

# Study of the Vibronic Transitions of $Gd^{3+}$ and $Eu^{3+}$ in Crystalline Materials and Glasses of the Same Composition

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**The electron–phonon coupling strength of  $Gd^{3+}$  and  $Eu^{3+}$  ions in crystalline and glass phases of the same chemical composition are studied by measuring the vibronic transition probabilities of the  $4f^n$  transitions of these ions. The experimentally derived vibronic transition probabilities are very small. Within the experimental error, the electron–phonon coupling strength of the lanthanide ions in the different phases is the same.** © 1998 Academic Press

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## 1. INTRODUCTION

The interaction of the 4f electrons of lanthanide ions with the lattice vibrations (electron–phonon coupling) is weak but has a significant influence on the spectroscopy of lanthanide ions. Knowledge of the electron–phonon coupling is therefore not only interesting from a fundamental point of view, but also important for the research on the application of systems containing lanthanide ions, like lasers, scintillators, and phosphors (1, 2).

Up to now, vibronic transitions and vibronic transition probabilities ( $A_{\text{vib}}$ ) were mainly measured in crystalline host materials. In this study we compare the vibronic transition probabilities of lanthanide ions in crystalline materials and glasses of the same chemical composition. On the basis of the less dense structure of glasses, the ion–ligand distances will be larger, and hence one might expect weaker electron–phonon coupling of the lanthanide 4f electrons with the lattice vibrations in the glasses than in the crystalline material. We present the results on the vibronic transition probabilities of  $Gd^{3+}$  and  $Eu^{3+}$  as dopants in the crystalline and the glass modifications of  $LaB_3O_6$  and  $LiLaP_4O_{12}$ . The reason that we have chosen to investigate the ions  $Gd^{3+}$  and  $Eu^{3+}$  is that vibronic transitions of these ions have been investigated thoroughly in other systems (3–5). The

${}^6P_{7/2} \Rightarrow {}^8S_{7/2}$  transition of  $Gd^{3+}$  was measured because this transition is an excellent one to study the vibronic interaction of the ion with its surroundings (3, 6). For  $Eu^{3+}$  the  ${}^5D_{0,2} \Leftarrow {}^7F_0$  transitions were studied.

$LaB_3O_6$  and  $LiLaP_4O_{12}$  have been chosen as hosts since these compounds show vibrational frequencies at high energies, so that the corresponding vibronic features are well separated from the inhomogeneously broadened zero-phonon line in the glass. Besides, these materials are known to have the same chemical composition and the same short-range ordering in the crystalline material as in the glass (7–9).

## 2. EXPERIMENTAL

Crystalline  $LaB_3O_6$  and  $LiLaP_4O_{12}$  doped with  $Gd^{3+}$  or  $Eu^{3+}$  were prepared according to way described in Refs. (10) and (11), respectively. To obtain glasses, the starting materials were heated at 1200°C for half an hour in quartz crucibles and subsequently poured out in carbon crucibles (at room temperature).

The crystalline samples were checked by X-ray powder diffraction analysis, and were found to be single phase. The glass samples did not contain crystalline material, as far it could be detected by X-ray powder diffraction. Transmission spectroscopy showed that the crystalline and the glass samples did not contain optical impurities.

Low- and high-resolution excitation and emission measurements and decay time measurements were performed using a SPEX DM3000F spectrofluorometer, an excimer-laser pumped-dye laser, and a Nd:YAG laser setup, described elsewhere (6).

## 3. STRUCTURE

The structure of crystalline  $LaB_3O_6$  is based on the boron–oxygen units  $[B_6O_{12}]_{\infty}^{6-}$  which consist of two  $BO_4$  tetrahedra and four  $BO_3$  triangles linked to each other and forming long chains. Parallel chains of these boron–oxygen units are joined together by lanthanide ions, situated

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between the chains. The lanthanide ion is at the center of a distorted ten-cornered polyhedron of oxygen ions. The unit cell of crystalline LaB<sub>3</sub>O<sub>6</sub> is monoclinic with space group *I2/c* (10, 12).

The unit cell of crystalline LiLaP<sub>4</sub>O<sub>12</sub> is monoclinic with space group *C2/c*. The basic structural units are helical ribbons (PO<sub>3</sub>)<sub>n</sub> formed by corner-sharing PO<sub>4</sub> tetrahedra. The lanthanide ion is at the center of a LaO<sub>8</sub> dodecahedron (13).

#### 4. RESULTS

##### Gd<sup>3+</sup>

In Figs. 1a and 1b, the low-resolution emission spectra of the <sup>6</sup>P<sub>7/2</sub> ⇒ <sup>8</sup>S<sub>7/2</sub> transition in glass and crystalline LaB<sub>3</sub>O<sub>6</sub>:Gd<sup>3+</sup> at 4.2 K are presented as examples. At about 32,000 cm<sup>-1</sup> the zero-phonon line is found, and at lower energies (around 30,500 cm<sup>-1</sup>) vibronic transitions are observed. These vibronic transitions are due to coupling with the high-energetic vibrations of the host lattice. In the crystalline material (Fig. 1b) vibronic transitions are also found at lower energies, but in the glass phase (Fig. 1a) these vibronics cannot be separated from the inhomogeneously broadened zero-phonon line.

The high-energetic vibronics, which can clearly be distinguished from the zero-phonon line, are in the crystalline phase at a distance of 1250 cm<sup>-1</sup> from the zero-phonon line (due to vibrations of the BO<sub>4</sub> group) and at 1410 cm<sup>-1</sup> (due to B–O stretching vibrations of the BO<sub>3</sub> group). The

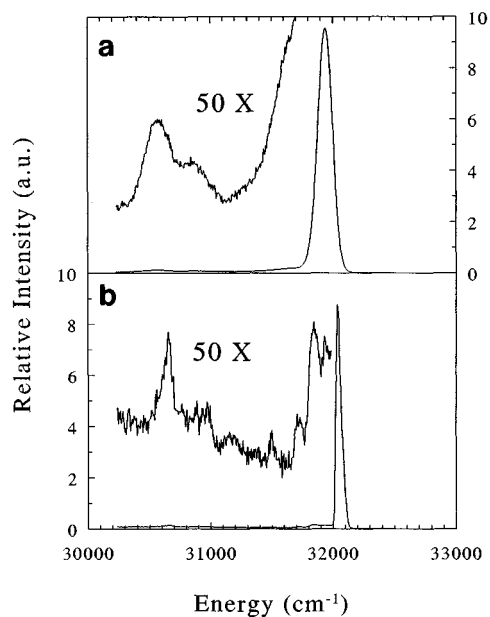


FIG. 1. Emission spectrum in the <sup>6</sup>P<sub>7/2</sub> ⇒ <sup>8</sup>S<sub>7/2</sub> region of Gd<sup>3+</sup> in (a) glass and (b) crystalline LaB<sub>3</sub>O<sub>6</sub>, both at 4.2 K. Excitation is in the <sup>6</sup>I<sub>7/2</sub> level of Gd<sup>3+</sup>. The vibronic regions are magnified 50×.

positions of these vibronic transitions are in agreement with the data from the literature (10). The fact that the energetic position of the vibronic transitions are within the experimental error the same in the glass and the crystalline material is in agreement with the results from Refs. (7–9) that these metaborate glasses contain the same borate groups which are found in the crystalline modification.

In the emission spectra of LiLaP<sub>4</sub>O<sub>12</sub>:Gd<sup>3+</sup> glass and crystalline powder, not shown here, the high-energetic vibronics are found at about 1090 and 1220 cm<sup>-1</sup>. The position of these vibronic transitions is in agreement with data from the literature on Raman and IR spectroscopy on these materials. These vibronic transitions are ascribed to coupling with P–O stretching vibrations (9–11).

From the decay times and the *R* values (defined as the ratio of the integrated vibronic intensity and the integrated zero-phonon line intensity), the transition probabilities for the zero-phonon line (*A*<sub>zp</sub>) and the vibronics (*A*<sub>vib</sub>) of the <sup>6</sup>P<sub>7/2</sub> ⇒ <sup>8</sup>S<sub>7/2</sub> transitions of Gd<sup>3+</sup> can be calculated, as has been described for other systems (3, 6, 14). The results for the Gd<sup>3+</sup> containing systems are given in Table 1.

It should be realized that for the *R* value and hence the vibronic transition probabilities, only the high-energetic vibronics have been taken into account. The total error in the vibronic transition probabilities is about 50%, mainly due to the fact that they are so weak relative to the zero-phonon line.

The *R* value obtained for crystalline LaB<sub>3</sub>O<sub>6</sub>:Gd<sup>3+</sup> (0.026) differs from the result presented by Verweij *et al.* (10) on GdB<sub>3</sub>O<sub>6</sub> (0.12). This difference can be explained by the fact that Verweij *et al.* used a 100% Gd<sup>3+</sup> crystalline material in which reabsorption may occur. The reabsorbed light is then redistributed over the zero-phonon and vibronic lines, and so the intensity of the vibronic sideband is enhanced with respect to the zero-phonon line (15). To obtain a correct *R* value, measurements should be performed on a diluted Gd<sup>3+</sup> sample.

##### Eu<sup>3+</sup>

For Eu<sup>3+</sup> in the glass and crystalline modifications of LaB<sub>3</sub>O<sub>6</sub> and LiLaP<sub>4</sub>O<sub>12</sub>, two excitation transitions were

TABLE 1  
*R* Values, Decay Times, and Transition Probabilities of Gd<sup>3+</sup> in Crystalline and Glassy LaB<sub>3</sub>O<sub>6</sub> and LiLaP<sub>4</sub>O<sub>12</sub> at 4.2 K

System	<i>R</i> values	Decay (μs)	<i>A</i> <sub>zp</sub> (s <sup>-1</sup> )	<i>A</i> <sub>vib</sub> (s <sup>-1</sup> )
	<sup>6</sup> P <sub>7/2</sub> ⇒ <sup>8</sup> S <sub>7/2</sub>			
LaB <sub>3</sub> O <sub>6</sub> :Gd <sup>3+</sup>	0.026	4000	244	7
	0.02	3400	288	6
LiLaP <sub>4</sub> O <sub>12</sub> :Gd <sup>3+</sup>	0.035	6570	147	5
	0.02	4550	215	4

studied: the  ${}^5D_0 \leftarrow {}^7F_0$  and the  ${}^5D_2 \leftarrow {}^7F_0$  transitions. These transitions were chosen because the vibronic sidebands in the spectra of these transitions were not obscured by the presence of the zero-phonon lines of other transitions. Due to the very low oscillator strength of the  ${}^5D_0 \leftarrow {}^7F_0$  transition, the transitions on  $\text{Eu}^{3+}$  were studied with the laser setups.

Here we show only the spectra of the  ${}^5D_0 \leftarrow {}^7F_0$  transition of  $\text{Eu}^{3+}$  in glass and crystalline  $\text{LaB}_3\text{O}_6$ , see Figs. 2a and 2b, respectively. The spectra are corrected for the dye laser intensity. The zero-phonon line is found at some  $17,300 \text{ cm}^{-1}$ , and vibronic transitions, due to coupling with high-energy vibrations, are found at a distance of some  $1100$  and  $1400 \text{ cm}^{-1}$ . In the crystalline materials (Fig. 2b) low-energetic vibronics are also found, which in the glass (Fig. 2a) cannot be separated from the zero-phonon line. From the spectra it is clear that the relative intensity ( $R$ ) of the vibronic transitions in the crystal is much larger than in the glass.

The  $R$  values and the vibronic transition probabilities, calculated for the  ${}^5D_0 \leftarrow {}^7F_0$  and the  ${}^5D_2 \leftarrow {}^7F_0$  transitions, are given in Table 2. The vibronic transition probability of the  ${}^5D_0 \leftarrow {}^7F_0$  transition is derived from the decay time of the  ${}^5D_0$  level and the relative emission intensity of the  ${}^5D_0 \Rightarrow {}^7F_0$  transition in the total  ${}^5D_0$  emission spectrum (branching ratio). From  $A_{zp}$  of the  ${}^5D_0 \Rightarrow {}^7F_0$  transition, which is the same in emission as in excitation and the

**TABLE 2**  
 **$R$  Values, Decay Times, and Transition Probabilities of  $\text{Eu}^{3+}$  in Crystalline and Glass  $\text{LaB}_3\text{O}_6$  and  $\text{LiLaP}_4\text{O}_{12}$  at 4.2 K of Transitions  ${}^5D_0 \leftarrow {}^7F_0$  and  ${}^5D_2 \leftarrow {}^7F_0$**

System	$R$ values		Decay ( $\mu\text{s}$ ) ${}^5D_0$	$A_{zp} (\text{s}^{-1})$ ${}^5D_0 \leftarrow {}^7F_0$	$A_{vib} (\text{s}^{-1})$ ${}^5D_0 \leftarrow {}^7F_0$
	${}^5D_0 \leftarrow {}^7F_0$	${}^5D_2 \leftarrow {}^7F_0$			
<b><math>\text{LaB}_3\text{O}_6:\text{Eu}^{3+}</math></b>					
Crystal	0.51/0.10		3366	1.5/35	1/3
Glass	0.02/0.01		1356	8/200	0.2/2
<b><math>\text{LiLaP}_4\text{O}_{12}:\text{Eu}^{3+}</math></b>					
Crystal	0.21/0.18		4500	0.3/14	0.1/3
Glass	0.03/0.01		3500	2/175	0.03/2

$R$  value, the vibronic transition probability of the  ${}^5D_0 \leftarrow {}^7F_0$  transition can be calculated.

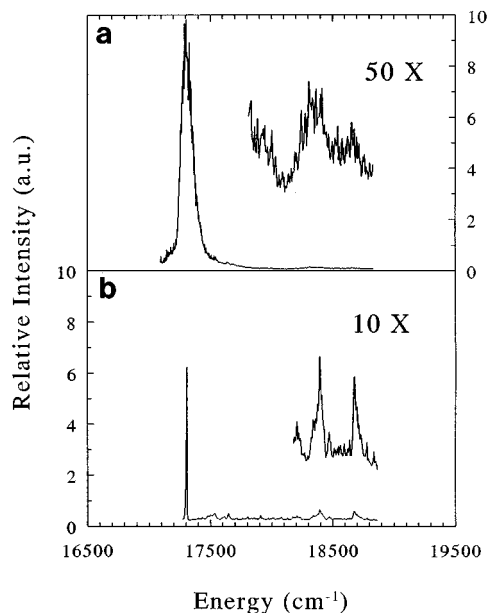
The transition probability of the  ${}^5D_2 \leftarrow {}^7F_0$  transition is calculated by relating the intensities of the zero-phonon lines of the two transitions studied ( ${}^5D_0 \leftarrow {}^7F_0$  and the  ${}^5D_2 \leftarrow {}^7F_0$ ) in the excitation spectra. Hence, from the transition probability derived for the  ${}^5D_2 \leftarrow {}^7F_0$  transition and the  $R$  value, the vibronic transition probability for this transition can be derived. Because the branching ratio of the  ${}^5D_0 \Rightarrow {}^7F_0$  transition is very small, the procedure to derive the vibronic transition probabilities via the branching ratio of the  ${}^5D_0 \Rightarrow {}^7F_0$  transition introduces a large error ( $\sim 100\%$ ) in the values of the vibronic transition probabilities for  $\text{Eu}^{3+}$ .

## 5. DISCUSSION AND CONCLUSIONS

The data presented in Tables 1 and 2 show that the transition probabilities of the zero-phonon lines differ significantly between the crystalline materials and the glasses, especially for  $\text{Eu}^{3+}$ . The larger values for the transition probabilities of the zero-phonon lines in the glass can be due to the lower symmetric environment of the lanthanide ion in the glasses. Since the transitions on  $\text{Eu}^{3+}$  are more sensitive to the environment (4), lowering of symmetry will have a larger influence on the transition probabilities of  $\text{Eu}^{3+}$  than on those of  $\text{Gd}^{3+}$ .

For a good comparison of vibronic intensities of lanthanide ions in different systems, not the  $R$  value but the vibronic transition probabilities must be compared (6), because the  $R$  value is dependent on the value of the zero-phonon line transition probability.

Vibronic transition probabilities scale with the ion–ligand distance  $R_L^{-6}$  (static coupling) or  $R_L^{-10}$  (dynamic coupling), and hence (14) smaller vibronic intensities are expected for the glasses, which are less dense. Since the differences in density between the crystalline and the glasses are small, a small effect is expected. It is clear from the tables



**FIG. 2.** Excitation spectrum in the  ${}^5D_0 \leftarrow {}^7F_0$  region of  $\text{Eu}^{3+}$  in (a) glass and (b) crystalline  $\text{LaB}_3\text{O}_6$ , both at 4.2 K. The emission of the  ${}^5D_0 \Rightarrow {}^7F_2$  transition is monitored. The vibronic regions in the figures are magnified  $50\times$  for the glass and  $10\times$  for the crystalline material.

that the differences in the vibronic transition probabilities are smaller than the experimental errors, which are estimated to be some 50% for the values of Gd<sup>3+</sup> and more than 100% for Eu<sup>3+</sup>. These large errors are mainly due to the very low intensities of the vibronic transitions, and the very small  $A_{zp}$  values for Eu<sup>3+</sup>. This means that the differences in vibronic transition probabilities between the crystalline material and the glass are too small to be estimated from these systems and with this method. Possibly in other systems with a stronger electron–phonon coupling than Gd<sup>3+</sup> and Eu<sup>3+</sup> (see for example Refs. (6, 16–18)) and more intense vibronic transitions, the vibronic transition probabilities can be determined with higher accuracy. This is required if there is a difference in the electron–phonon coupling strength between the glass and crystalline material.

Hence, within the experimental error, the electron–phonon coupling of the lanthanide ions Gd<sup>3+</sup> and Eu<sup>3+</sup> are the same in the glass and the crystalline phases of the studied host lattices.

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