The Gd^{3+} Luminescence in Lanthanide Hydroxycarbonate ($LnOHCO_3$) and Hydrated Carbonate ($Ln_2(CO_3)_3 \cdot 6H_2O$)

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Abstract

The X-ray excited emission of Gd^{3+} in $YOHCO_3$:Gd and $Gd_2(CO_3)_3 \cdot 6H_2O$ is reported. The vibronic lines due to coupling with the carbonate, the hydroxyl and the water vibrations are discussed.

Introduction

Recently we have reported the vibronic emission of the Gd^{3+} ($4f^7$) ion in a large number of host lattices [1]. The intensities of the vibronic emission lines belonging to the $^6P_{7/2} \rightarrow {}^8S$ emission transition have been qualitatively discussed [2]. In the case of $Y(OH)_3$:Gd it was possible to analyse the vibronic intensity quantitatively [3]. This analysis relates to the cooperative vibronic emission line in which the electronic transition is on the Gd^{3+} ion ($^6P_{7/2} \rightarrow {}^8S$) and the vibrational transition on the OH^- group (OH^- stretching mode).

In ref. 1 vibronic lines due to coupling with carbonate vibrations were reported for $BaCO_3$:Gd. The aim of the present study was to investigate emission spectra of Gd^{3+} in a mixed coordination containing CO_3^{2-} as well as OH^- or H_2O. For this purpose we selected $YOHCO_3$:Gd, $GdOHCO_3$ and $Gd_2(CO_3)_3 \cdot 6H_2O$. The crystal structure of the former is of the bastnaesite type [4], that of the hydrated carbonate is unknown [5].

Experimental

Samples were prepared as follows.

The Hydroxycarbonates

These compounds were obtained inadvertently when attempting to prepare single crystals of the rare earth carbonates by a hydrothermal high pressure procedure described in ref. 6. The nominal Gd concentration in $YOHCO_3$ was 2 mol.%. The obtained material was indexed and refined in the $P\bar{6}2c$ space group of bastnaesite [4] and yielded the following parameters: $a = 11.947(3)$, $c = 9.688(4)$ Å; $\gamma = 120°$.

The Carbonate Hydrates

While Sungur and Kizilyalli [5] used the thermal decomposition of the trichloroacetate as a procedure to make $Gd_2(CO_3)_3 \cdot nH_2O$, we found that the precipitation of the rare earth carbonates from nitrate solutions with a boiling solution of excess $(NH_4)_2CO_3$ reproducibly yielded $Ln_2(CO_3)_3 \cdot 6H_2O$, at least for the cases of Ln = Pr, Sm, Eu, Gd, Tb and Dy. We indexed the pattern of $Tb_2(CO_3)_3 \cdot 6H_2O$ in the orthorhombic space group $I222$, suggested by Sungur and Kizilyalli [5], and obtained the following refined parameters: $a = 6.140(2)$, $b = 9.265(4)$, $c = 15.236(4)$ Å; $V = 866.8(4)$ Å^3. This space group has to be considered as tentative. Only a detailed structure determination on a single crystal will allow final structural characterization. The assignment of six water molecules of hydration is based on repeated TGA measurements with a Du Pont 1090 B thermal analyzer. For $Gd_2(CO_3)_3 \cdot 6H_2O$ the calculated loss of all CO_2 and H_2O is 39%. Weight loss found between 600 and 1030 °C was (40 ± 0.5)%.

The performance of the optical measurements has been described in previous papers [1, 3].

Results and Discussion

(a) The Hydroxycarbonates

$YOHCO_3$:Gd

Under X-ray excitation the samples of $YOHCO_3$:Gd show an intense luminescence of a complicated character. Figure 1 shows the emission spectrum. The $^6P_{7/2} \rightarrow {}^8S$ emission line is dominating, but there are many weaker features present. They have been tabulated in Table 1. There is a thermally activated

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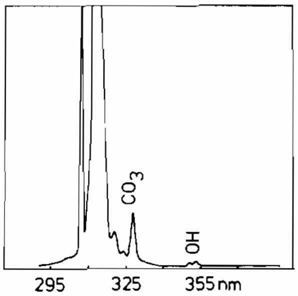

Fig. 1. Emission spectrum of $YOHCO_3$:Gd under X-ray excitation at 300 K.

TABLE 1. The Gd^{3+} emission spectrum of $YOHCO_3$:Gd at 300 K (see also Fig. 1)

Position emission feature (cm^{-1})	Assignment	Infrared frequency (cm^{-1}) [a]
32.545	$^6P_{5/2} \rightarrow {}^8S$	
31.950	$^6P_{7/2} \rightarrow {}^8S$ (e)	
31.225	(e)–725; $\nu_4(CO_3^{2-})$	720
30.890	(e)–1060; $\nu_1(CO_3^{2-})$	1090
30.490	(e)–1460; $\nu_3(CO_3^{2-})$	1450
28.510	(e)–3440; $\nu(OH^-)$	3475
28.290	(e)–3660; $\nu(OH^-)$	3620

[a] Derived from the infrared absorption spectrum of $NdOHCO_3$ [7].

$^6P_{5/2} \rightarrow {}^8S$ electronic emission line and a couple of weaker vibronic lines. Their assignment is given in Table 1. Use has been made of the infrared spectrum of isomorphous $NdOHCO_3$ reported by Dexpert *et al.* [7].

These vibronic lines are cooperative in nature. They are due to coupling between the $^6P_{7/2} \rightarrow {}^8S$ electronic transition and vibrational transitions on the carbonate group and the hydroxyl group. The intensities of these lines decrease in the sequence $\nu_3(CO_3^{2-}) > \nu_2(CO_3^{2-}) > \nu(OH^-) > \nu_1(CO_3^{2-})$, where the vibronic lines are indicated by the coupling vibrational mode. The same sequence is found for the intensities of the respective vibrational transitions in the infrared spectrum [7]. This is satisfying, since the expression for the vibronic emission intensity contains the matrix element which measures the infrared intensity [2]. Actually the vibronic line with the Raman-active $\nu_1(CO_3^{2-})$ is completely forbidden. The corresponding feature in Fig. 1 and Table 1 is considered to be a classical Franck-Condon replica [2].

The presence of two vibronic lines due to coupling with the OH^- vibration is due to the presence of two crystallographic sites for OH^- in the crystal structure [4].

The intensity of the vibronic lines is extremely weak. As before, we characterize this intensity by a factor *r* which gives the integrated intensity relative to that of the parent electronic transition. The total *r* for the hydroxide vibronics is ~0.1%, and for the carbonate vibronics ~1%. In $Y(OH)_3$:Gd the *r* value is ~0.2% [3], in $BaCO_3$:Gd ~1.5% (derived from data reported in ref. 1).

The lower *r* value for the hydroxide vibronics in the case of $YOHCO_3$:Gd can be ascribed to the lower number of OH^- groups around Gd^{3+} (3 in the $YOHCO_3$ structure against 9 in the $Y(OH)_3$ structure). The expression for the intensity contains this number in a factor which comprises also the charge, the polarizability and the radius of the ligand [2].

In $BaCO_3$:Gd the Gd^{3+} ion is coordinated by nine oxygens belonging to carbonate groups, in $YOHCO_3$:Gd by eight, so that the difference between the *r* values, which may be small anyhow in view of the inaccuracy, cannot be explained from the number of coordinating ligands. It may be that the excess positive charge of Gd^{3+} relative to Ba^{2+} plays a role in determining the value of the polarizability [2].

The fact that the *r* value in the case of $YOHCO_3$:Gd is an order of magnitude larger for the carbonate than for the hydroxide group is for an important part due to the fact that the intensity of the infrared bands involved is more than an order of magnitude larger for the CO_3^{2-} than for the OH^- group [7].

$GdOHCO_3$

The emission spectrum of $GdOHCO_3$ under X-ray excitation is given in Fig. 2. It shows an overview of the total spectrum. The emission of $GdOHCO_3$ consists only partly of Gd^{3+} emission. There is also a broad band emission in the visible and Tb^{3+} $^5D_4$ emission. The integrated intensity ratio Gd^{3+}:band:Tb^{3+} is about 10:2:1.5. The Tb^{3+} ions are present as an impurity in the starting material Gd_2O_3 (99.99%, Rhône-Poulenc). This shows that in $GdOHCO_3$ energy migration occurs over the Gd^{3+} ions to Tb^{3+} ions [8, 9].

Obviously the migrating energy is also trapped by the broad-band emitting centre. This might be OH^- or H_2O on the surface as observed also for the $[Gd \subset 2.2.1]^{3+}$ cryptate containing $[Tb \subset 2.2.1]^{3+}$ [10].

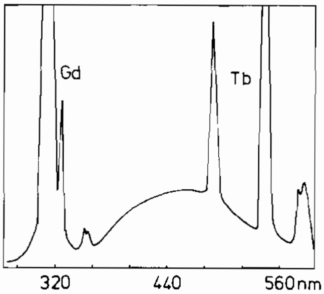

Fig. 2. Emission spectrum of $GdOHCO_3$ under X-ray excitation at 300 K. The lines in the visible are due to Tb^{3+}.

It is interesting to note the complete absence of Tb^{3+} $^5D_3$ emission. Cross relaxation can be ruled out in view of the very low Tb^{3+} concentration. The non-radiative $^5D_3$–$^5D_4$ transition will be very fast due to the presence of vibrating species with very high frequencies in close proximity. The energy gap between the $^5D_3$ and $^5D_4$ levels is about 5.500 cm^{-1} which is only slightly more than $\nu_3(CO_3^{2-}) + \nu(OH^-)$ (see Table 1).

$Gd_2(CO_3)_3 \cdot 6H_2O$

The compound $Gd_2(CO_3)_3 \cdot 6H_2O$ shows an intense emission under X-ray excitation at 300 K. Figure 3 shows the spectrum of the Gd^{3+} emission and Table 2 an analysis of the lines. Figure 4 shows an overall emission spectrum with dominating Tb^{3+} emission.

The interpretation of the Gd^{3+} vibronic emission lines is straight forward (Table 2). There is coupling with the vibrational modes of H_2O and CO_3^{2-}, and with the Gd–ligand mode. Although the crystal structure of $Gd_2(CO_3)_3 \cdot 6H_2O$ is unknown, the emission pattern shows that the Gd^{3+} ion is coordinated by carbonate ions and by one or more water molecules.

The ratio *r* amounts to 1% (H_2O), 2% (CO_3^{2-}) and a few % (Gd–O). The latter value cannot be determined with any accuracy, since there is overlap with the intense parent electronic transition. The *r* value for the water vibronics is an order of magnitude larger than for the hydroxyl vibronics as discussed before [2, 3]. Further discussion is difficult in view of the lack of structural data.

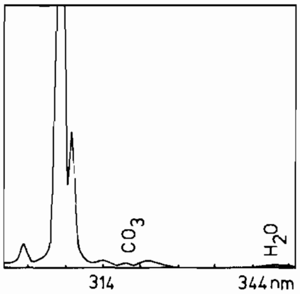

Fig. 3. Gd^{3+} emission of $Gd_2(CO_3)_3 \cdot 6H_2O$ under X-ray excitation at 300 K.

TABLE 2. The Gd^{3+} emission spectrum of $Gd_2(CO_3) \cdot 6H_2O$ at 300 K (see also Fig. 3)

Position emission feature (cm^{-1})[a]	Assignment	Infrared frequency (cm^{-1})[b]
32.545	$^6P_{5/2} \rightarrow {}^8S$	
31.925	$^6P_{7/2} \rightarrow {}^8S$ (e)	
31.745 (sh)	(e)–180; ν(Gd–O)	
31.200	(e)–725; $\nu_4(CO_3^{2-})$	720
30.865	(e)–1060; $\nu_1(CO_3^{2-})$	1070
30.555	(e)–1370; $\nu_3(CO_3^{2-})$	1380
~30.400 (sh)	(e)–1525; $\nu_b(H_2O)$	1525
28.775 (br)	(e)–3150; $\nu_s(H_2O)$	3120

[a] sh: shoulder, br: broad. [b] After ref. 5 and own measurements.

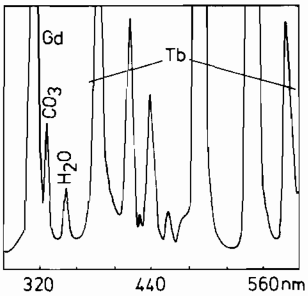

Fig. 4. Emission spectrum of $Gd_2(CO_3)_3 \cdot 6H_2O$ under X-ray excitation at 300 K. The lines at $\lambda \geq 380$ nm are due to Tb^{3+}.

It was observed that the carbonate loses water upon heating (see above). Simultaneously a decrease of the intensity of the water vibronic line was observed, in agreement with the present assignment.

Figure 4 shows that the greater part of the emission of $Gd_2(CO_3)_3 \cdot 6H_2O$ under X-ray excitation does not originate from Gd^{3+}, but from Tb^{3+}. The ratio of Gd^{3+} to Tb^{3+} emission is about 1:2. This shows that the energy migration over the Gd^{3+} sublattice is very efficient (see above). The Gd–Gd distances in the crystal lattice must be relatively short (<4 Å, see ref. 11).

The greater part of the Tb^{3+} emission is from the $^5D_4$ level (~75%). This points to non-radiative $^5D_3 \rightarrow {}^5D_4$ decay which is again an indication that H_2O molecules are directly coordinated to the lanthanide ion. This was confirmed by the fact that the emission intensity of $Eu_2(CO_3)_3 \cdot 6H_2O$ is an order of magnitude weaker. This can be ascribed, among others, to non-radiative $^5D_0 \rightarrow {}^7F_6$ decay due to interaction with the water vibrations (see, for example, ref. 9).

Conclusions

The Gd^{3+} emission spectra of $YOHCO_3$:Gd and $Gd_2(CO_3)_3 \cdot 6H_2O$ show vibronic lines due to coupling with vibrational modes of the carbonate ion, the hydroxyl ion and the water molecule. The intensity of the hydroxyl vibronics is weak. The vibronic intensities can be qualitatively understood from existing theories.

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