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Absorption spectra due to the $4f^7 \rightarrow 4f^7$ transitions of Gd^{3+} ions in $GdAl_3(BO_3)_4$ crystals

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Abstract. Optical absorption spectra due to the $4f^7 \rightarrow 4f^7$ transitions of Gd^{3+} ions in $GdAl_3(BO_3)_4$ crystals have been measured. The Stark splittings have been observed in the transitions from the ground state $^8S_{7/2}$ to the excited states 6P_J ($J = 7/2, 5/2, 3/2$), 6I_J ($J = 7/2, 9/2, 17/2, 11/2, 15/2, 13/2$) and 6D_J ($J = 9/2, 1/2, 7/2, 3/2, 5/2$). It is suggested that the splittings are consistent with the D_{3h} site symmetry of Gd^{3+} . The $4f^7 \rightarrow 4f^7$ spectrum is compared with that of Gd^{3+} in solution.

1. Introduction

The Gd^{3+} ion has the electronic configuration $4f^7 5s^2 5p^6$ (named $4f^7$ hereafter) in the outer shell. The $4f^7$ configuration has the ground state $^8S_{7/2}$ and the excited state multiplets 6P_J ($J = 7/2, 5/2, 3/2$ in order of increasing energy), 6I_J ($J = 7/2, 9/2, 17/2, 11/2, 15/2, 13/2$) and 6D_J ($J = 9/2, 1/2, 7/2, 3/2, 5/2$) with increasing energy. These excited states are located at 32 000–41 000 cm^{-1} above the ground state [1, 2]. The positions and order of the multiplets are almost the same in various materials (even if they are aqueous solutions) since the $4f^7$ electrons are shielded by the outer $5s^2 5p^6$ electrons from the surrounding ions of Gd^{3+} . In addition to these excited states the other $4f^7$ states (e.g. 6F_J and 4H_J) and the $4f^6 5d$ states are located in the vacuum-ultraviolet region, which have been studied in $LiYF_4$ [3] and CaF_2 [4], respectively.

The $4f^7(^8S_{7/2}) \rightarrow 4f^7$ ultraviolet absorption spectra of Gd^{3+} ions have been studied in various materials including not only ionic crystals like SrF_2 with Gd^{3+} impurity [5] but also Gd compounds like $Cs_2NaGdCl_6$ [6], where the observation of absorption lines related to the 6P_J , 6I_J and 6D_J excited states has been observed together with their Stark components. However, to our knowledge, all Stark components of the 6P_J , 6I_J and 6D_J states have not been observed in any Gd^{3+} materials except $Gd^{3+}:LaBr_3$ [7]: e.g. the Stark components of the $^6D_{3/2}$ and $^6D_{5/2}$ states in $LaCl_3$ are missing [8], and the Stark components of the $^6I_{15/2}$ and $^6I_{13/2}$ states in $GdCl_3 \cdot 6H_2O$ are missing [9], and additionally the $^6P_{3/2}$ lines are missing in many materials (see e.g. [7, 10, 11]).

Although the $4f^7 \rightarrow 4f^7$ absorption spectra have been studied in many Gd^{3+} compounds, the absorption spectra of Gd^{3+} in the $GdAl_3(BO_3)_4$ (called GAB hereafter) crystal have not been studied yet. Wang *et al* have reported the presence of weak absorption due to $^8S_{7/2} \rightarrow ^6P$ transitions at 300–310 nm in $Cr^{3+}:GAB$, but the detailed study has not been made yet [12]. GAB is used as the bulk crystal of the $Ti^{3+}:GdAl_3(BO_3)_4$ laser [13], and

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additionally crystals with the same crystal structure are used for lasers, e.g. $\text{NdAl}_3(\text{BO}_3)_4$ laser [14] and $\text{Cr}^{3+}:\text{YAl}_3(\text{BO}_3)_4$ laser [15]. Therefore not only doped but also undoped GAB might be laser active. In this sense, it is important to study the optical fundamental properties of GAB. Here, taking into account that the whole Gd^{3+} spectra containing all Stark components of the ${}^6\text{P}_J$, ${}^6\text{I}_J$ and ${}^6\text{D}_J$ states have not been shown for any material, we show the $4f^7 \rightarrow 4f^7$ absorption spectrum covering from the lowest-energy ${}^6\text{P}_{7/2}$ state up to the highest-energy ${}^6\text{D}_{5/2}$ state in the GAB crystal.

2. Experimental procedures and results

Single crystals of GAB used in the present study were grown by Dr Guofu Wang at the University of Strathclyde, Glasgow, UK. Absorption spectra were measured using a Cary-5E spectrophotometer at various temperatures in the range 15–300 K. The slit width was set to be 0.03 nm.

The GAB crystal is transparent in the infrared–visible region, while many sharp absorption lines appear in a limited ultraviolet region, i.e. in a $31\,900\text{--}41\,000\text{ cm}^{-1}$ range (corresponding to about 313–243 nm range in wavelength). The line spectrum does not change on decreasing temperature to 15 K: no change is observed in the line widths and peak heights for all the lines. The line width is almost the same (about 7 cm^{-1}) for all the Stark-split lines. Figures 1 and 2 show the enlarged spectra in the $31\,800\text{--}33\,400\text{ cm}^{-1}$ and $35\,600\text{--}41\,000\text{ cm}^{-1}$ ranges, respectively. From comparison with the previous studies of Gd compounds and Gd^{3+} impurities in ionic crystals, these absorption lines are attributed to the $4f^7 \rightarrow 4f^7$ intraconfigurational transitions of Gd^{3+} , e.g. the lowest-energy line is attributed to the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{7/2}$ transition. The excited states responsible for the observed lines are shown in figures 1 and 2.

Four, three and two absorption lines are observed in the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{7/2}$, ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{5/2}$ and ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{3/2}$ transitions, respectively as seen in figure 1. Of the three transitions, the last one is the weakest. At high energies, four, five, one, four, two and three lines are observed

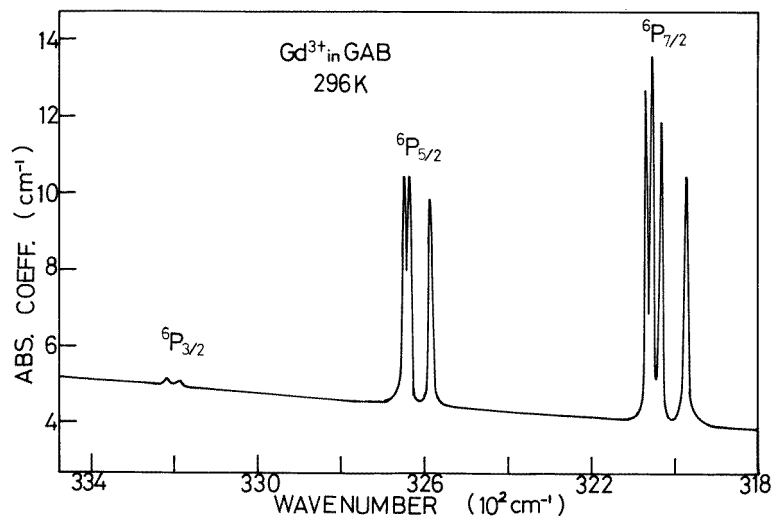


Figure 1. Absorption bands due to the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{7/2}$, ${}^6\text{P}_{5/2}$ and ${}^6\text{P}_{3/2}$ transitions of Gd^{3+} ions in the $\text{GdAl}_3(\text{BO}_3)_4$ crystal at 296 K. ABS. COEFF., absorption coefficient.

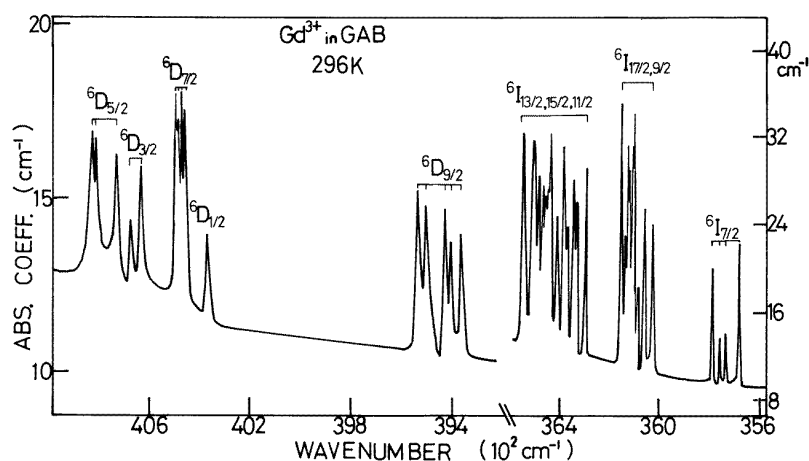


Figure 2. Absorption bands due to the ${}^8S_{7/2} \rightarrow {}^6I_J$ and 6D_J transitions of Gd^{3+} ions in the $GdAl_3(BO_3)_4$ crystal at 296 K. ABS. COEFF., absorption coefficient.

Table 1. Absorption line positions due to Gd^{3+} in the $GdAl_3(BO_3)_4$ crystal.

States	Energy (cm ⁻¹)	States	Energy (cm ⁻¹)	States	Energy (cm ⁻¹)	
${}^6P_{7/2}$	31 974	${}^6I_{11/2} + {}^6I_{15/2} + {}^6I_{13/2}$	36 301	${}^6D_{1/2}$	40 358	
	32 073		36 338		${}^6D_{7/2}$	40 446
	32 055		36 348			40 462
	32 070		36 374			40 477
${}^6P_{5/2}$	32 591		36 385		40 483	
	32 641		36 413	${}^6D_{3/2}$	40 623	
	32 653		36 444		40 666	
${}^6P_{3/2}$	33 191		36 453			
	33 219		36 463	${}^6D_{5/2}$	40 723	
${}^6I_{7/2}$	35 686		36 474		40 803	
	35 736		36 489		40 818	
	35 759		36 502			
	35 792		36 505			
${}^6I_{9/2} + {}^6I_{17/2}$	36 031		36 510			
	36 064		36 550			
	36 094	${}^6D_{9/2}$	39 353			
	36 113		39 396			
	36 117		39 420			
	36 129		39 493			
	36 134		39 527			
	36 143					
36 162						

in the ${}^8S_{7/2} \rightarrow {}^6I_{7/2}$, ${}^6D_{9/2}$, ${}^6D_{1/2}$, ${}^6D_{7/2}$, ${}^6D_{3/2}$ and ${}^6D_{5/2}$ transitions, respectively, as summarized in table 1. On the other hand, nine lines are observed in the ${}^8S_{7/2} \rightarrow {}^6I_{9/2} + {}^6I_{17/2}$ transitions, while 15 lines in the ${}^8S_{7/2} \rightarrow {}^6I_{11/2} + {}^6I_{15/2} + {}^6I_{13/2}$ transitions, where it is difficult to identify which line belongs to which excited state. In table 2 we give the absorption intensities (i.e. the integrated absorption areas of the whole Stark components) relative to the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ absorption intensity. It is observed the intensity of the ${}^8S_{7/2} \rightarrow {}^6P_{3/2}$ absorption is the smallest, and the next is that of the ${}^8S_{7/2} \rightarrow {}^6D_{1/2}$ absorption.

Table 2. Relative intensity of Gd^{3+} absorption.

Excited states	$\text{GdAl}_3(\text{BO}_3)_4$	SrF_2 [5]	Solution [18]
${}^6\text{P}_{7/2}$	1.0	1.0	1.0
${}^6\text{P}_{5/2}$	0.651	0.55	0.56
${}^6\text{P}_{3/2}$	0.017	—	0.019
${}^6\text{I}_{7/2}$	0.781	0.44	1.65
${}^6\text{I}_{9/2} + {}^6\text{I}_{17/2}$	4.175	4.20	11.57
${}^6\text{I}_{11/2} + {}^6\text{I}_{15/2} + {}^6\text{I}_{13/2}$	10.255	8.85	26.22
${}^6\text{D}_{9/2}$	1.146	0.16	1.07
${}^6\text{D}_{1/2}$	0.066	—	—
${}^6\text{D}_{7/2}$	0.774	0.24	1.12
${}^6\text{D}_{3/2}$	0.365	—	—
${}^6\text{D}_{5/2}$	0.788	—	—

3. Discussion

Although the positions of the $4f^7 \rightarrow 4f^7$ absorption lines are little dependent on material, the absorption line shape and the Stark splitting are different from material to material. A relatively small splitting is caused by the crystal field. The ${}^8\text{S}_{7/2}$ ground state has a very small Stark splitting of the order of 0.1 cm^{-1} , so that the absorption spectra reflect directly the excited states [9, 11, 16], providing information on the surroundings of Gd^{3+} .

The GAB crystal has the trigonal crystal structure which is isomorphous with the mineral huntite $\text{CaMg}_3(\text{BO}_3)_4$ belonging to the space group $R\bar{3}2$ as the cases of other borate crystals such as $\text{YAl}_3(\text{BO}_3)_4$ and $\text{NdAl}_3(\text{BO}_3)_4$. The Gd^{3+} ion occupies a crystallographic site without a centre of inversion and its immediate surroundings consist of a trigonal prism of oxygen anions (symmetry D_{3h}) [17]. The D_{3h} symmetry crystal field removes all but Kramers degeneracy in the electronic states, and the ${}^6\text{P}_{7/2}$ state is split into four Kramers degenerate crystal field states [11]. Therefore we expect four absorption lines in the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{7/2}$ transition in GAB as the cases of $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ [11] and $\text{Gd}^{3+}:\text{LaCl}_3$ [7] with the same D_{3h} site symmetry as GAB. Similarly the electronic term with J (J : quantum number of total angular momentum) is expected to show $(2J + 1)/2$ absorption lines since the number of Stark components in the excited state is $(2J + 1)/2$ in the D_{3h} crystal field: e.g. the transition to the ${}^6\text{D}_{9/2}$ (i.e. $J = 9/2$) state gives rise to five lines. This agrees with the observation except the absorption spectra in the ranges of $36\,000\text{--}36\,150$ and $36\,300\text{--}36\,600 \text{ cm}^{-1}$ (see figures 1 and 2). On the other hand, in the case of Gd^{3+} in LaCl_3 , the identification of the observed lines has been made for all the ranges [7]. The reason why the identification is difficult in the two ranges in GAB is that the ${}^6\text{I}_{9/2}$ and ${}^6\text{I}_{17/2}$ energy states appearing at the former range are located close to each other and the same is true for the ${}^6\text{I}_{11/2}$, ${}^6\text{I}_{15/2}$ and ${}^6\text{I}_{13/2}$ states appearing in the latter range.

In table 2 we summarize the integrated absorption areas of various excited states in GAB, relative to the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{7/2}$ absorption area (i.e. the absorption area related to the ${}^6\text{P}_{7/2}$ state is given as 1.0). The absorption related to the ${}^6\text{P}_{5/2}$ state consists of three lines. The integrated absorption area of this state means the sum of these integrated areas. In this table we also show the cases of Gd^{3+} in the SrF_2 crystal [5] and in dilute acid solution [18]. There is not much difference in the intensity ratios between GAB and SrF_2 crystals. However, there is an obvious difference between crystals and solution: the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{I}_J$ absorption intensity is considerably larger in solution than in crystals. According to the analysis by Downer *et al* [19], the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{I}_J$ absorption is caused by the electric dipole

(ED) transition, while the $^8S_{7/2} \rightarrow ^6P_J$ absorption is predominantly caused by the magnetic dipole (MD) transition. Therefore it is suggested that the relatively large $^8S_{7/2} \rightarrow ^6P_J$ absorption intensity observed in crystals (compared with the case of solution) is due to involvement of the ED transition in this parity-forbidden $^8S_{7/2} \rightarrow ^6P_J$ transition, because the ED transition is caused by the mixing of the $4f^65d$ state to the $4f^7$ state by the odd-parity crystal field and because the MD contribution to the absorption intensity is almost independent of the surroundings of the rare-earth ion.

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