Eu^{2+} Luminescence in the Borates $X_2Z(BO_3)_2$ (X = Ba, Sr; Z = Mg, Ca)

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Luminescence properties are reported for the Eu^{2+}-doped materials $Ba_2Mg(BO_3)_2$, $Ba_2Ca(BO_3)_2$, and $Sr_2Mg(BO_3)_2$; they exhibit red, green, and yellow emission, respectively. Results from these materials have been coupled with those from another extensive series of Eu^{2+}-doped borates to establish a correlation between the energy of the $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} and the coordination environments of the O atoms in these hosts. The transition occurs at low energies in those borates containing O atoms that are highly coordinated by regular arrangements of Ba or Sr atoms. Covalency effects are primarily responsible for the low-energy position of the excitation.

Introduction

The luminescence of the Eu^{2+} ion in inorganic hosts has been extensively investigated during the last three decades.[1−9] This ion is particularly unique because its broadband luminescence $4f^65d^1 \rightarrow 4f^7$ is strongly host dependent with emission wavelengths extending from the UV to the red portions of the spectrum. UV or blue-emitting Eu^{2+} phosphors are used in lamp and display applications, and many Eu^{2+}-doped materials are being examined for use in new flat-panel display technologies. Despite extensive research on the characteristics of Eu^{2+} luminescence, fundamental questions remain regarding the relationships between the electronic and crystal structures of the host and the resulting Eu^{2+} spectral features, i.e., the Stokes shift of the emission and the energetic position of the $4f^65d^1$ excited configuration.

We have undertaken a detailed investigation of a series of Ba and Sr borates that exhibit a wide range of Eu^{2+} excitation and emission behavior. In most Eu^{2+}-doped oxides, excitation takes place in the UV, with emission in the UV, violet, or blue. Recently, however, red luminescence of Eu^{2+} under UV excitation has been observed from the hosts $Ba_2LiB_5O_{10}$[1] and $Ba_2Mg(BO_3)_2$.[2] In addition, we recently described[3] green and yellow emission in the hosts $Ba_2Ca(BO_3)_2$ and $Sr_2Mg(BO_3)_2$, respectively. We have presented a simple model correlating the Stokes shifts of Eu^{2+} emission in these and related borates to the coordination environments of the O atoms in the hosts. Materials with O atoms richly bound by Ba or Sr atoms have longer Eu^{2+} emission wavelengths, and their Stokes shifts scale with the distortion of the coordination environments about the O atoms.

The Stokes shift, however, is only one factor that determines the resulting Eu^{2+} emission wavelength; the energetic position of the excited state is equally important. In the host SrB_4O_7, the $4f^7 \rightarrow 4f^65d^1$ excitation of Eu^{2+} occurs at 310 nm, leading to emission at 367 nm.[4] In the host $Sr_3(BO_3)_2$, the excitation wavelength is shifted to about 430 nm, and the emission occurs at 585 nm.[5] These shifts in excitation and emission wavelengths have been attributed to combinations of crystal-field and nephelauxetic effects[6] and, more recently, to preferred orientations of Eu d orbitals and their interactions with neighboring cations.[7] We present here an analysis of the luminescence properties of several Eu^{2+}-doped hosts with particular emphasis on the materials $Ba_2Mg(BO_3)_2$, $Ba_2Ca(BO_3)_2$, and $Sr_2Mg(BO_3)_2$. The latter materials are structurally similar, providing an opportunity to examine the factors that influence the energetic position of the lowest excited state of Eu^{2+}. As in our consideration of Stokes shifts,[3] emphasis is placed on the environments of the O atoms. From this study, we propose that covalency effects are primarily responsible for affecting the energy of the $4f^65d^1$ excited level. Here, following, we correlate low-energy excited levels of the Eu^{2+} ion in borate hosts to the presence of O atoms that are highly coordinated in symmetrical environments of Ba or Sr atoms.

Experimental Section

Powder samples of $Ba_{1.99}Eu_{0.01}Mg(BO_3)_2$ and $Ba_{1.99}Eu_{0.01}Ca(BO_3)_2$ were prepared from stoichiometric quantities of $BaCO_3$ (Cerac, 99.9%), $CaCO_3$ (Aesar, 99.999%), MgO (Aldrich, 99.95%), Eu_2O_3 (Aesar, 99.998%), and B_2O_3 (Aesar, 99.98%). The mixtures were ground under hexane and then heated in a Pt crucible under a 4% H_2/96% Ar atmosphere at 1273 K for 18 h. $Sr_{1.995}Eu_{0.005}Mg(BO_3)_2$ was synthesized by first preparing $Sr_{0.99}Eu_{0.01}B_4O_7$ ($SrCO_3$, Aesar, 99.99%) and then grinding and heating this material with an appropriate quantity of $SrCO_3$

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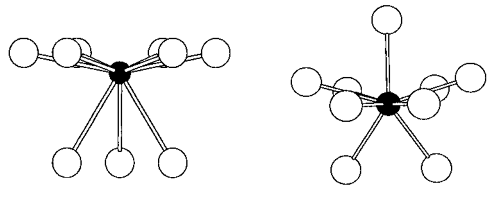

Figure 1. Ba sites in (a) $Ba_2Mg(BO_3)_2$ and (b) $Ba_2Ca(BO_3)_2$. Filled circles = Ba; open circles = O.

and MgO. Samples for the solid solutions $Sr_{2-x}Ba_xMg(BO_3)_2$ ($0 \le x \le 2$) and $Ba_2Mg_{1-y}Ca_y(BO_3)_2$ ($0 \le y \le 1$) were prepared with the same reagents and a heating period of 18 h.

Excitation and emission spectra were recorded as previously described.[2] All data have been corrected for lamp output, monochromator throughput, and sensitivity of the photomultiplier tube. Variable-temperature spectra were obtained by using a Cryo Industries helium-flow cryostat equipped with a Conductus temperature controller. Lifetime data were acquired by using a Q-switched, Quanta-Ray Nd:YAG laser equipped with a frequency-mixing crystal to provide excitation at 355 nm; the pulse width (fwhm) of the laser was measured as 10 ns. The sample emission signal was detected with a PMT that was connected to a 500 MHz Tektronix digital oscilloscope (Model TDS350) and interfaced to a PC for data collection; 256 emission curves were averaged and saved to disk for analysis. Emission lifetimes were determined from natural log plots of the decay curves. Each reported value was obtained as the slope of the best straight-line fit to the plot. All curves were found to be single exponential ($r^2 > 0.996$).

Results

Eu^{2+} Luminescence in $Ba_2Mg(BO_3)_2$, $Ba_2Ca(BO_3)_2$, and $Sr_2Mg(BO_3)_2$. The compounds $Ba_2Ca(BO_3)_2$ and $Sr_2Mg(BO_3)_2$ are isotypic (monoclinic, $C2/m$).[10,11] $Ba_2Mg(BO_3)_2$ is structurally distinct (trigonal, $R\bar{3}m$),[2] but related to the monoclinic structure as noted below. Each contains a single crystallographic Ba or Sr site coordinated by nine O atoms. In $Ba_2Mg(BO_3)_2$, the Ba atom has an unusual coordination environment with three O atoms in a trigonal plane below the Ba atom and six O atoms in a distorted hexagonal plane above the Ba atom; the site symmetry is C_{3v} (Figure 1a). In $Ba_2Ca(BO_3)_2$ and $Sr_2Mg(BO_3)_2$, the Ba and Sr atoms are slightly displaced from a more highly distorted hexagonal plane. In comparison with the Ba environment one atom is missing from the trigonal, triangular plane, moving to a capping position above the distorted hexagonal base; the site symmetry is C_s (Figure 1b).

Excitation and emission spectra measured at 4.2 K for doped samples of $Ba_2Mg(BO_3)_2$, $Ba_2Ca(BO_3)_2$, and $Sr_2Mg(BO_3)_2$ are depicted in Figure 2. The spectra for $Ba_2Mg(BO_3)_2:Eu^{2+}$ are similar to the room-temperature results previously reported.[2] The emission spectrum is characterized by a broad band with a maximum at about 617 nm. The other two materials exhibit similar emission spectra with maxima occurring at 530 nm for $Ba_2Ca(BO_3)_2:Eu^{2+}$ and at 605 nm for $Sr_2Mg(BO_3)_2:Eu^{2+}$. The emission maximum at 4.2 K of each compound is red-shifted (9 nm in $Ba_2Mg(BO_3)_2:Eu^{2+}$, 9 nm in $Ba_2Ca(BO_3)_2:Eu^{2+}$, and 15 nm in $Sr_2Mg(BO_3)_2:Eu^{2+}$) relative

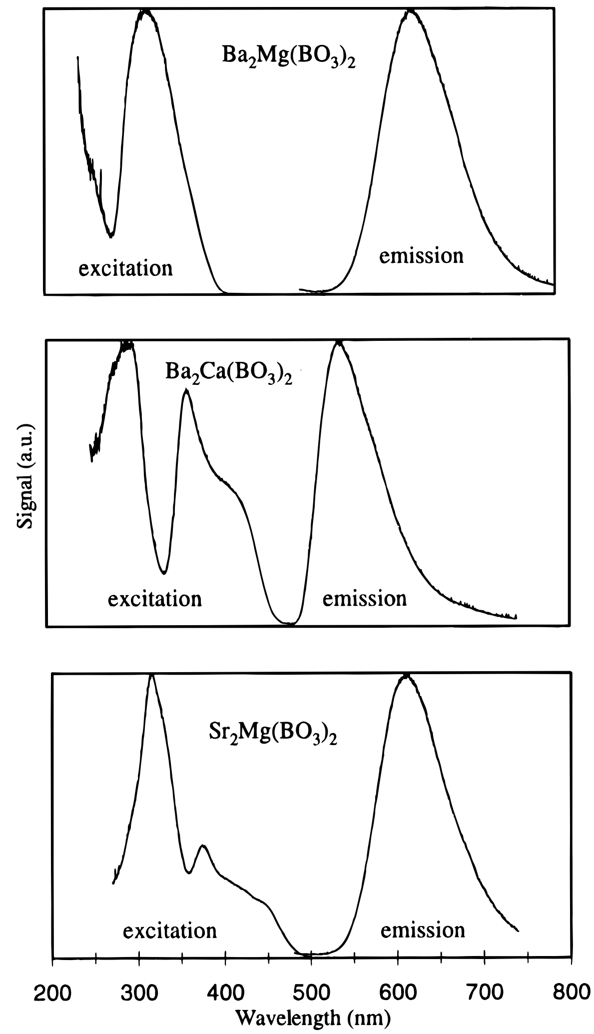

Figure 2. Excitation and emission spectra of $Ba_2Mg(BO_3)_2:Eu^{2+}$, $Ba_2Ca(BO_3)_2:Eu^{2+}$, and $Sr_2Mg(BO_3)_2:Eu^{2+}$ at 4.2 K. Excitation spectra were obtained for emission at the peak maxima. Emission spectra were obtained with $\lambda_{exc} = 355$ nm.

to room-temperature values. These shifts result in slightly larger values of the Stokes shifts relative to those previously reported.[3]

The emission band of $Ba_2Ca(BO_3)_2:Eu^{2+}$ appears to be somewhat more asymmetric than those from the other two compounds, particularly on the long-wavelength side. The unusual shape is likely associated with the presence of Eu^{2+} on both the Ba and Ca sites in this host; the Ca atom occupies a slightly distorted octahedral site. Further evidence for such a distribution is provided by examining the emission band at various temperatures. Two such spectra at 4.2 and 300 K are given in Figure 3. Each spectrum can be fit with two Gaussian profiles, as shown in the figure. At 4.2 K, the emission band consists of one profile centered at 18 850 cm^{-1} and another broader curve at 17 632 cm^{-1}. At 300 K, the signal of the lower-energy curve is reduced relative to the high-energy one, leading to a change in the emission-band shape. The excitation spectra are not significantly affected by the change in temperature. Assignment of these peaks is difficult without more detailed study. We note, however, that Eu^{2+} emission in Ca sites generally occurs at longer wavelengths than in Ba sites, and lower quenching temperatures generally occur in Ca sites relative to Ba sites.[12]

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Table 1. Spectroscopic Data for Eu^{2+} in $X_2Z(BO_3)_2$ Borates

compound	excitation peaks (nm)	emission max (nm)	T_{50}, K	τ 4.2 K	τ T_{50}	τ 300 K
$Ba_2Mg(BO_3)_2$	~240, 330	617	300	13.2 μs	5 μs	5 μs
$Sr_2Mg(BO_3)_2$	315, 375,420, 450	605	250	2.2 μs	1.2 μs	632 ns
$Ba_2Ca(BO_3)_2$	295, 360, 430	530	200	942 ns	537 ns	175 ns

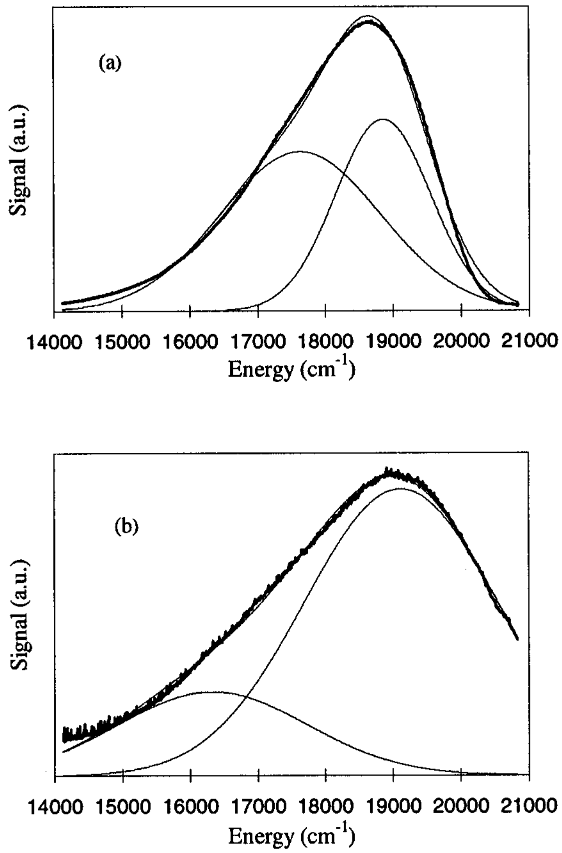

Figure 3. Emission spectra of $Ba_2Ca(BO_3)_2$:Eu^{2+} at (a) 4.2 K and (b) 300 K; λ_{exc} = 420 nm. Narrow lines are best-fit Gaussian profiles.

The excitation spectra of $Ba_2Ca(BO_3)_2$:Eu^{2+} and $Sr_2Mg(BO_3)_2$:Eu^{2+} are quite similar but very different from that of $Ba_2Mg(BO_3)_2$:Eu^{2+}. This is to be expected since the former compounds are isotypic and structurally distinct from $Ba_2Mg(BO_3)_2$. Excitation spectra of $Ba_2Ca(BO_3)_2$:Eu^{2+} and $Sr_2Mg(BO_3)_2$:Eu^{2+} exhibit three maxima (possibly four in $Sr_2Mg(BO_3)_2$:Eu^{2+}), with one excitation peak in each material occurring at a wavelength that is relatively long for Eu^{2+} (~425 nm in $Ba_2Ca(BO_3)_2$ and ~450 nm in $Sr_2Mg(BO_3)_2$). A similar excitation spectrum has been reported for $Sr_3(BO_3)_2$:Eu^{2+}.[5] Two excitation peaks appear for $Ba_2Mg(BO_3)_2$:Eu^{2+}, one at 330 nm and one at around 240 nm, though data at wavelengths shorter than 240 nm could not be collected on our system. From symmetry considerations, the C_{3v} Ba site in $Ba_2Mg(BO_3)_2$ affords a splitting of the Eu^{2+} 5d orbitals into 2e + a_1. From extended Hückel modeling calculations, one e level is found to occur at a higher energy than the remaining nearly degenerate e and a_1 levels. From the excitation spectrum the splitting between the e and e, a_1 levels is approximately 11 000 cm^{-1}. The absence of a large splitting between the lower e and a_1 levels indicates the Eu^{2+} ion occupies a position in the polyhedron similar to that of the Ba atom. Small shifts of the Eu^{2+} ion along or orthogonal to the C_3 symmetry axis leads to a significant splitting of these lower energy levels.

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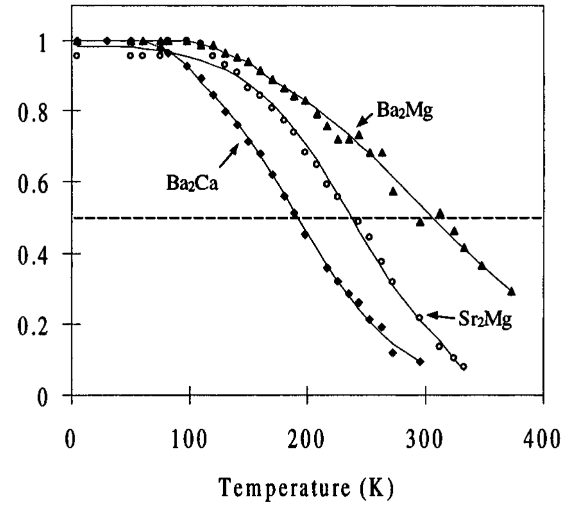

Figure 4. Normalized Eu^{2+} emission intensity as a function of temperature in the $X_2Z(BO_3)_2$ borates. The dashed horizontal line corresponds to a relative intensity of 50% of the value at 4.2 K.

Similar calculations with Eu^{2+} on the Ba site in $Ba_2Ca(BO_3)_2$ also yield results consistent with the excitation spectra. The C_s symmetry leads to accidentally degenerate a′ and a″ levels at highest energy, nearly degenerate a′ and a″ levels below these, and an a″ level at lowest energy. From the excitation spectrum of $Ba_2Ca(BO_3)_2$:Eu^{2+}, the two a′, a″ levels are split by 6100 cm^{-1}, and the lower a′, a″, and a″ levels are split by 4500 cm^{-1}. If the polyhedron is compressed to reflect the smaller Sr site in $Sr_2Mg(BO_3)_2$, a splitting of the middle a′ and a″ levels is observed. This is consistent with the excitation spectrum of $Sr_2Mg(BO_3)_2$:Eu^{2+}, where an additional peak is present at about 420 nm. On the basis of these results, we believe that the Eu^{2+} ion is occupying sites very similar to those of the substituted Ba (Sr) atom, i.e., the ion is not occupying an off-center position. The differences in energy between the lowest energy excitation peak and the emission maximum, the Eu^{2+} Stokes shifts, are 14 000 cm^{-1} for $Ba_2Mg(BO_3)_2$, 5600 cm^{-1} for $Sr_2Mg(BO_3)_2$, and 4300 cm^{-1} for $Ba_2Ca(BO_3)_2$. The Stokes shift for Eu^{2+} luminescence in $Ba_2Mg(BO_3)_2$ is among the larger values reported for this ion.

Spectroscopic data for each material are summarized in Table 1, and thermal quenching curves are drawn in Figure 4. Here, T_{50} is the temperature where the emission intensity falls to 50% of its value at 4.2 K. The T_{50} for $Ba_2Mg(BO_3)_2$:Eu^{2+} is around 300 K, a high value for a material having a Stokes shift >10 000 cm^{-1}. This could be attributed to the high excitation energy of Eu^{2+} in this host, which is expected to increase the quenching temperature.[13] Considering the very large Stokes shift

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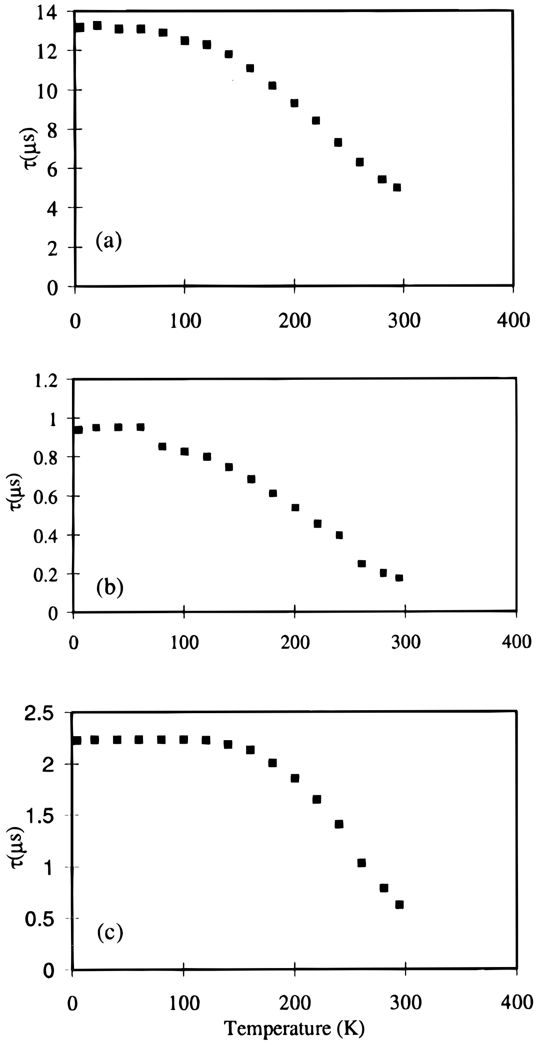

Figure 5. Eu^{2+} emission lifetime as a function of temperature in (a) $Ba_2Mg(BO_3)_2$ (λ_{em} = 617 nm), (b) $Ba_2Ca(BO_3)_2$ (λ_{em} = 530 nm), and (c) $Sr_2Mg(BO_3)_2$ (λ_{em} = 605 nm).

observed in this material, however, we might still expect the other two compounds to have higher quenching temperatures. It is also somewhat surprising that $Ba_2Ca(BO_3)_2:Eu^{2+}$ quenches at a lower temperature than $Sr_2Mg(BO_3)_2:Eu^{2+}$, as the latter exhibits a larger Stokes shift and a lower lying excitation energy. We suspect in this case that the data for $Ba_2Ca(BO_3)_2:Eu^{2+}$ are skewed by the presence of some Eu^{2+} ions on the Ca site, lowering the observed quenching temperature. The thermal quenching is consistent with the lifetime data shown in Figure 5 and in Table 1; the lifetime at T_{50} is approximately one-half the 4.2 K lifetime for each compound. $Sr_2Mg(BO_3)_2:Eu^{2+}$ and $Ba_2Ca(BO_3)_2:Eu^{2+}$ have decay times that are typical of Eu^{2+}. The emission lifetime of $Ba_2Ca(BO_3)_2:Eu^{2+}$ reported here is for emission from both the Ba and Ca sites. Because the observed decay curves appear to be single exponential, we expect that the decay lifetimes from the two sites are not markedly different. At 4.2 K, the lifetime of $Ba_2Mg(BO_3)_2:Eu^{2+}$ is 13 μs, a rather long, but fully reproducible, value for Eu^{2+} in this host. The room-temperature lifetime of 5 μs, however, is similar to the 5-μs lifetime reported for $BaFCl:Eu^{2+}$.[14] The low-energy

Table 2. Crystallographic Data for the Borates $X_2Z(BO_3)_2$

compound	space group	*a*	*b*	*c*	*β*
$Ba_2Mg(BO_3)_2$ [a]	$R\bar{3}m$	5.343	5.343	16.52	
$Ba_2Ca(BO_3)_2$ [b]	*C*2/*m*	9.635	5.432	6.635	119.38
$Sr_2Mg(BO_3)_2$ [c]	*C*2/*m*	9.035	5.146	6.099	118.59

[a] Reference 2. [b] Reference 10. [c] Reference 11.

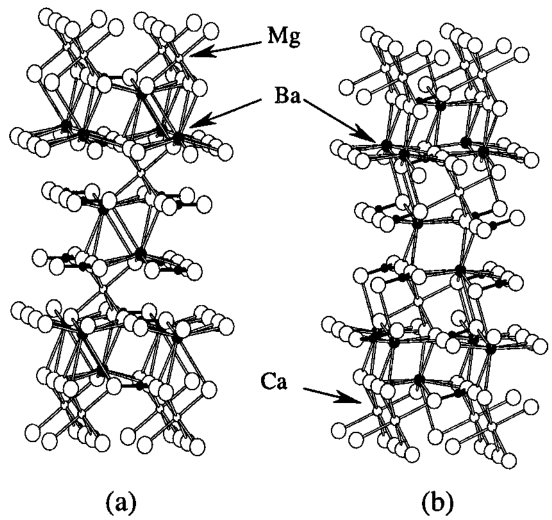

Figure 6. (a) Hexagonal unit cell of $Ba_2Mg(BO_3)_2$ and (b) the pseudohexagonal cell of $Ba_2Ca(BO_3)_2$.

emission in this material should lead to a longer lifetime, since the transition probability decreases as λ^3. But, the observed lifetime is too long to be caused by this effect alone. The rather long lifetime may be associated with an energetic overlap of the Eu^{2+} excited levels and the conduction band of the host, leading to emission from an impurity-trapped exciton.[7,15] We noted earlier the high-energy position of the excitation band in this material.

Solid Solutions $Sr_{2-x}Ba_xMg(BO_3)_2$ and $Ba_2Mg_{1-x}Ca_x(BO_3)_2$. The structures of the borate hosts involved in this study have been previously determined in our lab.[2,10,11] $Ba_2Ca(BO_3)_2$ and $Sr_2Mg(BO_3)_2$ crystallize in the monoclinic space group *C*2/*m*, while $Ba_2Mg(BO_3)_2$ forms in the trigonal space group $R\bar{3}m$. Crystallographic data for these compounds are given in Table 2. Despite the apparent differences between the hexagonal and monoclinic phases, a definite structural relationship exists between the materials. In fact, the monoclinic cell can be transformed to a pseudohexagonal setting with the matrix

$$\begin{bmatrix} 0 & 1 & 0 \\ 1/2 & -1/2 & 0 \\ 1/2 & 1/2 & 3 \end{bmatrix}$$

Here the *b* axis of the monoclinic cell becomes the *a* axis of the approximate hexagonal cell. The pseudohexagonal cell of $Ba_2Ca(BO_3)_2$ has a = 5.432, b = 5.530, c = 18.24, α = 108.7°, β = 81.4°, and γ = 119.4°. A similar, though smaller, cell can be derived for $Sr_2Mg(BO_3)_2$. This transformation is best understood by considering Figure 6, where the $Ba_2Mg(BO_3)_2$ and $Ba_2Ca(BO_3)_2$ structures are drawn adjacent to one another. When viewed in this way, it can be seen that the hexagonal and monoclinic structures are related by a rotation of the small cation-centered (Mg or Ca) octahedra and a

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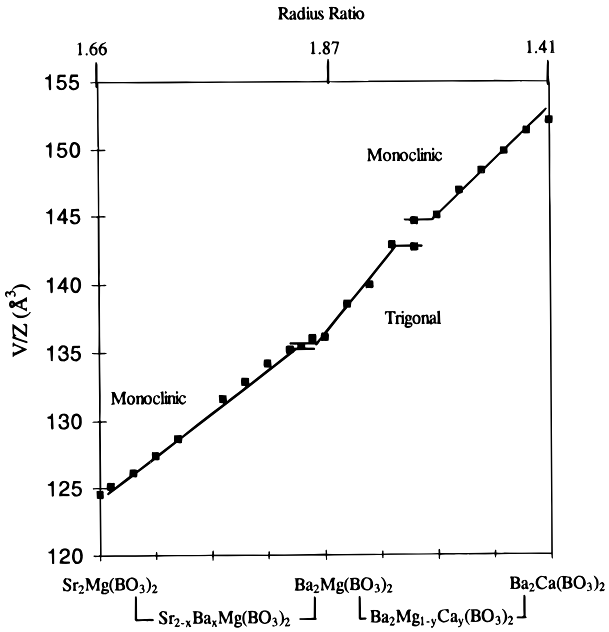

Figure 7. V/Z vs composition for the series $Sr_{2-x}Ba_xMg(BO_3)_2$ and $Ba_2Mg_{1-y}Ca_y(BO_3)_2$.

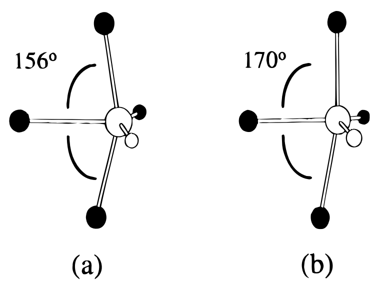

Figure 8. O atom coordination environments in (a) $Ba_2Mg(BO_3)_2$ and (b) $Ba_2Ca(BO_3)_2$. Central atom = O; large filled circles = Ba; small open circles = Mg or Ca; small filled circles = B. The angle indicated is the axial Ba−O−Ba angle.

tilting of the BO_3 groups. This rotation and tilting move one of the three O atoms from the triangular, trigonal plane of the 6 + 3 coordination sphere about Ba in $Ba_2Mg(BO_3)_2$ to a position outside the distorted hexagonal plane of the BaO_9 polyhedron in $Ba_2Ca(BO_3)_2$ (cf. Figures 1 and 6.)

Unit-cell volumes for the series $Sr_{2-x}Ba_xMg(BO_3)_2$ ($0 \le x \le 2$) and $Ba_2Mg_{1-y}Ca_y(BO_3)_2$ ($0 \le y \le 1$) are presented in Figure 8. Extensive solubility of Ba in the series $Sr_{2-x}Ba_xMg(BO_3)_2$ is observed with a solubility limit at $x_{max} \approx 1.6$. At slightly larger values of x, a two-phase region is observed, representing the maximum solubility of Ba in monoclinic $Sr_2Mg(BO_3)_2$ and Sr in trigonal $Ba_2Mg(BO_3)_2$; the maximum Sr solubility in $Ba_2Mg(BO_3)_2$ is represented by the formula $Ba_{1.8}Sr_{0.2}(BO_3)_2$. In the series $Ba_2Mg_{1-y}Ca_y(BO_3)_2$, the maximum Ca solubility in the $Ba_2Mg(BO_3)_2$ structure occurs at $y \approx 0.3$, while the maximum Mg solubility in the $Ba_2Ca(BO_3)_2$ structure occurs at $y \approx 0.5$. A two-phase region comprised of varying proportions of the limiting compositions exists between these two values of y.

By considering the ratios of the radii[16] for the cations occupying the 9- and 6-coordinate sites in these compounds, we find that the trigonal phase exists within the range of ratios 1.71−1.87.[17] For the monoclinic phases $Sr_2Mg(BO_3)_2$ and $Ba_2Ca(BO_3)_2$, the corresponding ratios are 1.66 and 1.41, respectively. As seen in Figure 7, the existence field for the trigonal structure is asymmetrically placed with respect to the highest radius ratio of 1.87 at the composition $Ba_2Mg(BO_3)_2$. Substitution of a smaller cation on the Ba site more readily affords the monoclinic structure in comparison to substitution of a larger cation on the Mg site. Occupation of the large and symmetrical 6 + 3 coordination environment by a cation of sufficient size appears to be a precondition for existence of the trigonal phase.

In $Ba_2Mg(BO_3)_2$, there is one crystallographically unique O atom, while in $Ba_2Ca(BO_3)_2$ there are two. The monoclinic−hexagonal transition leads to differences in the coordination environments of the O atoms in these structures. In Figure 8, one such environment from $Ba_2Ca(BO_3)_2$ is compared to a similar environment in $Ba_2Mg(BO_3)_2$. Each atom occupies a distorted trigonal bipyramid of three Ba, one Ca or Mg, and one B atom, but the axial Ba−O−Ba angle is 170° in $Ba_2Ca(BO_3)_2$ and only 156° in $Ba_2Mg(BO_3)_2$. We have already correlated the differences in these O-atom environments to the magnitudes of the Eu^{2+} Stokes shifts,[3] in that greater distortion leads to a larger Stokes shift. We will now discuss the relationship between these structural features and the excitation energy of the Eu^{2+} ion.

Discussion

Several models have already been proposed to correlate Eu^{2+} excitation and emission properties to the structure of the host. For example, large Stokes shifts have been commonly associated with a more asymmetric dopant-site geometry.[1] Here, an off-center displacement of the Eu^{2+} ion in the ground state can be considered to lead to a large rearrangement of the coordination environment in the excited state and hence to a large Stokes shift. From an extensive study of borate hosts[3] we have shown, however, that no strong correlation exists between the site asymmetry and the Stokes shift associated with Eu^{2+} Stokes luminescence. We also noted above that the observed excitation spectra are consistent with the splitting expected for a normal position of the Eu^{2+} ion in the dopant site, particularly in $Ba_2Mg(BO_3)_2$:Eu^{2+}, where the largest Stokes shift is observed. In addition, EPR studies of Eu^{2+} in some sulfide hosts have indicated that no such rearrangement of the ground state is occurring in these materials.[18]

In a report on Eu^{2+} luminescence in $BaAl_2O_4$ and $SrAl_2O_4$, the authors proposed that long-wavelength emission of Eu^{2+} will be observed when the host structure allows for the preferential orientation of a Eu 5d orbital.[7] $BaAl_2O_4$:Eu^{2+} contains two sites, and exhibits emission at 510 and 540 nm with Stokes shifts of 5000 and 6000 cm^{-1}, respectively. $SrAl_2O_4$:Eu^{2+} exhibits emission at 445 and 520 nm with Stokes shifts of 3000 and 4000 cm^{-1}. According to this model, the energy of a 5d orbital oriented toward an area of low electrostatic potential will be depressed. In $BaAl_2O_4$, the Ba atoms occupy channels within an $[Al_2O_4]^{-2}$ framework. One of the d orbitals of the Eu^{2+} dopant on a Ba site is assumed to orient along the channel axis and thus into an area of lower electrostatic potential

(16) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(17) $r(Ba^{2+})/[0.7r(Mg^{2+}) + 0.3r(Ca^{2+})] = 1.71$; $r(Ba^{2+})/r(Mg^{2+}) = 1.87$.

(18) Nakao, Y. *J. Phys. Soc. Jpn.* **1980**, *48*, 534.

resulting from the cationic neighbors in that direction. This d orbital is stabilized, leading to a lower excitation energy and a larger Stokes shift. The authors also proposed that such an effect may be operating in $Ba_2Mg(BO_3)_2:Eu^{2+}$, because of the unusual dopant-site geometry and the disposition of the neighboring cations. We feel, however, that this model may not adequately describe the results presented here. For example, a preferred orientation of orbitals should lower the excitation energy in $Ba_2Mg(BO_3)_2:Eu^{2+}$, whereas the observed excitation energy is rather large (30 300 cm^{-1}). In addition, the dopant-site geometry is more symmetric in $Ba_2Ca(BO_3)_2$ than in $Ba_2Mg(BO_3)_2$,[3] yet the excitation energy for Eu^{2+} is lower in the former compound by some 7000 cm^{-1}. And, many borates, like BaB_8O_{13}, have channel structures but still exhibit high-energy excitation and emission for Eu^{2+}.[19,20] We also note that such a model should be applicable when the metal d orbitals are essentially nonbonding with respect to the ligands, a situation not encountered in these hosts.

Another model commonly employed to explain the red-shift of Eu^{2+} excitation bands is covalency, or the nephelauxetic effect. This model stems from the observation that interelectron repulsion and energy levels are lower for an ion in a solid relative to that same ion in the gas phase. In the solid, the electrons with excited Eu^{2+} 5d character diffuse into the solid as a result of their interaction with the surrounding anions. An electron placed in the 5d shell from the $^8S_{7/2}$ level ($4f^7$ configuration) therefore experiences reduced repulsion from the other electrons in the Eu^{2+} core. Even though the ligand-centered molecular orbitals are expected to be antibonding, the electron−electron repulsion energy is of a magnitude comparable to the antibonding interaction.[21] As a result, the covalency effect lowers the barycenter of the 5d levels. We also note in this context that the term covalency refers to the bonding interaction between the Eu dopant and the ligands, rather than to the ionic or covalent character of the undoped host. The nephelauxetic model has been discussed in detail by Jørgensen.[22,23] It has been used to explain the low-lying excitation bands of Eu^{2+} in SrO,[24] as well as in some sulfides, where the covalency effect is expected to be stronger.[6] In the following, we will examine those structural features that are expected to produce a strong covalency effect in a given host.

In Table 3, structural and spectroscopic data are given for 14 borates doped with Eu^{2+}. The data for $Ba_2Ca(BO_3)_2:Eu^{2+}$ are included with the understanding that some Eu^{2+} is present on the Ca site in this material. This table is similar to that published previously,[3] except the position of the lowest energy excitation level of Eu^{2+} in each compound has been included. The average deviation of the angles about the O atoms from ideal polyhedral angles are listed in the column labeled "% angular deviation." The hosts that exhibit blue or UV emission are separated from those that exhibit emission at wavelengths longer than 500 nm. We have noted already that the long-wavelength emitters are distinguished by the presence of at least one O atom coordinated by three or more Ba or Sr atoms. We have also described the correlation between the angular deviations of the O polyhedra and the magnitudes of the Eu^{2+} Stokes shifts.[3] A few additional consequences of this structural feature are now readily recognized from the table. First, excitation energies are generally lower for those hosts containing O atoms highly coordinated by Ba or Sr atoms, usually lower than about 30 000 cm^{-1}. Those hosts containing O atoms minimally coordinated by Ba or Sr atoms exhibit excitation energies that are generally greater than 30 000 cm^{-1}. Also, in the long-wavelength emitters there exists a reasonable correlation between the percent angular deviation and the position of the lowest-energy excitation band. That is, it appears that regular O polyhedra lead to lower lying excitation energies in those materials containing O atoms bound by three or more Ba (Sr) atoms. Finally, note that no apparent correlation exists between the Eu^{2+} spectroscopic properties and the angular deviations in the hosts with O atoms bound mainly to B atoms.

Table 3. Spectroscopic Data for Eu^{2+} in Borates[a]

compound	excitation energy[b] (cm^{-1})	Stokes shift (cm^{-1})	emission λ (nm)	% angular deviation
Borates with Emission > 500 nm				
$Ba_2Mg(BO_3)_2$	30 300	14000	617	10.2
$Ba_2LiB_5O_{10}$	27 400	11000	612	9.9
$BaLiBO_3$	(25 000)	(5400)	510	7.4
$Ba_2Ca(BO_3)_2$	23 300	4300	530	6.6
$Sr_2Al_2B_2O_8$	(26 500)	(8000)	529	11.7
$Sr_3(BO_3)_2$	23 300	6000	585	7.0
$Sr_2Mg(BO_3)_2$	22 200	5600	605	6.3
Borates with UV or Blue Emission for Eu^{2+}				
$BaBe_2(BO_3)_2$	(27 200)	(1700)	392	8.5
$BaLiB_9O_{15}$	30 300	5300	400	14.9
$BaNaB_9O_{15}$	30 300	5700	407	11.5
BaB_8O_{13}	32 200	7200	400	7.0
$SrLiB_9O_{15}$	29 700	4100	390	8.8
SrB_4O_7	33 100	5900	367	11.1
$SrAl_2B_2O_7$	(31 700)	(7600)	415	9.3

[a] Complete references for the data in this table can be found in ref 3. [b] Refers to the lowest energy excitation peak. Values in parentheses are at room temperature, all others are at 4.2 K.

We must now consider those factors that distinguish, structurally and electronically, hosts that contain O atoms highly coordinated by Ba or Sr atoms. The expectation is that such a material will be more covalent (with respect to the dopant site). This can be considered either from the point of view that the material will be more polarizable, or from the related idea that more Ba (Sr) atoms will lead to a greater electron density on the O atoms and therefore to orbitals with a larger radius. In this case, the O−Eu overlap will likely increase, creating a more pronounced nephelauxetic effect. It has been suggested, for example, that covalency effects on Pb^{2+} and Eu^{3+} spectra become stronger as the SrO/B_2O_3 ratio is increased in Sr borates.[5] Folkerts and Blasse have also made this argument to explain the low-lying excitation band of Pb^{2+} in $Ca_4LaO(BO_3)_3$. One of the O atoms in that material is bound only to the Ca atoms, creating a highly charged O atom that binds in a

(19) Krogh-Moe, J.; Ihara, M. *Acta Crystallogr., Sect. B* **1969**, *25*, 2153.
(20) Blasse, G.; Bril, A.; De Vries, J. *J. Electrochem. Soc.* **1968**, *115*, 977.
(21) Piper, T. S.; Brown, J. P.; McClure, D. S. *J. Chem. Phys.* **1967**, *46*, 1353.
(22) Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*; North-Holland Publishing Co.: Amsterdam, 1971.
(23) Jørgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon Press: Oxford, 1962.
(24) Yamashita, N. *J. Lumin.* **1994**, *59*, 195.

covalent manner to the Pb center, lowering the excitation energy.[6]

From the data in Table 3, it appears that the effects of covalency on the Eu^{2+} 5d energies are more evident when a borate host contains O atoms surrounded by three or more Ba (Sr) atoms. Thus, in general we do not see excitation energies below about 30 000 cm^{-1} in the hosts where the O atoms are richly coordinated by B atoms. For those materials that are expected to produce a stronger nephelauxetic effect, the magnitude of the effect also depends to some extent on the geometry of the O polyhedra. Regular O polyhedra give better overlap with the Eu^{2+} 5d orbitals and lower the energy of the 5d levels.

For those materials that do not contain O atoms highly coordinated by Ba or Sr, we attribute the high Eu^{2+} excitation energies to the fact that the Eu−O interactions are less covalent, being similar to Eu−O interactions in a phosphate or sulfate or Eu−F interactions in a fluoride, and therefore exhibit a weaker nephelauxetic effect. The excitation energies in these hosts do not correlate with the distortion of the O polyhedra because the covalency effects are being dominated by the binding of the O atoms to highly electronegative atoms. In these materials it is also evident that the magnitudes of the Stokes shifts do not correlate well with the distortion of the O-centered polyhedra. As expected, the nature of the other small cations in these materials will have significant effects on the excitation energies and Stokes shifts. Note for example the increasing Stokes shift in the series $BaBe_2(BO_3)_2$ < $BaLiB_9O_{15}$ < $BaNaB_9O_{15}$, where the increasing size of the small cation correlates to an increasing magnitude of the Stokes shift.

Conclusions

We have shown that Eu^{2+} luminescence properties in borates can be correlated to the environment of the O atoms in these hosts. Materials can be divided into two types: those that exhibit long-wavelength ($\lambda > 500$ nm) emission, and those that exhibit short-wavelength emission ($\lambda < 500$ nm.) Those emitting at long wavelengths contain O atoms coordinated by three or more Ba or Sr atoms, while those emitting at short wavelengths contain O atoms coordinated by only one or two Ba or Sr atoms. Long-wavelength emission will result either from a low-lying excitation band or from a large Stokes shift. Structures with regular O polyhedra will produce a stronger nephelauxetic effect and consequently a lower excitation energy, while structures with more distorted O polyhedra will exhibit higher excitation energies and larger Stokes shifts. In those hosts that contain O atoms highly coordinated by B atoms, the excitation energies will in general be high, and short-wavelength emission will be observed. In this case, the magnitude of the Stokes shift is expected to depend strongly on the nature of the other cations in the structure.

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