Europium doped BaMgF₄, an EPR and optical investigation

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Abstract

Eu⁺⁺ was introduced into pure and oxygen codoped BaMgF₄ single crystals. A detailed EPR study of this ion (S=7/2) was realized on both types of systems. The result is that only one spectrum was observed involving a strong crystal field. The associated site symmetry of the impurity is C₁. It occupies very closely a Barium lattice site as was established by correlating the EPR results with those of a refined X-ray structure analysis on a Ba₀.₈ₓEu₀.₂ₓMgF₄ single crystal realized in our laboratory. The oxygen codoped crystals exhibited this same Eu⁺⁺ EPR spectrum (the only one). Optical emission and excitation experiments were performed between 13 000 and 53 000 cm⁻¹. The results due to the Eu⁺⁺ impurity are given and discussed qualitatively within the 4f⁴→4f⁵d¹ scheme. © 1998 Elsevier Science S.A.

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1. Introduction

Barium Magnesium Fluoride, BaMgF₄, belongs to the isomorphous compounds of the BaMF₄ type (M=Mn, Fe, Co, Ni and Zn). They all crystallize in the orthorhombic system with space group Cmc₂₁ (No 36) with four molecules per unit cell [1]. The BaMgF₄ structure has recently been characterized by single crystal X-ray diffraction [2]. It consists of distorted MgF₆ octahedra sharing corners to form puckered sheets parallel to (010). These are linked by Ba²⁺ ions. Both cations, Ba²⁺ and Mg²⁺ are on the Wyckoff site 4a, located in a mirror plane parallel to (100). BaMgF₄ is pyroelectric and piezoelectric [3] similar to all the compounds of the BaMF₄ type. Its conventional symmetry group allows for a polar axis parallel to c. This material is a very suitable host for transition metal (TM) and rare earth (RE) ion impurities and has promising properties for solid state laser applications. Within this context, identification of the site(s) occupied by the impurity cations in the crystal is important and needs to be clarified. Further, as many fluorides are notorious for oxygen contamination the question arose as to whether oxygen compensated impurity cations could be identified. We chose Eu⁺⁺ ions as the probe and EPR as the method to study these questions. Several publications give results of luminescence studies on Europium doped BaMgF₄ (e.g. [4–7]). But there is disagreement, in particular regarding the published excitation spectra. To the best of our knowledge, there seem to be no publications about single crystal EPR results on this system.

2. Experimental

2.1. Sample preparation and equipment

The compound BaMgF₄ doped with 4% of EuF₃ was synthesized from a stoichiometric melt of the fluorides BaF₂ (Merck, suprapure), MgF₂ (Balzers, oxygen-free vacuum deposition grade) and EuF₂ (Cerac, 99.9% pure). Single crystals were grown (using a pyrolytic graphite crucible) by the Czochralski method under 0.2 atm of Argon, or in our Bridgman furnace. The greatest care was taken to avoid oxygen contamination during growth. In particular BaF₂ was precrystallized beforehand and the absence of oxygen was verified by UV absorption and luminescence spectroscopy. During pulling, the nominal temperature of the crucible was 965°C while the melting point of BaMgF₄ is 920°C [8]. A typical single crystal size in the as-grown boule was 10×5×5 mm³. They cleave well parallel to {010}. The samples used for the EPR experiments were oriented precisely with the aid of a polarizing microscope and by the Laue X-ray technique.

As-grown Ba₁₋ₓMgF₄; Eu⁺⁺ crystals with nominally x =
0.004 were studied. A crystal was subsequently hydrolysed during 80 hours according to the method described in [9] at a nominal furnace temperature of 850°C. Further, a polycrystal of composition \((\text{BaMgF}_4)_1-x: (\text{BaO})_x; \text{EuF}_2\) with \(x = 0.04\) was grown in a vitreous carbon crucible under otherwise unchanged conditions with respect to the pure ones. Single crystals of typical dimensions \(5 \times 1.5 \times 8\) mm\(^3\) were cleaved from the as-grown material. The optical measurements were carried out with a home-built spectrophotometer. The excitation light of a Varian 300 W Xenon lamp was spectrally decomposed with the aid of a H2O monochromator. Part of the light was directed on a Hamamatsu photodiode with the aid of an appropriately positioned beamsplitter. The luminescence signal was analyzed with a Cary 16 double monochromator and detected by a Hamamatsu PM. Our home-made photon counting card (3 entrance ports) allows simultaneous measurement of the reference and the luminescence signals and normalization of the latter at each measured point. The recorded spectra were normalized this way. The Cary 16 monochromator had been calibrated with a low pressure mercury arc lamp. Lenses, dewar windows and beam splitters used were of Suprasil quality.

EPR spectra were obtained at 9.26 GHz on a laboratory-modified X-band E-line Varian spectrometer, and at 36.4 GHz on a home-built Ka-band spectrometer. Both instruments are fully computer-controlled and provided with low temperature equipment of our design. The magnetic field is computer-controlled and stabilized through feedback type electronics and is calibrated with a Metrolab PT2025 proton magnetometer. The microwave frequency is measured with a HP5342A frequency counter.

2.2. Data analysis and computer simulations

From a measured spectrum (in digital form) we determine the EPR line positions as a function of the magnetic field \(B\) and record them in a file together with the microwave frequency. The ensemble of files obtained when a complete angular variation of the B field has been performed, forms the input data for our home made SPINHAM computer program. This program allows treatment of the results of a large number of EPR and ENDOR situations. The general form of the spin Hamiltonian treated is \([10-12]\):

\[
H = g_\beta B \cdot S + S \cdot A \cdot I + I \cdot Q \cdot I - g_\mu_B B \cdot I
+ \sum_{k=2,4,6} \sum_{q=-k}^{+k} b_k^q O_k^q + \sum I \cdot A \cdot I,
\]

(1)

The symbols have their usual meaning, \(q\) has unit increments. The program builds up the matrix from all the terms (with the exception of the super hyperfine interaction terms in the \(SQ\) spin product space). In the simplest situation where the magnetic field and the spin Hamiltonian constants are given, the matrix is generated and diagonalized. In a usual EPR experiment the microwave frequency is known and the magnetic field values of the spectral components are obtained. The spin Hamiltonian parameters are in this case determined with the aid of a least squares optimization process. This numerical approach involves iteration of the magnetic field and diagonalization of the matrix at each step. The iteration step is adjustable, smaller increments being needed when the system is of low symmetry and/or the spin Hamiltonian matrix has important nondiagonal contributions, usually because the crystal field part of the Hamiltonian is not small in comparison with the Zeeman term. This situation actually applies for the present system. The program calculates the transition probabilities by evaluating the squared matrix elements of the projections of \(S\) and \(I\) along the microwave field.

The only limitations regarding the values of \(S, I\) and the number of interacting nuclei are the amount of computer time and memory. Super hyperfine interaction terms are evaluated within second order perturbation theory, to avoid matrices which are too large.

3. Results

3.1. EPR

3.1.1. X-band

Most of these spectra were recorded at 77 K. A few experiments were performed at 4.2 K to take advantage of the S/N ratio and to determine the absolute signs of the \(b_k^q\). Fig. 1a shows the spectrum obtained with \(B \parallel b\). It consists of an irregular pattern made up by five intense groups and three weaker ones spread over 700 mT. Its complexity is due to the fact that at the X-band the crystal field splitting is of the same order as the Zeeman splitting. This is fully

![Fig. 1. EPR spectra of BaMgF\(_4\)Eu\(^{2+}\) (4\%e). B parallel to the b axis. T=77 K. (a) X-band (\(\nu_{\text{microwave}} = 9.26\) GHz); (b) Ka-band (\(\nu_{\text{microwave}} = 36.4\) GHz).]
confirmed by the complexity of the experimental angular variation (Fig. 2) and the fact that individual packets become weak or disappear altogether when the magnetic field is rotated in the crystal planes. The strongest splitting between the groups is observed when the magnetic field is located in the (100) plane and forms an angle of 20° with respect to the b-axis. Fig. 2 presents the angular variation of the spectrum with B parallel to this plane.

3.1.2. Ka-band

The spectra recorded at these frequencies are simpler as the ratio of the Zeeman to the crystal field splitting increases approximately by a factor of 4. The spectrum presented in Fig. 1b was observed with B//b. It consists of seven fairly regularly disposed groups. Each one consists of twelve more or less resolved hyperfine structure lines, essentially due to the hyperfine interaction with the Eu nucleus (two isotopes 151Eu and 153Eu, each I=5/2). As the detailed treatment of hyperfine and super hyperfine structure effects is more conventional (e.g. [11]), and is not important in the following, its detailed analysis is not given at present. Experimental angular variations are given in Fig. 3. The angular variation in the (100) plane (Fig. 3a) shows extremal line positions at the same orientation of the magnetic field (20° from the b-axis) as at X-band frequency. The better resolution obtained at Ka-Band allowed the study of the angular variation with B situated in a (001) plane (Fig. 3b). It proves that, indeed, the (100) plane is a symmetry plane. Thus the Eu²⁺ sit symmetry group is C₄, and only one paramagnetic center was observed.

Both the X-band and the Ka-band EPR data were successfully parametrized with the SPINHAM program as explained in the preceding paragraph. The following spin Hamiltonian was used for both

\[
H = g\beta_B \cdot S + (b_0^0 O_0^0 + b_1^1 O_1^1 + b_2^2 O_2^2 + b_3^3 O_3^3) + (b_4^4 O_4^4 + b_5^5 O_5^5 + b_6^6 O_6^6 + b_7^7 O_7^7)
\]

In a first approach the \(b_6^6\) and \(b_7^7\) were included. But the spectral components have typical line widths of 70 MHz (due to super-hyperfine interaction with the fluorine ligands) and a residual error of 40 MHz/point was already attained with (2) from the angular variations. Inclusion of the 6th order terms resulted in an only marginal improvement with numerical values of these constants of nearly zero value. Thus, the \(b_6^6\) and \(b_7^7\) were neglected. The parameters obtained are given in Table 1. Table 2 presents the orthogonal transformation matrix from the crystal axes to the local principal axes of the crystal field tensor. The indicated deviations of the \(b_n^m\) correspond to doubling the residual error of the fit. The absolute signs with respect to the one of the \(g\) tensor (Table 1) were determined by measuring and analyzing the relative intensities of the Ka-band EPR spectra at 4.2 K. The theoretical angular variations calculated with the aid of the constants of Table 1 are presented in Figs. 2 and 3 as solid lines or sets of points.
Table 1

<table>
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<tr>
<th>$g_{\parallel}$</th>
<th>$b_x^0$</th>
<th>$b_y^0$</th>
<th>$b_z^0$</th>
<th>$b_x^1$</th>
<th>$b_y^1$</th>
<th>$b_z^1$</th>
<th>$b_x^2$</th>
<th>$b_y^2$</th>
<th>$b_z^2$</th>
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<td>−0.24</td>
<td>0.14</td>
<td>4.89</td>
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</tr>
<tr>
<td>±0.004</td>
<td>±3.0</td>
<td>±14.5</td>
<td>±6.2</td>
<td>±0.06</td>
<td>±10.37</td>
<td>±0.31</td>
<td>±1.56</td>
<td>±0.41</td>
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</tr>
</tbody>
</table>

Spin-Hamiltonian parameters (in $10^{-4}$ [cm$^{-1}$]) for Eu$^{2+}$ in BaMgF$_4$ at 77 K.

Table 2

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
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<td>−0.9361</td>
</tr>
<tr>
<td>$y$</td>
<td>−1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$z$</td>
<td>0</td>
<td>0.9361</td>
<td>0.3516</td>
</tr>
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</table>

Orthogonal transformation matrix between crystal axes ($a$, $b$, $c$) and local EPR axes ($x$, $y$, $z$).

3.2. Optical experiments

3.2.1. Crystals produced under no-oxygen conditions

Emission and excitation spectra were obtained at 300 K and 77 K from the BaMgF$_4$:Eu (4%) sample previously studied by EPR, typical results are shown in Fig. 4. The emission spectrum exhibits one broad and structureless 4f–5d fluorescence band (maximum emission at 23 900 cm$^{-1}$). This result obtained from transparent single crystals agrees with the powder emission spectra already published [4–7]. These authors used powders synthesized by solid state reactions. The excitation spectrum consists of a large feature (Fig. 4) formed by several unresolved bands (at about 29 400 cm$^{-1}$, 31 500 cm$^{-1}$, 35 900 cm$^{-1}$, 39 400 cm$^{-1}$, 45 200 cm$^{-1}$). Its structure differs from the published results [4–7]. Neither the excitation nor the emission spectrum showed narrow lines due to 4f–4f transitions of the Eu$^{2+}$ ion between room temperature and 77 K. Further, efforts to identify Eu$^{3+}$ in these crystals gave negative results.

3.2.2. Hydrolysed crystals

A monocrystal of the same batch was hydrolysed according to the method described above. Its emission spectrum exhibits additional bands, in particular a broad one around 17 200 cm$^{-1}$. The excitation spectrum between 18 200 and 53 000 cm$^{-1}$ of this latter band shows that an absorption at 50 000 cm$^{-1}$ is associated with the 17 200 cm$^{-1}$ emission whereas none of the Eu$^{2+}$ absorption bands contributes to this emission. The EPR experiments realized on this same sample revealed the presence of only one Eu$^{2+}$ EPR spectrum. Its detailed analysis demonstrated that this one is due to the same Eu$^{2+}$ center as the one obtained in the non-hydrolyzed sample described above. Within the sensitivity of our equipment no other EPR spectra were detected in the oxygen doped samples (hydrolysis and BaO doping).

4. Discussion

On the basis of ionic radius arguments the Eu$^{3+}$ ions is expected to occupy preferentially the Ba$^{2+}$ sites in the BaMgF$_4$ crystal lattice [4]. This is corroborated by substitution experiments. The X-ray structure data [13] obtained from the series of compounds Sr$_x$Ba$_{1-x}$MgF$_4$ (with 0 < $x$ < 0.55) show that the Sr$^{2+}$ ions (which have an ionic radius very close to that of Eu$^{2+}$) substitute for Ba$^{2+}$. This is further confirmed by a refined X-ray structure analysis of Ba$_{0.8}$Eu$_{0.2}$MgF$_4$ [14].

The C$_s$ point symmetry group of the Ba$^{2+}$ site in BaMgF$_4$ involves a mirror plane (the only one) parallel to (100) [2]. The local coordination environment is presented in Fig. 5. Four fluorine ions (2 F2 and 2 F3) ‘below’ the Ba$^{2+}$ ion form a distorted square whereas the symmetrically arranged fluorine ions (2 F1) are above this one. The three remaining fluorine neighbors (F2’, F3’ and F4’) are located in the mirror plane of the Ba$^{2+}$ site. The EPR results are in agreement with this structure and we conclude that the Eu$^{2+}$ center is substituting for a host Ba ion. Note that the local symmetry group does not impose an identical position for the two—with the exception of the constraint to lie in $m$. The Eu$^{2+}$ ion is indeed slightly off the Ba position as was shown for the mixed compound by an X-ray diffraction study [14].

The Newman superposition model [15] was applied to the local coordination cluster of this ion. As the second order crystal field terms are dominating, only these ones were considered. The local Hamiltonian of ligand $j$ is axially symmetric and assumed to consist of a term...
It is transformed by a matrix $U_2$ from the local coordinate system (with $z$-axis along the Eu$^{2+}$-F$_j$ bond) to the referential chosen for the interpretation of the EPR results, as defined above. This transformation is given by $U_2 = V_2 (\alpha, \beta, \gamma) V_1^{-1}$ where $V_2$ transforms the irreducible spherical tensors $T_{k}^{\sigma}$ [12] into the Stevens–Bleaney operators [11], denoted $O_{\sigma}^{(k)}$. Further, $D^{(2)}(\alpha, \beta, \gamma)$ is the rotation matrix as defined for instance in [16]. The sum of the transformations performed on the ligands gives the constants of the second degree terms in (1). Two geometries of the cluster were studied the one of BaMgF$_4$ and the one of Ba$_{0.8}$Eu$_{0.2}$MgF$_4$. In both cases the orientation of the EPR $z$-axis in the $m$ plane (specified by $\delta_0$) was considered as an available parameter. Several choices of the distance dependence of the $b_2(r_j)$ radial parameters were made. The assumption $b_2 = (r/r_0)^{-n}$ with $n = 3, 6$ gave at best an angle of $\delta_0 = 55^\circ$, strongly deviating from the experimentally determined value of $20^\circ$. For this reason a change in sign of the $b_2(r_j)$ as a function of $r$ was assumed. This constraint allowed obtaining reasonable parameters and $\delta_0 = 20^\circ$, but the number of possible solutions is too large for a meaningful interpretation.

The optical results obtained on the nonhydrolyzed samples consist of the spectra due to the substituting Eu$^{2+}$ as was shown above by correlating EPR and optical spectroscopy and with controlled crystal growth. There are five distinguishable components of the 77 K excitation band (Fig. 4). The lowest excited configuration is (4f$^6$, 5d$^1$). If we assume that the f–d coupling is not strong compared to the influence of the crystal field on the d electron, then the level structure may be due to the dominant splitting of the latter term into 5 levels by the low symmetry crystal field, each one being further split into a number of levels through the multiplets (4f$^6$(7F$^J$), 5d$^1$ where $J = 0 \ldots 6$) exchange coupled to the 5d electron [17]. If these latter effects are small (the total $^7$F splitting is approximately 3 800 cm$^{-1}$ for Sm$^{2+}$ in SrFCl) compared to the splitting between the d levels, then an ill resolved five-line structure is expected in absorption. As the symmetry at the Ba site is very low—in particular without an inversion center—the selection rules for the optical transitions are very much relaxed. This model would predict five not equidistant large absorption bands—in qualitative agreement with the experiment.

The same emission and absorption spectrum is also found in the hydrolysed samples. But additional bands are also present. This correlates with the EPR results. These show that with our hydrolysis methods only the same, a locally unaffected, Eu$^{2+}$ impurity center as in the nonhydrolyzed ones exists. Thus, the remaining of the optical spectrum of the hydrolysed sample is related to oxygen not correlated directly with Eu$^{2+}$.

5. Conclusions

The EPR and emission study of the Eu$^{2+}$ ion presented above indicate that only one (substitutional) Eu$^{2+}$ coordination complex exists in the pure BaMgF$_4$ host matrix. This is probably due to the rather densely packed crystal structure, in addition to the obvious iso-charge state of the substituting impurity. Remarkably, under the two oxygen doping schemes realized still only one (the same) Eu$^{2+}$ coordination complex was observed. This crystalline host material has very appealing properties for solid state laser applications involving bivalent rare earth ions. The fact that only the interconfiguration 4f$^5$ ↔ 4f$^5$5d$^1$ luminescence emission of the Eu$^{2+}$ ion was observed is probably associated with the very low symmetry crystal field of considerable strength together with the high ligand coordination number. The crystal field lifts most of the degeneracy and produces a comparatively important spread in energy of the resulting level structure whereas the high coordination number tends to decrease the energy of the 4f$^5$5d$^1$ levels with respect to the energy of the ground state as is exemplified experimentally in [4].

Acknowledgements

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References
