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Abstract. The optical properties (emission, excitation and lifetime data) of CaF$_2$ slightly contaminated with Eu^{2+} and Mn^{2+} ions have been analysed in the present investigation. The optical properties of the systems CaF$_2$:Eu^{2+} and CaF$_2$:Mn^{2+} have also been studied in order to obtain a better characterisation of the optical properties of the CaF$_2$:Eu:Mn phosphor material. The spectroscopic data obtained clearly indicate that energy transfer from the donor Eu^{2+} ions to the acceptor Mn^{2+} ions takes place in CaF$_2$ even at the very low impurity concentrations employed in our samples, suggesting therefore that the impurities are not randomly distributed in the lattice but rather occur as impurity clusters of Eu^{2+}–Mn^{2+}. Some insight into the possible nature of the impurity complexes as well as of the Eu → Mn energy transfer mechanism taking place inside them were gathered with the help of Dexter's theory for energy transfer phenomena. The results presented in this paper give support to the ionic radius criterion proposed by Rubio *et al* to predict impurity pairing in a solid material.

1. Introduction

The phenomenon of resonant energy transfer among impurity ions in a solid material has been the subject of a considerable amount of work during the last three decades. The interest in this field arises partially because energy transfer is important in the development of efficient phosphor materials and solid state lasers.

Recently, Rubio *et al* (1985, 1987, 1988a, b), Rubio (1989), Rubio and Muñoz (1989) and Rubio and Camarillo (1989) carried out detailed investigations of the energy transfer taking place from Eu^{2+} to Mn^{2+} ions in the alkali halide single crystals of NaCl, NaBr, NaI and KCl. One of the most important findings of these investigations was the strong tendency for the divalent europium and manganese ions to form close pairs in the sodium halide lattices. In this latter type of crystal, the average ionic radius (0.96 Å) of the Eu^{2+} and Mn^{2+} ions is nearly identical with that of the host cation Na$^+$ ions (0.99 Å) for which they substitute. Therefore, if the Eu^{2+} and Mn^{2+} ions couple through a halogen ion (Cl$^-$, Br$^-$ or I$^-$) along a $\langle 100 \rangle$ direction, then they fit quite well into the allotted space of the alkali halide lattice. In fact, the calculations performed using Dexter's theory of energy transfer indicated that the experimentally determined data could only be explained if the Eu^{2+} → Mn^{2+} energy transfer occurred in the Eu–Mn close pairs which were preferentially formed in the alkali halide matrix.

The strong tendency for the Eu^{2+} and Mn^{2+} ions to form close pairs in the sodium halides may be due to the reduction in strain in the lattice induced by the presence of each

impurity alone. This conclusion may be supported by the experimental data obtained in the system KCl:Eu:Mn (Capelletti *et al* 1987, Rubio *et al* 1988b) which revealed that Eu–Mn pair formation is much less favourable in this host crystal than in any of the sodium halides. This result is also in agreement with the expectation of the ionic radius criterion proposed by Rubio *et al* (1985, 1987) and Rubio and Muñoz (1989). In fact, in the KCl:Eu:Mn system, the average radius of the Eu^{2+} and Mn^{2+} ions is much smaller than that of the K^+ ion (1.33 Å) for which they substitute in the lattice. Therefore, impurity pair formation appears to be, in this case, an unimportant phenomenon in the minimisation of lattice distortion introduced by each impurity alone.

The experimental finding mentioned above is an uncommon situation and is in contrast with most impurity-sensitised luminescence situations where a random distribution of sensitisers and activators through the solid material is found. It seems to be, however, a quite relevant finding since then the fluorescence efficiency of a manganese-doped phosphor material may be strongly enhanced by pumping through the Eu^{2+} ions introduced into the material simultaneously during preparation.

If the ionic radius criterion is applicable to other kinds of crystalline host different from the alkali halides, then it will provide a reasonable basis for selecting impurity ions and host crystals which maybe lead to the development of efficient phosphor materials and solid state lasers. In particular, according to this criterion, compounds containing sodium, calcium or cadmium as host cation ions might be good candidates for the preferential formation of Eu^{2+}–Mn^{2+} complexes which maybe lead to very efficient phosphor systems.

Taking into account the importance of supporting the validity of this expectation, in this paper an investigation of the optical properties of CaF_2 slightly doped with Eu^{2+} and Mn^{2+} ions is presented.

2. Experimental details

All measurements described in this paper were performed on powder samples. The calcium fluoride phosphors codoped with doubly valent europium and manganese ions were synthesised in a solid state reaction by directly mixing CaF_2 with MnF_2 and EuO, the latter being previously reduced from Eu_2O_3 using standard reduction techniques. Mixtures were prepared by mixing into a paste with acetone, drying for 24 h under vacuum and then firing in evacuated quartz ampullas at 1173 K for 4 d. This preparation technique produced powder samples which were perfectly white by reflected light and free of any observable effects of manganese oxidation. Similar preparation procedures were followed to synthesise CaF_2:Eu^{2+} and CaF_2:Mn^{2+} whose optical properties were also analysed in order to obtain a better characterisation of the CaF_2:Eu:Mn system. The impurity concentration in the samples employed was determined by atomic absorption spectrophotometry.

Luminescence measurements were performed using a standard set-up consisting of a 150 W xenon lamp as light source, two Czerny–Turner monochromators (0.25 m PTI in the excitation arm and a Pacific 0.5 m in the detection arm) and a Hamamatsu R928 photomultiplier tube. All the emission and excitation spectra were corrected for lamp intensity, photomultiplier sensitivity and monochromator response.

For the lifetime measurements, the samples were excited with 1 ns pulses of a PAR-2100 Dyscan laser. The sample fluorescence was detected with a cooled Hamamatsu R943-03 photomultiplier tube and then processed by either a PAR model 165 gated
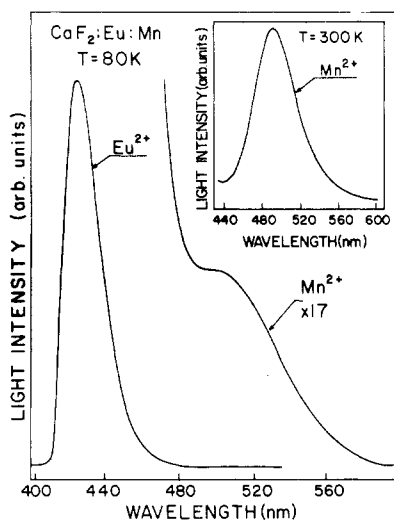
Figure 1. Liquid-nitrogen emission spectrum at 80 K of a CaF_2:Eu (47 ppm):Mn (180 ppm) powder specimen under excitation at 360 nm. The inset in this figure shows a Mn^{2+} phosphorescence emission spectrum at 300 K obtained 10 ms after the 360 nm excitation pulse.
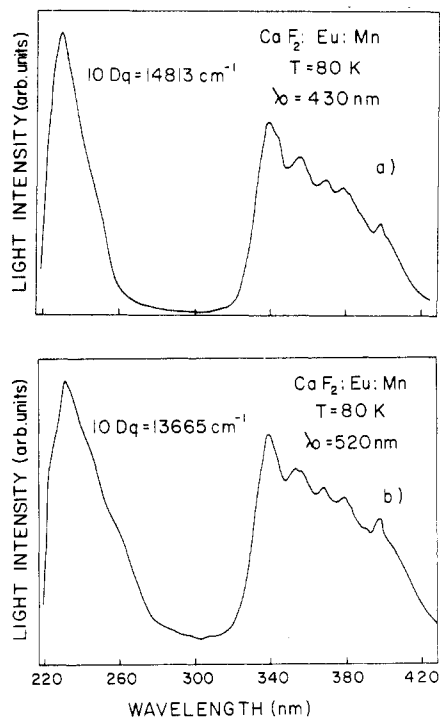

Figure 2. Liquid-nitrogen excitation spectrum at 80 K for (*a*) Eu^{2+} emission and (*b*) Mn^{2+} emission in our slightly doped CaF_2:Eu:Mn samples.

integrator connected to a PAR model 164 boxcar averager or by a Hewlett–Packard model 54201A digitising oscilloscope.

3. Results

Figure 1 portrays the liquid-nitrogen emission spectra observed in our CaF_2:Eu (47 ppm), Mn (180 ppm) powder samples, when the excitation is performed at 360 nm. Reference to this figure shows that the fluorescence spectrum consists of two broad bands which are located in the blue and in the green regions of the electromagnetic spectrum. The blue emission has the same characteristics (peak position, i.e. 424 nm, and width, i.e. 0.16 eV) as the europium-emission band observed in our CaF_2:Eu^{2+} (65 ppm) powder samples. These characteristics are also similar to those previously found for the Eu^{2+} emission in single-crystal CaF_2 (Kaplyanskii and Feofilov 1962, Kaplyanskii *et al* 1963, Kobayasi *et al* 1980). This band was therefore related to the electronic transition $4f^6 5d$ (E_g) $\rightarrow$ $4f^7$ in the europium ions taking place in our doubly doped CaF_2 specimens. On the other hand, the green emission was observed only after the CaF_2:Eu^{2+} phosphor material was simultaneously contaminated with Mn^{2+} ions. The peak position of this emission was found to shift to longer wavelengths when the

sample temperature was lowered, this behaviour being consistent with Mn^{2+} emission characteristics. This band was therefore attributed to the $^4T_{1g}(G) \rightarrow {}^6A_{1g}(S)$ transition of the divalent manganese ions.

In view of the strong overlap of the Mn^{2+} emission with that of Eu^{2+} in the CaF_2:Eu:Mn system, a phosphorescence emission spectrum, recorded 10 ms after the excitation pulse, was obtained to determine accurately the peak position and width of the manganese emission in our doubly doped specimens. This spectrum is shown in the inset of figure 1 for a sample temperature of 300 K, and for an excitation wavelength of 360 nm. From this spectrum the peak position of the Mn^{2+} emission was determined to be 489 nm and its width 0.27 eV.

The 80 K excitation spectra associated with the Eu^{2+} and Mn^{2+} emissions, observed in our doubly doped materials, are displayed in figure 2. In both cases, the intense excitation bands are due to the $4f^7\ {}^8S_{7/2} \rightarrow 4f^65d$ (T_{2g}; E_g) transitions of the Eu^{2+} ions. From the centres of gravity of the two broad excitation bands, values for the $10Dq$ splitting of the 5d orbital of the $4f^65d$ configuration into its T_{2g} and E_g components were determined in both cases and the results obtained are given in the same figure.

Lifetime measurements performed on the Eu^{2+} and Mn^{2+} emission transitions observed in our powder samples of CaF_2:Eu (65 ppm), CaF_2:Mn (5000 ppm) and CaF_2:Eu (47 ppm), Mn (180 ppm) were carried out in the range of temperatures 80–300 K. The Eu luminescence decay in the doubly doped samples was found to consist, in all the temperature range investigated, of a single-exponential decay with a time constant of $0.74 \pm 0.02\ \mu s$ at 300 K and $0.66 \pm 0.02\ \mu s$ at 80 K. This decay scheme was found to be equal, within experimental error ($\pm 3\%$), to that determined in our powder samples of CaF_2 contaminated with only Eu^{2+} ions. It is also similar to that found by Kisliuk *et al* (1968) for the europium emission in single-crystal CaF_2. These results indicate that the decay pattern of the Eu^{2+} luminescence in CaF_2:Eu is *not affected* by the presence of the manganese ions in our slightly doubly doped samples.

The decay scheme of the Mn^{2+} emission was found to consist of a single-exponential decay with a time constant which increased as the sample temperature decreased, i.e. 87 ± 5 ms at 300 K and 164 ± 9 ms at 80 K. A nearly identical Mn luminescence decay was found to occur in our powder samples of CaF_2 containing 5000 ppm Mn^{2+}. This decay scheme was also very similar to that reported by Alonso and Alcalá (1981) for the manganese emission in single-crystal CaF_2:Mn.

4. Discussion

The excitation spectrum corresponding to the Mn^{2+} luminescence observed in the doubly doped specimens reveals the presence of the $4f^7 \rightarrow 4f^65d$ (T_{2g}; E_g) absorption transitions of the Eu^{2+} ions. This result gives evidence that $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer occurred in our CaF_2:Eu:Mn phosphor materials. This process occurred even for the very low concentrations of the donor and acceptor ions in the samples employed. This conclusion can be also inferred from the following facts.

(i) Direct excitation of the Mn^{2+} ions cannot be produced in a CaF_2:Mn^{2+} sample using an excitation wavelength of 360 nm (as used to obtain the emission spectrum shown in figure 1).

(ii) Direct excitation of the manganese ions could not be produced in a CaF_2:Mn sample containing a very similar concentration of manganese ions as that in our doubly
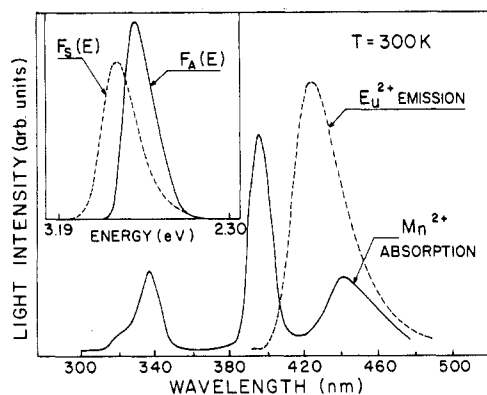
Figure 3. Room-temperature (300 K) overlap region of the europium emission (---) and manganese absorption (——). The inset in this figure shows the normalised lineshape functions in the overlap region.
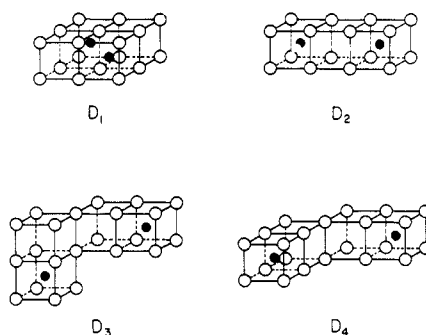

Figure 4. Four of the most simple configurations for the Eu–Mn complex in the lattice of CaF_2 which were considered to calculate the rate of energy transfer via multipolar interaction mechanisms.

doped specimens even under excitation at 398 nm which is in the wavelength region of the prominent $^6A_{1g} \rightarrow {}^4A_{1g}$; ^4E_g absorption transition of the Mn^{2+} ions in this material.

$Eu^{2+} \rightarrow Mn^{2+}$ energy transfer is expected to occur in CaF_2 since the Eu^{2+} emission overlaps the $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ Mn^{2+} absorption, as can be appreciated from the spectra portrayed in figure 3. However, for the concentrations of the donor and acceptor ions in our specimens, the interaction distance between donors and acceptors calculated from a truly random distribution of the impurities is so large that this process should not have occurred in our phosphor materials. Therefore, the observation of europium–manganese fluorescence in the samples analysed suggests that the impurities are not randomly distributed in the lattice but rather occur as impurity clusters of Eu^{2+}–Mn^{2+}.

The magnitude of the cubic $10Dq$ splitting calculated from the excitation spectrum of the Eu^{2+} emission in the $CaF_2:Eu^{2+}$ powder samples (14 854 cm^{-1}) is nearly identical with that obtained from the excitation spectrum of the Eu^{2+} emission in the doubly doped samples (14 813 cm^{-1}). These two values are, however, larger than that obtained from the excitation spectrum of the manganese emission (13 959 cm^{-1}). This finding indicates that the crystal field acting at the site occupied by the europium ion when it is isolated in the lattice of CaF_2 is larger than at the site occupied by the same impurity ion when it is associated with manganese ions in the doubly doped specimens.

On the other hand, the observation in the slightly doubly doped samples that the sensitised Mn^{2+} emission appears at shorter wavelengths (489 nm) than the 'normal' Mn^{2+} emission (about 495 nm) in $CaF_2:Mn$ (Alonso and Alcalá 1981) gives an indication that the crystal field acting at the site occupied by the Mn^{2+} ions when they are associated with the europium ions is smaller than in the case in which they are isolated in the lattice of CaF_2. Thus, in the Eu–Mn associated complexes, the crystal field acting on both impurities is smaller than that acting on them when they are completely dispersed in the lattice, this finding being probably one of the main reasons for the formation of impurity clusters in the lattice of CaF_2.

The ratio for the number N_p of Eu^{2+} ions which were associated with the manganese ions to the total concentration N_T of europium in the specimens analysed could be

roughly estimated using a simple model in which both the donor and acceptor ions are treated as two-energy-level systems. The basic assumptions of this model have been described elsewhere (Muñoz and Rubio 1988). According to them, N_p/N_T in the limit of weak pumping is given by (Muñoz and Rubio 1988)

$$N_p/N_T = I_{Mn}(\beta^r_{Eu}/\beta_{Eu})/I_{Eu}[\beta^r_{Mn}/\beta_{Mn} + (I_{Mn}/I_{Eu})(\beta^r_{Eu}/\beta_{Eu})]. \tag{1}$$

Considering that the radiative decay rates are equal to the inverse of the low-temperature (4 K) lifetime values ($\beta^r_{Eu} \simeq 1.6 \times 10^6 \, s^{-1}$, $\beta^r_{Mn} \simeq 3.3 \, s^{-1}$), N_p/N_T is found to be about 0.09 when our experimentally determined liquid nitrogen data, i.e. $\beta_{Eu} \simeq 1.35 \times 10^6 \, s^{-1}$, $\beta_{Mn} \simeq 11.36 \, s^{-1}$ and $I_{Mn}/I_{Eu} \simeq 0.025$ are employed in equation (1). Thus, about 9% of the total concentration of europium ions in our CaF_2:Eu:Mn specimens appeared to be associated with the manganese ions.

This finding along with those previously reported in the sodium halides doped with Eu^{2+} and Mn^{2+} ions (Rubio *et al* 1985, 1987, Rubio 1989, Rubio and Muñoz 1989, Rubio and Camarillo 1989) and in the systems $RbMgF_3$:Eu:Mn (Shinn and Sibley 1984), CaF_2:Ce:Mn (McKeever *et al* 1986) and CaF_2:Ce:Eu (Caldiño *et al* 1989) indicate that some kinds of ion when they are introduced into 'addecuate' crystalline matrices tend to form impurity clusters even at very low concentrations. It also gives support to the ionic radius criterion proposed by Rubio *et al* (1985, 1987) and Rubio and Muñoz (1989) to explain the preferential impurity pairing. In fact, the average radius of the Eu^{2+} and Mn^{2+} ions (0.96 Å) is nearly identical with that of the host Ca^{2+} ions (0.99 Å) for which they substitute in the calcium fluoride lattice.

From the model depicted above, it can also be obtained that the intensity of the activator ion reaches a maximum value after pulse excitation of the donor ions at a time t_{max} given by

$$t_{max} = [1/(K - \beta_a)] \ln(K/\beta_a). \tag{2}$$

From this equation and our experimentally determined data, i.e. $t_{max} < 25$ ns and $\beta_a = 11.36 \, s^{-1}$, the rate of $Eu^{2+} \to Mn^{2+}$ energy transfer was estimated to be greater than $8 \times 10^8 \, s^{-1}$ at 300 K.

Taking into account that the 3d $\to$ 3d Mn^{2+} absorption transitions are forbidden, it might be expected that the $Eu^{2+} \to Mn^{2+}$ energy transfer mechanism which takes place in CaF_2 is of the electric dipole quadrupole type. The transfer rate for such interaction is given by (Dexter 1953)

$$W^{DQ}_{SA} = \frac{3\hbar^4 c^4 f_q \lambda^2_S}{4\pi n^4 \tau^0_S f_d} \left(\frac{1}{R_{SA}}\right)^8 Q_a \int \frac{F_S(E)F_A(E)}{E^4} \, dE \tag{3}$$

where the integral $\Omega = \int[F_S(E)F_A(E)/E^4] \, dE$ represents the spectral overlap between the normalised shapes of the europium emission ($F_S(E)$) and manganese absorption ($F_A(E)$). The meaning of the other symbols in equation (3) has been described elsewhere (Dexter 1953). The overlap integral was calculated using the room-temperature Eu emission and the Mn absorption portrayed in figure 3. The inset in this figure shows the normalised lineshape functions in the overlap region. From this information, the value of Ω was found to be $4.6 \times 10^{-2} \, eV^{-5}$. In order to calculate Q_a, we followed the same procedure as that employed previously (Rubio *et al* 1987), the result being $Q_a = 4.8 \times 10^{-23} \, eV \, cm^2$. Now, using the fluorescence decay data for the europium emission, the values for Q_a and Ω mentioned above, $f_d \simeq 10^{-7}$ and $f_q \simeq 10^{-10}$, the critical interaction distance for energy transfer was found to be about 12 Å at 300 K. Hence, within the

Table 1. Theoretical calculated values for the rate of energy transfer from europium to manganese ions in CaF_2 at 300 K using the complex configurations shown in figure 4.

Complex configuration	Sensitiser–activator distance (Å)	Energy transfer rate (s^{-1})	
		W_{SA}^{DD}	W_{SA}^{DQ}
D_1	3.86	8.2×10^6	9.9×10^9
D_2	5.45	1.0×10^6	6.2×10^8
D_3	6.68	3.0×10^5	1.2×10^8
D_4	7.71	1.3×10^5	3.9×10^7

lifetime of the donor excitation, only those acceptor ions within a radius of around 12 Å will be sensitised.

Although the nature of the Eu–Mn clusters cannot be inferred from our optical data, different kinds of small aggregate in which the Eu and Mn ions are separated by at most 12 Å can be imagined in the lattice of CaF_2. Some of the simplest are illustrated in figure 4. The rate of Eu → Mn energy transfer via a dipole–quadrupole interaction mechanism was calculated using these dimer configurations and the results obtained are given in table 1 along with those which were calculated from the use of an electric dipole–dipole interaction mechanism for comparison. As expected, more reasonable values are obtained when a dipole–quadrupole interaction mechanism is employed rather than an electric dipole–dipole mechanism to perform the calculations. Moreover, the closer agreement between the calculated values for W_{SA}^{DQ} and that estimated experimentally is achieved when one assumes that the Mn^{2+} ion occupies the positions of first and/or second neighbours to the europium ion, as is the case in the complexes D_1 and D_2 in figure 4.

Although it is recognised that the calculations described above are phenomeno-logical, they may suggest that, in order to account for the high magnitude of the Eu → Mn energy transfer rate, the europium and manganese ions should be separated by at most 5.6 Å in the lattice of CaF_2. This condition is fulfilled by the dimer complexes D_1 and D_2. However, other small aggregate complexes in which a europium ion is surrounded by several manganese ions occupying the positions of first or second neighbours to the europium ion could also be appropriate to account for the high rate of energy transfer between the europium and manganese ions. In these small complexes, however, it appears to be unreasonable that several europium ions will be involved. In fact, the calculated rate of Eu^{2+} → Eu^{2+} energy transfer using a dipole–dipole interaction mech-anism with $\tau_S^0 = 0.74 \mu s$, $Q_a = 4.8 \times 10^{-18} eV cm^2$, $\Omega = 2.2 \times 10^{-2} eV^{-5}$ and R_{SA} in the range 3.86–5.6 Å is about 10^{11}–10^{10} s^{-1} which is much larger than the estimated rate of transfer between the Eu^{2+} and Mn^{2+} ions in the slightly doped samples from our experimental data. Therefore, in the small europium–manganese aggregates, Eu → Eu transfer will be more probable than Eu → Mn transfer and this is not in agreement with our experimental observations.

Finally, one may conclude that our spectroscopic data give evidence that small Eu–Mn clusters are formed in the lattice of CaF_2, in agreement with the expectation of the ionic radius criterion proposed by Rubio *et al* (1985). This preferential impurity clustering, which has been considered to be infrequent in most studies of energy transfer between impurities in solids, appears to be a quite relevant finding which may help to design more efficient phosphor and laser systems.

Acknowledgments

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