OPTICAL ABSORPTION AND EMISSION FROM IRRADIATED RbMgF$_3$:Eu$^{2+}$ AND KMgF$_3$:Eu$^{2+}$

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The optical properties of irradiated RbMgF$_3$:Eu$^{2+}$ and KMgF$_3$:Eu$^{2+}$ have been investigated. Previous research has shown that Eu$^{2+}$ ions in unirradiated RbMgF$_3$ give rise to broad band absorption around 250 nm and sharp intense line emission at 360 nm. When this material is irradiated little or no change occurs in the 250 nm absorption, but the lifetime of the Eu$^{2+}$ 360 nm transition is reduced. In addition, new emission is observed at 680 nm. In the case of irradiated KMgF$_3$:Eu$^{2+}$ two new emission bands are observed at 600 and 800 nm. All of these transitions have short lifetimes and are not due to Eu$^{3+}$ ions.

1. Introduction

Optical transitions of divalent europium ions have been investigated in a number of halide crystals [1—21]. In unirradiated Eu$^{2+}$-doped fluorides both broad band absorption and emission and a sharp intense line emission have been observed. These luminescent transitions could make these materials good candidates for tunable lasers. A detailed study of the temperature dependence of the absorption, emission, and excitation spectra from RbMgF$_3$:Eu$^{2+}$ as well as the lifetimes of the transitions has been made by Alcala et al. [16].

In some materials the optical properties can be drastically modified by the presence of impurity ions and/or radiation induced defects [22]. We have studied irradiated RbMgF$_3$:Eu$^{2+}$ to determine if there are modified optical effects. This material is ideal for radiation damage studies because radiation induced vacancies do not aggregate during irradiation at 300 K [22—24]. When irradiated specimens are annealed at 500 K or higher the vacancies become mobile and defect aggregation occurs. Therefore it is possible to independently investigate point defects and aggregates. In this paper we report on the radiation effects in Eu$^{2+}$-doped RbMgF$_3$ and KMgF$_3$. Many times it is helpful to compare the optical transitions of an impurity when it resides in different

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host crystals. Optical transitions of Eu$^{2+}$ ions in unirradiated KMgF$_3$ have been previously investigated [18–21]. In this investigation we compare the optical properties of Eu$^{2+}$ in RbMgF$_3$ and KMgF$_3$.

2. Experimental procedures

The single crystals were grown by J.J. Martin at the Oklahoma State University Crystal Growth Facility using the Bridgeman technique. The crystal growth melts contained 1 at% Eu$^{2+}$ for both the RbMgF$_3$ and KMgF$_3$ ingots. The concentration of Eu$^{2+}$ ions in the as-grown crystals was not uniform. However, most of the Eu$^{2+}$ ions were randomly distributed in Rb$^+$ and K$^+$ sites in the samples [16].

Optical absorption spectra were measured using a Cary-14 spectrophotometer. Emission spectra were detected using a 0.8 m Spex monochromator with a cooled RCA 31034 PMT and associated electronics. Excitation spectra were taken by exciting the samples with light from a 75 W Xe lamp chopped at selected frequencies and passed through a 0.22 m Spex monochromator. Lifetime measurements were performed using a Biomation Model 610B connected to a Nicolet Model 1070 digital signal averager.

In the thermal-annealing experiments the samples were held at the desired temperatures for 10 min and then the heated samples were air-cooled. Low-temperature measurements were taken using a Sulfrian helium cryostat, or a CTI Cryodyne Cryocooler with a resistance heater which allowed temperature control from 12 to 300 K.

3. Results

3.1. RbMgF$_3$

3.1.1. Radiation damage

The room-temperature absorption spectrum from a RbMgF$_3$:Eu$^{2+}$ crystal irradiated with 1.5 MeV electrons to a dose of $10^{16}$ MeV/cm$^2$ at 300 K is portrayed in fig. 1. The Eu$^{2+}$ absorption band peaks at about 250 nm, and the broad, intense radiation induced F-center band is observed at about 315 nm. The Eu$^{2+}$ absorption band intensity remains almost unchanged with irradiation. A detailed investigation of F centers in pure and impurity-doped RbMgF$_3$ was made previously [22–25]. Fig. 2 illustrates the growth of F centers as a function of radiation dose for RbMgF$_3$:Eu$^{2+}$. Three such growth curves are shown for samples containing different Eu$^{2+}$ concentrations. An estimate of the Eu$^{2+}$ content can be obtained by using an oscillator strength of $f \approx 4 \times 10^{-2}$ [26]. Concentrations of Eu$^{2+}$ greater than 500 ppm result in higher F-center
Fig. 1. Optical absorption at 300 K from RbMgF₃:Eu²⁺ irradiated with 1.5 MeV electrons for 15 min at 300 K.

concentrations. The cross-hatched area in fig. 2 represents the range of F-center formation curves for nominally pure, Er³⁺-, and Mn³⁺-doped RbMgF₃ crystals irradiated at 300 K with 1.5 MeV electrons [25].

Fig. 3 portrays the absorption spectrum from RbMgF₃:Eu²⁺ at 80 K.

Fig. 2. F-center absorption as a function of irradiation dose for RbMgF₃ crystals containing different Eu²⁺ concentrations at 300 K.
obtained by irradiating the sample with 1.5 MeV electrons to a dose of 10^{14} MeV/cm^3. Again the Eu^{2+} absorption band at 250 nm is unchanged but two new bands at 330 and 500 nm are observed. In the past, it was found that X_2 (V_K) centers are formed by a brief 80 K irradiation [23]. These defects absorb 330 nm light and are bleached with 330 nm light [23]. In the present case, the intensities of the 330 and 500-nm bands decrease simultaneously with bleaching. The growth of F centers as a function of radiation dose at 80 K is
illustrated in fig. 4. This result is in excellent agreement with that of Podinsh and Sibley [24]. The cross-hatched area depicts the range of F-center growth curves for pure, Er$^{3+}$-, and Mn$^{2+}$-doped RbMgF$_3$ crystals irradiated at 300 K. The F-center concentration can be calculated using the so-called Smakula's equation: $N_f = 7.3 \times 10^{15}f \alpha_m W \text{ cm}^{-3}$, where $f$ is the oscillator strength, $N$ the concentration, $W$ the width at half maximum, and $\alpha_m$ the maximum absorption coefficient. Using $f = 0.5$, $W = 0.9$ eV, and $\alpha_m = 70$ cm$^{-1}$ for a radiation dose of $\sim 10^{16}$ MeV/cm$^2$, the F-center concentration is calculated to be $\sim 10^{18}$ cm$^{-3}$.

As mentioned earlier, irradiation at 300 K produces only a statistical number of F aggregates in RbMgF$_3$. However, when crystals are annealed at higher temperatures numerous F$_2$(M) and F$_3$(R) centers are formed [22–24]. Fig. 5 displays the annealing stages of F centers and the growth of F$_2$ and F$_3$ centers at different annealing temperatures. The F$_2$(M) centers absorb 387 nm light while the F$_3$(R) centers absorb 300 nm light. The F$_2$-center concentration reaches its maximum at about 500 K, whereas the maximum F$_3$-center concentration occurs around 700 K. By 800 K most of the observable defect centers have been annihilated. The annealing process shown in fig. 5 essentially follows the same pattern as in the pure RbMgF$_3$ crystals [23–25]. This suggests Eu$^{2+}$ has little influence on the formation of F-center aggregates. It is important to mention that the maximum F$_3$-center concentration shown in fig. 5 is less than the value reported previously. This most likely is due to error from the uncertainty in measuring the F$_3$-center absorption band which occurs

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**Fig. 5.** Normalized thermal annealing data for RbMgF$_3$:Eu$^{2+}$ crystals after electron irradiation at 80 K and 300 K with 1.5 MeV electrons for 15 min.
on the shoulder of the intense Eu$^{2+}$ absorption band and is difficult to extract accurately.

In the annealing process the total F-center concentration is conserved to within 90% of its initial value. This was determined by annealing crystals at 700 K and then reirradiating them with a short burst of electrons. The F-center concentration in this case returned to 95% of the value prior to annealing.

3.1.2. Emission and excitation

When RbMgF$_3$:Eu$^{2+}$ is irradiated a new broad red emission band at 680 nm is observed. Fig. 6 illustrates the 680 nm emission band (dashed line) and its excitation spectrum (solid line). The lifetime of this transition is short (< 10 μs).

The original 360 nm emission line intensity decreases with radiation dose while the 680 nm emission intensity increases. However, as shown in Fig. 7, the variation of the intensities of these bands with radiation dose is not the same. The 680 nm band grows rapidly only after F-center formation reaches a saturation value while the 360 nm line emission intensity decreases at much lower radiation doses. It was mentioned earlier that the Eu$^{2+}$ absorption at 250 nm does not decrease with dose. The lifetime of the 360 nm transition at 300 K from unirradiated sample was measured before irradiation to be 1.4 ms [16], whereas after irradiation the lifetime of this transition was found to be 1 ms.

![Fig. 6. The 680 nm emission band (dashed line) at 15 K from RbMgF$_3$:Eu$^{2+}$ crystal irradiated with 1.5 Mev electrons at 300 K and its excitation spectrum (solid line).](image)
3.2. KMgF₃

In order to obtain a better idea of the Eu²⁺ transitions in irradiated and unirradiated materials it was felt that a comparison of KMgF₃:Eu and RbMgF₃:Eu would be helpful. The temperature dependence of the ~360 nm line emission for KMgF₃:Eu²⁺ is shown in fig. 8 for 80 and 600 K. The transition has a lifetime of 1.9 ms at 80 K. The temperature dependence of the line emission intensity decreases with increasing temperature while the underlying broad band emission at 345 nm increases with temperature. At about 650 K the line emission intensity becomes negligible. A semilog plot of the 360 and 345 nm emission intensities vs. $T^{-1}$ yields an activation energy of about 1250 cm⁻¹. The Eu²⁺ absorption spectrum from KMgF₃:Eu²⁺ was shown in a previous paper [16]. Although the lower energy band shows a characteristic “staircase” structure, the two bands are not well resolved. From the above observations a configuration coordinate diagram for Eu²⁺ in KMgF₃ similar to that for RbMgF₃:Eu²⁺ has been constructed. It is depicted in fig. 9. The observed Eu²⁺ absorption band (250 nm) and the emission (360 and 345 nm) are shown by cross-hatched areas. The crystal field splitting of 10 $Dq$ separates the 4f⁶5d¹ level into 4f⁶5d¹(e₅) and 4f⁶5d¹(t₂g). This splitting is about ~7500 cm⁻¹.
When KMgF₃: Eu²⁺ is irradiated with 1.5 MeV electrons to a dose of ~10¹⁶ MeV/cm³ at 300 K the Eu²⁺ absorption remains almost the same but two new broad emission bands (600 and 800 nm) are observed. Fig. 10 illustrates the 600 nm emission band (dashed) from irradiated KMgF₃: Eu²⁺ and its excitation spectrum (solid line). Fig. 11 depicts the 800 nm broad emission (dashed line) from the irradiated sample and the excitation spectra of this emission (solid line).

When KMgF₃: Eu²⁺ is irradiated with electrons (10¹⁴ MeV/cm³) at 80 K, in addition to the broad 250 nm absorption bands, two other absorption bands are observed at 330 and 550 nm. The 330 nm band is due to X₅ (VK) centers, while the 550 nm band is difficult to identify. The optical bleaching of the X₅ (VK) centers results in the simultaneous decrease of both bands.

*Fig. 8. Temperature dependence of 360 nm line emission from KMgF₃: Eu²⁺ crystal. Two spectra taken at 80 and 600 K are shown.*

*Fig. 9. Configuration coordinate diagram for the lower levels of Eu²⁺ in KMgF₃. The observed absorption and emissions are shown by cross-hatched areas.*

cm⁻¹ which agrees with the electrostatic model of the crystal field [16,26]. Usually two broad absorption bands are observed due to transitions from the 4f⁷ ground state of Eu²⁺ to states in the 4f⁶5d¹ configuration [2,3,19,21,26,29].

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Fig. 10. The 600 nm emission band (dashed line) at 80 K from KMgF₃:Eu²⁺ crystal irradiated with 1.5 MeV electrons for 15 min at 300 K and its excitation spectrum (solid line).

Fig. 11. The 800 nm emission band (dashed line) at 80 K from the irradiated KMgF₃:Eu²⁺ crystal and its excitation spectrum (solid line).
4. Discussion and summary

A number of observations from this work can be summarized for the benefit of those continuing to study radiation effects in highly ionic materials:

1. The substitution of impurities such as Mn$^{2+}$ or Er$^{3+}$ for Mg$^{2+}$ ions in RbMgF$_3$ apparently has no effect on the photochemical damage process.

2. The substitution of Eu$^{2+}$ for Rb$^+$ ions in RbMgF$_3$ results in a greater early stage coloration reminiscent of that observed for KCl:Ca. Irradiation at 300 K produces a statistical distribution of F$_2$, F$_3$ and F$^-$-Mn$^{2+}$ aggregate centers.

3. The optical transitions of Eu$^{2+}$ in RbMgF$_3$ and KMgF$_3$ are similar and can be explained on the basis of simple configuration coordinate models.

4. After extended irradiation at 300 K new emission bands occur at 680 nm for RbMgF$_3$:Eu$^{2+}$ and 600 and 800 nm for KMgF$_3$:Eu$^{2+}$. These transitions arise from an unidentified Eu center.

Most of the results summarized above are typical of photochemical defect production in highly ionic materials. There are, however, two observations which require more detailed investigation. The first puzzle is why the substitution of an Er$^{3+}$ ion for Mg$^{2+}$ which requires a positive-ion vacancy for charge compensation results in different radiation damage effects than when a Eu$^{2+}$ ion substitutes for Rb$^+$ even though a positive ion vacancy is also required for charge compensation in this case. Fig. 2 clearly suggests that Eu$^{2+}$ enhances the early stage room-temperature coloration of RbMgF$_3$, while Er$^{3+}$ does not.

The second interesting observation which requires more research is that late stage room-temperature coloration produces stable centers in RbMgF$_3$:Eu and KMgF$_3$:Eu which absorb 500 nm light in the former case and 450 and 590 nm light in the latter case. Emission occurs at 680 nm and at 600 and 800 nm, respectively. The decrease in intensity of the 360 nm Eu$^{2+}$ emission as seen in fig. 7 is most likely due to energy transfer since the lifetime of this transition decreases from 1.4 ms in unirradiated crystals to 1.0 ms in irradiated specimens.

It is possible that the irradiation-induced red emissions arise from Eu$^{1+}$ centers stabilized by radiation defects. The purpose of the low-temperature irradiation was to see if Eu$^{1+}$ ions could be stabilized by the formation of X$^2_+$ hole centers. The 500 nm band in RbMgF$_3$ and 550 nm band in KMgF$_3$ appear and disappear with the X$^2_+$ centers. This suggests that these bands might be associated with Eu$^{1+}$. If so, then the room-temperature radiation-induced bands in RbMgF$_3$ and KMgF$_3$ might arise from defect stabilized Eu$^{1+}$ centers. Of course, the formation of Eu$^{1+}$ by irradiation is also possible but the spectra, in figs. 6, 10, and 11, do not correspond to the well-known Eu$^{3+}$ transitions [32,33]. The luminescent transitions for Eu$^{3+}$ arise from $^5D_0$ level to the $^7F_j$ manifold. In RbMgF$_3$ host, the Eu$^{3+}$ emission peaks are found at 569, 580, 620 and 700 nm [32]. None of these peaks corresponds to the broad red emission at 680 nm from the irradiated RbMgF$_3$:Eu$^{2+}$ crystal. Similarly, the broad
emissions at 600 and 800 nm from irradiated KMgF$_3$:Eu$^{2+}$ do not resemble the Eu$^{3+}$ emissions observed from KMgF$_3$:Eu$^{3+}$ crystals [32,33].

References