JOURNAL OF SOLID STATE CHEMISTRY **67**, 104–108 (1987)

Different Sites for Divalent Europium Luminescence in $BaMgF_4$

E. BANKS, A. M. SRIVASTAVA, AND A. HALPERIN†

Department of Chemistry, Polytechnic University, 333 Jay Street,
Brooklyn, New York 11201

Received March 17, 1986; in revised form June 23, 1986

The Eu^{2+} luminescence of the compound $Ba_{1-x}Eu_xMgF_4$ ($x = 0.10, 0.20, 0.30, 0.55$) depends strongly on the conditions for synthesis and on the temperature. Two $5d$–$4f$ emission bonds whose relative intensities depend on the europium concentration and on the conditions of preparation, have their maxima at about 420 and 470 nm, respectively. A $4f$–$4f$ ($^6P_{7/2}$–$^8S_{7/2}$) line emission is observed in the low europium concentration samples. © 1987 Academic Press, Inc.

1. Introduction

Compounds of the type $BaMF_4$ (M = Mn, Fe, Co, Ni, Zn, Mg) crystallize in the orthorhombic system with the space group $A2_1am$ (*1*). The structure consists of MF_6 octahedra sharing corners to form puckered sheets parallel to (010) which are linked by Ba^{2+} ions only. The Ba^{2+} ions are coordinated to eight F^- ions. In a recent communication we have described the luminescence of Eu^{2+}-doped $BaMgF_4$ in considerable detail (*2*). This report limits the Eu^{2+} concentrations to 10, 20, 30, and 55 mol% where a different type of luminescence, originating from a different center is observed. Luminescence spectra of these compounds at 300 and 77 K are described.

2. Experimental

Samples have been prepared by firing intimate mixtures of stoichiometric amounts of the fluorides BaF_2, MgF_2, and EuF_2 in sealed graphite crucibles in a nitrogen atmosphere at 950°C. EuF_2 has been obtained by the hydrogen reduction of EuF_3 at 900°C.

The optical measurements were carried out by the method described previously (*3, 4*).

3. Results

Two types of emission were observed for this system, thereby necessitating the classification of samples into Types 1 and 2. These are briefly discussed below:

Type 1. The wavelength of maximum emission is 2.95 eV (420 nm) and that of excitation is 3.82 eV (352 nm).

Type 2. The wavelength of maximum

---

* Work supported by National Institute of Health, Grant 5R01 CA34676-02.

† Permanent address: Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel.

0022-4596/87 $3.00

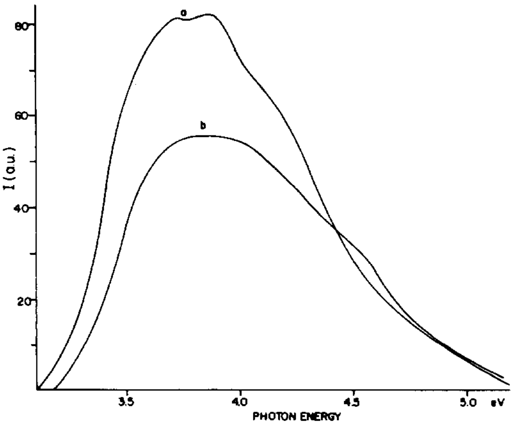

FIG. 1. Room-temperature excitation spectra of (a) Type 1 (E_{em} = 2.95 eV), and (b) Type 2 samples (E_m = 2.69 eV).

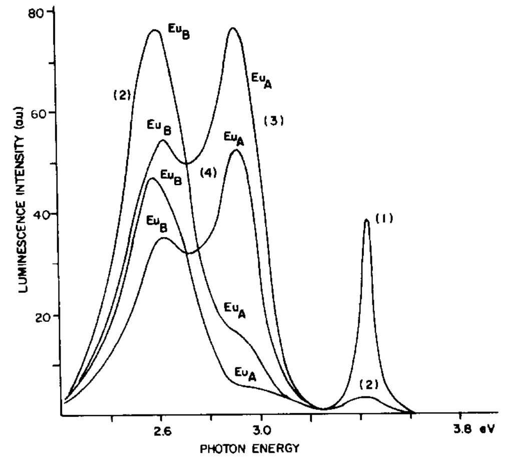

FIG. 3. Emission spectra of Type 2 samples at 77 K, (1)–(3) same as Fig. 2, (4) $Ba_{0.45}Eu_{0.55}MgF_4$. Sites Eu_A and Eu_B are explained in text.

emission is 2.67 eV (464 nm) and that of excitation 3.82 eV (325 nm).

The Type 1 luminescence which corresponds to the normal emission of Eu^{2+} in $BaMgF_4$ has been reported (*2, 5*). Figure 1a shows a room-temperature excitation spectrum of a Type 2 sample and compares it with that of a Type 1 material (Fig. 1b). These are practically the same. However, the emission spectra shown in Fig. 2 are completely different. The wavelength of maximum emission appears now at 2.67 eV (460 nm). At 300 K, this band has a full width at half maximum of 0.42 eV. Also, samples with low Eu^{2+} concentrations (x = 0.10 and 0.20) exhibit weak line emission ($4f$–$4f$) at 3.46 eV (358 nm) (*6*).

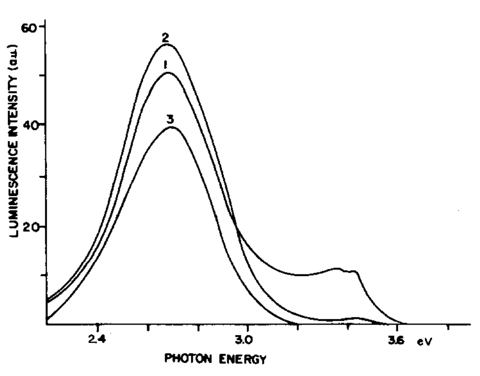

FIG. 2. Emission spectra of Type 2 samples at 298 K: (1) $Ba_{0.90}Eu_{0.10}MgF_4$, (2) $Ba_{0.80}Eu_{0.20}MgF_4$, and (3) $Ba_{0.70}Eu_{0.30}MgF_4$; E_{ex} = 3.82 eV.

Emission spectra of Type 2 samples at 77 K are shown in Fig. 3. A band at 2.95 eV appears now in addition to the 2.62-eV band and grows in intensity with increasing Eu^{2+} concentration. For x = 0.30 and 0.55, two separate bands at 2.95 and 2.62 eV are observed. For x = 0.10 and 0.20, this band appears only as a weak shoulder on the high-energy side of the 2.62-eV emission. Strong $4f$–$4f$ line emission is seen for x = 0.10 at 77 K and a weaker line emission appears for x = 0.20.

4. Discussion

The fact that the excitation spectrum of a Type 2 sample is practically the same as that observed for a Type 1 sample implies that the luminescent center for excitation in both cases is the same (see Fig. 1). We call this center Eu_A. However, the emission at 300 K appears at considerably lower energies. This implies the existence of a second luminescent center in Type 2 samples, Eu_B, with efficient energy transfer from Eu_A to Eu_B occurring at 300 K. Thus, for Type 2 materials excited at 3.82 eV, the emission takes place mainly in Eu_B after efficient energy transfer from Eu_A.

The excitation spectra of Type 2 samples at 77 K remain practically the same as that at 300 K. It can thus be deduced that the concentration of Eu_B centers is much lower than that of Eu_A centers. This is also confirmed by the existence of a very weak band in the excitation spectrum at 3.65 eV (340 nm) only at 77 K, which is now ascribed to Eu_B. The energy transfer from Eu_A to Eu_B at 300 K is apparently very efficient since no Eu_A emission is observed.

The emission spectra at liquid nitrogen temperature show the presence of an additional band at 2.95 eV, which is attributed to the emission from the Eu_A sites in the lattice under 3.82 eV excitation. This may be explained as follows. At room temperature there exists a favorable spectral overlap between the emission at the 2.95-eV (Eu_A centers) and 3.65-eV (Eu_B centers) excitation bands. At these temperatures the thermally stimulated energy transfer process is thus efficient; emission is observed from the Eu_B centers after excitation into the Eu_A centers. At low temperatures, due to narrowing of the corresponding bands, the spectral overlap decreases; this leads to inefficient energy transfer between the two centers. Thus, under 3.82-eV excitation, emission from both centers Eu_A (2.95 eV) and Eu_B (2.72 eV) is observed (see Table I).

TABLE 1

RATIO OF Eu_B TO Eu_A EMISSION (77 K) AS A FUNCTION OF Eu^{2+} CONCENTRATION

x in $Ba_{1-x}Eu_xMgF_4$	$I(Eu_B)/I(Eu_A)$
0.10	9.5
0.20	4.8
0.40	0.71
0.55	0.66

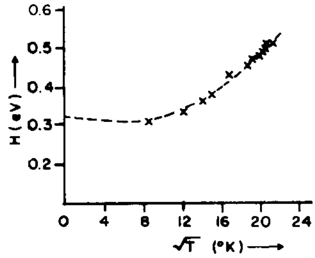

FIG. 4. Temperature dependence of the half width of a Type 2 samples. Experimental points are represented by (×), while the dashed curves is the best fit to Eq. (1). See text.

As can be seen from Table I, the emission from Eu_A sites becomes more favorable than that from the Eu_B sites with increasing Eu^{2+} concentration. For $x = 0.10$ and 0.20 the 2.95-eV emission appears only as a shoulder on the high-energy side of the 2.72-eV emission and at $x = 0.30$ and 0.55 a complete separation of the two band appears. This is due to the fact that with an increase in Eu^{2+} concentration the number of Eu_A sites (normal sites) increases relative to that of Eu_B sites. This also follows from the disappearance of the weak 3.65-eV band in the excitation spectrum of samples with $x = 0.30$ and 0.55 at 77 K.

The temperature dependence of the half width of the emission band has been investigated and is shown in Fig. 4. It follows the equation (7)

$$H = H_0\,[\coth(h\nu/2kT)]^{1/2} \qquad [1]$$

within experimental accuracy and yields $H_0 = 0.32$ eV for the half width at zero temperature and $7.73 \times 10^{12}s^{-1}$ for the vibrational frequency associated with the excited electronic state.

Type 2 emission may be explained by assuming the presence of traps. A possibility exists for occurrence of some Eu^{2+} ions near defects. Since fluorides are notorious for oxygen contamination, it can be assumed that Eu^{2+} next to O^{2-} ions on F^- sites are involved. Also, since the ionic radii of O^{2-} and F^- in different coordinations are very similar (*9*), it would seem reasonable that oxygen would be capable of substituting fluorine in a fluoride crystal lattice. These Eu^{2+} ions will have their energy levels at somewhat lower energies than Eu^{2+} ions surrounded only by fluorines. Thus, the formation of low-energy and high-energy sites for the Eu^{2+} ions and the corresponding emission from the Eu^{2+} (O^{2-}) ions can be explained. The energy transfer can thus be described by Eu^{2+} (F^-)–Eu^{2+} (O^{2-}). Effects of this type have been used to explain luminescence in certain fluoride systems [10].

To test for this hypothesis, a sample of $Ba_{0.85}Eu_{0.15}MgF_4$ was quenched in air after heating it to beyond the melting point. The excitation and emission spectra are shown in Figs. 5 and 6. The excitation spectrum consists of two bands whose intensity ratio depends on the emission wavelength. The excitation band at 4.0 eV corresponds to the Type 1 or Eu_A centers, while that at 3.67 eV corresponds to the Type 2 or Eu_B center. However, excitation into either band yields the same emission spectrum with a maximum at 2.67 eV. The emission intensity is, however, stronger under 4.0 eV excitation, thus confirming the efficient energy transfer from Eu_A centers to Eu_B centers.

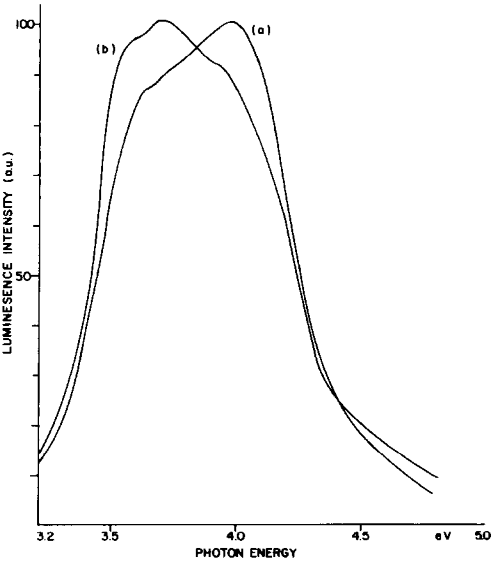

FIG. 5. Excitation spectra of an air-quenched $Ba_{0.85}Eu_{0.15}MgF_4$ sample at two different emissions (a) E_{em} = 2.95 eV and (b) E_{em} = 2.69 eV.

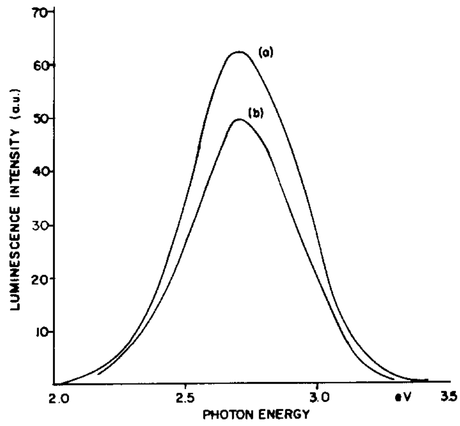

FIG. 6. Emission spectra of the sample in Fig. 6 at two different excitations: (a) E_{ex} = 3.94 eV and (b) E_{ex} = 3.65 eV.

Further confirmation for the presence of O^{2-} ions in the lattice comes from the following experiment. A Type 2 sample was heated in a reducing atmosphere consisting of 97% N_2–3% H_2 mixed gas for 5 hr. The luminescence spectrum of this sample had changed to Type 1 upon this treatment. Obviously, hydrogen helps in the removal of the oxide ions from the lattice, thus effectively decreasing the number of traps.

The occurrence of line emission in Type 2 samples at low Eu^{2+} concentrations can be explained on the basis of the defect nature of the host lattice. Substituting O^{2-} for F^- ions leads to fluorine ion vacancies, which lead to lattice distortion; this is responsible for the 4*f*–4*f* line emission of Eu^{2+}. A similar observation has been made for Eu^{2+} doped KCl and KI (*11*). It should be noted that for Type I emission no 4*f*–4*f* transition is observed for low concentration of Eu^{2+} in $BaMgF_4$ at temperatures down to 10 K (*2*).

Finally, we note that energy transfer between inequivalent Eu^{2+} ions has been reported before. More recently, Blasse (*12*) has shown that energy transfer is possible between inequivalent Eu^{2+} ions in Rb_2ZnBr_4. In this host lattice there exist two different crystallographic sites for the Eu^{2+} ion replacing the Rb^+ ion. In $BaMgF_4$ there exists only one site for the Eu^{2+} ion. The inequivalent sites become possible due to the presence of oxide ions in the lattice; the defect Eu^{2+} ions act as traps for the migrating excitation energy of the intrinsic Eu^{2+} ions in the host lattice.

5. Conclusion

Despite the fact that in the $BaMgF_4$ structure only one crystallographic site is available for Eu^{2+}, two luminescence centers are observed. The center with emission at low energy is ascribed to an Eu^{2+} ion near a defect (O^{2-}, Eu_B center), while the center with its emission at high energy is ascribed to Eu^{2+} ions free of defects (Eu_A centers). The fact that the shorter wavelength emission peaks are replaced by longer wavelength peaks with increasing temperatures indicates energy transfer between different europium centers. Excitation occurs in the Eu_A centers and the excitation energy migrates through the lattice until it is trapped at Eu_B centers near defects; this gives rise to the long wavelength emission. It is concluded that the Type 2 emission is due to the presence of O^{2-} ions in the lattice and that the presence of these ions has a very pronounced effect on the Eu^{2+} luminescence. This is not surprising since the 5*d* band of the Eu^{2+} ion is sensitive to very subtle crystal field effects brought about by only minor distortions of the local environment of the ion.

References

1. E. T. Keve, S. C. Abrahams, and J. L. Bernstein, *J. Chem. Phys.* **51,** 4928 (1961).
2. E. Banks and A. M. Srivastava, *J. Electrochem. Soc.,* submitted.
3. E. Banks, Liu Xingren, A. M. Srivastava, and A. Halperin, *J. Luminesc.* **31/32,** 216 (1984).
4. E. Banks, S. Nakajima, and M. Shone, *J. Electrochem. Soc.* **127,** 2234 (1980).
5. C. Fouassier, B. Latourrette, and P. Hagenmuller, *Mater. Res. Bull.* **11,** 933 (1973).
6. R. A. Hewes and M. V. Hoffman, *J. Luminesc.* **3,** 261 (1971).
7. C. C. Klick and J. H. Shulman, *in* "Solid State Physics," Vol. 5 (Seitz and Turnbull, Eds.), Academic Press, New York, 1957.
8. W. Bollman, *Phys. Status Solidi A* **57,** 601 (1980).
9. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect B* **1325,** 925 (1968).
10. G. Blasse, *Phys. Status Solidi A* **73,** 205 (1983).
11. J. M. Moret and R. Lacroix, *Helv. Phys. Acta* **49,** 313 (1976).
12. G. Blasse, *J. Solid State Chem.* **62,** 207 (1986).