

## PRESSURE-INDUCED ENHANCEMENT OF THE PHOTOLUMINESCENCE IN $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2:\text{Mn}^{2+}$

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The surprising disappearance of the  $\text{Mn}^{2+}$  photoluminescence (PL) on passing from  $\text{CaF}_2$  to  $\text{SrF}_2$  through the  $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2:\text{Mn}^{2+}$  series is investigated through pressure spectroscopy, and as a function of the temperature. The PL quenching which is observed along the series is explained on the basis of multiphonon relaxation mechanisms, which are described by a thermally activated process. In non-luminescent crystals, PL can be recovered by applying pressure. The results are accounted for through an universal equation relating the PL lifetime as a function of  $P$  (or  $V$ ) and  $T$ , using an activation energy and a transition rate that are strongly dependent on the lattice parameter (crystal volume).

*Keywords:* High-pressure spectroscopy; Photoluminescence; Radiationless process;  $\text{Mn}^{2+}$ ; Fluorite series

### 1 INTRODUCTION

The compound series of  $\text{Mn}^{2+}$ -doped fluorites  $\text{MF}_2$  (M: Ca, Sr, Ba) forms attractive photoluminescent systems. Their luminescence properties experience profound changes along the series. Whereas  $\text{CaF}_2:\text{Mn}^{2+}$  exhibits the longest  $\text{Mn}^{2+}$  green photoluminescence (PL) lifetime ( $\tau = 182$  ms) ever measured at low temperature among transition metal ions with quantum yields close to 1 [1–3], the isomorphous  $\text{SrF}_2:\text{Mn}^{2+}$  is not luminescent at room temperature (RT):  $\tau = 0$ ,  $\eta = 0$  [1, 2]. The optical properties of these systems have been investigated for a long time [1, 2, 4, 5]. In particular, the emission and excitation spectra along the  $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2:\text{Mn}^{2+}$  series can be understood on the basis of the formed  $\text{MnF}_8^{6-}$  cubal complex [2, 5, 6]. The small shifts undergone by the PL and the corresponding excitation bands along the series ( $a[\text{CaF}_2] = 5.46$  Å;  $a[\text{SrF}_2] = 5.81$  Å), are explained by the slight decrease of  $10 Dq$  due to changes of the local Mn-F distance which is estimated to vary from 2.26 to 2.31 Å on passing from  $\text{CaF}_2:\text{Mn}^{2+}$  to  $\text{SrF}_2:\text{Mn}^{2+}$  [4, 5]. Nevertheless, the PL intensity ( $I$ ) and the associated lifetime ( $\tau$ ) strongly decrease upon increasing the temperature in the 10–750 K range. The quenching temperature is known to decrease linearly with the strontium fraction,  $x$  [2]. At RT the PL intensity along the series abruptly decreases for

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$x = 0.75$ . The  $\text{BaF}_2:\text{Mn}^{2+}$  fluorite is an exception to this behaviour. Although the presence of isolated  $\text{MnF}_8^{6-}$  units in  $\text{BaF}_2:\text{Mn}^{2+}$  was revealed by EPR, the complex however is not PL ( $\tau = 0$ ) either at RT or at  $T = 10$  K [5] since the only red PL at  $T = 10$  K was ascribed to  $\text{BaMnF}_4$  precipitates [5].

This work investigates the surprising disappearance of the  $\text{Mn}^{2+}$  green PL ( $20000 \text{ cm}^{-1}$ ) observed at RT on passing from  $\text{CaF}_2$  to  $\text{SrF}_2$  along the  $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2:\text{Mn}^{2+}$  series [1, 2, 5, 6]. The aim is to understand the microscopic origin of the excited-state relaxation phenomena leading to radiationless processes and how the host crystal affects them. This knowledge is noteworthy in order to control the PL properties of these scintillator materials [7]. The peculiar PL behaviour shown by  $\text{Mn}^{2+}$  along the fluorite series is studied by optical spectroscopy as a function of the temperature and the pressure. Attention is paid on the variation of  $I$  and  $\tau$  with temperature through the complete series and pressure in  $\text{Ca}_{0.25}\text{Sr}_{0.75}\text{F}_2:\text{Mn}^{2+}$  and  $\text{CaF}_2$  [6]. This procedure is important to elucidate whether the loss of PL is due to the different nature of the host cation (*i.e.*  $\text{Ca}^{2+}$  compared to  $\text{Sr}^{2+}$  or  $\text{Ba}^{2+}$ ), or it is simply related to changes of lattice parameter with  $x$ , independently on the substituted cation.

## 2 EXPERIMENT

Single crystals of  $\text{MF}_2$  (M: Ca, Sr) doped with  $\text{Mn}^{2+}$  (1 mol%) and the solid solutions  $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2:\text{Mn}^{2+}$  were grown by the Bridgman technique as indicated elsewhere [2]. PL spectra and lifetime measurements at room pressure were obtained using a ISA Fluoromax-2 fluorimeter and a Chromex 500 IS monochromator with a Tektronix 2430 A oscilloscope, respectively. For lifetime measurements, the  $\text{Mn}^{2+}$  was excited with the 407 nm line of a Coherent I-302-K Krypton laser which was modulated by a Newport 35085-3 acousto-optic modulator. Experiments in the 290–750 K range were accomplished through a Leitz 350 heating stage. For low temperature (10–350 K), we used a Scientific Instruments 202 closed-circuit cryostat and an APD-K controller. Hydrostatic pressure experiments were performed with a Diamond Anvil Cell (High Pressure Diamond Optics, Inc.). We used a special microscope setup for measuring the PL lifetime and the corresponding spectrum of weakly luminescent  $\text{Ca}_{0.25}\text{Sr}_{0.75}\text{F}_2:\text{Mn}^{2+}$  microcrystals under pressure. The pressure was calibrated from Ruby chips.

## 3 EXPERIMENTAL RESULTS

Figure 1(a) shows the variation of the PL spectrum upon increasing the temperature in the 10–350 K range. The observed variation is similar along the whole series although the maximum intensity and the subsequent quenching of luminescence take place at different temperatures depending on the strontium content. The strong decrease of PL in the investigated compounds follows Arrhenius-type behaviour. A noteworthy result of this work deals with the activation energy and the associated pre-exponential factor, which are both strongly dependent on the strontium content,  $x$ . The activation energy was directly obtained from  $I(T)$  through fits shown in Fig. 1(b). The time-dependence of the PL decay  $I(t)$  as a function of  $x$  at RT is depicted in Fig. 1(c). The corresponding variation with the temperature along the  $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2:\text{Mn}^{2+}$  series is shown in Fig. 1(d). Curves  $\tau^{-1}(T)$  fit to the equation:

$$\tau^{-1} = \tau_0^{-1} + \tau_{\text{ED}}^{-1} \text{Coth}\left(\frac{\hbar\omega_u}{2KT}\right) + p \exp\left(-\frac{E_a}{KT}\right) \quad (1)$$

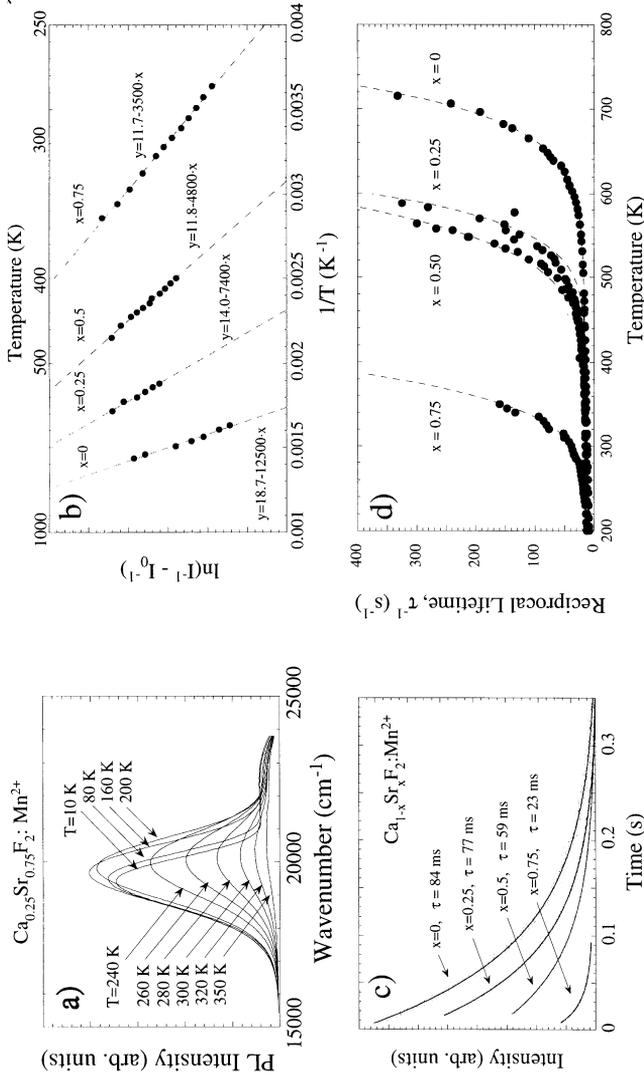


FIGURE 1 a) Variation of the PL spectrum for  $\text{Ca}_{0.25}\text{Sr}_{0.75}\text{F}_2:\text{Mn}^{2+}$  with the temperature. Note the abrupt decrease of intensity above 240 K. b) Analysis of the exponential part of the PL intensity decay in temperature.  $I_0$  is the maximum value of intensity of the  $I(T)$  Curve. c) PL time dependence decays for the  $\text{Mn}^{2+}$ -doped  $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2$  series at room temperature. Excitation wavelength 407 nm. The decays show an exponential behaviour,  $\exp(-t/\tau)$ . d) Experimental  $\tau^{-1}$  data and the corresponding fits to Eq. (1) (see text). The activation energy corresponds to the fit values given in Fig. 2(a).

The three terms represent the temperature-independent transition rate, the electric-dipole vibronic-assisted mechanism and the rate for radiationless processes, respectively [1, 2, 6]. Non radiative deexcitation is described by means of a thermally activated process as  $W_{\text{NR}} = p \cdot \exp(-E_a/KT)$ , where  $E_a$  is the activation energy and  $p$  is the associated rate. Fig. 2(a) shows the values of  $E_a$  obtained by fitting from  $I(T)$  and  $\tau^{-1}(T)$  through Eq. (1). This figure clearly indicates that the decrease of  $I(T)$  and  $\tau^{-1}(T)$  are both associated with thermally activated mechanisms whose activation energy changes with  $x$  as  $E_a(x) = 8200 - 7500x$ . By using  $E_a(x)$ , we obtain pre-exponential factors  $p$  by fitting  $\tau^{-1}(T)$  to Eq. (1). The results are shown in Fig. 1(d) and the corresponding pre-exponential

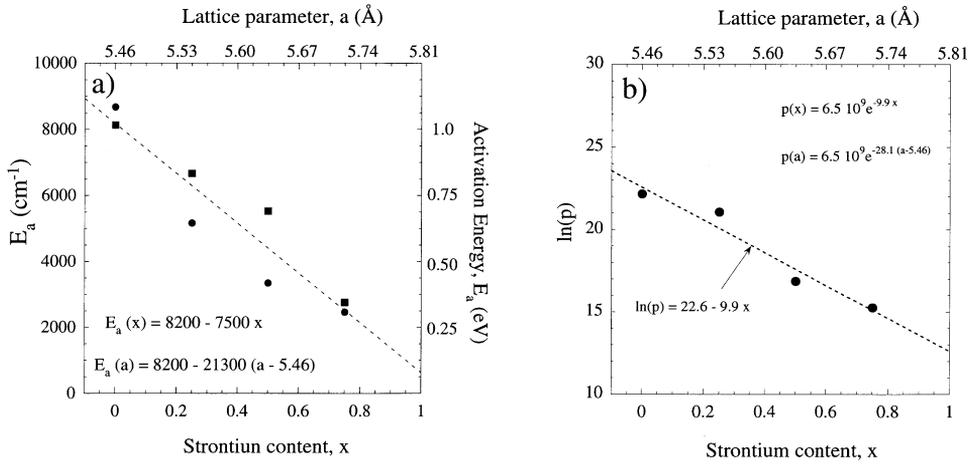


FIGURE 2 a) Variation of the activation energy,  $E_a$  obtained by fitting from the  $I(T)$  and  $\tau^{-1}(T)$  curves of Fig. 1(a) and (b) as a function of the strontium content  $x$ , along the  $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2:\text{Mn}^{2+}$  series. b) Variation of the corresponding pre-exponential factor  $p$  obtained from Fig. 1(d). Note the important reduction of  $p$  with the strontium content.

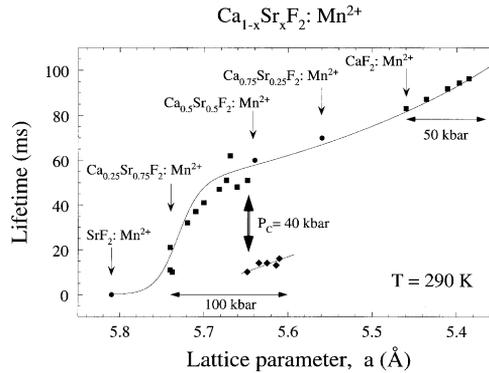


FIGURE 3 PL lifetime values of the  $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2:\text{Mn}^{2+}$  series measured at room temperature as a function of  $x$  (circles) and as a function of pressure for  $\text{Ca}_{0.25}\text{Sr}_{0.75}\text{F}_2:\text{Mn}^{2+}$  and  $\text{CaF}_2$  (squares). The pressure and the strontium content,  $x$ , have been normalized to the lattice parameter through the equation:  $a = 5.46 + 0.352x$  and the corresponding equation of state respectively. The continuous line is the calculated lifetime using Eq. (1) with following parameters:  $\tau_0^{-1} = 2.6 \text{ s}^{-1}$ ,  $\tau_{\text{ED}}^{-1}(P) = 3.5 - 0.012P$  (kbar and  $\text{s}^{-1}$  units),  $p(x) = 6.5 \times 10^9 \cdot e^{-9.9x}$  ( $\text{s}^{-1}$ ) and  $E_a(x) = 8200 - 7500x$  ( $\text{cm}^{-1}$ ).

factors in Fig. 2(b). Interestingly, these findings reveal that  $p$  depends exponentially on  $x$  as  $p(x) = 6.5 \times 10^9 e^{-9.9x}$ . The microscopic origin of the strong variation of  $p$  along the series will be discussed in a forthcoming paper. Figure 3 shows the lifetime data obtained along the series at ambient conditions, and as a function of pressure for  $\text{CaF}_2:\text{Mn}^{2+}$  and  $\text{Ca}_{0.25}\text{Sr}_{0.75}\text{F}_2:\text{Mn}^{2+}$ . In this plot, the values of  $x$  and pressure are re-normalised to the lattice parameter,  $a$ , which is known to vary with  $x$ :  $a = 5.46 + 0.352x$  [2]. The relation between pressure and  $a$  was accomplished through the bulk modulus of each crystal [6, 8, 9].

## 4 DISCUSSION

The results of Fig. 3 clearly point out that the PL quenching and the variation of  $E_a$  along the series, are not directly associated with the different chemical nature of Ca and Sr, but they are related to the crystal volume. Therefore, the radiationless process which is involved in this  $\text{MnF}_8^{6-}$  complex, is governed by changes of the lattice parameter induced by replacing Sr for Ca. The shorter the lattice parameter, the higher activation energy, thus leading to an enhancement of the PL quantum yield.

A salient feature of this work is that the PL intensity  $I(T, P)$  and the corresponding lifetime  $\tau(T, P)$  as a function of either the temperature or the pressure, can be accounted for simply on the basis of Eq. (1). The radiationless mechanism is described by thermally activated process with pre-exponential factor and activation energy depending only on the crystal volume. Aside Fig. 1(d), the curve of Fig. 3 was drawn through Eq. (1) by re-normalising  $x$  and  $P$  to  $a$ .

This conclusion is also supported by findings in impurity-related PL materials. The luminescence quantum yield is enhanced whenever the impurity is introduced into smaller host sites [10]. According to this, the decrease of  $E_a$  with increasing the crystal volume favours radiationless relaxation phenomena.

In conclusion, the variation of PL along the series and upon pressure is related to changes of  $E_a$  that we associate with multiphonon relaxation within the  $\text{MnF}_8^{6-}$  complex. The origin of the exponential dependence of  $p$  with the crystal volume as well as the corresponding variation of  $E_a$  are currently in progress. Jahn-Teller and anharmonic effects in the  ${}^4\text{T}_{1g}$  excited state probably play a crucial role in the observed variations.

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