

Luminescence from BaF₂:Mn²⁺ samples: substitutional Mn²⁺ ions are ‘silent’

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Abstract. Through this work it is shown that the luminescence observed in BaF₂:Mn²⁺ samples is related to the formation of BaMnF₄ microcrystalline precipitates. This conclusion is supported by the experimental emission and excitation spectra as well as by the temperature dependence displayed by the emission intensity. Also the EPR spectrum of most doped samples clearly shows the presence of a signal (superimposed on that coming from isolated Mn²⁺ ions) whose temperature dependence is similar to that displayed by BaMnF₄ crystals. The absence of luminescence associated with *isolated* Mn²⁺ ions in the BaF₂ host lattice is discussed. It is pointed out that luminescence quenching is probably related to a multiphonon non-radiative process rather than to a ⁴T₁(G) excited state close to the bottom of the BaF₂ conduction band.

Although luminescence quenching appears for a Dexter–Klick–Russell parameter Λ probably close to 0.1, this is qualitatively related to a high radiative lifetime ($\tau_R \simeq 100$ ms). The analysis made also shows that firstly Λ increases by a factor of about 1.7 on going from Mn²⁺-doped fluoroperovskites to Mn²⁺ in fluoride-type crystals, and secondly Λ increases on going from CaF₂:Mn²⁺ to SrF₂:Mn²⁺. Both variations mainly reflect a parallel increase in the Stokes shift.

1. Introduction

By means of EPR performed at room temperature it is known that, in Mn²⁺-doped MF₂ crystals (M=Ca, Cd, Sr or Ba), *substitutional* cubic centres are formed where Mn²⁺ is surrounded by eight equivalent F⁻ ions at a distance R [1,2]. The analysis of the experimental isotropic superhyperfine constant A_s shows that the M²⁺ → Mn²⁺ replacement gives rise to an inward relaxation which is maximum for the case of BaF₂:Mn²⁺ [3]. For this system $R = 232$ pm is smaller than $R_0 = 268$ pm corresponding to the perfect lattice.

Recent EPR [4] and ENDOR [5] data on BaF₂:Mn²⁺ have shown that the structure of the Mn²⁺ centre changes when the temperature T decreases below about 45 K. In this situation the new local structure displays a T_d symmetry, thus involving two inequivalent F⁻ ions and two different Mn²⁺–F⁻ distances denoted as R_s and R_l corresponding to the short bond and the long bond, respectively. The values of R_s and R_l derived from the experimental isotropic superhyperfine tensor are found to be $R_s = 224$ pm and $R_l = 250$ pm [6].

As regards Mn²⁺-doped fluorides the emission coming from the first excited state ⁴T₁(G) is usually detected, a fact which allows one to measure the excitation spectrum and thus to obtain also information on the metal–ligand distance R and local geometry [7].

As good examples the cases of Mn^{2+} -doped fluoroperovskites [7, 8] and $\text{CaF}_2 : \text{Mn}^{2+}$ and $\text{CdF}_2 : \text{Mn}^{2+}$ can be quoted [9, 3].

By virtue of these reasons a study of the luminescence of different samples of $\text{BaF}_2 : \text{Mn}^{2+}$ at different temperatures has been undertaken. The main results of such an investigation are shown in this work. Because of some unexpected results, luminescence and EPR measurements on BaMnF_4 together with additional X-band EPR measurements on $\text{BaF}_2 : \text{Mn}^{2+}$ have also been carried out. Details of the experimental set-up have been given elsewhere [4, 8]. The results obtained through this work clearly show that the Mn^{2+} luminescence detected in $\text{BaF}_2 : \text{Mn}^{2+}$ samples comes from the formation of BaMnF_4 microcrystalline precipitates. The absence of luminescence due to isolated cubic MnF_8^{6-} complexes formed in $\text{BaF}_2 : \text{Mn}^{2+}$ is discussed.

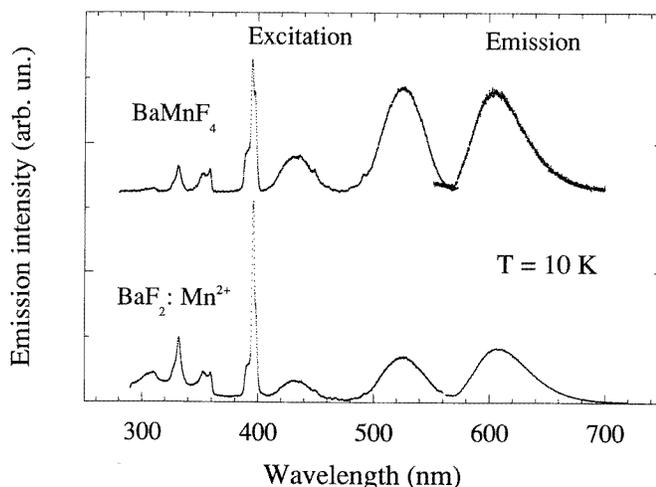


Figure 1. Emission and excitation spectrum found at $T = 10$ K in the $\text{BaF}_2 : \text{Mn}^{2+}$ samples analysed. For comparison the corresponding spectrum associated with BaMnF_4 are also shown.

2. Results and discussion

Figure 1 shows the only emission spectrum and associated excitation spectrum related to Mn^{2+} detected for all the $\text{BaF}_2 : \text{Mn}^{2+}$ samples investigated.

The excitation spectrum is typical of an octahedral MnF_6^{4-} complex as is found for $\text{KZnF}_3 : \text{Mn}^{2+}$ [7] or MnF_2 [10] for instance. The fingerprint of Mn^{2+} in a sixfold (instead an eightfold) coordination appears in the separation Δ_{31} between the energy of the sharp third excitation peak (associated with a ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}, {}^4\text{E}_g$ (D) transition) and that corresponding to the first peak assigned to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_1$ (G) transition. For the present case, Δ_{31} is equal to 6300 cm^{-1} while, for Mn^{2+} -doped fluoroperovskites [7, 8], Δ_{31} goes from 5500 cm^{-1} (for $\text{CsCaF}_3 : \text{Mn}^{2+}$) to 7000 cm^{-1} (for $\text{KMgF}_3 : \text{Mn}^{2+}$). By contrast, for $\text{CaF}_2 : \text{Mn}^{2+}$ where the MnF_8^{6-} complex is formed, Δ_{31} is only equal to 2400 cm^{-1} [9] and is thus less than half the value measured for $\text{CsCaF}_3 : \text{Mn}^{2+}$. As a first approximation, Δ_{31} can be written as $10Dq - C$ [10]; the significant difference between the Δ_{31} -values displayed by the MnF_6^{4-} and MnF_8^{6-} units has been explained on the following grounds.

- (1) Experimental [7–9] and theoretical [11] data on systems containing MnF_6^{4-} and

MnF_8^{6-} complexes indicate that the Racah parameters B and C are nearly independent of the metal–ligand distance R .

(2) By contrast, $10Dq$ turns out to be strongly dependent upon R . For MnF_6^{4-} it has been determined that, in the vicinity of $\bar{R} = 212$ pm $10Dq$ follows the law

$$10Dq = KR^{-n} \quad (1)$$

where $n = 4.7$ [7, 8]. In the case of the MnF_8^{6-} complex the exponent n would have a value almost coincident with that for MnF_6^{4-} following the theoretical results in [12]. The microscopic origin of this dependence is explored in [13].

(3) On passing from octahedral MnF_6^{4-} to cubic MnF_8^{6-} complexes there is a significant increase in the $\text{Mn}^{2+}\text{--F}^-$ distance [3] according to the Pauling rules. The true $\text{Mn}^{2+}\text{--F}^-$ distance for the whole series of Mn^{2+} -doped fluoroperovskites has been determined through the experimental isotropic superhyperfine constant [14] and the crystal-field spectrum [7, 8]. The average R -value is equal to 212 pm. By contrast the $\text{Mn}^{2+}\text{--F}^-$ distance for $\text{Mn}^{2+}:\text{MF}_2$ ($M = \text{Ca}, \text{Cd}, \text{Sr}$ or Ba) lies between 226 and 232 pm from the analysis of the experimental superhyperfine constant A_s [3]. This conclusion is in agreement with recent EXAFS measurements [15] and theoretical calculations [16] on $\text{CaF}_2:\text{Mn}^{2+}$.

Trying to understand what species having MnF_6^{4-} units are responsible for the excitation spectrum depicted in figure 1, we have verified that the energy of each crystal-field peak is the same as that found in *absorption* spectrum of BaMnF_4 [17]. Moreover, to clarify this situation, we have recorded the emission and excitation spectrum of a small sample of BaMnF_4 at $T = 10$ K and the results are also collected in figure 1. A comparison of both spectra strongly supports the fact that microcrystalline precipitates of BaMnF_4 are formed in the $\text{BaF}_2:\text{Mn}^{2+}$ samples.

This conclusion is not in contradiction with what is found on looking at other optical parameters. Figure 2 shows the temperature dependence displayed by the integrated emission intensity, together with the peak energy and band width of the emission band corresponding to the BaMnF_4 sample. The temperature dependence of the band width reflects well the magnetic phase transition at $T_N = 28$ K undergone by BaMnF_4 . The behaviour exhibited by the emission intensity and the peak energy is comparable with that reported in [17] and is characteristic of a multitrapping emission process. Luminescence produced on traps after excitation migration has been found for ionic compounds such as RbMnF_3 , MnF_2 [18] and RbMnCl_3 [19] where Mn^{2+} is not an impurity but a component of the perfect lattice.

Also this kind of luminescence has been found for instance for $\text{RbCl}:\text{Mn}^{2+}$ [20] or $\text{NaCl}:\text{Mn}^{2+}$ [21] where microcrystalline precipitated phases are formed.

Figure 3 shows the temperature dependence displayed by the emission intensity (measured at $\lambda = 600$ nm) for the $\text{BaF}_2:\text{Mn}^{2+}$ samples. It exhibits a similar behaviour to that corresponding to BaMnF_4 . Also a red shift of the emission peak energy as the temperature is increased, similar to that reported in figure 2, has been observed.

To correlate the present luminescence results with previous EPR data on $\text{BaF}_2:\text{Mn}^{2+}$ it was necessary, however, to discover some reasonable indication of the existence of BaMnF_4 microcrystals in the EPR spectra. As shown in figure 4 this was achieved in most doped samples. In this figure are compared the EPR spectrum of BaMnF_4 at different temperatures with the EPR spectrum corresponding to $\text{BaF}_2:\text{Mn}^{2+}$. The EPR spectrum of BaMnF_4 at $T > T_N$ is composed of *only one* Lorentzian band and is thus characteristic of pure insulator crystals but with a transition-metal cation involved in their composition. The effective exchange and magnetic dipole interactions between close Mn^{2+} ions are now more important than the hyperfine and superhyperfine interactions which can be observed

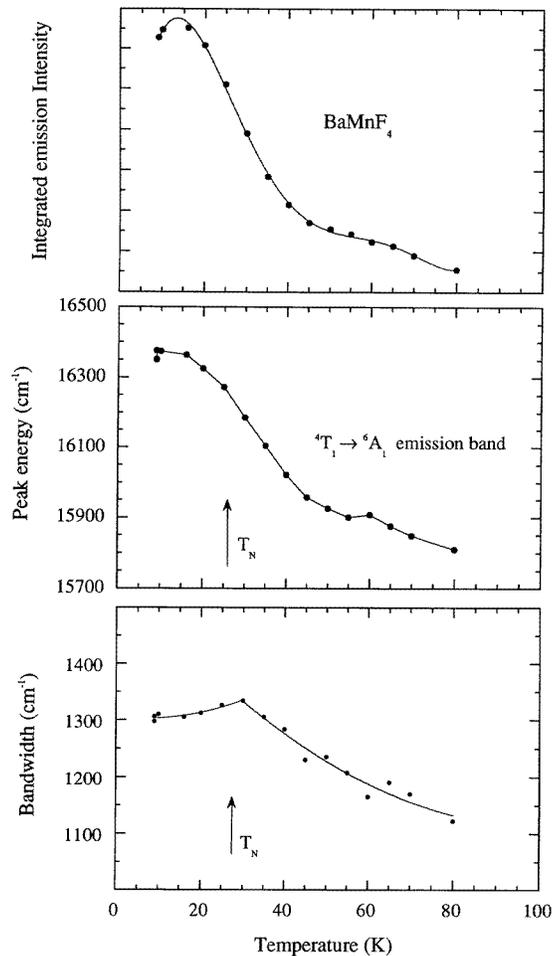


Figure 2. Temperature dependence of the integrated emission intensity of the BaMnF₄ sample together with that displayed by the emission peak energy and band width.

in the case of *isolated* Mn²⁺ ions. The disappearance of the paramagnetic resonance signal for $T = T_N$ reflects the advent of the antiferromagnetic phase transition. Below T_N an antiferromagnetic resonance can exist but at a different frequency because of an internal molecular field. The EPR spectrum of BaF₂ : Mn²⁺ taken at 25 K clearly reveals the existence of isolated Mn²⁺ ions where the hyperfine and superhyperfine structures are clearly visible. From the previously made analysis of such a spectrum it was concluded [4] that *isolated* Mn²⁺ ions have a T_d symmetry at $T = 25$ K. At $T = 60$ K the superhyperfine structure changes with respect to what is seen at $T = 25$ K, a fact connected to the cubic symmetry of isolated Mn²⁺ centres above $T = 45$ K. Moreover, in the EPR spectrum of BaF₂ : Mn²⁺ at $T = 60$ K, *another* signal is also present, indicated by the broken curves. We have verified that this signal disappears at $T = 30$ K and in fact it is absent in the EPR spectrum measured at $T = 25$ K (figure 4). The EPR results in figure 4 thus support the fact that BaMnF₄ microcrystals are formed in the most highly doped BaF₂ : Mn²⁺ samples although the concentration of isolated Mn²⁺ ions appears to be higher than that

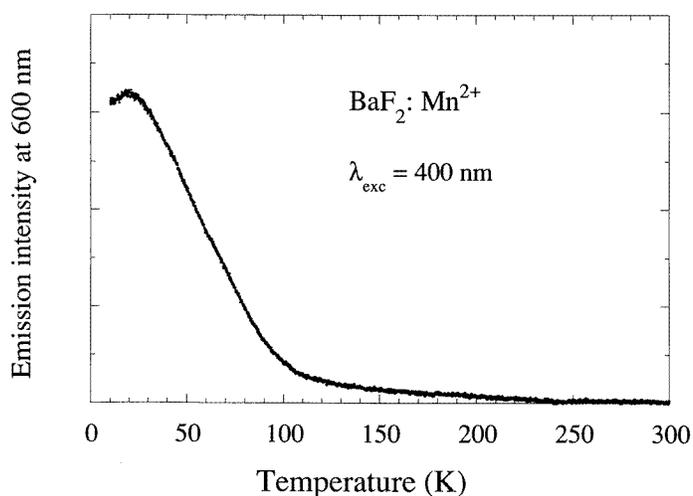


Figure 3. Temperature dependence of the emission intensity (measured at $\lambda = 600$ nm) displayed by $\text{BaF}_2 : \text{Mn}^{2+}$ samples.

corresponding to Mn^{2+} ions forming BaMnF_4 precipitates.

The present EPR and optical results on $\text{BaF}_2 : \text{Mn}^{2+}$ thus indicate that, although isolated Mn^{2+} ions are the dominant species, nevertheless the only luminescence detected comes from BaMnF_4 precipitates. As the ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1$ emission maxima in $\text{CaF}_2 : \text{Mn}^{2+}$ and in $\text{CdF}_2 : \text{Mn}^{2+}$ appear at around 500 nm, this region has been carefully explored but without success. It is worth noting that for $\text{SrF}_2 : \text{Mn}^{2+}$ the luminescence associated with isolated Mn^{2+} ions has been found but at temperatures $T \leq 190$ K [22].

Searching for an explanation for the absence of luminescence in the case of isolated Mn^{2+} ions in BaF_2 , we have firstly investigated the possibility that the first excited state ${}^4\text{T}_1(\text{G})$ lies in the conduction band or close to the bottom of the conduction band as happens for rare-earth ions (such as Tm^{2+} , Eu^{2+} or Yb^{2+}) in crystals with a fluorite structure [23, 24].

As a first approximation the energy to extract a d electron from a Mn^{2+} ion embedded in a lattice such as BaF_2 can simply be written as

$$E_d = I(\text{Mn}^{2+}) - e\{V_M + V_{RL}\} \quad (2)$$

where $I(\text{Mn}^{2+}) = 33.7$ eV is the first ionization potential of free Mn^{2+} and V_M is the Madelung potential at the cation site in the perfect lattice. For cases such as $\text{BaF}_2 : \text{Mn}^{2+}$ or $\text{CaF}_2 : \text{Mn}^{2+}$ where there is a lattice relaxation of the first neighbours around the impurity it is necessary to add the V_{RL} term which is given by

$$V_{RL} = 8e\{1/R - 1/R_0\} \quad (3)$$

in the case of eightfold coordination.

For $\text{CaF}_2 : \text{Mn}^{2+}$, $eV_M = 19.0$ eV, $eV_{RL} = 1.9$ eV and thus $E_d = 11.9$ eV. As the bottom of the conduction bands of CaF_2 and BaF_2 appear to be about 1 eV below the zero level [25, 26] this simple reasoning demonstrates that the ground and first excited states of MnF_8^{6-} in CaF_2 lie at an energy well below that associated with the bottom of the conduction band of CaF_2 . This idea is reinforced by recent XPS results [27] on $\text{CaF}_2 : \text{Mn}^{2+}$ showing that the binding energy corresponding to the ground state of MnF_8^{6-} lies around 11 eV. For $\text{BaF}_2 : \text{Mn}^{2+}$ it is found that $eV_M = 17.5$ eV and $eV_{RL} = 6.9$ eV, indicating a much

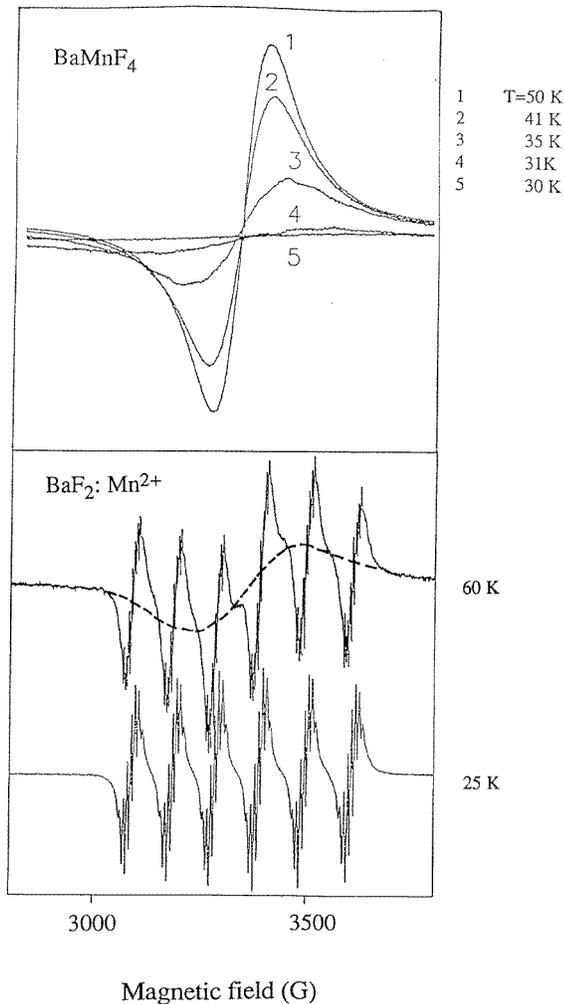


Figure 4. (a) EPR spectrum of BaMnF₄ taken at different temperatures. (b) EPR spectrum associated with a BaF₂: Mn²⁺ sample recorded at $T = 60$ K and $T = 25$ K. ($H \parallel (100)$): ---, guide to the eye.

stronger inward relaxation of ligands than for CaF₂: Mn²⁺. Therefore E_d would be equal to 9.4 eV and thus although smaller than for CaF₂: Mn²⁺, it favours the fact that both the ground and the first excited states of MnF₈⁶⁻ in BaF₂ are well below the bottom of the host lattice conduction band [24]. The present situation would be different from that observed for divalent rare-earth cations in lattices such as CaF₂, SrF₂ or SrCl₂, where the first excited state can be in the conduction band. This is favoured by the low ionization potential displayed by ions such as Tm²⁺, Dy²⁺ or Eu²⁺ with respect to $I(\text{Mn}^{2+}) = 33.7$ eV. For instance $I(\text{Tm}^{2+}) = 23.3$ eV. Taking into account these facts we have also explored whether the absence of luminescence for isolated Mn²⁺ can be explained through a normal non-radiative process involving multiphonon emission for the first excited state. The non-radiative emission probability is related to the Stokes shift E_s and to the gap E_g between

the first excited and ground-state energy. E_s can be written as

$$E_s = 2\bar{S}\hbar\bar{\omega} \quad (4)$$

in terms of an average mode with frequency $\bar{\omega}$ linearly coupled to the electronic excited state. \bar{S} denotes the corresponding Huang–Rhys factor. The gap E_g is also written as

$$E_g = \bar{p}\hbar\bar{\omega} \quad (5)$$

and thus \bar{p} is the number of phonons required to bridge the gap.

Dexter *et al* [28] pointed out that the occurrence of luminescence is governed by the Λ parameter defined by

$$\Lambda = \frac{1}{2} \frac{E_s}{E_g} = \frac{\bar{S}}{\bar{p}} \quad (6)$$

in such a way that an increase in Λ favours the disappearance of the luminescence. Moreover in the case of F centres it was found [29] that luminescence exists when $\Lambda < \Lambda_M$ where $\Lambda_M = 0.25$.

Table 1. The energies of the ${}^6A_1 \rightarrow {}^4T_1(G)$ excitation peak (E_g), the associated emission peak and the Stokes shift (E_s) measured at room temperature for Mn²⁺ in some fluoroperovskites and in Mn²⁺-doped MF₂ (M = Ca, Cd or Sr), together with the Λ -value (defined in (6)) corresponding to each system. The energy of the ${}^6A_1 \rightarrow {}^4T_1(G)$ excitation peak for SrF₂: Mn²⁺ (where $R = 213$ pm) has been derived from that corresponding to CaF₂: Mn²⁺ (where $R = 226$ pm) taking into account the dependence of $10Dq$ upon R (equation (1)) and assuming the same values of the Racah parameters.

Host lattice	References	Energy (cm ⁻¹)			Λ
		${}^6A_1 \rightarrow {}^4T_1(G)$ peak	Emission peak	Stokes shift	
KMgF ₃	[7, 8]	18 160	16 955	1205	0.033
KZnF ₃	[7, 8]	18 530	17 200	1330	0.036
CsCaF ₃	[7, 8]	19 880	18 350	1530	0.038
CaF ₂	[9]	22 625	20 202	2432	0.055
CdF ₂	[9]	22 075	19 493	2582	0.060
SrF ₂	[22]	23 000	20 000	3000	0.065

In table 1 are collected representative values of E_s and E_g for Mn²⁺-doped fluoroperovskites as well as for Mn²⁺ in CaF₂ and SrF₂. In the latter case, only the emission peak has been measured. The value of the ${}^6A_1 \rightarrow {}^4T_{1g}(G)$ absorption maxima has been calculated from $10Dq = 4250$ cm⁻¹ found for CaF₂, equation (1) and the distances $R = 226$ pm and $R = 231$ pm derived from the experimental isotropic superhyperfine constant A_s for CaF₂: Mn²⁺ and SrF₂: Mn²⁺, respectively. It can be seen in table 1 that the Λ -values for Mn²⁺ in fluoroperovskites are all close to 0.035. By contrast, Λ experiences a significant increase on passing from these cases to CaF₂: Mn²⁺ (where $\Lambda = 0.055$). Also on going from CaF₂: Mn²⁺ to SrF₂: Mn²⁺, Λ experiences approximately a 20% increase.

Therefore the Λ -values shown in table 1 suggest that firstly the system SrF₂: Mn²⁺ is less favourable than CaF₂: Mn²⁺ for observing luminescence and secondly Mn²⁺ in fluoroperovskites are more suitable systems than Mn²⁺ in crystals with a fluorite structure, mainly because the latter systems involve a Stokes shift which is about 70% higher than that displayed by the former.

As regards CaF₂: Mn²⁺ the data collected in [9] indicate that luminescence strongly decreases when $T > 550$ K. For SrF₂: Mn²⁺ the luminescence is only seen [22] for

temperatures $T < 200$ K. Although these experimental facts are in qualitative agreement with the preceding conclusions, the present analysis indicates that the quenching of luminescence for Mn^{2+} in BaF_2 can be related to a Λ_M -value close to about 0.1. This value is certainly smaller than the value $\Lambda_M = 0.25$ reached in the study of F centres [29].

Also in the recent study on $\text{CaF}_2 : \text{Cu}^+$ the Cu^+ luminescence is well observed [30]. The experimental values $E_g = 28\,000 \text{ cm}^{-1}$ and $E_s = 8\,000 \text{ cm}^{-1}$ lead to $\Lambda = 0.14$, thus implying that $\Lambda_M > 0.14$ for this system. Very recent results on Cr^{4+} in several oxides [31] reveal that firstly luminescence is favoured upon decreasing Λ and secondly, among the systems analysed, the lowest value of the quantum efficiency η is reached for $\text{YSGG} : \text{Cr}^{4+}$ where $\eta = 9\%$ and $\Lambda = 0.20$.

Let us now try to explain the quenching of the luminescence in $\text{BaF}_2 : \text{Mn}^{2+}$ despite the fact that Λ would be about 0.1. As is well known the total decay probability τ^{-1} involves the radiative contribution τ_R^{-1} as well as the non-radiative contribution τ_{NR}^{-1} . Roughly speaking the quenching of luminescence starts when the two parameters τ_R and τ_{NR} become comparable [32]. A great difference appears, however, between Mn^{2+} for fluorites and systems with F centres, and Cr^{4+} as regards τ_R in oxides. In fact, in these systems, τ_R is of the order of some microseconds while for $\text{Mn}^{2+} : \text{CaF}_2$ it is about 100 ms [9].

If τ_{NR} in $\text{BaF}_2 : \text{Mn}^{2+}$ is dominated by multiphonon processes, then τ_{NR} depends on Λ . Thus τ_{NR} can become comparable to τ_R at Λ -values smaller than those reached in cases where τ_R is of the order of 1 μs .

In conclusion, at variance with what is found for $\text{CaF}_2 : \text{Mn}^{2+}$ where $\eta = 1$ at room temperature, we have discovered no luminescence arising from substitutional Mn^{2+} impurities in BaF_2 down to 10 K. By contrast, from the analysis of emission and excitation spectra, direct evidence of the existence of BaMnF_4 precipitates inside the samples analysed has been reached. The progressive quenching of the isolated Mn^{2+} luminescence through the series $\text{CaF}_2 \rightarrow \text{SrF}_2 \rightarrow \text{BaF}_2$ of host lattices could partially be related to an increase in the Stokes shift E_s . As recently analysed for the symmetric mode [12] the Stokes shift depends on ω^{-2} , and the angular frequency ω decreases upon increasing the metal–ligand distance R . This feature probably explains the higher Stokes shift encountered in $\text{CaF}_2 : \text{Mn}^{2+}$ than in Mn^{2+} -doped fluoroperovskites because R increases on passing from sixfold to eightfold coordination.

On the other hand the existence of the symmetry change undergone by the substitutional Mn^{2+} centre in BaF_2 [4] suggests the existence of a soft local mode which again tends to favour an increase in E_s .

Further work on this problem is planned for the near future.

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