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Eu^{+2} Fluorescence in $BaCl_2$

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The $Ba_{1-x}Eu_xCl_2$ system was studied over wide ranges of x, particularly regarding the fluorescent emission of Eu^{2+}. In addition to the commonly observed $5d \rightarrow 4f$ band emission sharp line, $f \rightarrow f$ transitions were observed. Single crystals of Eu^{2+} containing $BaCl_2$ were grown via the Czochralski technique and many of the optical properties, such as transmission, fluorescence, and excitation, were measured. X-ray and thermal parameters for the $Ba_{1-x}Eu_xCl_2$ system are also reported.

Introduction

Since the discovery of sharp line $f \rightarrow f$ transitions for Eu^{2+} in $SrAlF_5$ and similar compounds by Hewes and Hoffman in 1970 (*1*), many other hosts were reported in which the same type of emission is observed. These hosts include fluorochlorides, oxides, and most recently even pure sulfates (*2–4*). The present paper describes such $f \rightarrow f$ transitions for the first time in a pure chloride and thereby adds yet another structural type and crystal field environment to the growing list of hosts supporting sharp line emission of Eu^{2+}.

Experimental

The samples were prepared from high purity $BaCl_2$ (Merck, optical grade) and $EuCl_2$ [obtained as previously described (*5*)] by either melting under purified argon, nitrogen, or HCl in vitreous carbon boats (a solid-state reaction at temperatures about 100°C below the melting point of the specific composition), or by pulling single crystals from the melt also contained in a vitreous carbon crucible. Typical growth conditions were: pulling speed 5 to 10 mm/hr, rotation 30 to 40 rpm. Since $BaCl_2$ is hygroscopic, readily converting to the dihydrate $BaCl_2 \cdot 2H_2O$, moisture must be excluded as much as possible during the preparation and measurements. Single crystals are much more stable than powders and stay clear and transparent for days even in the laboratory atmosphere. For the X-ray parameters, powder patterns were obtained with a Guinier–Hägg camera at 25°C with $CuK\alpha_1$ radiation and an internal standard of KCl ($a = 6.2931$ Å). Refined cell dimensions were obtained by a least-squares treatment of the Guinier data. Fluorescent emission, excitation, and absorption spectra were run with a Cary Model 17 spectrophotometer. The specific heat anomalies were measured with a Du Pont Model 900 thermal analyzer by differential thermal analyses (DTA).

Results and Discussion

The $BaCl_2$ and $Ba_{1-x}Eu_xCl_2$ Structures

Anhydrous barium chloride is known to exist in two temperature-dependent structural modifications: the high temperature cubic β form (*6*) crystallizing in *Fm*3*m* symmetry and the low temperature orthrhombic α form (*7*) which is the thermodynamically stable room temperature form and crystallizes in *Pnam* symmetry. Both Brackett et al. (*7*) and Paulick et al. (*8*) mention a monoclinic $BaCl_2$ modification which originally was listed as ASTM file card 1-1177 but has since been deleted. We

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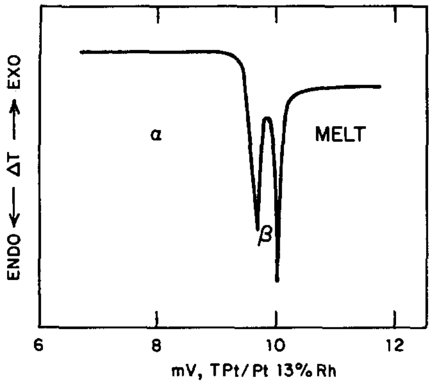

FIG. 1. DTA run of pure $BaCl_2$.

did not find any experimental evidence that monoclinic $BaCl_2$ exists. There exists, however, a monoclinic dihydrate, $BaCl_2 \cdot 2H_2O$ (*9*). The stability range for pure β-$BaCl_2$ is extremely limited, as can be seen from the DTA plot in Fig. 1. The melting point of 964°C and the transition temperature of 939°C agree well with the reported (*10*) values (960 and 925°C, respectively). Brackett et al. showed that the cubic modification also can be obtained in a metastable state at 60°C. According to these authors, it readily converted to the stable orthorhombic structure at 200°C. We found that certain concentrations of Eu^{2+} will also stabilize the cubic structure, particularly when fast cooling of the melt is used. $EuCl_2$ was first characterized by Döll and Klemm (*11*) as being isomorphous with orthorhombic $BaCl_2$. Because of the rather large discrepancy between ionic radii (1.17 Å for Eu^{2+} vs 1.36 Å for Ba^{2+}), this is somewhat surprising, as one would expect $EuCl_2$ to be isostructural with cubic $SrCl_2$ (*12*) since the radii of Eu^{2+} and Sr^{2+} are virtually identical. It is undoubtedly due to the higher polarizability of Eu^{2+} that it shares the same chloride structure with $BaCl_2$. We prepared extensive solid solutions of these two halides in the form of the $Ba_{1-x}Eu_xCl_2$ system. The lattice parameters and specific heat anomalies are listed in Table I. All samples were prepared via the melt and were furnace cooled. Only the 1:1 compound, $Ba_{0.5}Eu_{0.5}Cl_2$, was also quenched by rapidly removing the boat from the furnace. This procedure yielded a purely cubic composition with a cell edge of 7.117 ± 1 Å. The observed and calculated *d* values for this compound are in Table II. Actually, even some of the furnace-cooled samples contained small fractions of the cubic phase, at least when $x > 0.3$. An estimate of their relative concentrations is given in Table I. All compositions with $x \leqslant 0.3$ were purely orthorhombic. A typical pattern is indexed in Table III, giving the first 20 lines of the orthothombic modification. In all, 48 lines were

TABLE I

CELL CONSTANTS, TRANSFORMATION TEMPERATURES, AND MELTING POINTS OF THE $Ba_{1-x}Eu_xCl_2$ SYSTEM

Composition	*a* (Å)	*b* (Å)	*c* (Å)	*a* (Å) cubic	Percentage of cubic phase	T_t	T_m
$BaCl_2$	7.874 (2)[a]	9.431 (2)	4.731 (1)	—	0	933	964
$Ba_{0.99}Eu_{0.01}Cl_2$	7.873	9.429	4.730	—	0	928	961
$Ba_{0.95}Eu_{0.05}Cl_2$	7.859	9.406	4.719	—	0	916	956
$Ba_{0.90}Cu_{0.10}Cl_2$	7.842	9.388	4.692	—	0	901	949
$Ba_{0.70}Eu_{0.30}Cl_2$	7.768	9.290	4.663	7.171	5	807	899
$Ba_{0.5}Eu_{0.5}Cl_2$	7.673	9.174	4.620	7.118	10	772	880
$Ba_{0.4}Eu_{0.6}Cl_2$	7.636	9.123	4.599	7.093	10	683	863
$Ba_{0.2}Eu_{0.8}Cl_2$	7.581	9.119	4.528	7.042	20	637	838
$EuCl_2$[b]	7.499	8.914	4.493	—	—	537	757

[b] The numbers in parentheses are the standard deviations of the least significant digit.

[b] According to (*11*).

TABLE II

OBSERVED AND CALCULATED *d*-VALUES OF CUBIC $Ba_{0.5}Eu_{0.5}Cl_2$, $a = 7.119(1)$ Å

N	*I*	*h k l*	*d* obsd	*d* calcd
1	96	1 1 1	4.1106	4.1092
2	11	2 0 0	3.5587	3.5586
3	100	2 2 0	2.5162	2.5163
4	38	3 1 1	2.1469	2.1459
5	4	2 2 2	2.0552	2.0546
6	5	4 0 0	1.7797	1.7793
7	14	3 3 1	1.6334	1.6328
8	2	4 2 0	1.5900	1.5915

TABLE III

OBSERVED AND CALCULATED *d*-VALUES OF ORTHORHOMBIC $Ba_{0.7}Eu_{0.3}Cl_2$, $a = 7.768(2)$ Å, $b = 9.290(2)$ Å, $c = 4.663(1)$ Å

N	*I*	*h k l*	*d* obsd	*d* calcd
1	2	0 2 0	4.6671	4.6493
2	70	0 1 1	4.1873	4.1833
4	95	1 2 0	3.9922	3.9907
5	75	2 0 0	3.8901	3.8898
6	80	1 1 1	3.6859	3.6842
7	45	1 2 1	3.0385	3.0377
8	25	2 0 1	2.9895	2.9921
9	10	1 3 0	2.8776	2.8793
10	100	2 1 1	2.8483	2.8482
11	70	0 3 1	2.5839	2.5848
12	10	2 2 1	2.5197	2.5161
13	10	3 1 0	2.4968	2.4973
14	55	1 3 1	2.4526	2.4529
15	2	2 3 0	2.4246	2.4238
16	65	0 0 2	2.3430	2.3420
17	45	0 4 0	2.3245	2.3246
18	65	3 2 0	2.2637	2.2643
19	60	3 1 1	2.2033	2.2037
20	55	2 3 1	2.1521	2.1527

observed and indexed with 98 % having unique assignments. As we are moving closer to pure $EuCl_2$, the phase field of the β structure increases and appears to be largest for $EuCl_2$. We do not have any high-temperature X-ray data at present and therefore can only assume that the transition is to the cubic fluorite structure. Pure $EuCl_2$ is white, while many of the molten solid solutions with high Eu contents exhibit a slightly blue color. Presently, we do not have an explanation for this coloration.

Optical Properties

Clearly, the most interesting optical property of Eu^{2+}-doped $BaCl_2$ is the sharp line luminescence from the $6\ P_{7/2} \rightarrow 8\ S_{7/2}$ transition within the *f* electrons. This constitutes the first reported chloride host which exhibits $f \rightarrow f$ transitions for Eu^{2+}. Apparently the $4f^{n-1}\ 5d$ configuration lies at a high enough energy level combined with a weak crystal field surrounding the 9-coordinated Eu^{2+} to support an $f \rightarrow f$ transition. This condition was previously believed to be restricted to more ionic fluorides (*13*). While the $f \rightarrow f$ emission is practically not observable at room temperature (Fig. 2), it comes up strongly at liquid nitrogen temperatures (Fig. 3). The $d \rightarrow f$ band emission is still strong at liquid nitrogen temperatures, very similar to the emissions in tetragonal EuFCl and distinctly different from some pure fluoride hosts (*14*) where the $f \rightarrow f$ emission dominates even at room temperature. The peak emission of the $f \rightarrow f$ transition is at 363.5 nm, and one might expect crystal field splitting into several individual lines as has been observed in

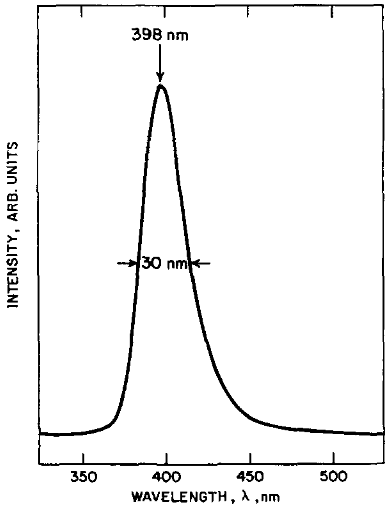

FIG. 2. Fluorescent emission spectrum of $Ba_{0.99}$-$Eu_{0.01}Cl_2$ at room temperature.

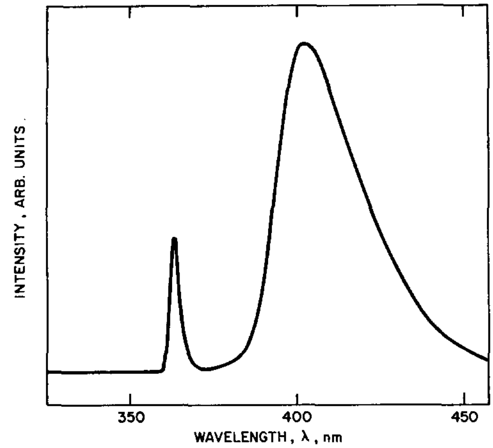

FIG. 3. Fluorescent emission spectrum of $Ba_{0.99}Eu_{0.01}Cl_2$ at 77°K.

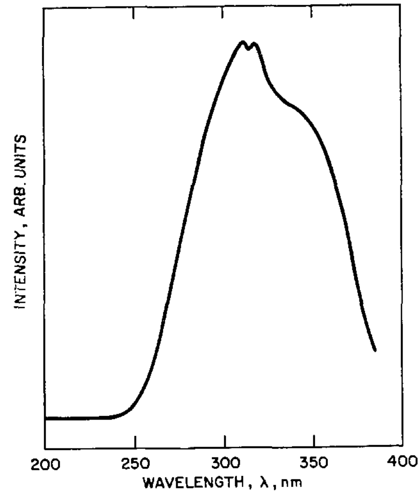

FIG. 4. Excitation spectrum of $Ba_{0.99}Eu_{0.01}Cl_2$.

$SrFCl$ or $BaLiF_3$ (*15*). We attempted to resolve this peak into components by combining the minimum slit-width with maximum sensitivity of the CARY 17 spectrophotometer. This produced a second peak at 366.5 nm with about one-tenth the intensity of the high-energy emission. The room temperature excitation spectrum for $Ba_{0.99}Eu_{0.01}Cl_2$ is shown in Fig. 4. Since all measurements were carried out with single crystals, it should be pointed out that the Eu concentration is only nominal since a segregation coefficient of $K < 1$ yielded a lower Eu content in the crystal. Magnetic susceptibility measurements indeed confirmed the Eu concentration to be <0.01. In the solid-state preparations used in measuring the concentration dependence of the luminescence, this is not a problem as the samples do not melt. The intensity dependence as a function of x is shown in Fig. 5 and, as can be seen from the numbers at the data points, there is a shift of the peak emission toward lower energies as the Eu content increases. Peak intensities are observed near $x = 0.05$, but total concentration quenching never occurs as even pure $EuCl_2$ still fluoresces strongly in the blue (*15*).

While pulled single crystals of $BaCl_2$: Eu are clear and transparent to the eye, we did have O^{2-} or OH^- impurities as is indicated in Fig. 6. We believe the tail around 320 nm to be due to OH and the absorption of the superimposed narrow band at 270 nm to stem from O^{2-}, similar to observations made on KCl (*16*).

Since we observed $f \rightarrow f$ transitions in chlorides, we considered the possibility that the isostructural bromide $BaBr_2$ could support the same emission, although this is an even less ionic and more covalent compound. Eu^{2+} emits efficiently in a narrow band in $BaBr_2$ as can be seen in Fig. 7. Neither at room temperature nor at 77°K could we observe sharp line emission, so we must conclude that the less ionic bromide cannot support an $f \rightarrow f$ transition of Eu^{2+}. We assume this to be due to the fact that the larger Br ion lowers the $f \rightarrow d$ absorption energy sufficiently

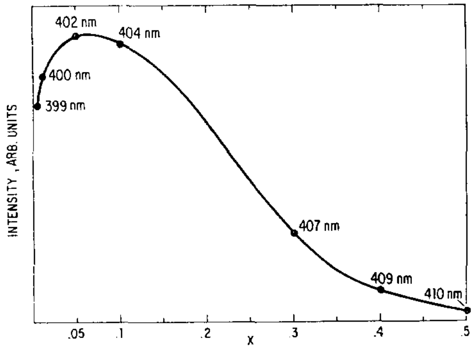

FIG. 5. Intensity of fluorescent emission as a function of x for the $Ba_{1-x}Eu_xCl_2$ system.

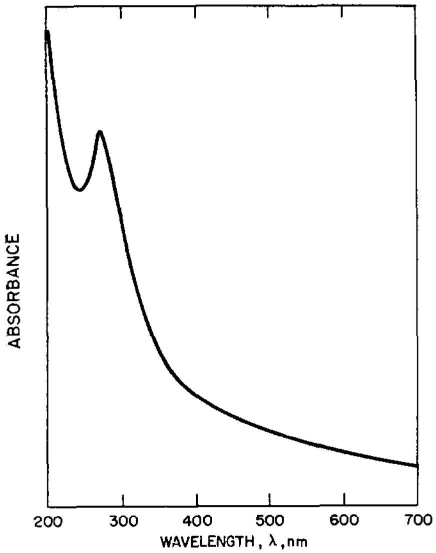

FIG. 6. Absorption spectru of $Ba_{0.99}Eu_{0.01}Cl_2$ at *RT*.

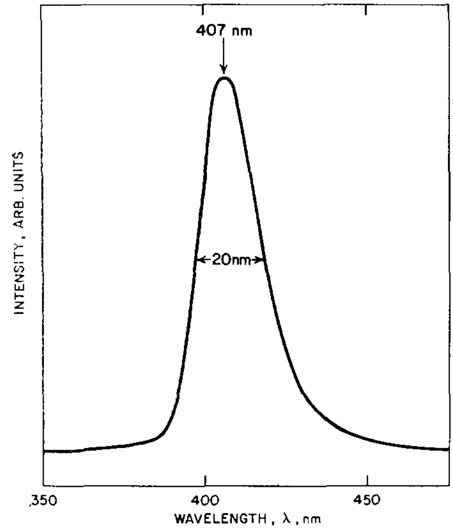

FIG. 7. Fluorescent emission spectrum of $Ba_{0.99}$-$Eu_{0.01}Br_{1.98}Cl_{0.02}$ at 77°K.

near the $f \rightarrow f$ level to effectively quench the $f \rightarrow f$ luminescence.

Finally we doped cubic (*Fm3m*) $SrCl_2$ and orthorhombic (*Pnmm*) $CaCl_2$ with Eu^{2+}. Both hosts support efficient blue Eu^{2+} luminescence with rather narrow band emission as seen in Figs. 8 and 9. The halfwidth of $SrCl_2$:Eu

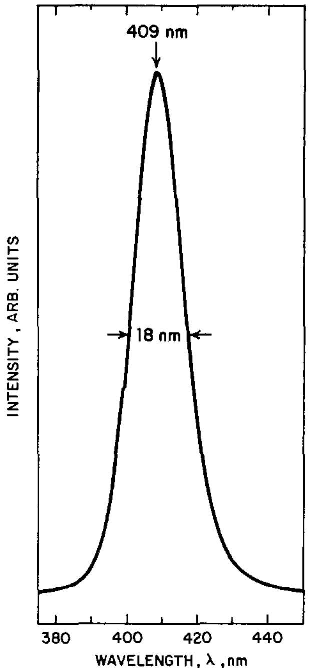

FIG. 8. Fluorescent emission spectrum of $Sr_{0.99}$-$Eu_{0.01}Cl_2$ at *RT*.

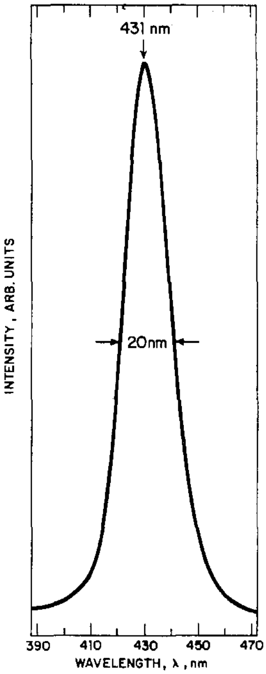

FIG. 9. Fluorescent emission spectrum of $Ca_{0.99}$-$Eu_{0.01}Cl_2$ at *RT*.

narrowed to 10 nm at liquid nitrogen temperature and that of $CaCl_2$:Eu to 12 nm. Neither composition showed any indication of $f \rightarrow f$ emission. With $SrCl_2$, we assume the strong cubic crystal field to be responsible for the nonexistence of $f \rightarrow f$ transitions and with $CaCl_2$ the general band emission appears to be located at too low an energy.

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