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Optically detected magnetic resonance investigations of oxygen luminescence centres in BaFCl

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Abstract. The structure of oxygen-related luminescence centres in oxygen-doped BaFCl was investigated by photoluminescence-detected electron paramagnetic resonance (PL-EPR). It turned out that one of the oxygen-related luminescence centres is due to an excited triplet state. The fine structure parameters of this $S = 1$ system are $D = 188$ mT and $E = 28$ mT with an angle of 17° in the ca plane between the z axis of the D tensor and the c axis of the crystal. The structure of the centre can be described as an oxygen–vacancy complex where the oxygen substitutes for fluorine with a next nearest chlorine vacancy.

1. Introduction

BaFBr doped with Eu is known as one of the best x-ray storage phosphors. It was previously shown that it is very difficult to avoid oxygen contamination in this material [1]. The incorporation of oxygen influences significantly the performance of this storage material. The structure of an oxygen-related photoluminescence centre in BaFBr was investigated by detecting the microwave-induced changes in the photoluminescence [2]. The analysis of the photoluminescence-detected electron paramagnetic resonance (PL-EPR) spectra yielded an excited triplet state of an $O_F^{2-}-v_{Br}$ complex (O_F = oxygen on an F lattice site, v_{Br} = bromine vacancy). The bromine vacancy was proposed to be in the next nearest neighbourhood of O_F .

BaFCl is also contaminated with oxygen. This was shown by luminescence [3] as well as by EPR [4] techniques. Luminescence measurements yielded two different oxygen-related luminescence centres [3], whereas EPR showed three oxygen defects: oxygen substitutes for fluorine, oxygen substitutes for chlorine and an oxygen molecule which substitutes for chlorine [4].

In this paper we present a PL-EPR investigation of the oxygen-related luminescence centres in BaFCl.

2. Experiment

2.1. Sample preparation

BaFBr and BaFCl single crystals were grown in graphite crucibles with the Bridgman method from a stoichiometric mixture of BaF_2 , $BaBr_2/BaCl_2$ and 200 ppm BaO. BaFBr and BaFCl crystallize in the matlockite structure, with tetragonal space group $P4/nmm$ (No 129) (figure 1) [5–7].

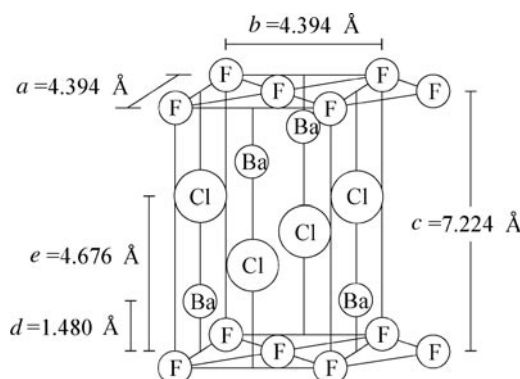


Figure 1. Matlockite structure of BaFCl with the lattice parameters of the unit cell [5]. The value d represents the distance between the fluorine and the barium plane, the value e the distance between the fluorine and the chlorine plane.

2.2. Spectroscopy

Luminescence and luminescence excitation spectra were measured with a single-beam spectrometer in which 0.25 m double monochromators (Spex) were available for excitation and luminescence. The excitation was carried out with a deuterium lamp; the photoluminescence (PL) was detected using single photon counting with a photomultiplier.

Photoluminescence-detected electron paramagnetic resonance (PL-EPR) spectra were recorded at 1.5 K with a custom-built, computer-controlled spectrometer working at 24 GHz (K band). The samples were excited in the ultraviolet (UV) spectral range with a deuterium lamp and subsequent interference filters in the range between 210 and 300 nm. PL was detected by a photomultiplier in the spectral range between 300 and 800 nm using edge filters. The microwave modulation frequency was between 270 Hz and 10 kHz; the EPR angular dependence was recorded for a microwave modulation frequency of 270 Hz.

3. Experimental results

The UV-excited luminescence band of oxygen-doped BaFCl peaks at 540 nm (2.30 eV) (figure 2(a)). The corresponding excitation band peaking at 244 nm (5.08 eV) is shown in figure 2(b). The ground state of an O^{2-} impurity is diamagnetic and thus cannot be detected by EPR. However, the excited state of O^{2-} can become paramagnetic if the excited electron and the remaining unpaired electron have parallel spins, i.e. if the excited $(O^{2-})^*$ is in a triplet state [2]. Figure 3 shows a PL-EPR spectrum of oxygen-doped BaFCl in the K band (24.85 GHz) for a magnetic field orientation in the ca plane with an angle of approximately 30° with respect to the c axis. The spectrum is characteristic for a triplet EPR spectrum with two lines symmetrical about $g = 2$ split by the fine structure interaction. The angular dependence of these lines 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 lines.

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

where $\underline{\underline{g}}$ and $\underline{\underline{D}}$ are the g and D tensor, respectively. μ_B is the Bohr magneton, \vec{B} is the magnetic field vector and \vec{S} the electron spin operator. The orientations of the g and D tensor

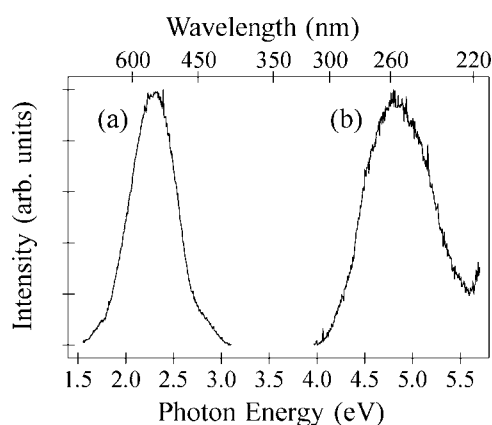


Figure 2. (a) Luminescence spectrum of oxygen-contaminated BaFCl excited at 244 nm (5.08 eV) and (b) excitation spectrum of the luminescence peaking at 540 nm (2.30 eV). Both spectra were recorded at RT.

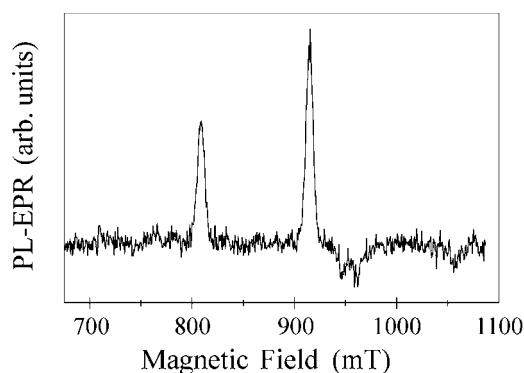


Figure 3. PL-EPR spectrum of oxygen-doped BaFCl for an orientation of the magnetic field in the ca plane with an angle of approximately 30° with respect to the c axis. The spectrum was recorded as microwave-induced changes in the integral PL at 1.5 K applying a microwave frequency of 24.85 GHz (270 Hz microwave modulation). The PL was excited with a 280 nm interference filter and detected in the integral luminescence with a 450 nm edge filter.

can be described with a set of Euler angles. In the principal axis 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 ($D = \frac{3}{2}D_{zz}$) and non-axial ($E = \frac{1}{2}(D_{xx} - D_{yy})$) parts, respectively (see e.g. [8]). The calculated EPR angular dependence is shown in figure 4 by solid lines. The parameters are collected in table 1. It turned out that two of the principal axes of the g and the D tensor, respectively, are in a ca (cb) mirror plane. Thus, the tensor orientation with respect to the crystal axes is described by one free angle only.

The analysis of the angular dependence yielded that there are four different centre orientations. For two centre orientations, the x and z axes of the g and the D tensor, respectively, are in the ca mirror plane; for the other two orientations they are in the cb mirror plane. For $\vec{B} \parallel \vec{c}$ all four centre orientations are magnetically equivalent. When rotating the magnetic field from the c axis to the a axis (figure 4(a)), the two centre orientations in the cb plane remain magnetically equivalent having only one fine structure split doublet. The small splitting of these

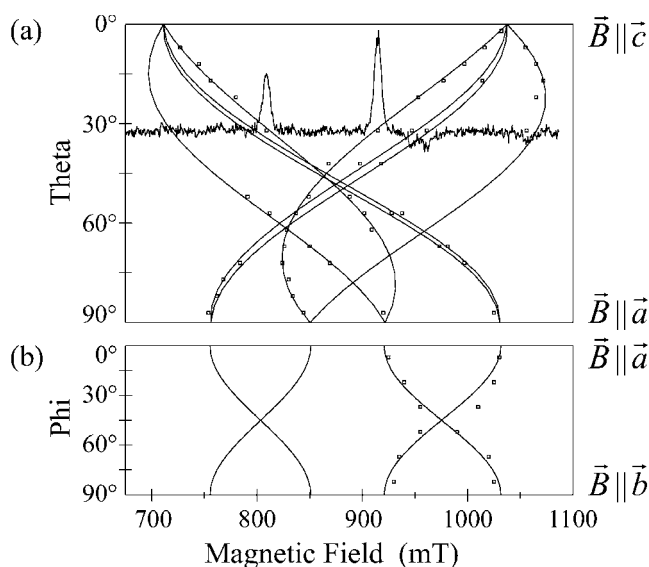


Figure 4. Angular dependence of the PL-EPR lines, measured (a) for a rotation from $\vec{B} \parallel \vec{c}$ to $\vec{B} \parallel \vec{a}$ and (b) for a rotation in the ab plane. The open squares represent the experimental line position; the solid lines are calculated by using the FS parameters of table 1.

Table 1. Parameters of the spin Hamiltonian (equation (1)) obtained from the analysis of the angular dependence. ϑ_g and ϑ_D describe the angles in the ca (cb) mirror plane between the z axes of the g and D tensors, respectively, and the c axis of the crystal. The x axis of the g and the D tensor, respectively, is also in the ca (cb) mirror plane; the y axis is parallel to the b axis (a axis). The precision is ± 0.005 for g , ± 50 MHz for D and E , and $\pm 1^\circ$ for ϑ_g and ϑ_D .

g_{xx}	g_{yy}	g_{zz}	ϑ_g ($^\circ$)	D/h (MHz)	E/h (MHz)	ϑ_D ($^\circ$)
1.970	1.979	2.045	-30	± 5270	± 780	17
				$(D/g_e\beta_e = 188 \text{ mT})$	$(E/g_e\beta_e = 28 \text{ mT})$	

two orientations in the cb plane is due to a slight misalignment. For a rotation of the magnetic field in the ab plane there are two pairs of two magnetically equivalent centre orientations (figure 4(b)).

Unfortunately, it was not possible to determine the sign of the FS parameter D experimentally. The observed line intensities cannot be explained by a simple Boltzmann distributed level population. They are obviously influenced by dynamical effects such as the radiative lifetime of the different m_S states. The PL-EPR line intensity decreased to half its value on changing the microwave modulation frequency from 270 Hz to 3 kHz and vanished for 10 kHz, indicating that the relaxation time of the spin polarization in the excited state is longer than several tenths of a millisecond.

The PL-EPR lines could be detected in a spectral range according to the luminescence spectrum of figure 2(a): the highest PL-EPR line intensity was obtained at a photon energy of 2.3 eV (540 nm) which is the maximum of the luminescence band. However, the spectral range of the excitation light was slightly shifted to longer wavelength with respect to the excitation spectrum of figure 2(b): the best excitation energy was found to be at approximately 4.75 eV (261 nm).

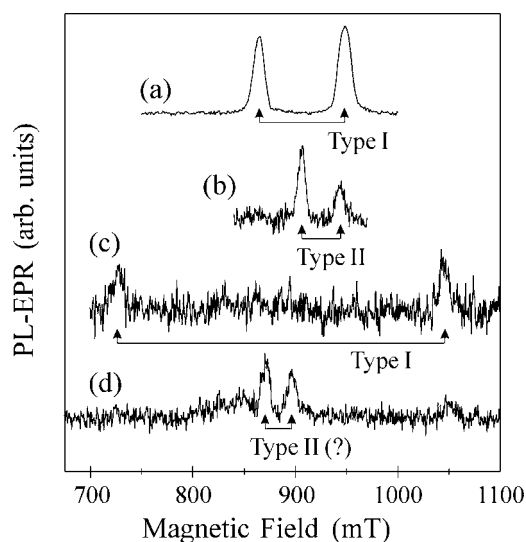


Figure 5. PL-EPR spectra of oxygen-doped BaFBr and BaFCl, recorded for $\vec{B} \parallel \vec{c}$ at $T = 1.5$ K applying a microwave frequency of 24.85 GHz (270 Hz microwave modulation frequency) using different interference filters (IF) and edge filters (EF): (a) BaFBr:O—260 nm (IF, exc.) and 503 nm (IF, lum.), (b) BaFBr:O—240 nm (IF, exc.) and 520 nm (EF, lum.), (c) BaFCl:O—280 nm (IF, exc.) and 450 nm (EF, lum.), (d) BaFCl:O—240 nm (IF, exc.) and 380 nm (EF, lum.).

3.1. Further oxygen centres in BaFCl and BaFBr

Besides the above described PL-EPR resonances (as shown in figure 5(c) for $\vec{B} \parallel \vec{c}$), we found PL-EPR from another luminescence centre with significantly different FS parameters (figure 5(d)). Due to the low line intensity it was not possible to measure a full angular dependence as for the other centre, but only for $\vec{B} \parallel \vec{c}$. These two luminescence centres could be separated by using different excitation energies. The PL-EPR was again detected at a photon energy of 2.3 eV (540 nm), while the best excitation energy was found to be at approximately 5.15 eV (241 nm).

In BaFBr we found not only PL-EPR resonances from the oxygen–vacancy complex described in [2] (see figure 5(a)), but also another centre with different FS parameters (figure 5(b)). Due to the low line intensity it was again not possible to measure a full angular dependence of this second luminescence centre. The two luminescence centres in BaFBr could be separated by using different excitation energies as in BaFCl, but also different spectral ranges for detection of the luminescence. We used an excitation energy of 5.17 eV (240 nm) and detected the luminescence at energies lower than 2.38 eV (520 nm) (figure 5(b)).

4. Discussion

According to the PL-EPR angular dependence of the main oxygen-related luminescence centre in BaFCl there are four centre orientations. The presence of a charge-compensating vacancy nearby will determine the orientation of the FS tensor as will be discussed later. From the present PL-EPR experiments alone we cannot decide whether O^{2-} resides on a fluorine or on a bromine site. However, it was possible to separate two different oxygen-related luminescence centres by growing specially prepared BaFCl crystals where mainly O_F^{2-} or O_{Cl}^{2-} defects, respectively, are formed [3]. The luminescence band of the O_F^{2-} centres (type I centres) peaks

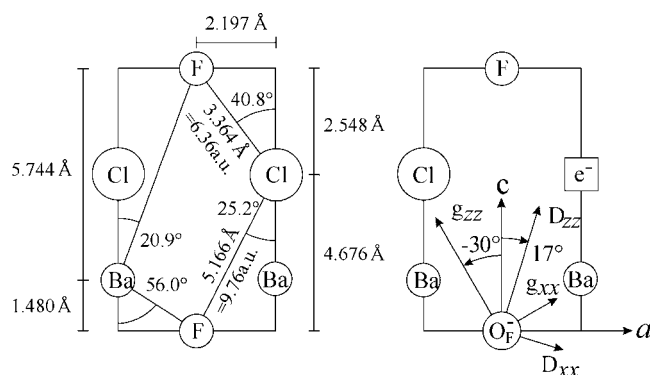


Figure 6. Model of the $\text{O}_F^{2-}-v_{\text{Cl}}$ complex in BaFCl.

at 2.30 eV (540 nm) whereas the $\text{O}_{\text{Cl}}^{2-}$ luminescence band (type II centres) has its maximum at 2.45 eV (506 nm). The type I centre has one of its absorption bands at 4.9 eV (253 nm); one of the absorption bands of the type II centre peaks at 4.5 eV (276 nm). The highest PL-EPR line intensity of the main centre was obtained at a photon energy of 2.3 eV (540 nm) which is in very good agreement with the peak position of the luminescence band of the O_F^{2-} centres (type I centres). Although the best excitation energy for the PL-EPR which was found to be at approximately 4.75 eV (261 nm) is slightly different from the absorption band at 4.9 eV we assign the PL-EPR resonances to an O_F^{2-} defect. It is not clear whether the PL-EPR lines of the second oxygen-related luminescence centre are due to $\text{O}_{\text{Cl}}^{2-}$ centres. The excitation band, where the PL-EPR lines could be detected best, do not coincide with the data for the type II centre according to [3].

In BaFBr there are also two different oxygen-related luminescence centres: the first one was analysed previously to be an $\text{O}_F^{2-}-v_{\text{Br}}$ complex [2, 3] whereas the second one is probably caused by $\text{O}_{\text{Br}}^{2-}$ centres as proposed in [3].

The zero-field splitting parameter D consists of the two parts D_{ss} and D_{so} , whereby D_{ss} is due to the spin-spin interaction and D_{so} due to the spin-orbit interaction [9]. In [2] it was already estimated that the latter one is probably very small and can thus be neglected, similarly as for the STEs in alkali fluorides [10]. In analogy to the situation in BaFBr [2] the optically excited oxygen 2p electron being in an s-like state resides on a nearby Cl^- vacancy. However, the 2p orbital of the oxygen hole is not orientated perpendicular to the $\text{O}_F^- - v_{\text{Cl}}$ connecting line, but towards the Cl^- vacancy. The orientation of the fine structure tensor $\vartheta_D = 17^\circ$ agrees quite well with the angle of 25.2° between the $\text{O}_F^- - v_{\text{Cl}}$ connecting line and the crystal c axis (figure 6). The axial part of the fine structure tensor D was estimated by assuming Gaussians, i.e. $\exp(-\alpha r^2)$ for the wavefunctions of the electron on the Cl^- vacancy ($\text{F}(\text{Cl}^-)$) and the p hole at the oxygen on the fluorine site. For the hole we assumed that $\alpha_{\text{hole}} = 0.3 (\text{au})^{-2}$ and $\alpha_{\text{electron}} = 0.08 (\text{au})^{-2}$ as in BaFBr [2]. The theoretical values for different distances and orientations are listed in table 2. It turned out that D_{theo} depends rather weakly on ϑ_{theo} and α_{electron} (not listed in table 2), but there is a very strong dependence on the distance d . The measured fine structure parameter D can be simulated quite well by considering a misalignment of the p hole with respect to the $\text{O}_F^- - v_{\text{Cl}}$ connecting line and a larger distance between the p hole and the F electron (11.0 au) as in the case of an unperturbed lattice (9.76 au). We cannot give a good explanation for the fact that in BaFBr the D_{zz} axis was oriented perpendicular to the $\text{O}_F^- - v_{\text{Br}}$ connecting line [2] while here the D_{zz} axis is nearly parallel to the $\text{O}_F^- - v_{\text{Cl}}$ connecting line. It is probably caused by a different interaction between the F electron and the

Table 2. Theoretical values for the axial part D of the fine structure interaction calculated for different distances and orientations ϑ_{theo} of the oxygen p hole with respect to the crystal c axis. For the calculations $\alpha_{\text{hole}} = 0.3 \text{ (au)}^{-2}$ and $\alpha_{\text{electron}} = 0.08 \text{ (au)}^{-2}$ were used.

d (au)	D_{theo} (mT)	ϑ_{theo} ($^{\circ}$)
	-252	18.0
10.0	-250	17.1
	-248	16.2
	-216	18.0
10.5	-215	17.1
	-213	16.2
	-188	18.0
11.0	-187	17.1
	-185	16.2

oxygen ion. In BaFCl, the repulsion between the F electron and the electron p orbitals of the oxygen ion seems to be stronger than in BaFBr. Thus, the p hole at the oxygen ions orientates towards the F electron.

References

- [1] Eachus R S, Nuttall R H D, Olm M T, McDugle W G, Koschnick F-K, Hangleiter Th and Spaeth J-M 1995 *Phys. Rev. B* **52** 3941
- [2] Koschnick F-K, Hangleiter Th, Song K S, and Spaeth J-M 1995 *J. Phys.: Condens. Matter* **7** 6925
- [3] Radzhabov E and Otroshok V 1995 *J. Phys. Chem. Solids* **56** 1
- [4] Eachus R S, Nuttall R H D, Olm M T, McDugle W G, Koschnick F-K, Hangleiter Th and Spaeth J-M 1995 *Phys. Rev. B* **52** 3941
- [5] Sauvage M 1974 *Acta Crystallogr. B* **30** 2786
- [6] Liebich B W and Nicollin D 1977 *Acta Crystallogr. B* **33** 2790
- [7] Beck H P 1979 *Z. Anorg. Allg. Chem.* **451** 73
- [8] Spaeth J-M, Niklas J R, and Bartram R H 1992 *Structural Analysis of Point Defects (Springer Series in Solid-State Sciences 43)* (Berlin: Springer) ch 3
- [9] Song K S and Williams R T 1993 *Self-Trapped Excitons (Springer Series in Solid-State Sciences 105)* (Berlin: Springer) ch 5
- [10] Song K S, Leung C H and Spaeth J-M 1990 *J. Phys.: Condens. Matter* **2** 6373