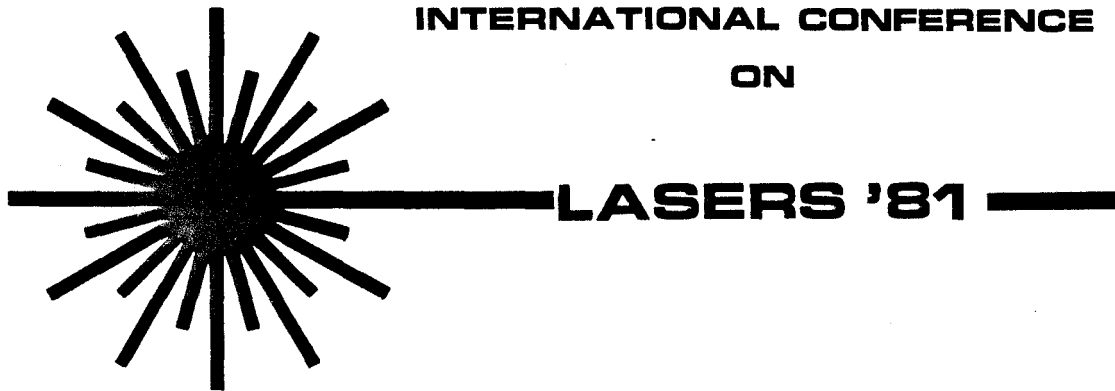


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OPTICAL TRANSITIONS OF $\text{RbMgF}_3:\text{Eu}^{2+}$ AND $\text{RbMgF}_3:\text{Mn}^{2+}, \text{Eu}^{2+}$
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Abstract

A number of studies have been made on the optical properties of Eu^{2+} in various crystal lattices. The strong blue emission from both $5d \rightarrow 4f$ and $4f \rightarrow 4f$ transitions of this ion embedded in alkali earth halides makes some of these systems likely candidate for tunable solid state lasers. In addition, several of the higher energy levels for Mn^{2+} ions appear to be resonant with those for Eu^{2+} ions in materials like RbMgF_3 . In this case, energy transfer can occur and the strongly spin forbidden Mn^{2+} emission should be observable around 600 nm. In this paper, we report on the optical absorption, emission, and excitation spectra of $\text{RbMgF}_3:\text{Eu}^{2+}$ and $\text{RbMgF}_3:\text{Mn}^{2+}, \text{Eu}^{2+}$.

Introduction

Recent experiments on free electron lasers, excimer lasers, fluorescence line narrowing, four wave mixing, and F-center lasers have created great interest in new techniques and materials. Solid state materials which lase in the ultraviolet, visible and near infrared regions of the spectrum are especially important at present. If solid state materials with broad band laser transitions and stable output can be found, then the possibility of replacing chemical dyes with small solid state devices is quite good. Our group is involved in systematic studies of the optical properties of potential laser materials. This paper reports on the optical characteristics of Eu^{2+} ions in RbMgF_3 and $\text{RbMg}_{.99}\text{Mn}_{.01}\text{F}_3$.

The intense absorption bands observed when Eu^{2+} is present in materials such as alkali halides and alkaline earth oxides are associated with the electric dipole allowed transitions between the $4f^n$ and the $4f^{n-1}5d$ configurations.¹⁻¹⁹ Because the 5d electron interacts with the lattice ions, the Eu^{2+} absorption is broad and the absorption energy depends strongly on the crystal host. In some crystals fine structure on the absorption band is observed which can be used to specify the particular transition responsible for the absorption.^{20,21} Emission from Eu^{2+} ions is observed to consist of both broad and narrow lines.¹⁵⁻¹⁹ The broad emission bands result from $4f^65d^1 \rightarrow 4f^7$ electronic transitions while the lines are due to transitions between different levels of the $4f^7$ configuration (usually from the $6P_J$ states to the $8S_{7/2}$ ground level). The narrow line transitions are forbidden. Thus, these transitions have long lifetimes (about 2 ms) and are not usually observed unless the $4f^7$ excited state level is lower in energy than the $4f^65d^1$ level. In this case the $4f^7$ relaxed excited state is fed by the higher levels and line emission is observed. If the $4f^7$ excited state level and the $4f^65d^1$ level have about the same energy, then a strong temperature dependence of the emission is observed.^{5,8}

The Eu^{2+} emission has been extensively studied because of the potential applications for phosphors or lasers.⁵ The presence of both broad band absorption and emission makes Eu^{2+} doped materials good candidates for tunable lasers in the UV-visible region. Laser action can also be obtained for the narrow lines, because the excited $4f^7$ levels can be populated through the intense absorption of the $4f^65d^1$ band. Moreover, since the energy levels of Eu^{2+} and Mn^{2+} are similar in energy, it is possible to obtain visible emission from the spin forbidden Mn^{2+} ions. This observation opens an even wider possibility for a tunable laser system throughout the visible region of the spectrum.

Experimental Procedure

The single crystals were grown by J. J. Martin at Oklahoma State University Crystal Growth Laboratory. The crystal growth melt contained 1 at % Eu^{2+} in one case, and in another case, 1 at % Eu^{2+} and 1 at % Mn^{2+} .

The absorption spectra were taken on a Cary 14 spectrophotometer. A 1-m Jarrell-Ash monochromator or a 0.8 m Spex monochromator with a cooled RCA 31034 PMT and associated electronics were used for luminescence detection. A 0.22-m Spex monochromator with 75 W or 300 W Xe lamps provided excitation. The exciting light was chopped at selected frequencies. The intensity of the exciting light through a 0.22 m Spex monochromator was measured with a Spectra Radiometer Model 301 and excitation spectra were corrected accordingly for wavelengths greater than 300 nm.

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Lifetime measurements ($> 10 \mu\text{s}$) were recorded using a Biomation Model 610B connected to a Nicolet Model 1070 digital signal averager. Lifetimes shorter than $10 \mu\text{s}$ were measured using a pulsed Nitrogen Laser and a Boxcar Integrator in the laboratory of R. C. Powell.

Experimental Results and Discussion

A broad absorption band is observed about 250 nm for crystals of $\text{RbMgF}_3:\text{Eu}^{2+}$. This band is composed of at least two superimposed absorption bands and has a width at half maximum of about 6300 cm^{-1} at 300 K. The band narrows at low temperature but no fine structure is observed. In our crystals which contain about 1000 ppm Eu^{2+} , the absorption coefficient at the peak of this band was about 100 cm^{-1} .

Three different emission spectra are observed from $\text{RbMgF}_3:\text{Eu}^{2+}$ crystals. The emission spectra taken at 300 K are illustrated in Figure 1(a). The emission consists of two broad bands centered around 405 nm and 525 nm and a line at about 360 nm. The line emission has been observed previously by Sommerdijk and his collaborators.^{7,8} The lifetimes of these transitions at 300 K are 1.44 ms for the 359.1 nm line and about 1 s for the two bands. The room temperature emission from $\text{RbMgF}_3:\text{Eu}^{2+}, \text{Mn}^{2+}$ is shown in Figure 1(b). The only major difference in these spectra and those in Figure 1(a) is the broad emission peak at 600 nm.

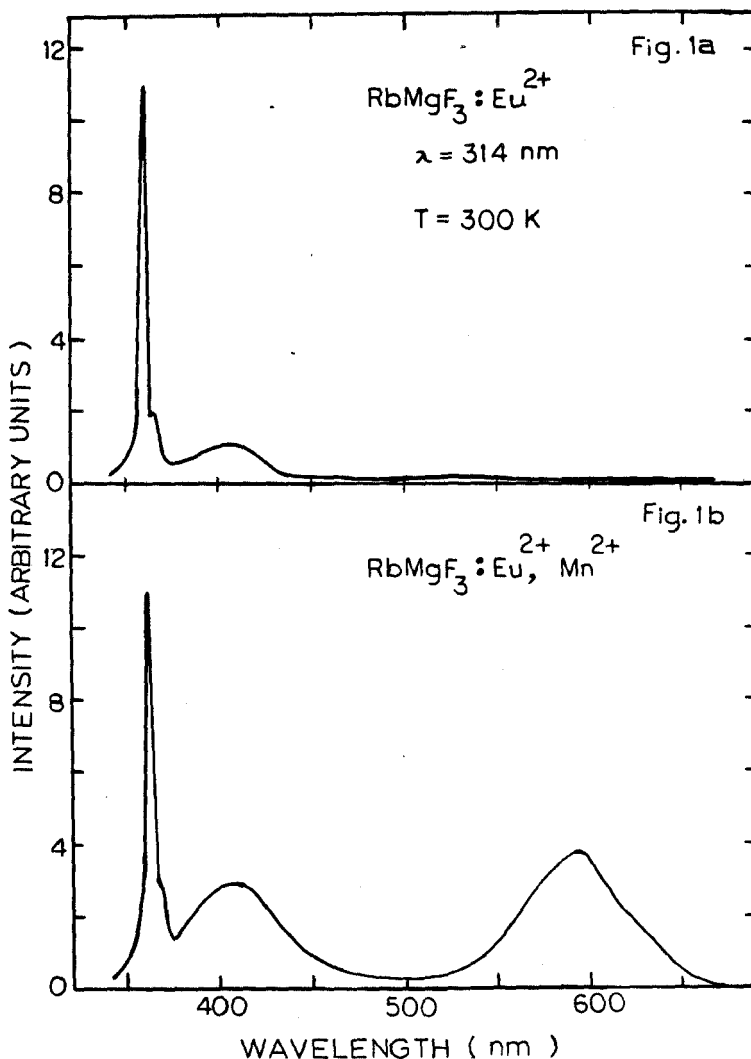


Figure 1(a): Emission spectrum at 300 K from $\text{RbMgF}_3:\text{Eu}^{2+}$ excited with 314 nm light.

Figure 1(b): Emission spectra at 300 K from $\text{RbMgF}_3:\text{Eu}^{2+}, \text{Mn}^{2+}$ excited with 314 nm light.

This transition has a very long lifetime (45 ms) which indicates it is forbidden. The temperature dependence of the 359.1 nm emission intensity and the intensity of a broad band that grows under this emission at higher temperature in $\text{RbMgF}_3:\text{Eu}^{2+}$ were measured for temperatures from 300 K to 650 K. The emission spectra at 300 K and 580 K are portrayed in

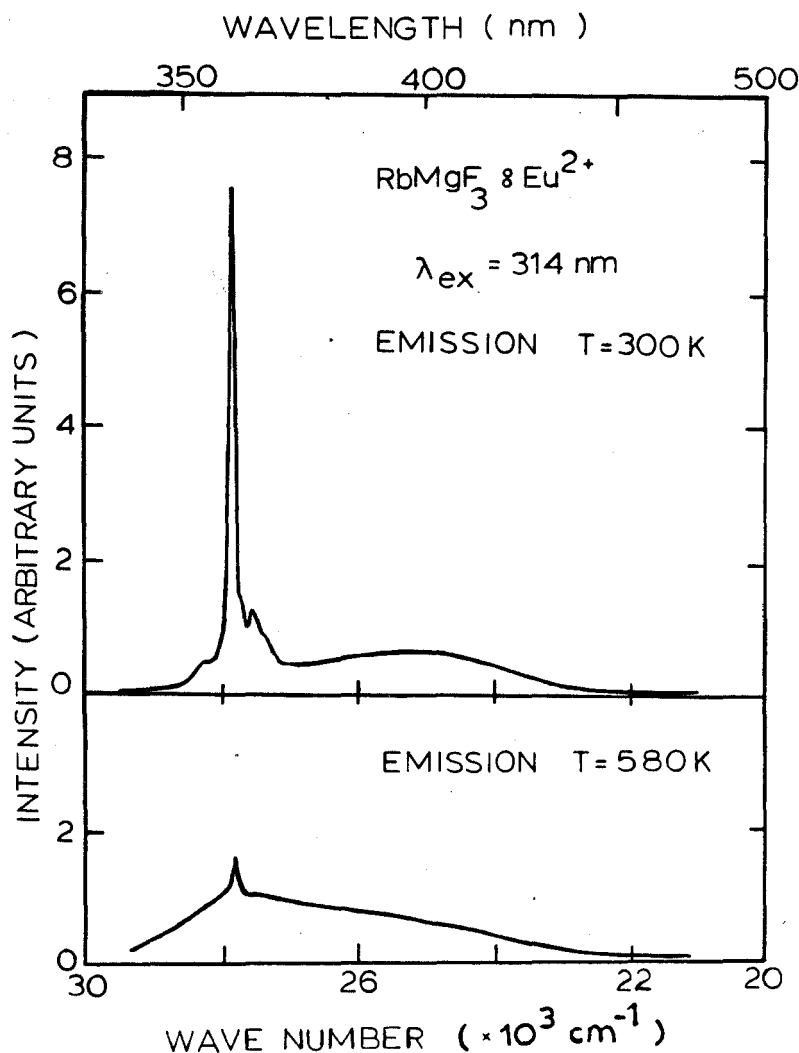


Figure 2: Temperature dependence of the 359.1 nm line emission from $\text{RbMgF}_3:\text{Eu}^{2+}$.

Figure 2. From these data, an activation energy of about 0.12 eV can be determined. This suggests that the relaxed excited states of the $4f^{65d^1}$ and $4f^7$ levels are about 970 cm^{-1} apart. Figure 3 shows a configuration coordinate diagram for $\text{RbMgF}_3:\text{Eu}^{2+}$ which has been derived from the absorption, emission, and heat treatment data. Notation for impurities with O_h site symmetry is used. The actual site symmetry is C_{3v} . The broad band at the top left side of the figure pictures the absorption. On the right hand side of the figure energy level diagrams for Eu^{2+} and Mn^{2+} are shown. Notice that the $4f^7$ and $4f^{65d^1}$ levels are resonant with the ${}^4T_{2g} 3d^5$ level of the manganese. Energy transfer undoubtedly occurs at this point and results in the bright Mn^{2+} visible emission. It is surprising that with only about 1000 ppm of both Eu^{2+} and Mn^{2+} in the crystal energy transfer occurs. Such long range energy transfer suggests strongly allowed electric dipole transitions. Similar long range energy transfer was observed for Er^{3+} and Mn^{2+} ions in RbMgF_3 .²²

A careful study of Figure 3 suggests that since the $4f^7 \rightarrow 4f^7$ transitions are relatively unaffected by crystal field, changes in the $10Dq$ value for the $5d$ levels might result in allowed $4f^6 5d^1 \rightarrow 4f^7$ broad band transitions. We feel this is the origin of the 405 nm and 525 nm bands. When Eu^{2+} ions are located near another impurity such as Ca^{2+} or dislocations, the crystal field could increase to make the $10Dq$ splitting greater and drive the $4f^6 5d^1$ energy level below the $4f^7(6P_j)$ level resulting in allowed $4f^6 5d^1 \rightarrow 4f^7$ emission.

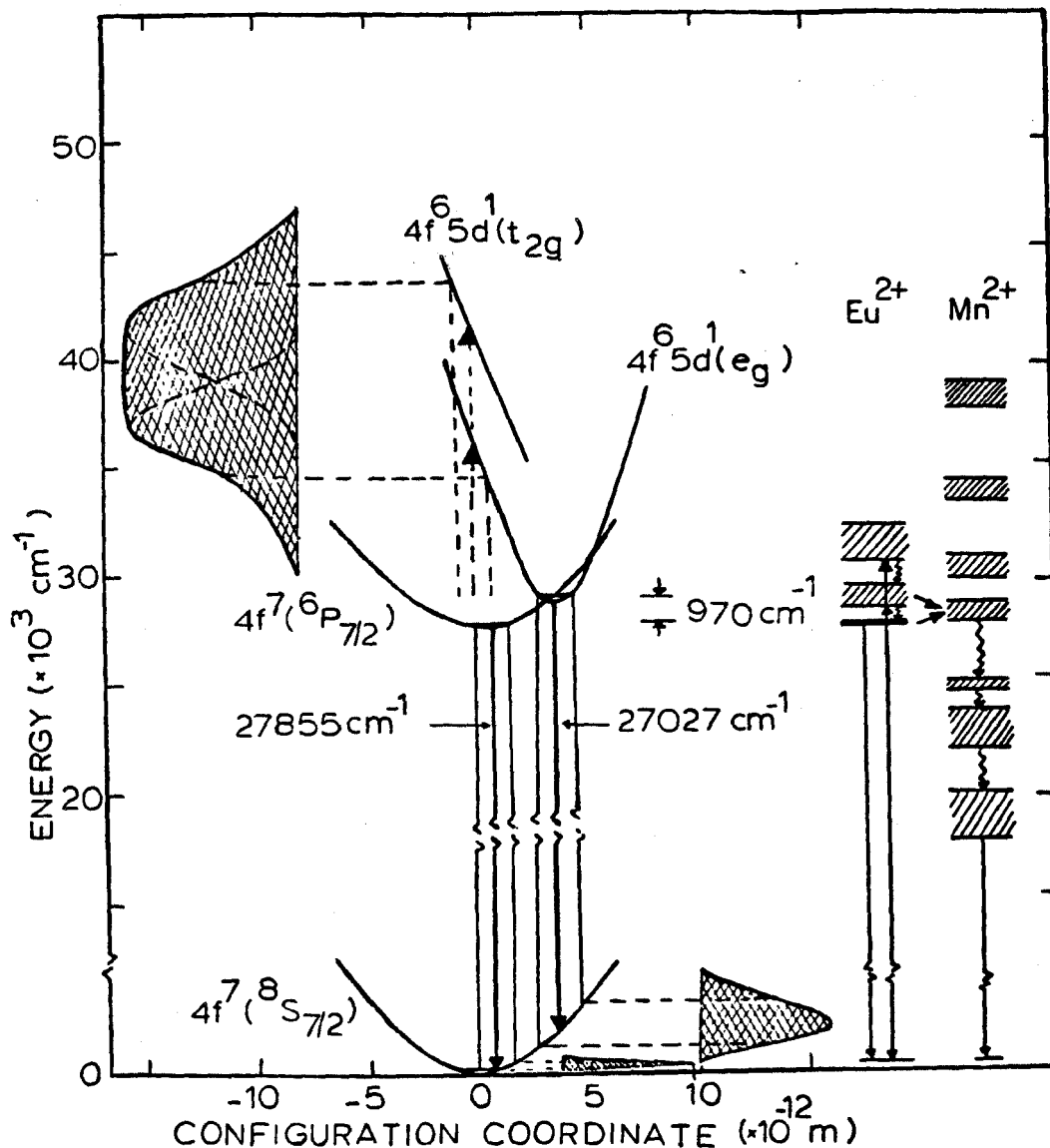


Figure 3: Configuration coordinate diagram for the lower levels of Eu^{2+} in RbMgF_3 . Observed absorption and emission bands are illustrated with cross-hatching. The right hand side of the figure depicts some of the energy levels for Eu^{2+} and Mn^{2+} .

Summary

1. Three emission bands at 359.1 nm, 405 nm, and 525 nm are observed in Eu^{2+} doped RbMgF_3 and $\text{RbMg}_{.99}\text{Mn}_{.01}\text{F}_3$.
2. The 359.1 nm emission is due to $4f \rightarrow 4f$ transitions which show a narrow half width and a lifetime of about 2 ns.
3. The broad 405 nm and 525 nm emissions have lifetimes at 300 K of 1.2 μs and 0.9 μs , respectively.
4. When Mn^{2+} is present in addition to Eu^{2+} , a new broad band emission is observed at about 600 nm which is due to energy transfer.

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