

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

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The optical properties of irradiated $\text{RbMgF}_3:\text{Eu}^{2+}$ and $\text{KMgF}_3:\text{Eu}^{2+}$ 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 $\text{KMgF}_3:\text{Eu}^{2+}$ 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 $\text{RbMgF}_3:\text{Eu}^{2+}$ 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 $\text{RbMgF}_3:\text{Eu}^{2+}$ 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 Eu²⁺ ions in unirradiated KMgF₃ have been previously investigated [18–21]. In this investigation we compare the optical properties of Eu²⁺ in RbMgF₃ and KMgF₃.

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% Eu²⁺ for both the RbMgF₃ and KMgF₃ ingots. The concentration of Eu²⁺ ions in the as-grown crystals was not uniform. However, most of the Eu²⁺ 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 Sulfrin helium cryostat, or a CTI Cryodyne Cryocooler with a resistance heater which allowed temperature control from 12 to 300 K.

3. Results

3.1. RbMgF₃

3.1.1. Radiation damage

The room-temperature absorption spectrum from a RbMgF₃:Eu²⁺ crystal irradiated with 1.5 MeV electrons to a dose of 10¹⁶ MeV/cm³ at 300 K is portrayed in fig. 1. The Eu²⁺ absorption band peaks at about 250 nm, and the broad, intense radiation induced F-center band is observed at about 315 nm. The Eu²⁺ absorption band intensity remains almost unchanged with irradiation. A detailed investigation of F centers in pure and impurity-doped RbMgF₃ was made previously [22–25]. Fig. 2 illustrates the growth of F centers as a function of radiation dose for RbMgF₃:Eu²⁺. Three such growth curves are shown for samples containing different Eu²⁺ concentrations. An estimate of the Eu²⁺ content can be obtained by using an oscillator strength of $f \approx 4 \times 10^{-2}$ [26]. Concentrations of Eu²⁺ greater than 500 ppm result in higher F-center

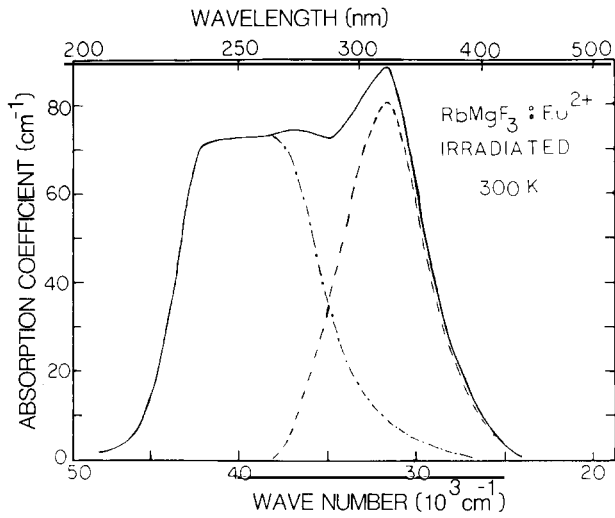


Fig. 1. Optical absorption at 300 K from $\text{RbMgF}_3:\text{Eu}^{2+}$ irradiated with 1.5 MeV electrons for 15 min at 300 K.

concentrations. The cross-hatched area in fig. 2 represents the range of F-center formation curves for nominally pure, Er^{3+} -, and Mn^{2+} -doped RbMgF_3 crystals irradiated at 300 K with 1.5 MeV electrons [25].

Fig. 3 portrays the absorption spectrum from $\text{RbMgF}_3:\text{Eu}^{2+}$ at 80 K

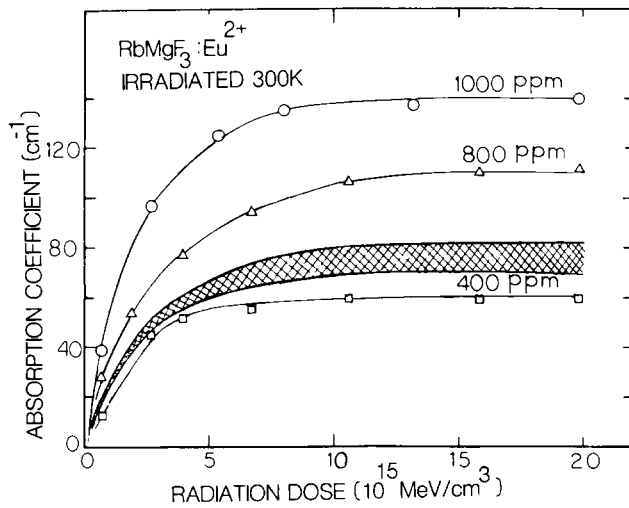


Fig. 2. F-center absorption as a function of irradiation dose for RbMgF_3 crystals containing different Eu^{2+} concentrations at 300 K.

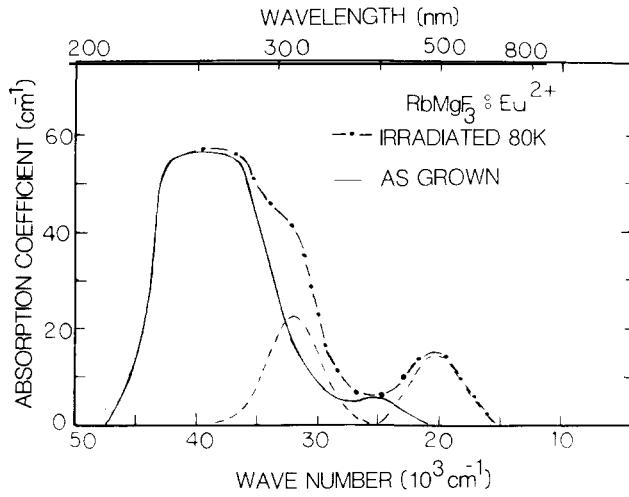


Fig. 3. Optical absorption at 80 K from $\text{RbMgF}_3:\text{Eu}^{2+}$ irradiated with 1.5 MeV electrons for 1 min at 80 K.

obtained by irradiating the sample with 1.5 MeV electrons to a dose of 10^{14} MeV/cm³. 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 $\text{X}_2(\text{V}_\text{K})$ 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

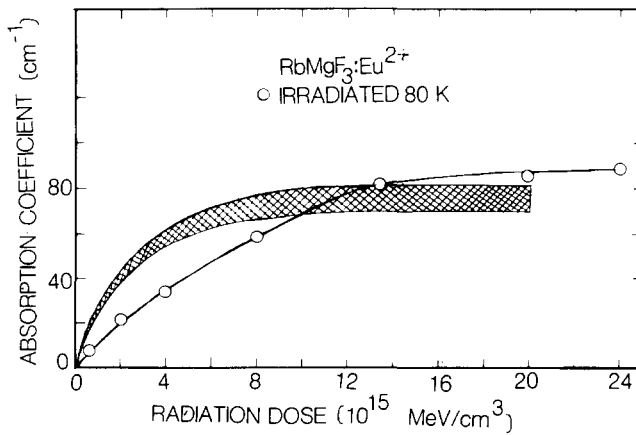


Fig. 4. F-center absorption as a function of irradiation dose at 80 K from $\text{RbMgF}_3:\text{Eu}^{2+}$.

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, Er³⁺-, and Mn²⁺-doped RbMgF₃ crystals irradiated at 300 K. The F-center concentration can be calculated using the so-called Smakula's equation: $Nf = 7.3 \times 10^{15} \alpha_m W \text{ cm}^{-3}$, where f is the oscillator strength, N the concentration, W the width at half maximum, and α_m the maximum absorption coefficient. Using $f = 0.5$, $W = 0.9 \text{ eV}$, and $\alpha_m = 70 \text{ cm}^{-1}$ for a radiation dose of $\sim 10^{16} \text{ MeV/cm}^3$, the F-center concentration is calculated to be $\sim 10^{18} \text{ cm}^{-3}$.

As mentioned earlier, irradiation at 300 K produces only a statistical number of F aggregates in RbMgF₃. However, when crystals are annealed at higher temperatures numerous F₂(M) and F₃(R) centers are formed [22–24]. Fig. 5 displays the annealing stages of F centers and the growth of F₂ and F₃ centers at different annealing temperatures. The F₂(M) centers absorb 387 nm light while the F₃(R) centers absorb 300 nm light. The F₂-center concentration reaches its maximum at about 500 K, whereas the maximum F₃-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 RbMgF₃ crystals [23–25]. This suggests Eu²⁺ has little influence on the formation of F-center aggregates. It is important to mention that the maximum F₃-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 F₃-center absorption band which occurs

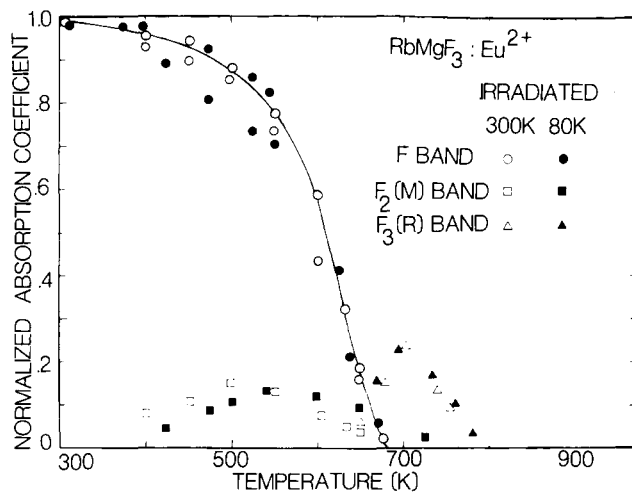


Fig. 5. Normalized thermal annealing data for RbMgF₃:Eu²⁺ crystals after electron irradiation at 80 K and 300 K with 1.5 MeV electrons for 15 min.

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 $\text{RbMgF}_3:\text{Eu}^{2+}$ 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 ($< 10 \mu\text{s}$).

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.

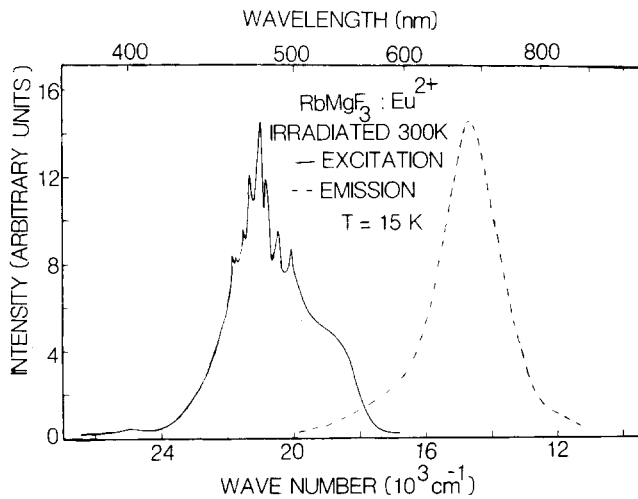


Fig. 6. The 680 nm emission band (dashed line) at 15 K from $\text{RbMgF}_3:\text{Eu}^{2+}$ crystal irradiated with 1.5 Mev electrons at 300 K and its excitation spectrum (solid line).

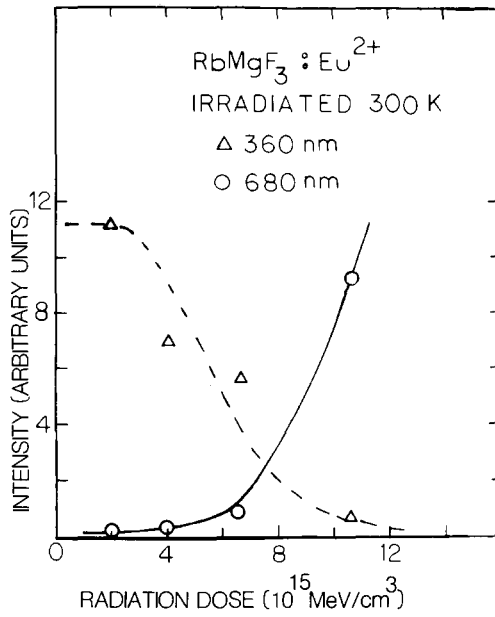


Fig. 7. The emission intensities of 360 and 680 nm as function of irradiation dose for $\text{RbMgF}_3:\text{Eu}^{2+}$ at 300 K.

3.2. KMgF_3

In order to obtain a better idea of the Eu^{2+} transitions in irradiated and unirradiated materials it was felt that a comparison of $\text{KMgF}_3:\text{Eu}$ and $\text{RbMgF}_3:\text{Eu}$ would be helpful. The temperature dependence of the ~ 360 nm line emission for $\text{KMgF}_3:\text{Eu}^{2+}$ 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 Eu^{2+} absorption spectrum from $\text{KMgF}_3:\text{Eu}^{2+}$ 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 Eu^{2+} in KMgF_3 similar to that for $\text{RbMgF}_3:\text{Eu}^{2+}$ has been constructed. It is depicted in fig. 9. The observed Eu^{2+} 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 $4f^6 5d^1$ level into $4f^6 5d^1(e_g)$ and $4f^6 5d^1(t_{2g})$. This splitting is about ~ 7500

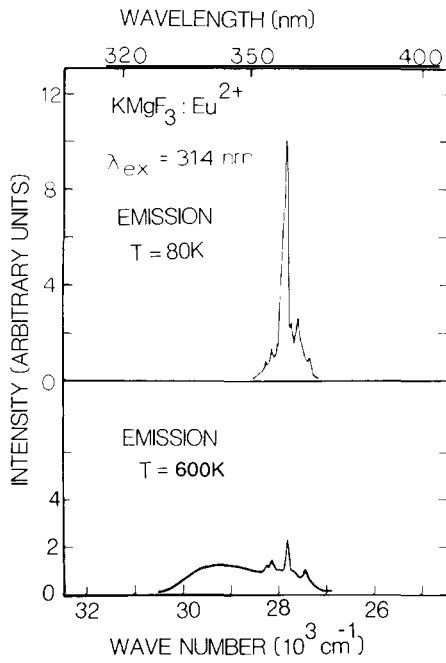


Fig. 8. Temperature dependence of 360 nm line emission from $\text{KMgF}_3:\text{Eu}^{2+}$ crystal. Two spectra taken at 80 and 600 K are shown.

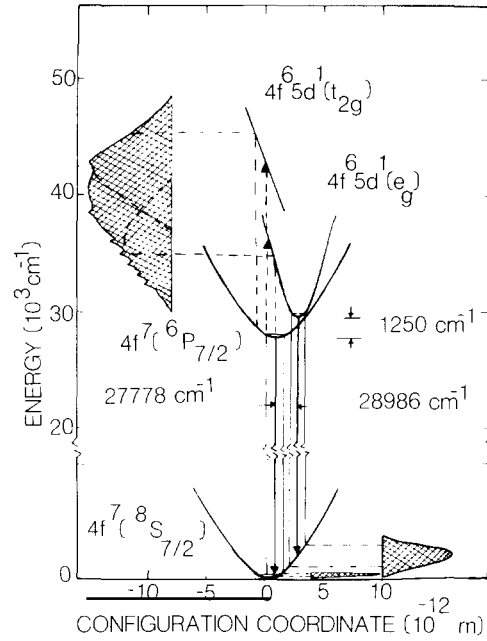


Fig. 9. Configuration coordinate diagram for the lower levels of Eu^{2+} in KMgF_3 . The observed absorption and emissions are shown by cross-hatched areas.

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 $4f^7$ ground state of Eu^{2+} to states in the $4f^65d^1$ configuration [2,3,19,21,26,29].

When $\text{KMgF}_3:\text{Eu}^{2+}$ is irradiated with 1.5 MeV electrons to a dose of $\sim 10^{16} \text{ MeV/cm}^3$ at 300 K the Eu^{2+} 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 $\text{KMgF}_3:\text{Eu}^{2+}$ 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 $\text{KMgF}_3:\text{Eu}^{2+}$ is irradiated with electrons (10^{14} MeV/cm^3) 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 $X_2^-(V_K)$ centers, while the 550 nm band is difficult to identify. The optical bleaching of the $X_2^-(V_K)$ centers results in the simultaneous decrease of both bands.

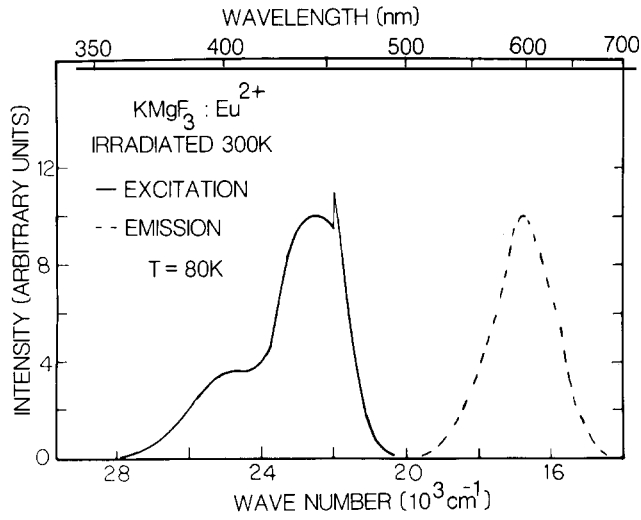


Fig. 10. The 600 nm emission band (dashed line) at 80 K from $\text{KMgF}_3:\text{Eu}^{2+}$ crystal irradiated with 1.5 MeV electrons for 15 min at 300 K and its excitation spectrum (solid line).

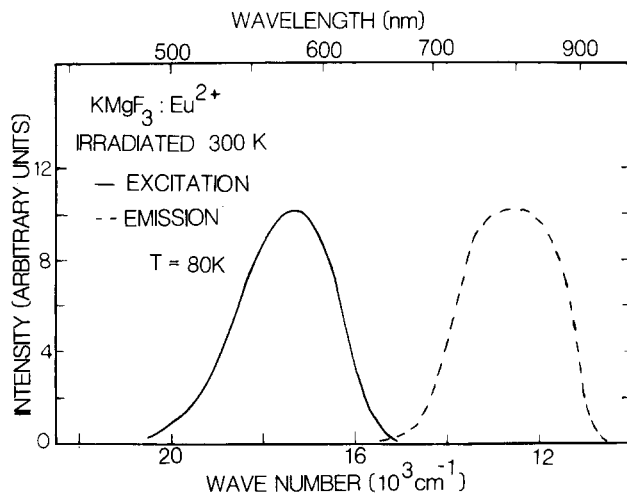


Fig. 11. The 800 nm emission band (dashed line) at 80 K from the irradiated $\text{KMgF}_3:\text{Eu}^{2+}$ crystal and its excitation spectrum (solid line).

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 Mn²⁺ or Er³⁺ for Mg²⁺ ions in RbMgF₃ apparently has no effect on the photochemical damage process.
- (2) The substitution of Eu²⁺ for Rb⁺ ions in RbMgF₃ results in a greater early stage coloration reminiscent of that observed for KCl:Ca. Irradiation at 300 K produces a statistical distribution of F₂, F₃ and F-Mn²⁺ aggregate centers.
- (3) The optical transitions of Eu²⁺ in RbMgF₃ and KMgF₃ 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 RbMgF₃:Eu²⁺ and 600 and 800 nm for KMgF₃:Eu²⁺. 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 Er³⁺ ion for Mg²⁺ which requires a positive-ion vacancy for charge compensation results in different radiation damage effects than when a Eu²⁺ ion substitutes for Rb⁺ even though a positive ion vacancy is also required for charge compensation in this case. Fig. 2 clearly suggests that Eu²⁺ enhances the early stage room-temperature coloration of RbMgF₃, while Er³⁺ does not.

The second interesting observation which requires more research is that late stage room-temperature coloration produces stable centers in RbMgF₃:Eu and KMgF₃: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 Eu²⁺ 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 Eu¹⁺ centers stabilized by radiation defects. The purpose of the low-temperature irradiation was to see if Eu¹⁺ ions could be stabilized by the formation of X₂⁻ hole centers. The 500 nm band in RbMgF₃ and 550 nm band in KMgF₃ appear and disappear with the X₂⁻ centers. This suggests that these bands might be associated with Eu¹⁺. If so, then the room-temperature radiation-induced bands in RbMgF₃ and KMgF₃ might arise from defect stabilized Eu¹⁺ centers. Of course, the formation of Eu³⁺ by irradiation is also possible but the spectra, in figs. 6, 10, and 11, do not correspond to the well-known Eu³⁺ transitions [32,33]. The luminescent transitions for Eu³⁺ arise from ⁵D₀ level to the ⁷F_{*j*} manifold. In RbMgF₃ host, the Eu³⁺ 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 RbMgF₃:Eu²⁺ crystal. Similarly, the broad

emissions at 600 and 800 nm from irradiated KMgF₃:Eu²⁺ do not resemble the Eu³⁺ emissions observed from KMgF₃:Eu³⁺ crystals [32,33].

References

- [1] G. Blasse, W.L. Wanmaker, J.W. ter Vrugt and A. Bril, Philips Res. Rpts. 23 (1968) 189.
- [2] T. Kobayasi, S. Mroczkowski, J.F. Owen and L.H. Brixner, J. Lumin. 21 (1980) 247.
- [3] J. Hernandez, W.K. Cory and J. Rubio, Jap. J. Appl. Phys. 18 (1979) 533.
- [4] G. Boulon, J.C. Gacon, D. Trottler and A. Bedrine, Phys. Stat. Sol. (b) 93 (1979) 775.
- [5] M.V. Hoffman, J. Electrochem. Soc. 118 (1971) 933.
- [6] R.A. Hewes and M.V. Hoffman, J. Lumin. 3 (1971) 261.
- [7] G. Blasse, Phys. Stat. Sol. (b) 55 (1973) K131.
- [8] J.L. Sommerdijk and A. Bril, J. Lumin. 10 (1975) 145.
- [9] M.V. Eremin, Opt. Spect. 26 (1969) 317.
- [10] J.L. Sommerdijk, P. Vries and A. Bril, Philips J. Res. 33 (1978) 117.
- [11] G. Blasse and A. Bril, Philips Tech. Rev. 31 (1970) 304.
- [12] F.J. Lopez, H. Murrieta, J. Hernandez and J. Rubio, Phys. Rev. B22 (1980) 6428.
- [13] N.S. Altshuler, E. Kh. Ivoilova, L.D. Livanova, V.G. Stepanova and A.L. Stolov, Sov. Phys. Solid State (1974) 1973.
- [14] J.L. Sommerdijk, J.M.P.J. Versteegen and A. Bril, J. Lumin. 8 (1974) 502.
- [15] J.L. Sommerdijk, A. Bril and F.M.J.H. Hoex-Strik, J. Lumin. 15 (1977) 115.
- [16] R. Alcala, D.K. Sardar and W.A. Sibley, J. Lumin. (in press).
- [17] J.L. Sommerdijk and A. Bril, J. Lumin. 11 (1976) 363.
- [18] N.S. Altshuler, L.D. Livanova and A.L. Stolov, Opt. Spect. 36 (1974) 72.
- [19] M.A. Dubiniski, L.D. Livanova and A.L. Stolov, Sov. Phys. Solid State 22 (1980) 711.
- [20] S.N. Bodrug, E.G. Valyashko, V.N. Mednikova, D.T. Sviridov and R.K. Sviridov, Opt. Spect. 34 (1973) 176.
- [21] N.S. Altshuler, E. Kh. Ivoilova and A.L. Stolov, Sov. Phys. Solid State 15 (1974) 1602.
- [22] W.A. Sibley and N. Koumvakalis, Phys. Rev. B14 (1976) 35.
- [23] N. Koumvakalis and W.A. Sibley, Phys. Rev. B13 (1976) 40509.
- [24] A. Podinsh and W.A. Sibley, Phys. Rev. B18 (1978) 5921.
- [25] D.K. Sardar, M.D. Shinn and W.A. Sibley, Phys. Rev. B26 (1982) 2382.
- [26] J. Hernandez, F.J. Lopez, H. Murrieta and J. Rubio, J. Phys. Soc. Japan, 50 (1981) 225.
- [27] Eugene Loh, Phys. Rev. 175 (1968) 533.
- [28] M.J. Freiser, S. Methfessel and F. Holzberg, J. Appl. Phys. 39 (1968) 900.
- [29] E. Munoz, J.L. Boldú, and G. Aguilar, J. Chem. Phys. 63 (1975) 4222.
- [30] J.L. Merz and P.S. Pershan, Phys. Rev. 162 (1967) 217.
- [31] D.S. McClure and Z. Kiss, J. Chem. Phys. 39 (1963) 3251.
- [32] J.L. Sommerdijk and A. Bril, J. Lumin. 12/13 (1976) 669.
- [33] M. Hirano and S. Shionoya, J. Phys. Soc. Japan, 28 (1970) 926.