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# Optically detected magnetic resonance investigation of a luminescent oxygen–vacancy complex in Mn-doped LiBaF<sub>3</sub>

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## Abstract

The structure of an oxygen-related luminescence centre in manganese-doped LiBaF<sub>3</sub> was investigated by means of photoluminescence (PL) and PL-detected electron paramagnetic resonance. At 20 K an oxygen-related complex shows two luminescence bands peaking at about 430 and 475 nm, when excited at 220 nm. These bands can be attributed to an excited triplet state ( $S = 1$ ) of an oxygen–vacancy complex with the  $z$  axis of the fine structure tensor parallel to the  $\langle 110 \rangle$  direction. This complex is believed to be next to a Mn<sup>2+</sup> impurity on a Ba<sup>2+</sup> site and can be described as an oxygen on a fluorine lattice site with a nearest fluorine vacancy along the  $\langle 110 \rangle$  direction.

## 1. Introduction

LiBaF<sub>3</sub> has a so-called inverse perovskite structure (space group  $O_h^1$ ) with a perfect cubic structure; its lattice constant is  $a = 3.995 \text{ \AA}$  [1]. Even at low temperatures it shows no distortions from its cubic structure [2]. This compound can be doped with Mn<sup>2+</sup>, which substitutes for Li<sup>+</sup> and is thus surrounded by six fluorine ions in octahedral symmetry [3].

Previous work [4] on Mn-doped LiBaF<sub>3</sub> revealed the optical properties of the Mn<sup>2+</sup> dopant. Mn<sup>2+</sup> emits at 712 nm and has a characteristic excitation spectrum. After x-irradiation the magnetic circular dichroism (MCD) of the optical absorption indicated that an F-type centre interacts with the Mn<sup>2+</sup> dopant.

For oxygen-doped LiBaF<sub>3</sub> Shiran and Voronova [5] found a luminescence band peaking at 420 nm which is caused by the oxygen dopant. Besides the Mn<sup>2+</sup> emission we found for Mn-doped LiBaF<sub>3</sub> luminescence bands peaking at 423 and 480 nm. These bands correspond to those observed for oxygen-doped LiBaF<sub>3</sub> [5] and are tentatively attributed to oxygen impurities which are difficult to avoid in fluoroperovskites.

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In order to get structural information on these oxygen-related centres we detected the electron paramagnetic resonance-induced changes in the oxygen-related photoluminescence (PL). This technique is usually called PL-detected electron paramagnetic resonance (PL-EPR). In the present work we analysed PL-EPR spectra and their angular dependences for the oxygen-related luminescence bands.

## 2. Experiment

### 2.1. Sample preparation

LiBaF<sub>3</sub> single crystals were grown in the Paderborn crystal growth laboratory using the Bridgman method with a vitreous carbon crucible, argon atmosphere and a stoichiometric mixture of LiF and BaF<sub>2</sub> powder to which 2000 ppm of MnF<sub>2</sub> were added. For the PL-EPR measurements the single crystals were oriented by the Laue technique and cut into a block, so that a rotation in a {110} plane is possible.

### 2.2. Spectroscopy

PL and PL excitation spectra were recorded using a single-beam spectrometer in which two 0.22 m double monochromators (Spex) were available for excitation and luminescence. The excitation was carried out with a deuterium and a xenon lamp; the PL was detected with a cooled photomultiplier using single-photon counting. The spectra were not corrected for the spectral sensitivity of the experimental set-up. The time-resolved PL measurements were carried out with a nitrogen flash lamp for excitation and a computer-controlled transient recording board. The pulse width was 20 ns.

PL-EPR spectra were recorded at 1.5 K with a custom-built, computer-controlled magneto-optical spectrometer working at 24 GHz (K-band). The samples were excited in the ultraviolet (UV) spectral range with a deuterium lamp and a subsequent 218 nm interference filter. PL was detected with a cooled photomultiplier in the spectral range between 380 and 800 nm using an edge filter (KV 380). The microwave modulation frequency was at 7 Hz.

## 3. Experimental results

### 3.1. Photoluminescence

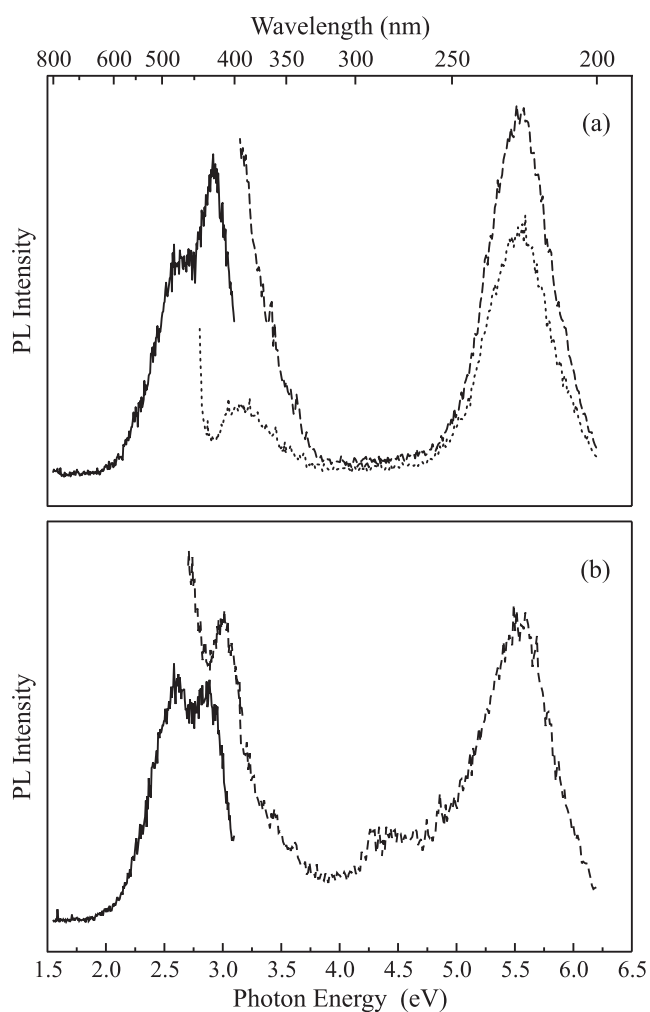
Figure 1(a) shows the PL and PL excitation spectra of an oxygen-related complex in Mn-doped LiBaF<sub>3</sub>. In PL, one band peaks at 423 nm and a weaker one at 480 nm. The corresponding excitation spectra show intense bands at 220 and 398 nm. The radiative lifetime of the 423 nm luminescence is  $(2.5 \pm 0.3)$  ms (figure 2). The 423 and 480 nm luminescence bands are not caused by the Mn dopant. The PL and PL excitation spectra of Mn<sup>2+</sup> in LiBaF<sub>3</sub> are shown in [4].

At 20 K the 423 and 480 nm PL bands do not change significantly. Here both luminescence bands have the same intensity and peak at about 430 and 475 nm. Their excitation spectra are identical with their maxima at 220 and 412 nm (figure 1(b)).

### 3.2. Photoluminescence-detected EPR

The ground state of an O<sup>2-</sup> impurity is diamagnetic and can thus not be detected using EPR. However, the excited state of O<sup>2-</sup> can become paramagnetic if the excited electron and the remaining unpaired electron have parallel spins, i.e. if the excited (O<sup>2-</sup>)<sup>\*</sup> is in a triplet state.

Figure 3 shows a PL-EPR spectrum detected in the oxygen-related luminescence bands found in Mn<sup>2+</sup>-doped LiBaF<sub>3</sub>. The spectrum was recorded in the K-band (23.73 GHz) for a magnetic field orientation parallel to [110]. The PL was excited at 1.5 K with a deuterium lamp

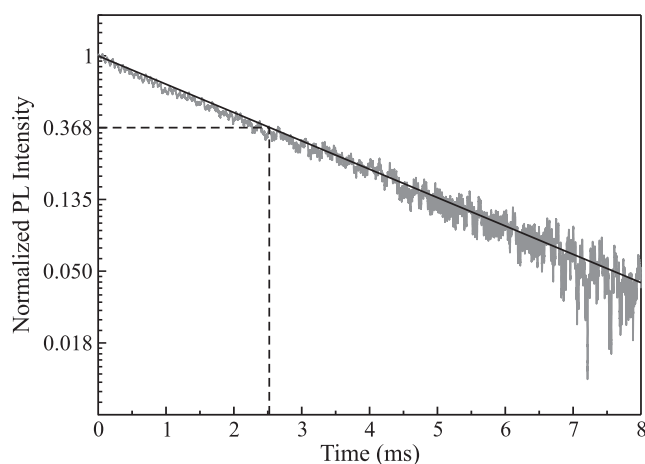


**Figure 1.** (a) PL (solid curve) and PL excitation (dashed, dotted curves) spectra of an oxygen-related complex in LiBaF<sub>3</sub>:Mn<sup>2+</sup> recorded at RT. The PL was excited at 220 nm. The excitation spectra were detected at 423 nm (dashed) and 480 nm (dotted). The increase in the excitation spectra is caused by incident excitation light. (b) PL (solid curve) and PL excitation (dashed curve) spectra of an oxygen-related complex in LiBaF<sub>3</sub>:Mn<sup>2+</sup> recorded at 20 K. The PL was excited at 220 nm; the excitation spectrum was detected at 475 nm. The excitation spectrum detected at 430 nm is not shown; it is identical to the one detected at 475 nm.

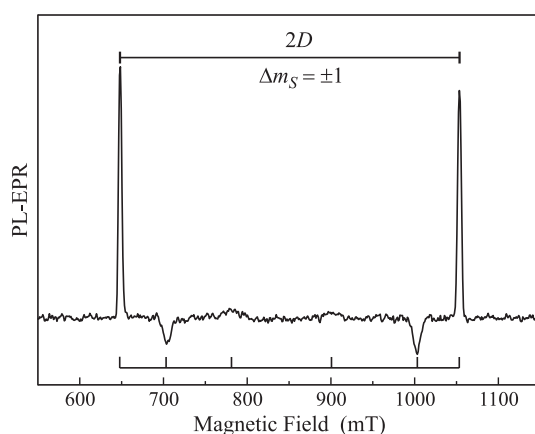
and a subsequent 218 nm interference filter and detected in the integral luminescence with a 380 nm edge filter. The angular dependence of these lines for a rotation of the magnetic field in a {110} plane is presented in figure 4. We used the spin Hamiltonian of a triplet spin ( $S = 1$ ) system with an orthorhombic fine structure (FS) tensor to analyse the angular dependence of the PL-EPR line, i.e.

$$\mathcal{H} = \mu_B \cdot \vec{B} \cdot \underline{\underline{g}} \cdot \vec{S} + \vec{S} \cdot \underline{\underline{D}} \cdot \vec{S} \quad (1)$$

where  $\underline{\underline{g}}$  and  $\underline{\underline{D}}$  are the  $g$  and  $D$  tensors,  $\mu_B$  is the Bohr magneton,  $\vec{B}$  is the magnetic field vector and  $\vec{S}$  is the electron spin operator. The orientations of the  $g$  and  $D$  tensors can be described

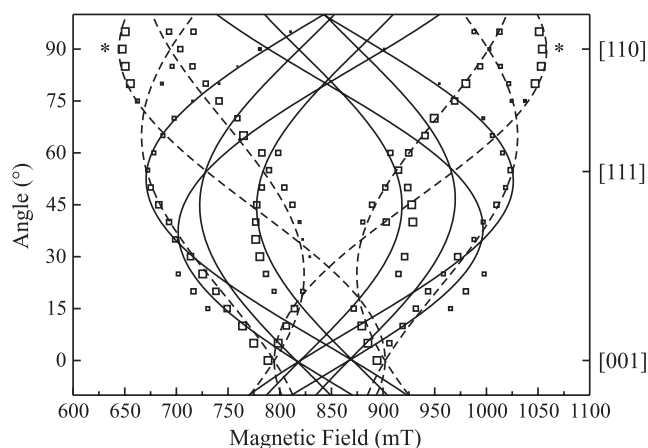


**Figure 2.** PL lifetime excited with a nitrogen flash-lamp and detected at 423 nm.



**Figure 3.** (a) PL-EPR spectrum of an oxygen-related complex in  $\text{LiBaF}_3:\text{Mn}^{2+}$  for an orientation of the magnetic field parallel to  $[110]$ . The spectrum was recorded as microwave-induced changes in the integral PL at 1.5 K applying a microwave frequency of 23.73 GHz. The PL was excited with a deuterium lamp and a subsequent 218 nm interference filter and detected in the integral luminescence with an edge filter (KV 380).

with a set of Euler angles. In the principal axes system the  $g$  tensor is characterized by its three principal values  $g_{xx}$ ,  $g_{yy}$  and  $g_{zz}$ . The  $D$  tensor can be expressed with the two FS values  $D$  and  $E$  in the principal axis system, which have the usual meaning as the axial ( $D = 3/2 \cdot D_{zz}$ ) and the non-axial ( $E = 1/2 \cdot (D_{xx} - D_{yy})$ ) parts, respectively (see for example [6]). The choice of the  $z$  axis corresponds to the maximum absolute value of the FS splitting. The calculated EPR angular dependence for a rotation of the magnetic field in a  $\{110\}$  plane is shown in figure 4 by solid and dashed lines. The parameters are listed in table 1. All observed resonances are due to ‘allowed’ ( $\Delta m_S = \pm 1$ ) transitions. The principal axes  $z$  of the  $g$  and the  $D$  tensors are assumed to be collinear and parallel to a  $\langle 110 \rangle$  direction. The  $x$  and  $y$  axes of the  $g$  and  $D$  tensors are rotated by an angle of  $25^\circ$  about the  $z$  axis and are thus not aligned along any crystal axes.



**Figure 4.** Angular dependence of the PL-EPR lines, recorded for a rotation of the magnetic field in a {110} plane. The spectra were recorded as microwave-induced changes in the integral PL at 1.5 K applying a microwave frequency of 23.73 GHz. The PL was excited with a deuterium lamp and a subsequent 218 nm interference filter and detected in the integral luminescence with a 380 nm edge filter. The open squares represent the experimental line position; the dashed and solid (twofold-degenerate) lines are calculated by using the FS parameters in table 1. The lines marked with ‘\*’ consist of two magnetically non-equivalent lines, which cannot be resolved here.

**Table 1.** Parameters of the spin Hamiltonian (equation (1)) for an oxygen-related luminescence centre in Mn-doped LiBaF<sub>3</sub>. The  $z$  axes of the  $g$  and  $D$  tensors are parallel to a  $\langle 110 \rangle$  direction. The  $x$  and  $y$  axes are not aligned along the crystal axes. The  $x$  axis is tilted in a {110} plane by an angle  $\vartheta$  with respect to a  $\langle 100 \rangle$  direction.

$g_{xx}$	$g_{yy}$	$g_{zz}$	$ D/g_e\beta_e $ (mT)	$ E/g_e\beta_e $ (mT)	$\vartheta$ (deg)
1.97	1.98	1.98	207	52	25
$\pm 0.01$	$\pm 0.01$	$\pm 0.01$	$\pm 2$	$\pm 2$	$\pm 1$

In principle, a triplet spin system having orthorhombic symmetry with the principal axis,  $z$ , along a  $\langle 110 \rangle$  direction should show six magnetically non-equivalent centre orientations, if the  $x$  and  $y$  axes of the  $D$  tensor are aligned exactly along the crystal axes  $\langle 100 \rangle$  and  $\langle 110 \rangle$ . In our case neither the  $x$  nor the  $y$  axis coincides with a  $\langle 100 \rangle$  or a  $\langle 110 \rangle$  direction. Thus, each of the six orientations mentioned above is split into two further magnetically non-equivalent centre orientations. The spectrum of each centre orientation should be split by the fine structure interaction into two lines symmetrical about  $g = 2$ . Altogether up to 24 resonance lines could appear in the PL-EPR spectra. The largest splitting of  $2D$  is for the magnetic field parallel to a  $\langle 110 \rangle$  direction. However, for a rotation of the magnetic field in a {110} plane the angular dependence shows up to 16 resonance lines, 8 of which are twofold degenerate (see figure 4). The number of lines is reduced to 8 for  $B \parallel \langle 110 \rangle$  and to 4 for  $B \parallel \langle 100 \rangle$ . Note that for  $B \parallel \langle 110 \rangle$  only 6 lines can be observed in the experimental spectrum (indicated by bars in figure 3). It was not possible to determine the sign of the FS parameter  $D$ , experimentally by e.g. magnetic circular polarization of emission (MCPE) measurements.

The highest PL-EPR line intensity was obtained for a photon energy of 2.7 eV (460 nm) which corresponds to the low temperature luminescence spectrum of figure 1(b) (solid curve). The best excitation energy using a set of interference filters was found to be at approximately

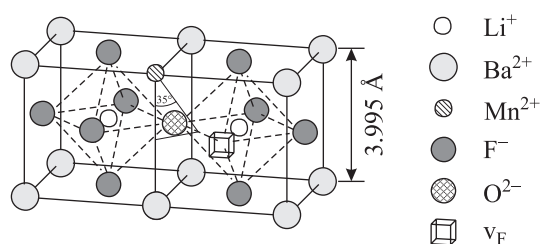


Figure 5. Model of the  $\text{O}_{\text{F}}^{2-}-\text{v}_{\text{F}}-\text{Mn}_{\text{Ba}}^{2+}$  complex in Mn-doped  $\text{LiBaF}_3$ .

5.7 eV (218 nm) which is in agreement with the excitation spectrum depicted in figure 1(b) (dashed curve).

#### 4. Discussion

The analysis of the PL-EPR data shows that the triplet state of the 460 nm luminescence can be described by  $g$  and  $D$  tensors with the  $z$  axes along a  $\langle 110 \rangle$  direction. The  $x$  and  $y$  axes are not aligned along the crystal axes. The  $x$  axis is tilted in a  $\{110\}$  plane by an angle of  $25^\circ$  with respect to a  $\langle 100 \rangle$  direction. The  $g$  values as well as the spectral position of the 460 nm luminescence are very similar to those found for oxygen–vacancy complexes in other fluoride crystals [7–9]. Thus, we assign our luminescent triplet state to an oxygen impurity centre in  $\text{LiBaF}_3$ .  $\text{O}^{2-}$  usually substitutes for fluorine and has an extra negative charge which is usually compensated by an fluorine vacancy nearby [7–9]. In  $\text{LiBaF}_3$  the  $\text{O}_{\text{F}}^{2-}-\text{v}_{\text{F}}$  complex is aligned along a  $\langle 110 \rangle$  direction which is in agreement with the orientation of the principal axis  $z$  of the  $D$  tensor. However, we still have to find an explanation for the observation that the  $x$  and  $y$  axes are not aligned along the crystal axes, but tilted in a  $\{110\}$  plane. We assume a perturbation close to the oxygen–vacancy complex, e.g.  $\text{Mn}^{2+}$  at a  $\text{Ba}^{2+}$  site (figure 5). In this case no additional charge compensation is necessary. The connecting line between the centre of an unrelaxed  $\text{O}_{\text{F}}^{2-}-\text{v}_{\text{F}}$  complex and the  $\text{Ba}^{2+}$  site nearby makes an angle of  $35^\circ$  with respect to a  $\langle 100 \rangle$  direction. However, relaxations in the  $\text{O}_{\text{F}}^{2-}-\text{v}_{\text{F}}-\text{Mn}_{\text{Ba}}^{2+}$  complex might lead to the measured angle of  $25^\circ$ . Note, that the ionic radius of the  $\text{Mn}^{2+}$  ion (0.80 Å) is much smaller than that of the  $\text{Ba}^{2+}$  ion (1.34 Å).

In principle, there would be two further alternatives for an oxygen-related complex considering the necessary charge compensation: (i)  $\text{Mn}^{2+}$  at a  $\text{Li}^+$  site or (ii) a Mn ion in its possible charge state of  $\text{Mn}^{3+}$  at a  $\text{Ba}^{2+}$  site. The first possibility can be excluded because the  $\text{O}_{\text{F}}^{2-}-\text{Mn}_{\text{Li}}^{2+}$  complex would be aligned along a  $\langle 100 \rangle$  direction. For (ii) the  $\text{O}_{\text{F}}^{2-}-\text{Mn}_{\text{Ba}}^{3+}$  complex would be aligned along a  $\langle 110 \rangle$  direction, but in this case we cannot explain the tilt of the  $x$  and  $y$  axes of the  $D$  tensor with respect to the crystal axes.

#### 5. Conclusion

PL-EPR measurements provided information on a luminescent oxygen-related complex in Mn-doped  $\text{LiBaF}_3$ . The luminescence at 2.7 eV (for an excitation energy of 5.7 eV) is due to a Mn-perturbed oxygen–vacancy complex consisting of an oxygen on a fluorine site with the nearest fluorine vacancy in a  $\langle 110 \rangle$  direction and  $\text{Mn}^{2+}$  in the vicinity, substituting for  $\text{Ba}^{2+}$ .

## Acknowledgments

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