

**Effect of symmetry reduction on the electronic transitions in polytypic
GdAl₃(BO₃)₄:Eu:Tb crystals**

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Abstract

The existence of a recently described monoclinic phase ($C2/c$, $Z=8$) [1] in addition to the well-known Huntite type rhombohedral ($R32$) polytypic modification of the $GdAl_3(BO_3)_4$ (GAB) crystal at room temperature provides a unique possibility to investigate the incorporation of rare earth dopants into slightly modified crystal lattice by spectroscopic methods. In these characteristic GAB structures the dopant ions, e.g. Tb^{3+} or Eu^{3+} , possess slightly different neighbor geometries and local symmetries. The Tb^{3+} : ${}^7F_6 \rightarrow {}^5D_4$ and Eu^{3+} : ${}^7F_{0,1,2} \rightarrow {}^5D_{0,1,2}$ electronic transitions were successfully identified in the absorption spectra using polarization, concentration and temperature dependent measurements in both polytypic modifications. The positions of the investigated Tb lines are shifted by up to 10 cm^{-1} due to symmetry changes. In addition, some of the Eu lines show splittings of about $4\text{--}30\text{ cm}^{-1}$ as a consequence of the change of the local environment. From the room temperature absorption measurements some of the low energy crystal field levels of 7F and 5D states of the Eu^{3+} ions were successfully determined for both modifications.

Keywords: electronic transition, absorption, polytypism, $GdAl_3(BO_3)_4$, Europium

1. Introduction

The huntite type aluminium borate crystals ($RA_3(BO_3)_4$, where R denotes rare earth elements including yttrium), have been investigated for a long time since the members of this crystal family exhibit strong chemical stability, outstanding physical and optical properties, such as

wide optical transmission range in the ultraviolet [1-3]. They are excellent hosts for laser active rare earths, since the substitution of these ions at the trigonal prism sites usually occurs without charge compensation and lattice distortion. The efficiency of the borate-based light sources depends in a complex way on the active rare earth ions present. Enhanced energy transfer rate was observed in the visible range luminescence of the Eu and Tb co-doped $\text{GdAl}_3(\text{BO}_3)_4$ (GAB) crystal after excitation the Gd^{3+} host ions in the VUV range [5,6]. In addition, the ${}^7\text{F}_2$ - ${}^5\text{D}_0$ transition of Eu^{3+} ion in the huntite type GAB crystal does not follow strictly the selection rules for electrical dipole transition [7, 8]. This effect has generated a series of detailed spectroscopic measurements and crystal field calculations [9-13] showing the induced electric dipole character of the ${}^7\text{F}_2$ - ${}^5\text{D}_0$ transition [9].

Although borate crystals are most useful for optical applications if possessing the huntite structure ($R32$) it has become clear that they could be grown in polytypic modifications with different symmetries (e.g. $C2$, $C2/c$ [4, 14]). Growth temperature and cooling rate were found to be important factors for producing the given polytypic modifications of these borate crystals. The possibility and realization of polytypic modifications in borate crystals has been investigated by Belokoneva and Timchenko in detail [15]. They have shown that the observed modifications can be explained in order-disorder theory by different arrangements of composition layers common for all polytypes and corresponding to the 'ab' plane of the monoclinic structures. In the unified model [15, 16] several possibilities of the polytypic packing were predicted. Some of those structures have already been experienced in various borate crystals, while others could not be produced so far. One of the missing structures with $C2/c$ space group with a unit cell consisting of 8 molecules has recently been prepared [1]. The emergence of polytypic phases as a function of the starting crystallization temperature was demonstrated in Eu and Tb co-doped GAB crystals grown by the high temperature top seeded solution growth (HTTSSG) method. Both the rhombohedral ($R32$) and the monoclinic ($C2/c$, $Z=8$) phases could be separately prepared with the same composition [1]. The dopant rare earth ions enter Gd sites in both cases, however their local site symmetry is lowered from trigonal to $C2$ in the monoclinic phase [1].

In this work the results of spectroscopic measurements of Tb and Eu doped GAB crystals with monoclinic ($C2/c$, $Z=8$) structure will be presented for the first time and compared to the case of the rhombohedral ($R32$) modification. The temperature, concentration and polarization dependences of the rare earth transition bands were investigated and the term structures of the low energy parts of ${}^7\text{F}$ and ${}^5\text{D}$ states of the Eu^{3+} ions were determined and compared for the different symmetries.

2. Experimental

The investigated GAB single crystals were grown by the HTTSSG method from a $\text{K}_2\text{Mo}_3\text{O}_{10}:\text{B}_2\text{O}_3$ flux (see details in [17]). The starting concentrations of the dopants in the solution are listed in Table 1. The structure of the as-grown crystals was identified by X-ray diffraction (XRD) measurements. Crystal samples were cut, oriented and polished to obtain optical quality.

No.	Eu [mol%]	Tb [mol%]	Symmetry
1	0	5	<i>R32</i>
2	0	10	<i>R32</i>
3	0	20	<i>R32</i>
4	20	20	<i>R32</i>
5	20	20	<i>C2/c</i>

Table 1. The concentrations of Tb^{3+} and Eu^{3+} ions in the starting solution and the space groups of the as-grown GAB crystals.

The absorption spectra were recorded by a BRUKER IFS 66/v FTIR spectrophotometer with a resolution at about 0.2 cm^{-1} . For the polarization dependent measurements an UV-visible polymer polarizer was used. Temperature dependent measurements in the range of 9–300 K were carried out in a closed-cycle helium cryostat.

3. Results and discussion

The huntite type borates are uniaxial optical crystals with the optical axis coinciding with the trigonal axis, while the monoclinic modifications are biaxial. The selection rules for the polarization dependent measurements are summarized in Table 2 [18, 19]. The electric or magnetic dipole behavior of the transitions have been shown by white and grey background of the columns, respectively.

D ₃	A1		A2		E	
A1	-	-	π	σ	$\alpha\sigma$	$\alpha\pi$
A2	π	σ	-	-	$\alpha\sigma$	$\alpha\pi$
E	$\alpha\sigma$	$\alpha\pi$	$\alpha\sigma$	$\alpha\pi$	$\alpha\pi\sigma$	$\alpha\pi\sigma$

C ₂	A		B	
A	z	Rz	x,y	Rx,Ry
B	x,y	Rx,Ry	z	Rz

Table 2. Selection rules for the polarization directions for both symmetry modifications (a: trigonal D₃, b: monoclinic C₂). The background of the cell is white or grey when the transition has electric or magnetic dipole behavior, respectively.

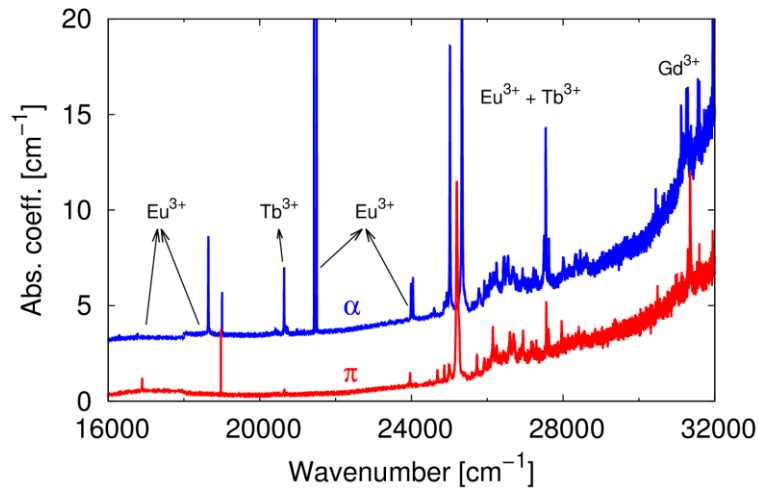


Fig. 1. Visible-UV absorption spectra of the rhombohedral GAB:Tb,Eu (No. 4) crystal measured in the α and π polarizations at room temperature.

Several absorption bands corresponding to the electronic transitions of Tb³⁺, Eu³⁺ and Gd³⁺ ions can be seen in the absorption spectra measured in the 16000-32000 cm⁻¹ range showing strong polarization dependence (see Fig. 1). Transitions up to 22000 cm⁻¹ wavenumber can be clearly distinguished, however, above that the absorption bands overlap each other. Since the electronic transitions of Gd³⁺ ions are situated above 31500 cm⁻¹, only the transitions of Tb³⁺ and Eu³⁺ ions have been studied in this work.

As was shown in ref. [1] a pseudo-trigonal axis behaving as a pseudo-optical axis can also be defined in the monoclinic GAB crystal. With this simplification the results of the polarization measurements can be treated in a similar way both for trigonal and monoclinic modifications using the following notations. In the case of rhombohedral GAB crystals for light propagating

perpendicular to the optical axis the π_r and σ_r polarizations mean electric fields parallel and perpendicular to the c axis, respectively, while the α_r symbol is used for light propagation coinciding with the optical axis. In the monoclinic case one of the dielectric axes coincides with the twofold axis (z), the second one with the pseudo-trigonal axis (x) and the third one (y) is perpendicular to those two. Samples with surfaces perpendicular and parallel to the pseudo-trigonal axis were prepared for comparison. However, due to complex growth and morphological reasons the normal of the surface parallel to the pseudo-trigonal axis has an angle of 60° to the z -axis. Accordingly, the π_m and σ_m symbols are used for light propagating perpendicular to the pseudo-trigonal axis whereby the polarization is parallel (E_x) and perpendicular ($E_y + E_z$) to the x axis, respectively (i.e. for the case of the sample cut parallel to pseudo-trigonal axis). The α_r symbol is used for light propagating along the pseudo-trigonal x axis where the E_x component is missing.

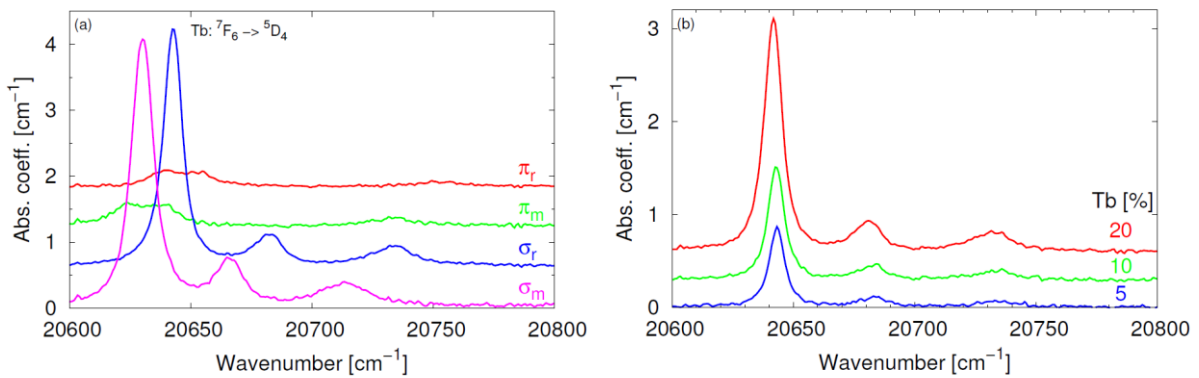


Fig. 2. Polarization (π and σ) dependence of the Tb: ⁷F₆ - ⁵D₄ transition in doped GAB crystals of both modifications (No. 4-5, r: rhombohedral, m: monoclinic phase as discussed in the text) (a). Absorption spectra of GAB:Tb crystals (No. 1-3) as a function of the Tb concentration (b).

Among the electronic transitions of Tb³⁺ ions only the ⁵D₄ multiplet falls into the visible spectral range. The ⁵D₄ multiplet due to the Coulomb repulsion between 4f electrons and the spin-orbit interactions is in the range of 20600-20800 cm⁻¹ (485-480 nm) above the ⁷F₆ ground state. A slight shift of these band positions by at about 12-19 cm⁻¹ can be observed in Fig. 2a for both polarizations due to the change from the rhombohedral to the monoclinic structure (crystals No. 4-5). In order to exclude the concentration change of the Tb³⁺ ions as the origin of the shift, the absorption bands have also been measured as a function of the Tb

content (see Fig. 2b). The change of the concentration of Tb^{3+} ions in a relatively wide range (5-20 mol%, No. 1-3) induces only a 1-2 cm^{-1} shift of the main absorption band corresponding to the ${}^7F_6 - {}^5D_4$ transition. This result supports the assumption that the difference of the band positions, present in the symmetry modifications, essentially originates from the specific environments of Tb^{3+} ions in the GAB crystal lattices changing both the crystal field (CF) symmetry and the crystal field strength. The common shift of all lines in the ${}^7F_6 - {}^5D_4$ transition indicates that not only the crystal field splitting pattern is altered within the 5D_4 multiplet, but also the barycenter of the 5D_4 multiplet is shifted due to changes of the Coulomb and spin-orbit interactions.

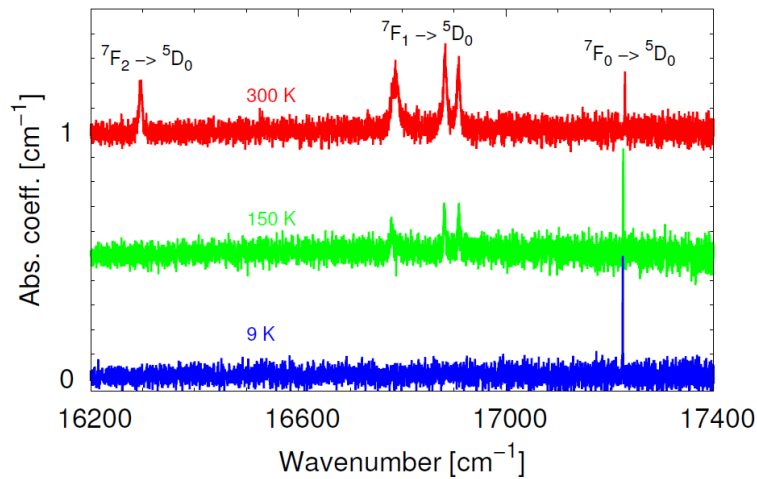


Fig. 3. Temperature dependence of the absorption bands of the ${}^7F_{0,1,2} - {}^5D_0$ transitions of Eu^{3+} in monoclinic GAB:Tb,Eu (No. 5) crystal.

For the assignation of the absorption bands to the electronic levels of the Eu^{3+} ions temperature dependent absorption measurements were also performed. The absorption spectra of Eu^{3+} ions in the rhombohedral GAB crystal (No. 4) show similar behavior as already measured in [10]. One can conclude from these measurements that the electronic transitions from the 7F_0 ground state and the thermally populated 7F_1 and 7F_2 multiplets of europium can be detected at room temperature [9, 10]. However, a shift and splitting of the bands by values in the range of 4–30 cm^{-1} depending on the electronic transitions were observed in the absorption spectra of the monoclinic structure due to the symmetry reduction and its consequences for the Coulomb, spin-orbit and crystal field interactions. E.g. the crystal field splitting of the 7F_1 hot transition results in three absorption bands in the high temperature spectra as can be seen in Fig 3.

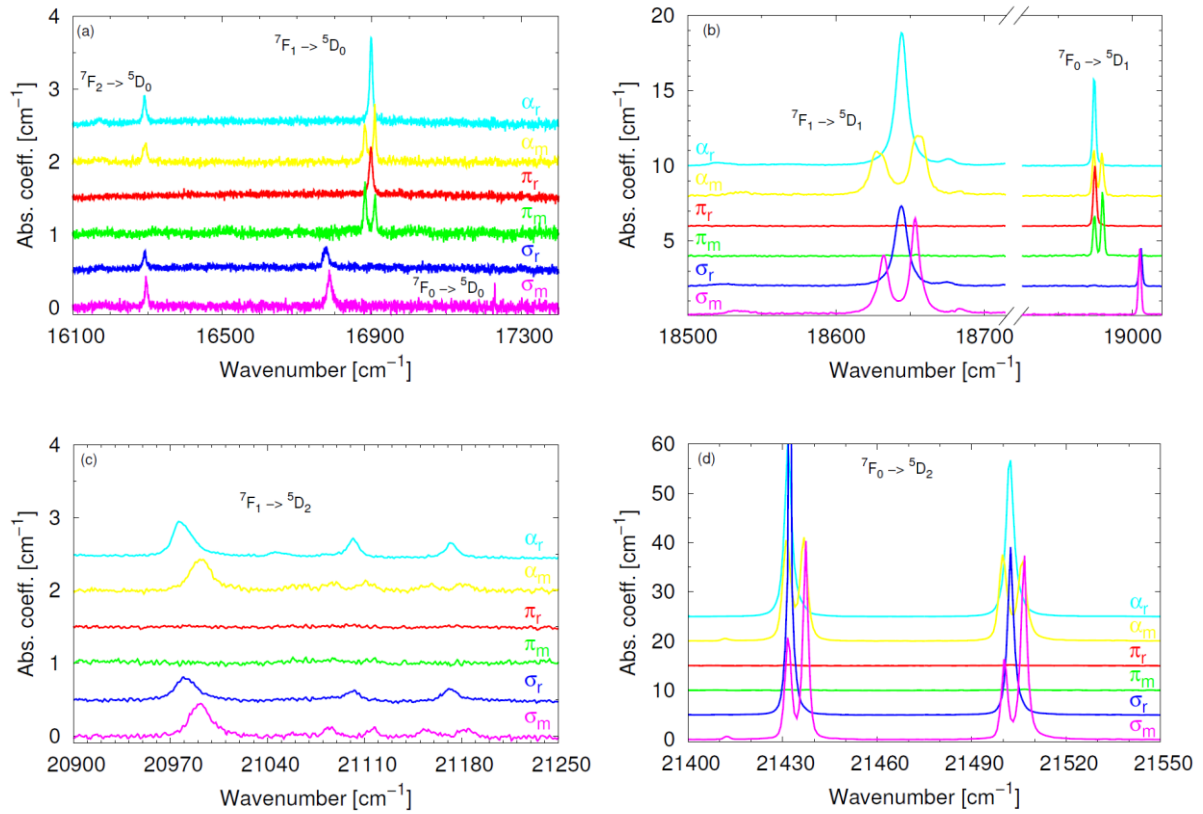


Fig. 4. Absorption spectra corresponding to the electronic transitions from the ${}^7F_{0,1,2}$ CF levels to the ${}^5D_{0,1,2}$ CF levels (a-d) of the Eu^{3+} ion with α , π and σ polarizations in both modifications, measured at room temperature (Samples No. 4-5).

Fig. 4. shows the polarization dependent absorption spectra of Eu^{3+} ions in both rhombohedral and monoclinic GAB crystals at room temperature. The electronic transitions from the ${}^7F_{0,1,2}$ multiplets to 5D_0 singlet can be observed in the 16100-17300 cm^{-1} wavenumber range (Fig. 4a.). The forbidden band of the 7F_0 - 5D_0 transition, that is invisible in rhombohedral symmetry, evolves into a σ polarized absorption spectrum of the monoclinic GAB crystal. The small change of the local symmetry makes it observable with a magnetic dipole behavior (Table 2). In both modifications the transitions from the 7F_1 and 7F_2 levels have magnetic and electric dipole character, respectively. Since 5D_0 is a singlet every splitting in the absorption spectra in this range is a consequence of the crystal field splitting of the fundamental ${}^7F_{1,2}$ multiplets in the monoclinic modification. So the splitting of the band by at about 16900 cm^{-1} into two bands at 16880 cm^{-1} and 16910 cm^{-1} corresponds to the break-up of the doubly degenerated 7F_1 multiplet.

Absorption bands corresponding to transitions to the 5D_1 level have been investigated in the 18500-19000 cm^{-1} wavenumber range. The magnetic dipole feature of the ${}^7F_0 - {}^5D_1$

transition can be clearly seen in the polarization dependent absorption spectra (see Fig. 4b and Table 2). Additionally, a small splitting of the band at 18974 cm^{-1} by at about 6 cm^{-1} shows the loss of the degeneracy of the corresponding ${}^5\text{D}_1$ CF level due to symmetry reduction. The hypersensitive ${}^7\text{F}_1 - {}^5\text{D}_1$ transition shows electric dipole behavior and a similar splitting by at about 30 cm^{-1} as it was already seen for the splitting of one of the ${}^7\text{F}_1$ CF levels in the ${}^7\text{F}_1 - {}^5\text{D}_0$ transition.

The absorption bands of the ${}^7\text{F}_{0,1} - {}^5\text{D}_2$ transitions were observed in the $20900\text{-}21550\text{ cm}^{-1}$ wavenumber range (Fig. 4c-d). Although the ${}^7\text{F}_1 - {}^5\text{D}_2$ transition gives only low intensity absorption bands the splitting by at about 30 cm^{-1} corresponding to the ${}^7\text{F}_1$ CF level is clearly observable (Fig. 4c). The most intense absorption bands in the spectra correspond to the ${}^7\text{F}_0 - {}^5\text{D}_2$ transition which shows electric dipole behavior (Fig. 4d and Table 2). Because of the single ground state the absorption band positions clearly correspond to the structure of the excited ${}^5\text{D}_2$ multiplet. It was found that the degenerate ${}^5\text{D}_2$ CF levels were split by at about $5\text{-}7\text{ cm}^{-1}$ due to the symmetry reduction.

Assigning the band positions in the room temperature absorption measurements and taking into consideration the polarization dependence one can determine the energies of the ${}^7\text{F}_{0,1,2}$ and ${}^5\text{D}_{0,1,2}$ CF levels. The resulting electronic energy level diagrams for both symmetry variations are shown in Fig. 5. These results can be used for crystal field calculations in a unique way because the crystal lattice and also the environment of the rare earth ions differ only nearly imperceptibly in these two modifications. According to [20] the energy levels of ${}^5\text{D}_1$ and ${}^7\text{F}_1$ multiplets of Eu^{3+} ion behave similarly in different environments. It was shown theoretically that the ratio of the splitting of these two terms has to be 0.298 independent from crystal symmetry, however, the experimental values usually differ (e.g. $1/5$ in [11]) from this prediction which was interpreted by intermediate coupling or J-mixing. The ratios for the rhombohedral and monoclinic GAB crystals are 0.24 and 0.258, respectively. These values indicate that the LS coupling model describes the Eu^{3+} ions better in the monoclinic structure than in the rhombohedral one.

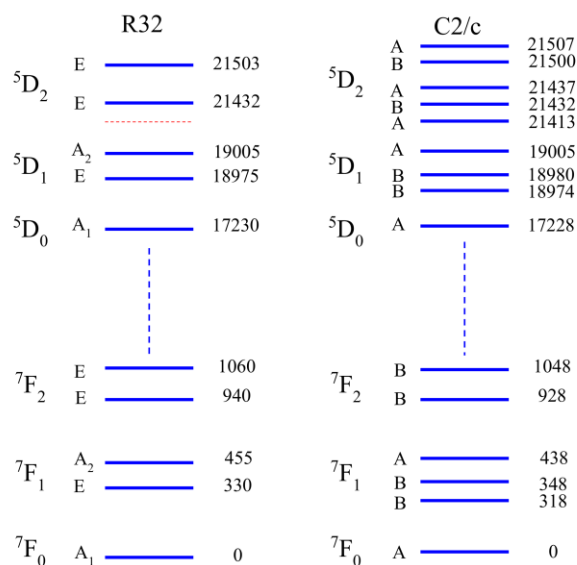


Fig. 5. The lower part of the electronic energy levels of Eu^{3+} ion determined from absorption measurements at room temperature for both rhombohedral and monoclinic modifications, the energy values are given in cm^{-1} .

4. Conclusions

Electronic transitions of the Eu^{3+} , Tb^{3+} and Gd^{3+} rare earth ions in doped GAB crystals with monoclinic ($C2/c$) and rhombohedral ($R32$) structure were successfully identified using temperature and concentration dependent absorption measurements in the $16000\text{--}32000\text{ cm}^{-1}$ wavenumber range. The absorption bands of Tb^{3+} ions shifted less than 20 cm^{-1} due to the symmetry change. The electronic transitions of the Eu^{3+} ions between the ${}^7F_{0,1,2}$ and ${}^5D_{0,1,2}$ levels were also successfully identified by additional polarization dependent absorption measurements at room temperature. The appearance of the strongly forbidden ${}^7F_0\text{--}{}^5D_0$ transition and the splitting of the degenerate levels due to symmetry reduction make detailed crystal field calculations most feasible. The ratios of the splitting of the 5D_1 and 7F_1 multiplets show that the LS coupling scheme is better for the description of the Eu^{3+} ions in the monoclinic structure than in the rhombohedral case.

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