bi_2O_3 and NH_4Cl as described for GdOCl-Bi^{3+} .

All samples were checked by X-ray powder diffraction using $\text{CuK}\alpha$ radiation. The X-ray diffraction patterns did not show the presence of the starting materials or of decomposition products. Only in the case of $\text{Bi}_{1-x}\text{La}_x\text{OCl}$ (with $x > 0.1$) we also observed the presence of LaOCl in the sample.

Apparatus.

The luminescence spectra were recorded using a Perkin-Elmer MPF-3A spectrofluorimeter. Low temperatures were obtained by mounting the sample in an Oxford-CF100 continuous flow cryostat. The excitation spectra were corrected for the lamp intensity and the transmittance of the monochromator with the use of Lumogen T-rot GG as a standard (10).

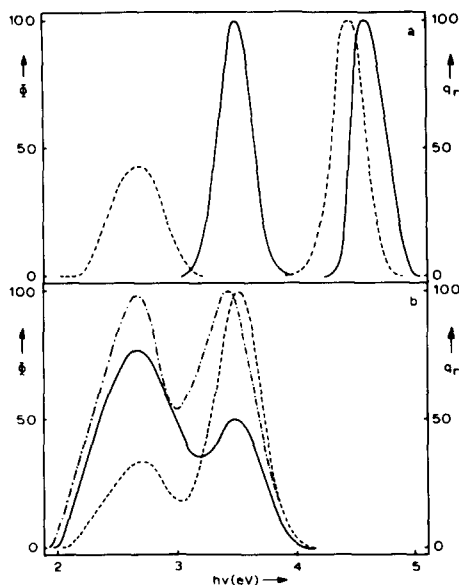
The emission spectra were corrected for the photomultiplier sensitivity. The photon flux per constant energy interval (Φ) is obtained by multiplying the radiant power per constant wavelength interval by λ^3 . The decay time measurements were performed using an EG & G 108Au Xe flashlamp (pulse width $\approx 1 \mu\text{s}$). The detection apparatus has been described in detail elsewhere (11).

Results

LaOCl-Bi^{3+} .

The Bi^{3+} activated LaOCl emits in the ultraviolet and the blue spectral region. The luminescence intensity is high and independent of temperature up

FIG. 1



1a. Emission and excitation spectra of $\text{La}_{0.99}\text{Bi}_{0.01}\text{OCl}$ at 8 K. Broken lines relate to the blue emission, drawn lines to the UV emission. Φ gives the spectral radiant power per constant energy interval in arbitrary units, q_r gives the relative quantum output.

1b. The emission spectra at 8 K of: $\text{La}_{0.99}\text{Bi}_{0.01}\text{OCl}$ (—) prepared by solid-state reaction, $\text{La}_{0.9}\text{Bi}_{0.1}\text{OCl}$ (---) prepared by solid-state reaction and $\text{La}_{0.99}\text{Bi}_{0.01}\text{OCl}$ (-.-) prepared from aqueous HCl. Excitation energy is 4.50 eV.

to 300 K. To the 3.53 eV emission band belongs an excitation band at 4.59 eV and to the 2.65 eV emission band belongs an excitation band at 4.48 eV (fig. 1a). It is possible to excite these emissions separately. This indicates the presence of two luminescent centers. The intensity ratio of these two emission bands depends on the Bi^{3+} concentration and the preparation of the sample (fig. 1b).

Increasing the Bi^{3+} concentration shows an increase of the 2.65 eV emission relative to the 3.53 eV emission. Samples prepared from aqueous HCl show also a stronger 2.65 eV emission relative to the 3.53 eV emission. The position of the emission and excitation bands is almost independent of temperature, in the region of 8 K up to 300 K.

$\text{YOCl}-\text{Bi}^{3+}$.

Two emission bands are observed for $\text{YOCl}-\text{Bi}^{3+}$ (fig. 2). A broad emission around 3.00 eV has its excitation band at 4.87 eV. The intensity of this emission is independent of temperature, in the region of 8 K up to 300 K. The emission band shifts slightly to lower energy at higher temperatures. The other emission band is also broad and peaks around 2.90 eV. The excitation band belonging to this emission is more complex. It consists of two

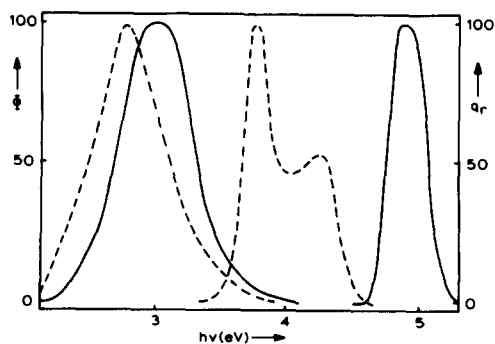


FIG. 2

Emission and excitation spectra of $\text{Y}_{0.998}\text{Bi}_{0.002}\text{OCl}$ at 8 K. See also fig. 1.

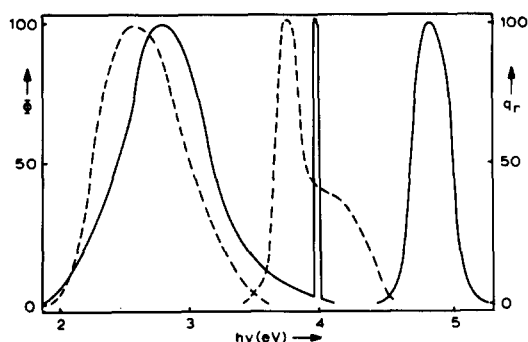


FIG. 3

Emission and excitation spectra of $\text{Gd}_{0.998}\text{Bi}_{0.002}\text{OCl}$ at 8 K. See also fig. 1.

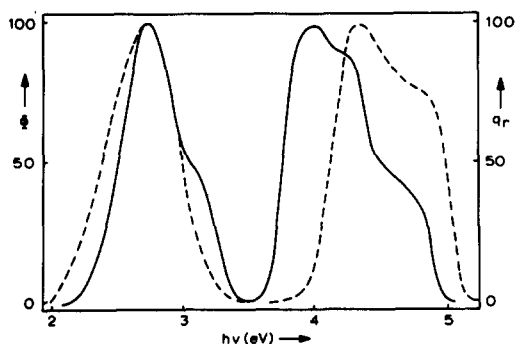


FIG. 4

Emission and excitation spectra of BiOCl (-) and $\text{Bi}_{0.8}\text{La}_{0.2}\text{OCl}$ (--) at 8 K.

at 3.03 eV and at 2.62 eV. The former emission is quenched at about 30 K, the latter at about 70 K. The excitation spectrum is the same for these two bands. It is rather complex (see fig. 4). The introduction of LaOCl into BiOCl has several effects (fig. 4). First the excitation bands shift to higher energy, although the shape of the excitation spectrum does not change. The changes in the emission spectrum are not large. The emission band can be dissolved into two Gaussian bands peaking at 2.62 eV and at 2.23 eV. The 2.62 eV band remains the dominating one. The other major change is the increase of the quenching temperature. In the case of $\text{Bi}_{0.8}\text{La}_{0.2}\text{OCl}$ the emission is quenched at a temperature of about 250 K. These features are also observed for BiOCl containing less LaOCl . Generally the increase of the LaOCl content in BiOCl leads to a continuous shift of the excitation bands to higher energy and an increase of the quenching temperature.

subbands at 4.25 eV and at 3.76 eV. This emission is quenched at 70 K. The intensity of this latter band relative to the former increases for increasing Bi^{3+} concentration. In samples prepared from aqueous HCl , the 2.90 eV emission is also strong relative to the 3.00 eV emission. This situation is comparable with that in LaOCl-Bi^{3+} .

GdOCl-Bi^{3+} .

GdOCl-Bi^{3+} shows the same spectral features as YOCl-Bi^{3+} . Two emission bands are observed (fig. 3). To the emission at 2.79 eV belongs an excitation band at 4.82 eV and to the emission at 2.50 eV belongs an excitation region with maxima at 3.67 eV and 3.98 eV. This is comparable with the YOCl-Bi^{3+} system. There are two differences. Excitation in the 4.82 eV band gives not only the broad emission band at 2.79 eV, but also a line at 3.97 eV. This line is the well-known gadolinium ${}^6\text{P}_{7/2}-{}^8\text{S}_{7/2}$ transition, so that excitation in the bismuth yields also gadolinium luminescence. The other difference with the YOCl-Bi^{3+} system is the quenching temperature. The 2.50 eV emission is quenched at 80 K, but in GdOCl-Bi^{3+} the 2.79 eV emission is quenched at 100 K.

$\text{Bi}_{1-x}\text{La}_x\text{OCl}$ (with $0 \leq x \leq 0.2$).

Pure BiOCl emits in the visible region (fig. 4). The broad emission band can be dissolved into two Gaussian bands peaking

Decay time measurements

The decay time of the emission is temperature dependent in the case of Bi^{3+} in LaOCl and YOCl (fig. 5). The measured decay curves are exponential. The temperature dependence could be analyzed with a three level scheme (12,13) (insert fig. 5). Levels 0, 1 and 2 correspond to the $^1\text{S}_0$, $^3\text{P}_0$ and $^3\text{P}_1$ level of the free Bi^{3+} ion. The Mulliken notation is used in the case of C_{4v} symmetry: $^1\text{A}_1$, $^3\text{A}_2$ and $^3\text{A}_1 + ^3\text{E}$. Excitation takes place in level 2, the transition $^1\text{A}_1 \rightarrow ^3\text{A}_1 + ^3\text{E}$. This transition is partially allowed by spin-orbit interaction. The $^1\text{A}_1 \rightarrow ^3\text{A}_2$ transition is forbidden. Emission is observed from both levels 1 and 2 to level 0 with probabilities $k_1 = \tau_1^{-1}$ and $gk_2 = \tau_2^{-1}$. gk_{12} and k_{21} are the non radiative probabilities between levels 1 and 2, $k_{12} = k_{21} \exp(-\Delta E/kT)$. The degeneracy of level 2 is called g . Assuming $k_2 \gg k_1$ and $k_{21} \gg k_{12}$ the decay time can be expressed as

$$\frac{1}{\tau} = k_1 + g \left(\frac{1}{k_{21}} + \frac{1}{k_2} \right)^{-1} \exp(-\Delta E/kT). \quad (1)$$

The experimental results were fitted to eq.1 with the parameters k_2 and ΔE . The value of k_1 is obtained from the low temperature decay time. In this model we assume that all transition probabilities, except k_{12} , are temperature independent. The parameters deduced from this fit are presented in table I. The decay time of the 2.90 eV emission of YOCl-Bi^{3+} (excitation at 3.76 eV) is about 600 μs at 4.2 K. This decay time does not change much until the quenching of the emission. The decay curve of BiOCl is not a single exponential at 4.2 K. The decay curve can be analysed as a two exponential decay curve. This results in two decay times, 100 μs and 670 μs . The decay time of the 2.74 eV emission in GdOCl-Bi^{3+} is about 7 μs , at 4.2 K. Up to 40 K this decay time decreases to 5 μs . Above this temperature quenching of the emission starts.

Table I

Parameters deduced from the fit
of the temperature dependent decay times to eq.1.

Host lattice	emission (eV)	k_1 (s^{-1})	gk_2 (s^{-1})	ΔE (eV)
LaOCl	3.53	$(425 \pm 5) \times 10$	$(9 \pm 2) \times 10^9$	$(68 \pm 4) \times 10^{-3}$
YOCl	3.00	$(92 \pm 2) \times 10^2$	$(75 \pm 4) \times 10^4$	$(49 \pm 4) \times 10^{-4}$

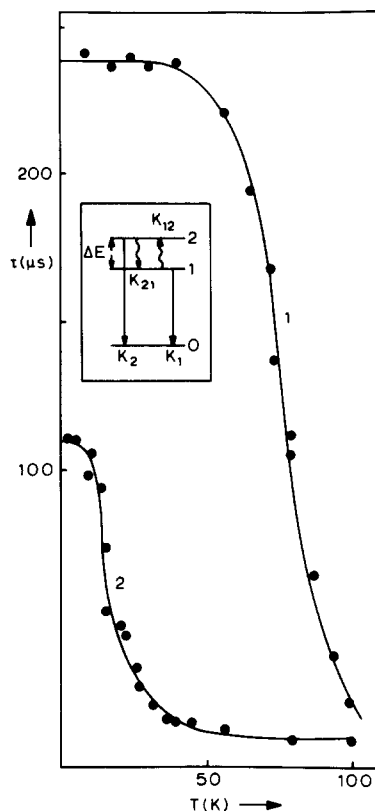


FIG. 5

The decay times of the 3.53 eV emission of $\text{La}_{0.99}\text{Bi}_{0.01}\text{OCl}$ (1) and of the 3.00 eV emission of $\text{Y}_{0.998}\text{Bi}_{0.002}\text{OCl}$ (2) as a function of temperature. The solid lines give the best fit of the experimental data to eq. 1. The three-level scheme (insert) is discussed in the text.

Discussion

LaOCl-Bi³⁺

In all the compounds studied only one lattice site is available for the Bi³⁺ ion. Yet at least two excitation and emission bands are observed. This implies that there are at least two different luminescent centers. A probable explanation for this is clustering of the Bi³⁺ ions. In that case it is obvious that the 3.53 eV emission belongs to the isolated Bi³⁺ ion and the 2.65 eV emission to Bi³⁺ clusters. The 3.53 eV emission has the characteristics of Bi³⁺ luminescence (12,13,14,15). At low temperature the forbidden transition $3P_0-1S_0$ ($3A_2-1A_1$) occurs and at higher temperature the partially allowed transition $3P_1-1S_0$ ($3A_2, 3E-1A_1$). The value of the Stokes shift (1.06 eV) and the energy difference between the $3A_2$ and $3A_1, 3E$ level (68 meV) are in agreement with the data reported by Blasse and Van der Steen (14).

The 2.65 eV emission belongs to a cluster of Bi³⁺ ions. The intensity of this emission increases when the Bi³⁺ concentration is increased. Further it depends on sample history. From the luminescence properties of pure and doped BiOCl we can get an indication about this type of luminescent center. In pure BiOCl the excitation peaks at about 3.95 eV, but in Bi_{0.8}La_{0.2}OCl at about 4.3 eV. The main emission is around 2.62 eV. This shows much resemblance with the 2.65 eV emission in LaOCl-Bi³⁺, which has its excitation band at about 4.45 eV. This emission can be from a BiOCl-rich phase, containing a certain amount of LaOCl, probably more than 20 %. We conclude therefore that the solubility of BiOCl in LaOCl is very small, because even at low Bi³⁺ concentrations the other phase is observed. The solubility of LaOCl in BiOCl is much greater.

The low solubility of BiOCl in LaOCl is not so surprising, when the cell parameters are taken into account. The cell parameters are gathered in table II.

Table II
Crystallographic data of the compounds studied (1)

compound	a (Å)	c (Å)	c/a	radius Ln ³⁺ ion a) (Å)
LaOCl	4.119	6.883	1.67	1.18
YOCl	3.903	6.597	1.69	1.02
GdOCl	3.950	6.672	1.69	1.06
BiOCl	3.891	7.369	1.89	1.11

a) The effective ionic radius in eight coordination (24).

The main difference between BiOCl and LnOCl is the c/a ratio. In BiOCl this ratio is 1.89, while in LnOCl it is about 1.68. Ln³⁺ ions have the Xe configuration, but Bi³⁺ has 6s² configuration. Probably this 6s² configuration is mixed with a 6s6p configuration, leading to a non-spherical charge distribution. This can be seen as a kind of polarisation of the cation. This polarisation leads to a repulsion between the Bi³⁺ ion and the chloride layer because of the greater electronegativity of the oxygen on the other side of the Bi³⁺ ion. This results in an elongation of the lattice along the c axis. This bonding difference may be responsible for the low solubility of BiOCl in LaOCl.

In conclusion, the UV emission is ascribed to the Bi³⁺ ion in LaOCl and the blue emission to a second, BiOCl-rich, phase. Such an effect has been overlooked by earlier investigators.

YOC1-Bi³⁺

The 2.90 eV emission with its low-energy excitation at 3.76 eV and 4.25 eV shows resemblance with the luminescence of pure BiOCl. Especially the position of the emission bands agree well. But this is not the only agreement, because the quenching temperatures are almost the same (70 K) and the decay times of the emission are comparable. In YOC1-Bi³⁺ 600 μ s in case of the 2.90 eV emission and in BiOCl a long component of about 670 μ s. So it seems that the 2.90 eV emission in YOC1-Bi³⁺ is almost the emission of pure BiOCl. This leads to the conclusion that we are dealing with a second, BiOCl-rich, phase so that the solubility of YOC1 in BiOCl is very low.

The interpretation of the 3.00 eV emission in YOC1-Bi³⁺ is more difficult. The Stokes shift of this luminescence is about 1.87 eV. In the case of the isolated Bi³⁺ ion in LaOCl the Stokes shift is about 1.06 eV. On replacing the La³⁺ in the host lattice by Y³⁺ the Stokes shift is expected to decrease. This is what is generally observed (14), for example in LiLnO₂ and NaLnO₂ (with Ln = Sc, Y, La, Gd, Lu) (16) or LnBO₃ (Ln = Sc, Y, La, Lu) (17). Another difference with the LaOCl-Bi³⁺ system is the high-temperature decay time. The probability of the transition from level 2 to level 0 (insert fig. 5) is roughly 10⁴ times smaller for YOC1-Bi³⁺ than for LaOCl-Bi³⁺. These differences are usually much smaller. In NaLaO₂ and NaYO₂, for example (16), it is about seven times. These observations lead to the conclusion that in the case of YOC1-Bi³⁺ we are not dealing with isolated Bi³⁺ ions. It may be that the Bi³⁺ ions enter the lattice in pairs. The shortest Y-Y distance in the lattice is about 3.64 Å. This value can be computed from the lattice parameters (1) and the interionic distances (18,19). So the Bi³⁺ ions can influence each other. We did not succeed in preparing YOC1-Bi³⁺ with "isolated" Bi³⁺ ions, i.e. with Bi³⁺ ions which show a luminescence which is comparable with the UV emission of LaOCl-Bi³⁺.

Table II suggests that the favorable pairing of Bi³⁺ ions in YOC1 is not only related to the different c/a ratio of YOC1 and BiOCl, but also to the relatively small ionic radius of the Y³⁺ ion. Luminescence from Bi³⁺ pairs, with comparable characteristics was also observed in LaBO₃ (17), where it will be discussed in more detail.

In conclusion, the luminescence properties of YOC1-Bi³⁺ suggest that the solubility of BiOCl in YOC1 is very small and that the (few) Bi³⁺ ions present in YOC1 show a strong tendency to cluster.

GdOCl-Bi³⁺

The position of the excitation and emission bands in GdOCl-Bi³⁺ is comparable with these of the YOC1-Bi³⁺ system. The 2.79 eV emission could be emission from Bi³⁺ pairs and the 2.50 eV emission could be emission from BiOCl containing some GdOCl. The ionic radii of Y³⁺ and Gd³⁺ do not differ much and are smaller than that of Bi³⁺ (see table II). Yet there is a major difference with the YOC1-Bi³⁺ system. The quenching of the 2.79 eV emission occurs at much lower temperature, viz. about 100 K. Excitation in the Bi³⁺ pair (4.82 eV) yields also Gd³⁺ luminescence. This seems to suggest energy transfer from Bi³⁺ to Gd³⁺. However, under this excitation also the Gd³⁺ ⁶D levels are excited. At least part of the Gd³⁺ emission is, therefore, due to direct Gd³⁺ excitation. This means that at 8 K only a very small amount of the Bi³⁺ excitation energy is transferred to Gd³⁺, viz. a few percent. At higher temperatures, however, the Bi³⁺→Gd³⁺ transfer becomes more efficient, resulting in quenching of the Bi³⁺ emission. Energy migration in the Gd³⁺ subsystem is known to be efficient. This has been demonstrated in several systems, for example GdF₃ (20) and GdAl₃B₄O₁₂ (21). The limiting step in the energy transfer process is, therefore, the energy transfer from the Bi³⁺ ion to the Gd³⁺ ion. The energy transfer from Gd³⁺ to Gd³⁺ is very efficient, because of the large spectral

overlap and the short Gd-Gd distance (about 3.90 Å). Quenching of the Bi^{3+} emission is due to energy transfer from Bi^{3+} to Gd^{3+} , and via Gd^{3+} to killer sites. This could be substantiated in studying $\text{GdOCl-Bi}_x\text{X}$, where X is a luminescent rare earth ion, which can trap the excitation energy which migrates among the Gd^{3+} sites. In the quenching region of the Bi^{3+} luminescence, the intensity of the X luminescence increases, if excitation is in the Bi^{3+} excitation band.

Another difference between GdOCl-Bi^{3+} and YOC1-Bi^{3+} is the decay time of the 2.79 eV emission of GdOCl-Bi^{3+} . Even at low temperature (4.2 K) this decay time is relatively short, viz. about 7 μs . Since energy transfer from Bi^{3+} to Gd^{3+} can be neglected at this temperature, this value presents a radiative life time. Such a short decay time was also observed for $\text{Gd}_2\text{O}_3\text{-Bi}^{3+}$ (22), LiGdO_2 (16) and NaGdO_2 (16). It has been suggested that the Gd^{3+} ion causes a magnetic field at the Bi^{3+} ion site. The $^3\text{P}_0$ and $^3\text{P}_1$ levels will be mixed by this effect (23), resulting in an increase of the $^3\text{P}_0\text{-}^1\text{S}_0$ transition probability and a shorter decay time.

In conclusion we note that only the data on the UV emission of LaOCl-Bi^{3+} give information on the luminescence of isolated Bi^{3+} ions in lanthanide oxychlorides. The properties of the corresponding bromides will be discussed in a forthcoming paper.

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