

Spectroscopy of Gd^{3+} and Eu^{3+} in the Calcite Structure

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The spectroscopy of Gd^{3+} in the compounds with calcite structure $ScBO_3$ and $CaCO_3$ is discussed. In $ScBO_3$, the Gd^{3+} ion replaces the smaller Sc^{3+} ion without distorting the inversion symmetry of the cation site. This is confirmed by measuring the spectroscopy of Eu^{3+} -doped $ScBO_3$. Transition probabilities are hard to derive for $ScBO_3:Gd^{3+}$ due to the presence of an impurity of unknown nature. In $CaCO_3$ the Gd^{3+} ion replaces the less charged Ca^{2+} ion. The charge compensation removes the inversion symmetry of the cation site, as is shown more clearly for $CaCO_3:Eu^{3+}$. Local charge compensation is dominant, but three sites with charge compensation at remote distance are observed as well. © 1992 Academic Press, Inc.

1. Introduction

In recent studies measurements of the vibronic emission transitions of Gd^{3+} and Eu^{2+} in several host lattices have been reported (1–5). Usually, the intensity of these vibronic transitions is weak, i.e., $\approx 1\%$ of the zero-phonon line. However, in some cases the intensities can be much higher (1, 3, 4). Actually, one must compare the electronic transition probability of the zero-phonon line and the vibronic transition probabilities. This is possible if decay measurements have been performed. For the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} in different host lattices, the vibronic transition probability, A_{vib} , differs by two orders of magnitude. The smallest value for A_{vib} is found for Gd^{3+} in LaF_3 , viz. 2 s^{-1} ; the largest value is found for Gd^{3+} in $YOCl$, viz. 114 s^{-1} . For Eu^{2+} , which is isoelectronic with Gd^{3+} , even higher values are found (5).

The differences in A_{vib} are ascribed to the

influence of the surroundings of Gd^{3+} . The polarizability of the ligands is, in this case, the main parameter. The difference between Gd^{3+} and Eu^{2+} is ascribed to the much lower position of the opposite parity configuration of Eu^{2+} .

Here we report results on the Gd^{3+} emission and its vibronic contribution for Gd^{3+} in the calcite structure. The cation site has inversion symmetry (S_6). $ScBO_3$ and $CaCO_3$ were used. The latter needs charge compensation. This will give rise to different sites (6–8).

In addition the Eu^{3+} luminescence in these host lattices was studied to check whether the site of the larger lanthanide ion still has inversion symmetry. For Eu^{3+} on a site with inversion symmetry only the magnetic-dipole (MD) transition ${}^5D_0 \rightarrow {}^7F_1$ will be observed in emission. Due to the selection rules for vibronic transitions (9, 10) this transition is not accompanied by vibronic transitions. The electric-dipole

(ED) transition ${}^5D_0 \rightarrow {}^7F_2$ is strictly forbidden as a purely electronic transition for such a Eu³⁺ site, so the position of the origin of the vibrational structure is unknown. Neither is this transition suitable for studying vibronic lines, mainly because of the overlap of the vibronic lines with other electronic transitions such as ${}^5D_0 \rightarrow {}^7F_3$ (11). Therefore, we do not compare the Eu³⁺ and Gd³⁺ vibronic spectra.

After the Gd³⁺-doped samples and the Eu³⁺-doped samples are prepared in a similar way, the latter are used to see whether the inversion symmetry of the cation site is conserved when Sc³⁺ and Ca²⁺ are replaced by a lanthanide ion. Here we make use of the fact that Gd³⁺ and Eu³⁺ have nearly the same size.

2. Experimental

2.1. Sample Preparation

Measurements are performed on crystalline powders with a dopant concentration of 0.1 mole%. The samples are checked by X-ray diffraction using CuK α radiation and by measuring the diffuse reflection spectrum. The borates are prepared using a method described in (12). The X-ray dia-

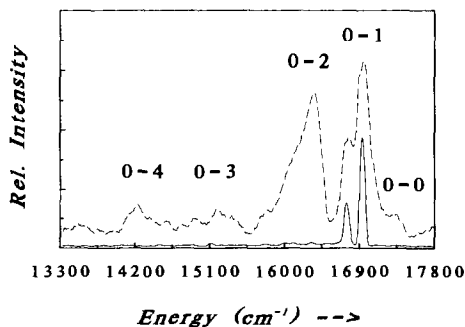


FIG. 1. Emission spectrum of Eu³⁺ in ScBO₃ at 4.2 K. Excitation is at 37,000 (upper spectrum) and at 43,500 cm⁻¹ (lower spectrum). The labels 0-*J* (*J* = 0-4) indicate the ${}^4D_0 \rightarrow {}^7F_J$ transitions. The upper spectrum is magnified by a factor of 100. See text.

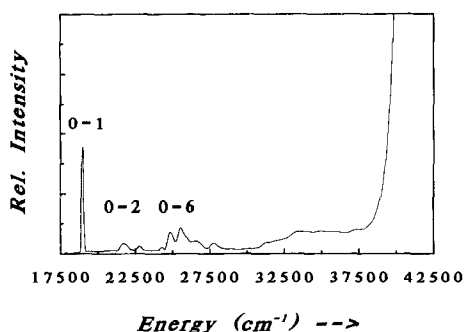


FIG. 2. Excitation spectrum of the ${}^5D_0 \rightarrow {}^7F_1$ emission of Eu³⁺ in ScBO₃ at 4.2 K. The labels 0-1, 0-2, and 0-6 indicate the ${}^7F_0 \rightarrow {}^5D_1$, 5D_2 , and 5L_6 transitions.

grams give no indication of the presence of a second phase. The carbonates are prepared using the "nonfiring" method described by Donker *et al.* in (13). The X-ray diffraction diagrams show only the calcite phase.

2.2. Optical Instrumentation

The Eu³⁺ spectra have been measured on a Spex Fluorolog and a Perkin-Elmer MPF-44B spectrofluorometer (14). The Gd³⁺ spectra have been measured on a frequency-doubled dye laser system, described in (4).

3. Results and Discussion

3.1. ScBO₃

We first briefly discuss the spectroscopy of Eu³⁺ in ScBO₃. Avella (15, 16), Hintzen (17), and Blasse and Dirksen (18) have reported earlier on this system.

After excitation into the charge transfer (C.T.) state at 43,500 cm⁻¹, the emission spectrum shows only the ${}^5D_0 \rightarrow {}^7F_1$ transition (Fig. 1). It is split in two crystal field components in agreement with S_6 site symmetry. The excitation spectrum of the ${}^5D_0 \rightarrow {}^7F_1$ emission is shown in Fig. 2. The MD transition ${}^7F_0 \rightarrow {}^5D_1$ yields the strongest line excitation. In the region of the (ED) ${}^7F_0 \rightarrow {}^5D_2$, 5L_6 transitions, only vibronic structures are observed.

The absence of forced ED transitions in emission as well as in excitation and the dominating ${}^5D_0 \rightarrow {}^7F_1$ emission after C.T. excitation indicate that the observed Eu^{3+} ions are at a site with inversion symmetry. These are Eu^{3+} ions that occur on a Sc^{3+} site without distorting the site symmetry of the cation site. The widths of the lines are relatively large. Due to the low Eu^{3+} concentration and the low intensity of the excitation lamp at $43,500 \text{ cm}^{-1}$ we had to open the slits of the monochromator, which decreases the resolving power significantly.

After excitation at $37,000 \text{ cm}^{-1}$ or into the 5L_6 term level, an emission spectrum is observed in which the ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 2,$ and 4) transitions dominate (Fig. 1). The excitation spectrum of these emissions shows that the corresponding C.T. state has moved to lower energy. The emission spectrum shows that there is a considerable deviation from inversion symmetry for the Eu^{3+} ions under consideration. The line widths of the emission lines observed after excitation via the ${}^7F_0 \rightarrow {}^5L_6$ transition are much larger than those measured after excitation at $43,500 \text{ cm}^{-1}$. This indicates that part of the Eu^{3+} ions is incorporated into a borate glass phase. The site symmetry of these Eu^{3+} ions

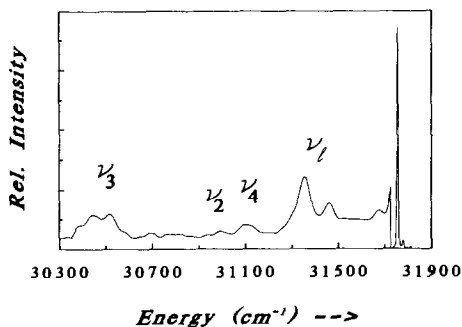


FIG. 3. Emission spectrum of Gd^{3+} in ScBO_3 at 4.2 K. The weak zero-phonon line at $31,777 \text{ cm}^{-1}$ is from Gd^{3+} in a borate glass phase. The vibronic spectrum is magnified by a factor of 100. The features indicated by ν_i indicate the Gd-(BO_3) vibration. See also text.

TABLE I
VIBRATIONAL STRUCTURE IN THE ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$
EMISSION TRANSITION OF Gd^{3+} IN ScBO_3 AT 4.2 K

Position	$\hbar\omega_{\text{vib}}$	IR data for ScBO_3 (19)	Raman data for ScBO_3 (20)
31,676	80		
31,461	295	{ 262 285	247
31,354	402	422	398
31,095	660	637	639
30,993	760	{ 740 764	923
{ 30,520 30,446	{ 1236 1310	{ 1200 1220 1240 1260	1220

is lowered and forced ED transitions appear. Therefore they can be excited selectively in the ${}^7F_0 \rightarrow {}^5L_6$ transition. From a comparison of the intensities of the MD ${}^5D_0 \rightarrow {}^7F_1$ transitions we estimate that less than 1% of the Eu^{3+} ions is in the glass phase.

We now turn to the spectroscopy of $\text{ScBO}_3 : \text{Gd}^{3+}$. The emission spectrum in the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ region is given in Fig. 3. The position of the main zero-phonon line is $31,756 \text{ cm}^{-1}$. The temperature-independent weak line at $31,777 \text{ cm}^{-1}$ shows a different excitation spectrum from the main line at $31,756 \text{ cm}^{-1}$. Therefore it is ascribed to Gd^{3+} in a borate glass phase. At energies lower than the zero-phonon line, vibronic lines are observed (Fig. 3). The ratio r of the integrated vibronic intensity to the integrated zero-phonon line intensity amounts to $r = 0.05$. Vibronic lines are observed from 300 to 1260 cm^{-1} from the zero-phonon line. The positions are to be compared with the frequencies of the strongest infrared (IR) active vibrations of ScBO_3 (19). These frequencies are summarized in Table I. For completeness the Raman frequencies (20) are also mentioned in the table.

The ν_3 (B-O stretching) vibration around

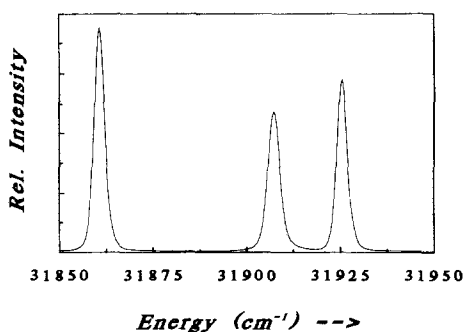


FIG. 4. Excitation spectrum of the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ emission at $31,756 \text{ cm}^{-1}$ of Gd^{3+} in ScBO_3 at 4.2 K.

1280 cm^{-1} and the ν_2 and ν_4 (B–O bending) vibrations of the borate group at 760 and 660 cm^{-1} , respectively, are indicated in Fig. 3. The stretching of $\text{Gd}^{3+}\text{--BO}_3$ is also indicated. The relative positions of the vibronic lines are a little higher than the values of the corresponding IR active vibrations. This reflects the change in bonding when replacing Sc^{3+} by Gd^{3+} .

The excitation spectrum in the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ region of the main ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ emission line is given in Fig. 4. Three crystal field (c.f.) components are observed at $31,860$, $31,906$, and $31,924 \text{ cm}^{-1}$. The ${}^6P_{7/2}$ term level is henceforth split into four crystal field components. This is in agreement with site symmetry S_6 for the lanthanide ion. The decay of the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ emission is exponential with a decay time of 4.0 ms at 4.2 K . This is much shorter than expected for this transition of Gd^{3+} on a site with inversion symmetry. The excitation spectrum in the purely ED ${}^8S_{7/2} \rightarrow {}^6I_{7/2}$ transition region consists, remarkably, of a broadband spanning the lasing region of the dye (Rhodamine 590). No excitations lines are observed in this region.

The diffuse reflection spectrum, measured at room temperature, shows an absorption band around $33,300 \text{ cm}^{-1}$ for $\text{ScBO}_3:\text{Eu}^{3+}$ as well as for $\text{ScBO}_3:\text{Gd}^{3+}$.

This absorption band is also observed in the reflection spectrum of the starting material Sc_2O_3 .

At room temperature and after low-resolution excitation at $35,970 \text{ cm}^{-1}$, i.e., in one of the ${}^6I_{7/2}$ levels, not only line emission of Gd^{3+} is observed, but also a structureless broad emission band ranging from $33,000$ to $20,000 \text{ cm}^{-1}$. The excitation spectrum of this broadband corresponds with the additional absorption band observed in the diffuse reflection spectrum. The excitation spectrum shows an overlap with the ${}^6P_{7/2}$, ${}^6I_{7/2} \rightarrow {}^8S_{7/2}$ emission transitions of Gd^{3+} . This allows energy transfer from Gd^{3+} to the impurity.

The origin of this emission is unknown. One might suggest that it is due to the presence of Ce^{3+} in the starting materials. The spectroscopy of $\text{ScBO}_3:\text{Ce}^{3+}$ has been investigated (21, 22). Comparison of the $\text{ScBO}_3:\text{Ce}^{3+}$ spectra with our spectra shows that an assignment to Ce^{3+} cannot be correct.

Due to the energy transfer process, the decay time does not reflect the radiative transition probability, A_{zp} , of the Gd^{3+} ion. It is clear that the Gd^{3+} site has inversion symmetry. In that case the ${}^6P_{7/2} \rightarrow {}^8P_{7/2}$ transition is totally due to magnetic-dipole interaction and the radiative transition probability can be calculated (23, 4). This yields $A_{zp} = (8.5 \text{ ms})^{-1}$. With the value of $r = 0.05$ the vibronic transition probability is found to be 6 s^{-1} . This value is comparable with those obtained for Gd^{3+} in other ionic host lattices. It is interesting to compare this result with the elpasolite $\text{Cs}_2\text{NaGdCl}_6$. Here, Gd^{3+} also possesses a site with inversion symmetry but the environment of the Gd^{3+} ion is more strongly polarizable than that in $\text{ScBO}_3:\text{Gd}^{3+}$. The vibronic transition probability found for the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} in $\text{Cs}_2\text{NaGdCl}_6$ is 28 s^{-1} (4). This is much larger than that for Gd^{3+} in ScBO_3 . The difference reflects the strong dependence of the vibronic transition probability on the polarizability.

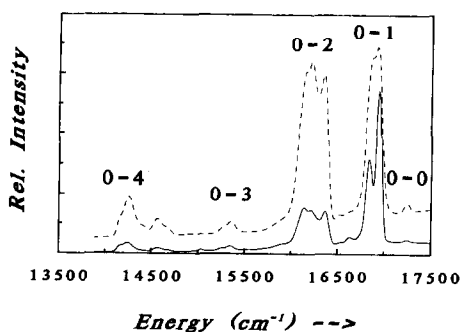


FIG. 5. Emission spectrum of Eu^{3+} in CaCO_3 at 4.2 K. The labels 0- J indicate the ${}^5D_0 \rightarrow {}^7F_J$ transitions. Excitation is at $19,000 \text{ cm}^{-1}$, the (${}^7F_0 \rightarrow {}^5D_1$ transition) for the lower spectrum and at $21,500 \text{ cm}^{-1}$ the (${}^7F_0 \rightarrow {}^5D_2$ transition) for the upper spectrum.

3.2. CaCO_3

The emission spectrum of Eu^{3+} in CaCO_3 is given in Fig. 5 for excitation via the MD ${}^7F_0 \rightarrow {}^5D_1$ transition and via the forced ED ${}^7F_0 \rightarrow {}^5D_2$ transition. The spectra differ from each other and from the emission spectrum of $\text{ScBO}_3 : \text{Eu}^{3+}$ (Fig. 1). Excitation into the 5D_2 term level yields stronger forced ED emissions. These emissions do not show individual c.f. components but are smeared out.

The excitation spectrum of the ${}^5D_0 \rightarrow {}^7F_1$ emission is shown in Fig. 6. The forced ED transitions ${}^7F_0 \rightarrow {}^5D_2$ and ${}^7F_0 \rightarrow {}^5L_6$ are the dominating line excitations. The C.T. transition has its maximum at $38,000 \text{ cm}^{-1}$. In the excitation spectrum of the ${}^5D_0 \rightarrow {}^7F_2$ emission the forced ED transitions are even more pronounced.

Excitation into the 5D_2 term level selectively excites the Eu^{3+} ions on a site without inversion symmetry, whereas the ${}^7F_0 \rightarrow {}^5D_1$ excitation is nonselective. There are, consequently, at least two different Eu^{3+} sites, one with the ${}^5D_0 \rightarrow {}^7F_1$ emission dominating, and another with ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ emissions of comparable intensity. For the former, the charge compensation hardly affects the site symmetry of the

Eu^{3+} ion. This is possible for remote charge compensation. For the latter Eu^{3+} ions the inversion symmetry is lost. This occurs for local charge compensation, for example, for a Ca^{2+} vacancy on a nearest or next-nearest cation site. The absence of individual c.f. components in the ED emissions indicates that this charge compensation results in considerable inhomogeneous broadening. In conclusion, we have for Eu^{3+} in CaCO_3 at least two different sites. Since charge compensation occurs by $3 \text{Ca}_{\text{Ca}}^x \rightarrow 2 \text{Eu}_{\text{Ca}}^{\cdot} + \text{V}_{\text{Ca}}''$, there is one group of sites ($\text{Eu}_{\text{Ca}}^{\cdot} \cdot \text{V}_{\text{Ca}}''$) and another group $\text{Eu}_{\text{Ca}}^{\cdot}$. The former shows a broader width.

Now we turn to $\text{CaCO}_3 : \text{Gd}^{3+}$. The emission spectrum of $\text{CaCO}_3 : \text{Gd}^{3+}$ at 4.2 K is given in Fig. 7. The emission consists of three sharp lines with an underlying broad line, the relative intensity of which increases with the Gd^{3+} concentration. The narrow lines are labeled A, B, and C, as in Fig. 7. The broad line has a FWHM of 65 cm^{-1} , which is a typical value for Gd^{3+} in a solid solution (24).

The excitation spectrum in the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ region of each of these three emission lines consists of three lines. These lines are assigned to the higher c.f. components of the ${}^6P_{7/2}$ term levels. The decay times of the emission lines are measured to be 5.1 (A),

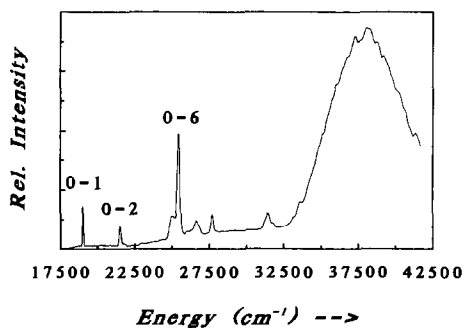


FIG. 6. Excitation spectrum of the ${}^5D_0 \rightarrow {}^7F_1$ emission of Eu^{3+} in CaCO_3 at 4.2 K. The labels 0-1, 0-2, and 0-6 indicate the ${}^7F_0 \rightarrow {}^5D_1$, 5D_2 , and 5L_6 transitions.

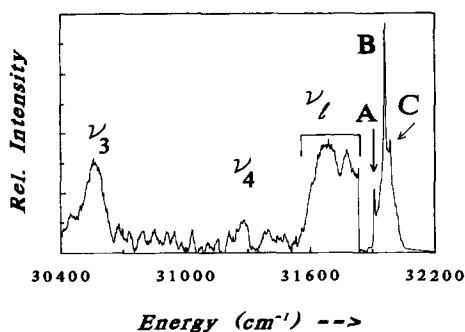


FIG. 7. Emission spectrum of Gd³⁺ in CaCO₃ at 4.2 K. Three different sites, labeled A, B, and C, can be distinguished. The vibronic spectrum is magnified by a factor of 100. See Fig. 3.

5.3 (B), and 6.7 (C) ms. At wavelengths longer than the zero-phonon lines, vibronic lines are observed (Fig. 7). After selective excitation of the sites, the distances to the main line are found to be 280, 700, and 1410 cm⁻¹. The first is ascribed to the Gd³⁺-CO₃²⁻ vibration; the latter two are ascribed to asymmetric bending and stretching vibrations of the CO₃²⁻ group, respectively (25, 26).

At 4.2 K only the lowest c.f. component of the ⁶P_{7/2} term is occupied, so that there should be only one emission line per Gd³⁺ site. Obviously, the extra charge of Gd³⁺ on a Ca²⁺ site is compensated in different ways. Lines A, B, and C correspond to Gd³⁺ sites with long decay times, i.e., with small deviations from inversion symmetry. They belong to the group Gd_{Ca} in the notation introduced above. They have also been obtained by ESR in CaCO₃:Gd³⁺ with very low Gd³⁺ concentration (10⁻⁴ at.%) (27). The broad line corresponds to the group (Gd_{Ca} · V_{Ca}''). Its existence makes it impossible to give a thorough interpretation of the vibronic intensities and of the measured decay times. This result agrees with that for Eu³⁺ and shows that CaCO₃ is not a suitable host for fundamental studies of trivalent lanthanide ions.

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