

Luminescence of Eu^{2+} in Barium and Strontium Aluminate and Gallate

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The luminescence of Eu^{2+} in alkaline earth aluminates and gallates of the type $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_{2-y}\text{Ga}_y\text{O}_4$ ($x = 0, 0.5, 1$ and $y = 0, 1, 2$) has been studied. In both $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, green Eu^{2+} luminescence is observed from Eu^{2+} on the two different alkaline earth sites present in the lattice. The Eu^{2+} luminescence is at low energies due to preferential orientation of a d orbital of Eu^{2+} on the barium or strontium sites in these lattices. Due to photoionization, no Eu^{2+} luminescence can be observed in $\text{BaGa}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{SrGa}_2\text{O}_4:\text{Eu}^{2+}$. When part of the gallium is replaced by aluminum, the characteristic Eu^{2+} luminescence as seen in $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ is again observed.

Introduction

The emission and absorption spectra of Eu^{2+} usually consist of broad bands due to transitions between the $^8\text{S}_{7/2}$ ($4f^7$) ground state and the crystal field components of the $4f^65d$ excited state configuration. The emission of Eu^{2+} varies from blue to red, depending on the structure it is built into. In SrO and CaO , for example, the Eu^{2+} emission is at 625 and 733 nm, respectively, while in $\text{Sr}_2\text{P}_2\text{O}_7$ the Eu^{2+} emission is at 420 nm.¹⁻³ In BaFCl the Eu^{2+} emission is at even shorter wavelength, viz., at 390 nm.⁴ In alkaline earth aluminates the Eu^{2+} emission is in many cases in the blue region of the spectrum. Divalent europium in $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ emits at 460 and 395 nm, respectively.^{3,5,6} In $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ the Eu^{2+} emission is at 450 nm, and in $\text{SrMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ it is at 465 nm.⁷ However, in $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, the Eu^{2+} ion shows a green emission at 505 and 520 nm, respectively.^{5,8-10} This different luminescence behavior of Eu^{2+} makes it worthwhile to study the luminescence of Eu^{2+} in these compounds in more detail.

The crystal structures of the compounds studied in this work are all derivatives of the stuffed tridymite structure. In this type of structure there are large open channels in the framework, which provide suitable sites for large cations.

In BaAl_2O_4 there are two different barium sites, one occurring 3 times more frequently than the other. Both barium sites are coordinated by nine oxygen ions, one slightly more regularly than the other.^{11,12} The struc-

ture of SrAl_2O_4 is less regular compared to the hexagonal structure of BaAl_2O_4 . In the monoclinic low-temperature form of SrAl_2O_4 , which is the form occurring at room temperature, there are two sites available for Sr^{2+} ions. Both sites occur in equal amounts in the lattice and are coordinated by nine oxygen ions. The coordination of strontium by oxygen is less regular than the coordination of barium by oxygen in BaAl_2O_4 . Due to the existence of a hexagonal form of SrAl_2O_4 at higher temperatures, mixed crystals with composition $\text{Ba}_x\text{Sr}_{1-x}\text{Al}_2\text{O}_4$ can be grown.¹³ BaGa_2O_4 is isostructural with BaAl_2O_4 . This implies that there are two different barium sites in BaGa_2O_4 , one site occurring 3 times more frequently than the other. Both sites are coordinated by nine oxygen ions.¹⁴ SrGa_2O_4 , finally, has two modifications: a low-temperature form which is monoclinic and a high temperature form which has a hexagonal structure.^{15,16} Although in the literature the structure of SrGa_2O_4 is not described as comprehensively as that of BaAl_2O_4 , it seems reasonable to compare the structure of SrGa_2O_4 with that of SrAl_2O_4 , just as BaGa_2O_4 can be compared with BaAl_2O_4 .

Thus, the structures described above are all derivatives of the stuffed tridymite structure. Therefore, it is interesting to study the Eu^{2+} luminescence in these compounds, in order to get a better understanding of the influence of the surroundings in the lattice on the Eu^{2+} luminescence.

Experimental Section

Preparation. The measurements were performed on powder samples with composition $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_{2-y}\text{Ga}_y\text{O}_4:\text{Eu}^{2+}$, with $x = 0, 0.5$, and 1 , and $y = 0, 1$, and 2 . The Eu^{2+} mole fractions were 1×10^{-2} . The starting materials were BaCO_3 (Philips Maarheze), SrCO_3 (Philips Maarheze), Al_2O_3 (Reynolds), Ga_2O_3

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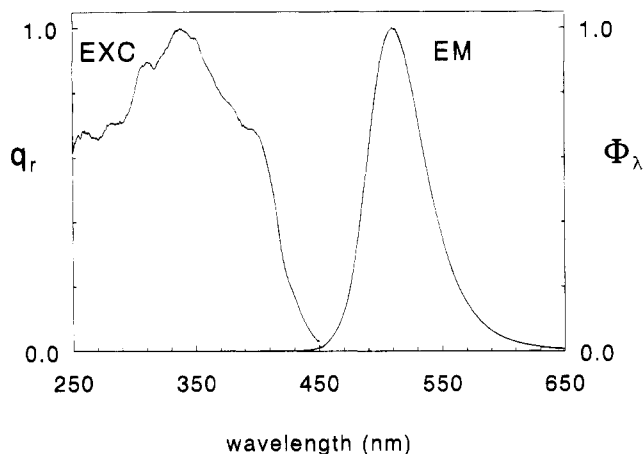


Figure 1. Excitation (EXC) and emission (EM) spectra of $\text{BaAl}_2\text{O}_4:1\%\text{Eu}^{2+}$ at 4.2 K ($\lambda_{\text{em}} = 510$ nm, $\lambda_{\text{exc}} = 350$ nm). q_r gives the relative quantum output in arbitrary units, Φ_λ gives the radiant power per constant wavelength interval in arbitrary units.

(Alusuisse), and Eu_2O_3 (Highways Int., 99.99%). All samples were prepared by solid state reactions. Stoichiometric amounts of the starting materials were thoroughly mixed in a planetary ball mill and subsequently fired at 600 °C for 1 h and at 1100 °C for 4 h. After milling for a second time, the samples were fired at 600 °C for 1 h, and at 1200 °C for 4 h. Both firing procedures took place in a reducing atmosphere (25% $\text{H}_2/75\%$ N_2). The samples were confirmed to be single phase by X-ray powder diffraction using $\text{Cu K}\alpha$ radiation.

Optical Measurements. Diffuse reflection spectra were recorded on a Perkin-Elmer Lambda 7 UV/vis spectrophotometer. BaSO_4 was used as a reference. The luminescence spectra were recorded on a SPEX Fluorolog spectrofluorometer equipped with two double-grating 0.22 m SPEX 1680-monochromators and a xenon lamp as an excitation source. Temperature dependent measurements were performed with the SPEX spectrofluorometer equipped with an Oxford Instruments liquid helium flow cryostat, for temperatures from 4.2 K to room temperature, and a homemade high-temperature cell,¹⁷ for temperatures above room temperature. The excitation spectra were corrected for the lamp output.

Results

Aluminates. The emission spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ at 4.2 K show a broad emission band at about 510 nm (Figure 1). This emission band corresponds to the $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} . On an energy scale this emission band appears to be asymmetric and can be divided into two Gaussian bands with maxima at 510 and 540 nm (Figure 2). At 4.2 K the band at 540 nm is about 3 times less intense than the band at 510 nm. At room temperature the emission maxima are at 495 and 530 nm, respectively. The excitation spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ at room temperature as well as at 4.2 K are broad and structureless and correspond to the $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} (Figure 1). No clear dependence of the excitation spectra on the emission wavelength is observed. The excitation spectra recorded at room temperature are consistent with the reflection spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$. Because the excitation spectra are broad and structureless, only a very rough estimation of the values of the Stokes shifts of both emissions can be made. The Stokes shift of the shorter wavelength emission is about 5000 cm^{-1} , whereas the longer wavelength emission has a Stokes shift of about 6000 cm^{-1} . The temperature at which half of the emission intensity

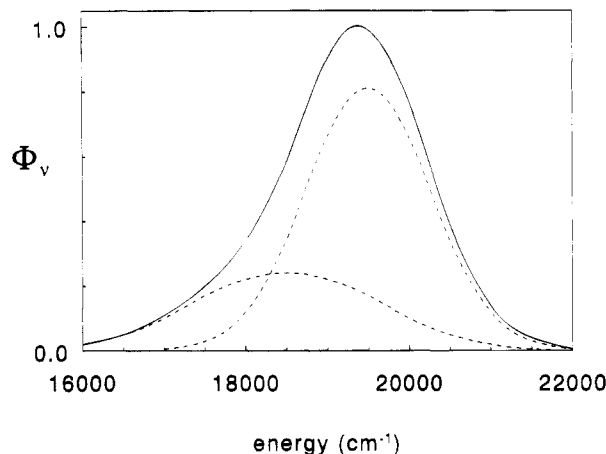


Figure 2. Gaussian fit of the emission spectrum of $\text{BaAl}_2\text{O}_4:1\%\text{Eu}^{2+}$ excited at 350 nm at 4.2 K into two components. Φ_v gives the radiant power per constant energy interval in arbitrary units.

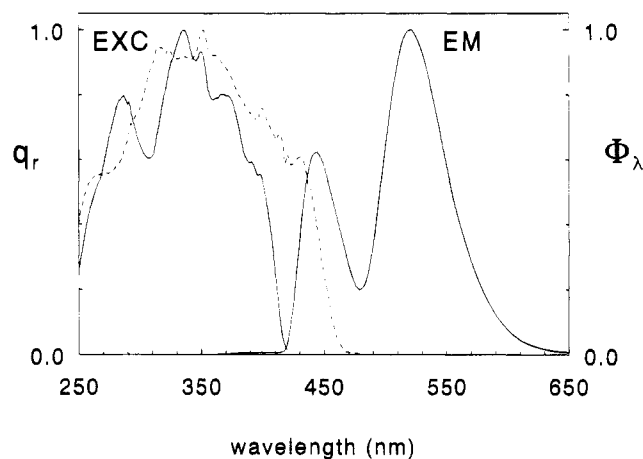


Figure 3. Excitation spectra (EXC) of $\text{SrAl}_2\text{O}_4:1\%\text{Eu}^{2+}$ at 4.2 K (solid curve: $\lambda_{\text{em}} = 443$ nm, dashed curve: $\lambda_{\text{em}} = 520$ nm). Emission spectrum (EM) of $\text{SrAl}_2\text{O}_4:1\%\text{Eu}^{2+}$ at 4.2 K ($\lambda_{\text{exc}} = 340$ nm).

Table 1. Temperature Dependence and Stokes Shifts of the Eu^{2+} Luminescence in $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4\text{Ga}_y\text{O}_4:\text{Eu}^{2+}$ ($x = 0, 0.5, 1$ and $y = 0, 1$; $T_{1/2}$ = Temperature at Which Half of the Emission Intensity at 4.2 K Is Reached; T_q = Temperature at Which the Emission Is Completely Quenched)

compound	emission maxima at 4.2 K (nm)	$T_{1/2}$ (K)	T_q (K)	Stokes shift (cm^{-1})
$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$	510	300	410	5000
	540	290	370	6000
$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$	445	170	320	3000
	520	440	>550	4000
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Al}_2\text{O}_4:\text{Eu}^{2+}$	505	320	440	5000
	550	270	360	6000
$\text{BaAlGaO}_4:\text{Eu}^{2+}$	510	220	370	5000
	555	100	270	6000
$\text{SrAlGaO}_4:\text{Eu}^{2+}$	450	120	250	3000
	540	150	420	5000

at 4.2 K is reached is 300 K for the emission at 510 nm and 290 K for the emission at 540 nm; the quenching temperatures are 410 and 370 K, respectively (Table 1).

The emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ at 4.2 K show two emission bands at about 445 and 520 nm (Figure 3). At room temperature the emission at 445 nm is almost quenched and only the longer wavelength emission is observed. The excitation spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ are dependent on the emission wavelength. The excita-

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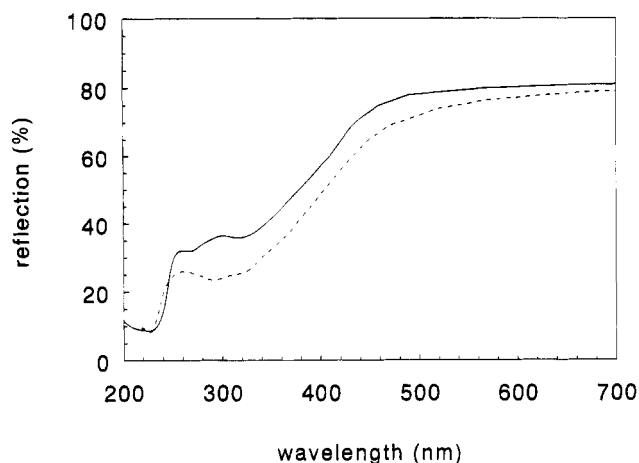


Figure 4. Diffuse reflection spectrum of $\text{BaGa}_2\text{O}_4:1\% \text{Eu}^{2+}$ (solid curve) and $\text{SrGa}_2\text{O}_4:1\% \text{Eu}^{2+}$ (dashed curve) at room temperature.

tion spectrum of the emission at 520 nm starts at about 460 nm, whereas the excitation spectrum of the emission at 445 nm starts at about 420 nm (Figure 3). At room temperature the excitation spectrum starts at about 480 nm and is consistent with the reflection spectrum of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$. A rough estimation of the Stokes shifts gives about 3000 and 4000 cm^{-1} for the emissions at 445 and 520 nm, respectively. The temperature at which half of the emission intensity at 4.2 K is reached is 170 K for the emission at 445 nm and 440 K for the emission at 520 nm; the quenching temperatures are 320 and >550 K, respectively (Table 1).

The luminescence behavior of Eu^{2+} in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Al}_2\text{O}_4$ is comparable to that of Eu^{2+} in BaAl_2O_4 . Again a broad emission band is observed, which can be divided into two bands: one at 505 nm and another less intense band at about 550 nm. The excitation spectra are broad and structureless and are consistent with the reflection spectrum. In contrast to the excitation spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$, the excitation spectra of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Al}_2\text{O}_4:\text{Eu}^{2+}$ are slightly dependent on the emission wavelength. When the emission wavelength is longer than 500 nm, the excitation spectrum is shifted to slightly longer wavelengths. This effect is less clear than a similar effect described for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$. A rough estimation of the Stokes shifts gives 5000 and 6000 cm^{-1} for the emission at 505 and 550 nm, respectively. The temperature dependence is also very similar to that of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ (Table 1).

Gallates. In the reflection spectrum of $\text{BaGa}_2\text{O}_4:\text{Eu}^{2+}$ as well as $\text{SrGa}_2\text{O}_4:\text{Eu}^{2+}$, the Eu^{2+} absorption is very clearly present (Figure 4). However, Eu^{2+} emission is observed in neither $\text{BaGa}_2\text{O}_4:\text{Eu}^{2+}$ nor in $\text{SrGa}_2\text{O}_4:\text{Eu}^{2+}$, at room temperature and even at 4.2 K. When part of the gallium is replaced by aluminum, Eu^{2+} luminescence is again observed.

The emission spectra of $\text{BaAlGaO}_4:\text{Eu}^{2+}$ are very similar to those of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$, except for the efficiency of the Eu^{2+} emission, which is lower in $\text{BaAlGaO}_4:\text{Eu}^{2+}$. At 4.2 K a broad emission band is observed, which can be divided into two bands. The maxima of these bands are at about 510 and 555 nm. The maximum of the emission band is slightly dependent on the excitation wavelength; the emission band shifts to longer wavelengths when the excitation position is at longer wavelengths. At room temperature only the

more intense shorter wavelength emission is observed. Besides the Eu^{2+} emission, a characteristic gallate emission is also observed at 430 nm.¹⁸ The excitation spectra of $\text{BaAlGaO}_4:\text{Eu}^{2+}$ at 4.2 K are broad and structureless. Just as for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Al}_2\text{O}_4:\text{Eu}^{2+}$, the excitation spectra are slightly dependent on the emission wavelength. For emission wavelengths longer than about 525 nm, the excitation spectrum is shifted to slightly longer wavelengths. A rather rough estimation of the Stokes shift gives 5000 and 6000 cm^{-1} for the emissions at 510 and 555 nm, respectively. Both emissions are much stronger temperature dependent than the Eu^{2+} emissions of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$. The temperature at which half of the emission intensity at 4.2 K is reached, is 220 K for the emission at 510 nm and 100 K for the emission at 555 nm; the quenching temperatures are 370 and 270 K, respectively (Table 1).

The emission spectra of $\text{SrAlGaO}_4:\text{Eu}^{2+}$, finally, are very similar to those of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, except for the efficiency of the Eu^{2+} emission, which is lower in $\text{SrAlGaO}_4:\text{Eu}^{2+}$. At 4.2 K two emission bands are observed at 450 and 540 nm, while at room temperature only the longer wavelength emission is observed. At 4.2 K, the emission at shorter wavelengths has a much lower intensity than the emission at longer wavelengths, whereas in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ both emissions are of comparable intensity. The excitation spectra are broad, both at room temperature and at 4.2 K. A similar dependence on the emission wavelength as described for the excitation spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ is observed. A rough estimation of the Stokes shift gives 3000 and 5000 cm^{-1} for the emissions at 450 and 540 nm, respectively. Just as in $\text{BaAlGaO}_4:\text{Eu}^{2+}$, the Eu^{2+} luminescence in $\text{SrAlGaO}_4:\text{Eu}^{2+}$ is strongly temperature dependent. The temperature at which half of the emission intensity at 4.2 K is reached, is 120 K for the emission at 450 nm and 150 K for the emission at 540 nm; the quenching temperatures are 250 and 420 K, respectively (Table 1).

Discussion

Aluminates. Both in $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ and in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, two Eu^{2+} emissions are observed, whereas in the literature only one Eu^{2+} emission is reported for these compounds.^{5,8-10} In BaAl_2O_4 and SrAl_2O_4 there are two different sites available for Eu^{2+} . In BaAl_2O_4 one of these barium sites occurs 3 times more frequently in the lattice than the other. This ratio is also found in the emission spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$. When the emission band, which is asymmetric on an energy scale, is divided into two Gaussian bands, the intensity ratio is found to be about 3:1, the longer wavelength emission being the less intense band. The most intense band corresponds to the Eu^{2+} emission mentioned in the literature for $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$.

In $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Al}_2\text{O}_4:\text{Eu}^{2+}$ the Eu^{2+} luminescence is quite similar to that in $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$. This is not surprising, because $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Al}_2\text{O}_4$ is isostructural with BaAl_2O_4 .¹³

In SrAl_2O_4 both strontium sites occur in equal amounts in the lattice. In the emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ at 4.2 K, two bands are observed. The emission at shorter wavelength is somewhat lower in intensity, but this is due to energy transfer. Since allowed electric-dipole transitions are involved in the case of Eu^{2+} , the

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value of the critical transfer distance (R_c) can be found from¹⁹

$$R_c = 0.36 \times 10^{28} \frac{4.8 \times 10^{-16} P}{E^4} \text{S.O.} \quad (1)$$

Here P is the oscillator strength of the involved absorption transition of the Eu^{2+} ion, E the energy of maximum spectral overlap, and S.O. the spectral overlap integral. For P a value of 10^{-2} for the broad $4f^7 \rightarrow 4f^6 5d$ absorption band is taken.²⁰ E and S.O. can be derived from the spectral data. The calculated value of R_c for the energy transfer between inequivalent Eu^{2+} ions in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ is 20 Å. This value can be compared to values of R_c found for Eu^{2+} in other lattices,²⁰ and indicates that energy transfer between the Eu^{2+} sites in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ ($\text{Eu}(1)$ and $\text{Eu}(2)$) will be efficient. This is confirmed by the fact that in SrAl_2O_4 with 0.1% Eu^{2+} the intensity of both Eu^{2+} emissions is equal.

The critical distance for energy transfer can also be determined from the relative intensities of the $\text{Eu}(1)$ and $\text{Eu}(2)$ bands in the emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$.²¹ To calculate R_c from the relative intensities, it is assumed that every $\text{Eu}(1)$ ion in the excited state that has one or more $\text{Eu}(2)$ ions within the critical distance for energy transfer, will transfer its excitation energy to a $\text{Eu}(2)$ ion. R_c can be found from

$$R_c = \left(\frac{n V_{\text{Eu}(2)}}{4/3\pi} \right)^{1/3} \quad (2)$$

Here $V_{\text{Eu}(2)}$ is the average volume per $\text{Eu}(2)$ ion, and n is the number of cation sites within R_c :

$$(1 - x)^n = I_{\text{Eu}(1)}/0.5 \quad (3)$$

Here $I_{\text{Eu}(1)}$ is the relative intensity of the emission band of $\text{Eu}(1)$ and x is the concentration Eu^{2+} in $\text{Sr}_{1-x}\text{Eu}_x\text{Al}_2\text{O}_4$.

The critical distance for energy transfer, determined from the relative intensities of the Eu^{2+} bands in the emission spectra of $\text{SrAl}_2\text{O}_4:1\%\text{Eu}^{2+}$, is 14 Å. This value of R_c is smaller than the one calculated using eq 1. Because the former method suffers from a large inaccuracy in the S.O. due to the broad and structureless absorption band, the value of R_c determined from the relative intensities of the Eu^{2+} emission bands is considered to be more accurate. When the intensity ratio of the emission bands in $\text{SrAl}_2\text{O}_4:0.1\%\text{Eu}^{2+}$ is calculated using eqs 2 and 3, with $R_c = 14$ Å, both emission bands should be of equal intensity. This is indeed observed in the emission spectra of $\text{SrAl}_2\text{O}_4:0.1\%\text{Eu}^{2+}$.

In the emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ at room temperature, only the emission at longer wavelengths, which is the emission reported in the literature, is found.

We now turn to the long-wavelength emission of Eu^{2+} in these samples.

Both in BaAl_2O_4 and in SrAl_2O_4 , the barium or strontium ions are in the channels, which are formed by $[\text{AlO}_4]^{5-}$ tetrahedra, and form chains in the structure.^{12,13} The barium or strontium ions are coordinated by nine oxygen ions, one site more regularly than the other. However, when the influence on the Eu^{2+} emis-

sion is assumed to be not restricted to the nearest coordination of the barium or strontium site, the following model can be proposed to explain the long-wavelength emission of Eu^{2+} in these lattices.

In BaAl_2O_4 , the channels are along the c axis, and the two different barium sites occur in separate chains. The less frequently occurring barium sites form chains in which the barium ions are exactly above each other. The other barium chain, which contains the more frequently occurring barium sites, is not exactly linear. In the latter chain the distance between two successive barium ions is slightly longer than in the perfectly linear chains.

When a europium ion is built into either of these chains, it experiences, in addition to the negative charges of the nearest anion neighbors, positive charges due to cation neighbors in the chain direction. As a consequence, the crystal field will orient the d orbital preferentially in the chain direction. This will lower its energy and therefore result in a Eu^{2+} emission at longer wavelengths. Since such a d orbital will be more delocalized than without preferential orientation, the Stokes shift of the emission will also be larger. This is an important difference from the situation in which a long wavelength emission is due to covalency, as in $\text{SrO}:\text{Eu}^{2+}$ and $\text{CaO}:\text{Eu}^{2+}$, for example.^{1,2} In these compounds the Eu^{2+} emission is at very long wavelengths, viz., 625 and 733 nm, respectively, but the low-energy excitation band spreads over the wide range of the visible region, resulting in a small Stokes shift. In the perfectly linear chain of BaAl_2O_4 , the preferential orientation of the d orbitals will be more pronounced than in the chain in which the barium ions are somewhat shifted toward each other. Therefore, Eu^{2+} in the linear chain will give an emission at longer wavelengths. In the emission spectra, two Eu^{2+} emissions are indeed observed. As expected, these emissions are close together and can be separated only by fitting the emission band, which is asymmetrical on an energy scale, into two Gaussian bands. At 4.2 K, the ratio of the intensity of the two emission bands at 510 and 540 nm is about 3:1. This intensity ratio fits very well with the ratio in which the two different barium sites occur in the lattice. According to this similarity, the Eu^{2+} emission at longer wavelengths is due to a europium ion in the perfectly linear chain. Further the observed Stokes shifts are relatively large. This is expected according to the model proposed above.

In SrAl_2O_4 , the strontium chains are along the a axis. In contrast to BaAl_2O_4 , the chains in SrAl_2O_4 consist of the two different strontium sites. These chains are not perfectly linear. The distance between two successive strontium ions is alternately 3.9 and 4.6 Å. However, the distances between the strontium ion and its neighboring oxygen ions are different for the two strontium sites. Looking along the a axis, the oxygen ions are rather close to one strontium site, whereas the oxygen ions are at a much larger distance from the other strontium site. Thus, on the former strontium site, no preferential orientation of d orbitals will occur, whereas on the latter preferential orientation of a d orbital is possible due to the fact that the negative charge is at a large distance. Eu^{2+} on the former site will give an emission at shorter wavelengths than Eu^{2+} on the latter site. At 4.2 K, two emission bands are indeed observed. The two Eu^{2+} emissions in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ are observed as two separate bands and not as two strongly overlapping bands, as in $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$. This difference can be

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explained by the fact that in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ the effect on the Eu^{2+} luminescence is due to the fact whether there exists a preferential orientation of a d orbital or not, whereas in $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ the effect on the Eu^{2+} luminescence is due to the degree of preferential orientation of a d orbital.

In $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$, a blue emission at 440 nm has been observed.⁵ CaAl_2O_4 is structurally related to tridymite, but the stuffed tridymite lattice is strongly distorted.²² Due to this distortion, no preferential orientation of the d orbitals is left, and the Eu^{2+} emission is at higher energy. Also in magnetoplumbite-type crystal structures, like $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}^{2+}$ and $\text{CaAl}_{12}\text{O}_{19}:\text{Eu}^{2+}$, a blue Eu^{2+} is observed.^{5,7} These structures can be described as a close packing of 19 oxygen ions and one large cation, with smaller cations occupying the interstitial sites.²³ In this structure no preferential orientation of d orbitals of Eu^{2+} on a large cation site can occur, and a blue Eu^{2+} emission will be observed.

On the other hand, in $\text{LiBaPO}_4:\text{Eu}^{2+}$ a Eu^{2+} emission at 483 nm is observed.²⁴ The excitation band is in the UV and the Stokes shift is about 6000 cm^{-1} .²⁵ LiBaPO_4 has the LiKSO_4 structure, which is closely related to the stuffed tridymite structure of BaAl_2O_4 . The most important difference between the structures of LiBaPO_4 and BaAl_2O_4 is the difference in size of the two kinds of tetrahedra in LiBaPO_4 ($[\text{LiO}_4]^{7-}$ and $[\text{PO}_4]^{3-}$), whereas there is only one kind of tetrahedron in BaAl_2O_4 ($[\text{AlO}_4]^{5-}$).^{26,27} Just as in BaAl_2O_4 , in LiBaPO_4 there is a preferential orientation of the d orbitals of Eu^{2+} on a barium site, and a Eu^{2+} emission at longer wavelengths is observed.

Finally, the Eu^{2+} luminescence in $\text{LiBa}_2\text{B}_5\text{O}_{10}:\text{Eu}^{2+}$ and $\text{Ba}_2\text{Mg}(\text{BO}_3)_2:\text{Eu}^{2+}$ will be discussed from the models point of view. In $\text{LiBa}_2\text{B}_5\text{O}_{10}:\text{Eu}^{2+}$ and $\text{Ba}_2\text{Mg}(\text{BO}_3)_2:\text{Eu}^{2+}$, a Eu^{2+} emission is observed at 630 and 608 nm, respectively.^{28,29} The excitation bands are in the UV and for both compounds a large Stokes shift of about 11000 cm^{-1} is found. In both structures, the Ba^{2+} ions are in an irregular oxygen coordination. In $\text{LiBa}_2\text{B}_5\text{O}_{10}$, the barium ions are coordinated by eight oxygen ions. The Ba-O distances range from 2.64 to 3.02 Å, the shorter distances being on one side of the Ba^{2+} ion.³⁰ In $\text{Ba}_2\text{Mg}(\text{BO}_3)_2$, the barium ions are coordinated by nine oxygen ions. There are six oxygen ions on the corners of a distorted hexagon, and there are three oxygen ions on the corners of a triangle. The barium ion is far from the triangle but close to the hexagon. Thus, on one site of the Ba^{2+} ion there are three oxygen ions, whereas at the other site there is nearly open space.²⁹ Due to the asymmetric coordination of the Ba^{2+} ions in these compounds, there will be a preferential orientation of a d orbital of Eu^{2+} on the Ba^{2+} site, which means that the Eu^{2+} emission will be at low energy.

Gallates. As mentioned above, both $\text{BaGa}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ do not show Eu^{2+} luminescence, not even at 4.2 K, although in the reflection spectra Eu^{2+} absorption is clearly observed. When part of the gallium

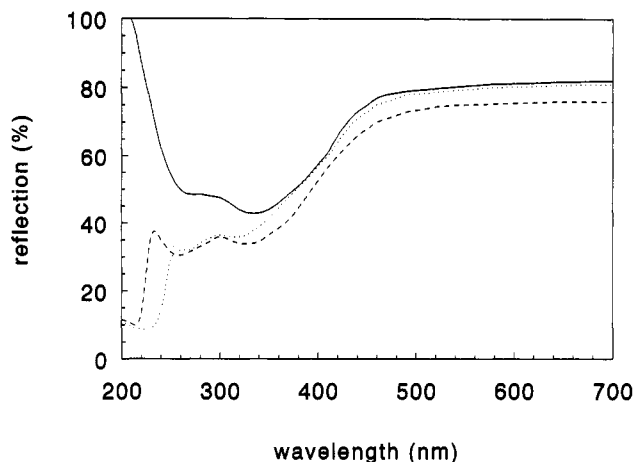


Figure 5. Diffuse reflection spectrum of $\text{BaAl}_2\text{O}_4:1\% \text{Eu}^{2+}$ (solid curve), $\text{BaAlGaO}_4:1\% \text{Eu}^{2+}$ (dashed curve), and $\text{BaGa}_2\text{O}_4:1\% \text{Eu}^{2+}$ (dotted curve) at room temperature. Due to Eu^{2+} luminescence, the spectrum of $\text{BaAl}_2\text{O}_4:1\% \text{Eu}^{2+}$ increases at the shorter wavelength side.

is replaced by aluminum, Eu^{2+} luminescence is again observed. The absence of the Eu^{2+} luminescence in $\text{BaGa}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{SrGa}_2\text{O}_4:\text{Eu}^{2+}$ can be explained by photoionization. In BaGa_2O_4 and SrGa_2O_4 the bottom of the conduction band is at lower energy than it is in BaAl_2O_4 and SrAl_2O_4 . In other words, when a noble gas ion (Al^{3+}) is replaced by a d¹⁰ ion (Ga^{3+}), the conduction band shifts to lower energy. This is also seen in the reflection spectra (Figure 5). In this situation the excited state levels of Eu^{2+} are overlapped by the conduction band and no normal Eu^{2+} luminescence can be observed.

The same effect has been observed when studying the luminescence of Pr^{3+} in InBO_3 , ScBO_3 , and LuBO_3 .³¹ The bottom of the conduction band of InBO_3 , with a d¹⁰ ion (In^{3+}), is at much lower energy than in the case of isostructural ScBO_3 and LuBO_3 , with noble gas ions (Sc^{3+} , Lu^{3+}).

In $\text{BaAlGaO}_4:\text{Eu}^{2+}$ and $\text{SrAlGaO}_4:\text{Eu}^{2+}$, the luminescence behavior of Eu^{2+} is comparable to that in $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, which of course is not very surprising. However, the efficiency of the Eu^{2+} emission in both $\text{BaAlGaO}_4:\text{Eu}^{2+}$ and $\text{SrAlGaO}_4:\text{Eu}^{2+}$ is lower than in $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, respectively. Further the temperature dependence is really different. In BaAlGaO_4 and SrAlGaO_4 the conduction band is closer to the excited state levels of Eu^{2+} than in BaAl_2O_4 and SrAl_2O_4 , which will result in a quenching of the Eu^{2+} luminescence at lower temperatures (Figure 5).

In conclusion, the Eu^{2+} luminescence in $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, $\text{BaAlGaO}_4:\text{Eu}^{2+}$, and $\text{SrAlGaO}_4:\text{Eu}^{2+}$ is at low energies. This is due to preferential orientation of a d orbital of Eu^{2+} on the barium or strontium sites in the lattices. Due to photoionization, no Eu^{2+} luminescence can be observed in $\text{BaGa}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{SrGa}_2\text{O}_4:\text{Eu}^{2+}$.

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