

MULTIPHONON RADIATIONLESS PHENOMENA IN Mn^{2+} -DOPED $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2$ AND BaF_2 FLUORITES

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This work investigates the surprising disappearance of the Mn^{2+} photoluminescence on passing from $\text{CaF}_2:\text{Mn}^{2+}$ to $\text{SrF}_2:\text{Mn}^{2+}$ or $\text{BaF}_2:\text{Mn}^{2+}$ using pressure spectroscopy. We show that the loss of luminescence in these systems is associated with non-radiative thermally activated processes whose activation energy and pre-exponential rates strongly depend on the crystal volume irrespective of the chemical composition. A salient feature is the PL enhancement observed in the cotunnite high-pressure phase along the series. This enhancement is explained in terms of the large volume reduction at the phase transition, as well as by the presence of low-symmetry crystal fields attained at the cation sites leading to an increase of the radiative transition rate by the electric-dipole mechanism.

Keywords: High-pressure spectroscopy; Photoluminescence; Radiationless process; Mn^{2+} -doped fluorites; Fluorite-Cotunnite phase transition

INTRODUCTION

Multiphonon relaxation plays a key role in the occurrence or absence of luminescence in transition metal complexes formed as impurity in inorganic materials. This study deals with excited-state relaxation phenomena in photoluminescence (PL) compound series of Mn^{2+} -doped fluorites MF_2 (M: Ca, Sr, Ba) leading to radiationless processes. The knowledge of the microscopic origin of these mechanisms is worthwhile in order to establish guidelines to be followed for the improvement of PL materials. The selected crystal series provides an attractive system for this purpose since PL properties experience profound changes along the series [1–3] and by applying pressure [4, 5]. Whereas $\text{CaF}_2:\text{Mn}^{2+}$ exhibits the longest Mn^{2+} green photoluminescence (PL) lifetime ($\tau = 182$ ms) ever measured at low temperature among transition metal ions with quantum yields close to 1 ($\eta \approx 1$) [1–3], the isomorphous $\text{SrF}_2:\text{Mn}^{2+}$ is not luminescent at room temperature (RT): $\tau = 0$, $\eta = 0$. $\text{BaF}_2:\text{Mn}^{2+}$ is an exception to this behaviour since PL associated with isolated MnF_8^{6-} units has never been observed ($\tau = 0$) either at RT or at $T = 10$ K [6].

The aim of this work is to investigate the disappearance of the Mn^{2+} green PL on passing from $\text{CaF}_2:\text{Mn}^{2+}$ to $\text{SrF}_2:\text{Mn}^{2+}$ and $\text{BaF}_2:\text{Mn}^{2+}$. The study follows a previous research focused on the $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2:\text{Mn}^{2+}$ and $\text{CaF}_2:\text{Mn}^{2+}$ crystals [4–6] that we now extend to the

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whole series including $\text{BaF}_2:\text{Mn}^{2+}$. Attention is paid on the effect of the fluorite-to-cotunnite structural phase-transition (PT) at high pressure. Excitation and emission spectra as well as PL lifetime measurements have been done in $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{F}_2:\text{Mn}^{2+}$, $\text{SrF}_2:\text{Mn}^{2+}$ and $\text{BaF}_2:\text{Mn}^{2+}$ as a function of pressure and temperature. This procedure is important to elucidate whether the loss of PL is due to the different nature of the host cation (*i.e.* Ca^{2+} compared to Sr^{2+} or Ba^{2+}), or it is simply related to changes of lattice parameter along the series, independently on the substituted cation ($a[\text{CaF}_2] = 5.46 \text{ \AA}$; $a[\text{SrF}_2] = 5.81 \text{ \AA}$, $a[\text{BaF}_2] = 6.20 \text{ \AA}$). In addition we are interested in revealing whether PL enhancement or non-radiative process is actually favoured in the high-pressure cotunnite phase.

EXPERIMENT

Single crystals of MF_2 (M:Ca, Sr, Ba) doped with Mn^{2+} (1 and 0.5 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 ambient pressure as a function of the temperature were done with the experimental setup described elsewhere [5]. Hydrostatic pressure experiments were performed with a Diamond Anvil Cell (High Pressure Diamond Optics, Inc.). A mixture methanol-ethanol-water 16:3:1 was used as pressure transmitter. We employed a special microscope setup for measuring the PL lifetime and the corresponding spectrum under pressure. A Jobin-Yvon HR-320 monochromator and a Ramanor U-1000 double monochromator were used for pressure experiments. The pressure was calibrated from Ruby.

RESULTS AND DISCUSSION

Figure 1 shows the excitation and PL spectra of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{F}_2:\text{Mn}^{2+}$ at ambient conditions and as a function of pressure. The spectra are very similar to those observed along the $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2:\text{Mn}^{2+}$ series with the exception of $x > 0.75$ and $\text{BaF}_2:\text{Mn}^{2+}$ which do not show any PL at ambient pressure. The small PL blueshift induced by pressure agrees with findings along the series. The variation of the PL energy with x , or the lattice parameter, a is $E_{\text{em}}(x) = 2.51 + 0.047x$, or $E_{\text{em}}(a) = 1.78 + 0.13a$ (in \AA and eV units). The PL lifetime increases with pressure according to the general behaviour found for the series on the basis of the equation [5]:

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

The three terms on the right side represent the transition rates due to temperature-independent mechanisms, electric-dipole vibronic-assisted transitions (ω_u is the vibrational frequency) and for radiationless processes, respectively [1, 2, 5]. The non-radiative rate 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 which depends on the lattice parameter (or pressure) like $E_a = 1.02 - 0.93a$ and $p(\text{s}^{-1}) = 6 \times 10^9 e^{-28.1(a-5.46)}$ [5]. The pressure dependence of the vibronic term as $\tau_{\text{ED}}^{-1}(\text{s}^{-1}) = 3.5 - 0.016P$ mainly accounts for the pressure variation of the lifetime of Figure 1. However there is an abrupt decrease of τ at $P = 52 \text{ kbar}$ upon increasing pressure which corresponds to the fluorite-to-cotunnite PT [7, 8]. A similar but opposite variation is observed upon releasing pressure at 22 kbar, thus indicating a pressure hysteresis of 30 kbar. Interestingly, the lifetime decrease that is observed in the cotunnite

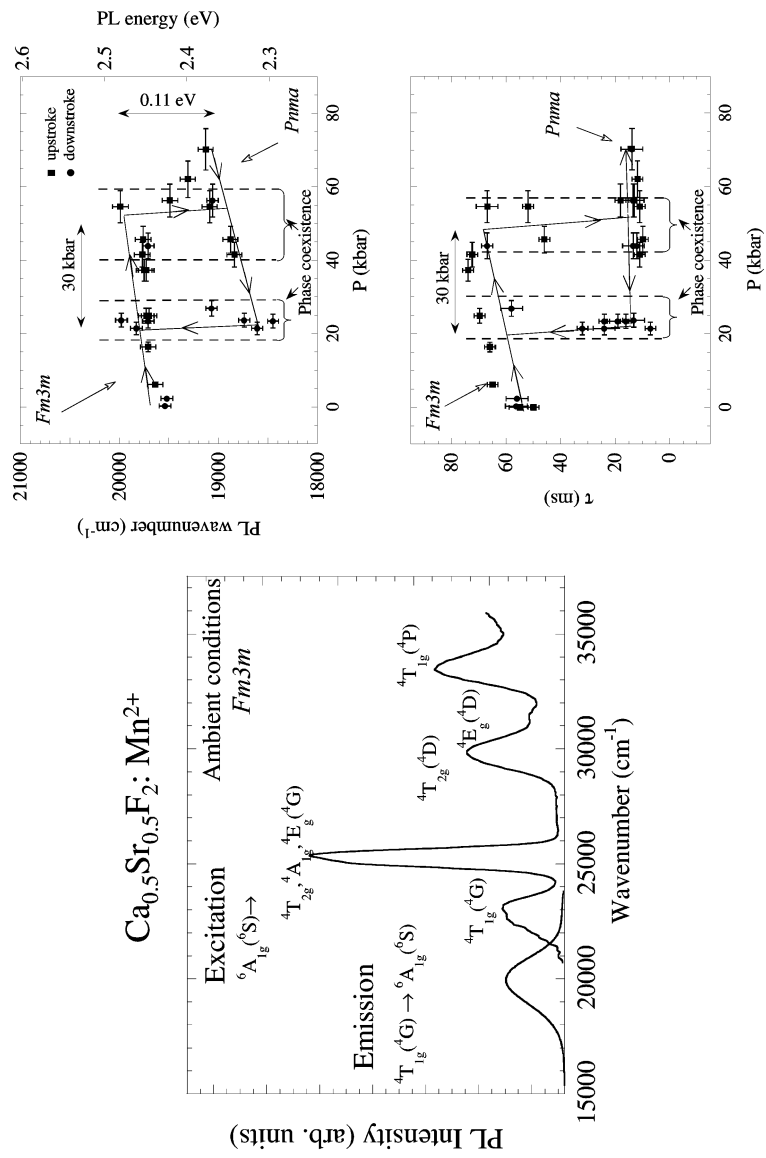


FIGURE 1 Excitation and PL spectra of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{F}_2:\text{Mn}^{2+}$ at ambient conditions (left). The variations of the PL transition energy and the lifetime as a function of pressure are plotted on the right.

phase, is in no way associated with an increase of radiationless phenomena given that the PL intensity increases with pressure in this phase. The loss of inversion centre in the MnF_8^{6-} complex in fluorite with respect to the non-centrosymmetric low-symmetry of Mn^{2+} in the nine-fold coordination site in the cotunnite can explain this feature. Thus the lifetime

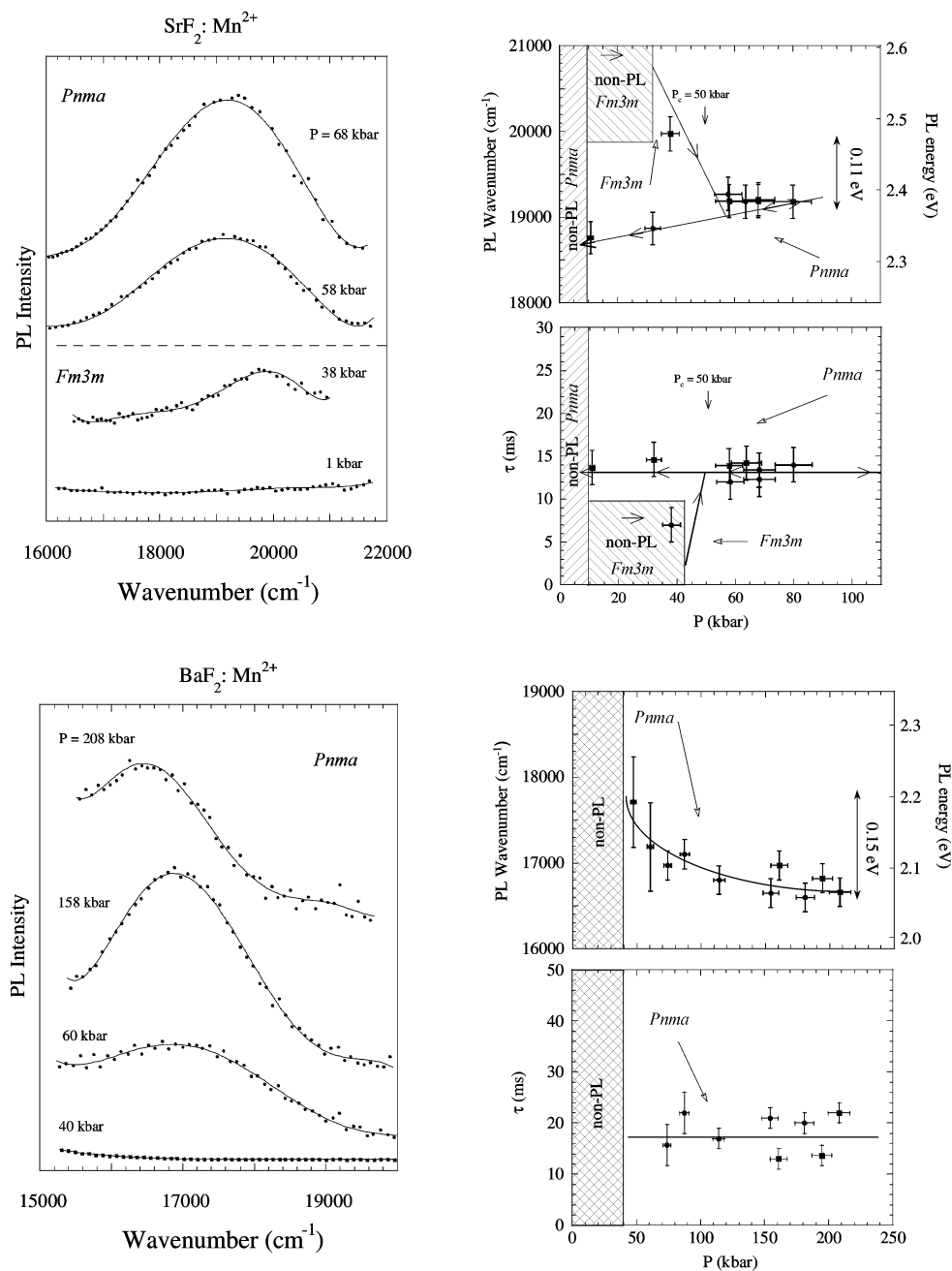


FIGURE 2 Variation of the PL spectra and the corresponding transition energy and lifetime for $\text{SrF}_2:\text{Mn}^{2+}$ (top) and $\text{BaF}_2:\text{Mn}^{2+}$ (bottom) as a function of the pressure. The shadowed areas indicate the pressure range where no PL was detected. Solid lines are guides for the eye.

decrease at the PT is mainly ascribed to the enhancement of τ_0^{-1} by non-centrosymmetric crystal-field.

On regarding the behaviour of $\text{SrF}_2:\text{Mn}^{2+}$ and $\text{BaF}_2:\text{Mn}^{2+}$ two main questions arise. (1) Could pressure induce PL in these non-PL systems? and (2) does the cotunnite phase enhance PL? The latter question suggests that non-radiative multiphonon relaxation can be reduced in the high-pressure phase and would provide new ways for obtaining more efficient PL materials.

Figure 2 shows the PL measurements performed on $\text{SrF}_2:\text{Mn}^{2+}$ and $\text{BaF}_2:\text{Mn}^{2+}$ as a function of pressure. It is noteworthy that pressure induces PL in both systems. PL can be efficiently detected upon compression above 40 and 100 kbar, respectively. In $\text{BaF}_2:\text{Mn}^{2+}$, the PL pressure range corresponds to the cotunnite phase whose transition pressure is 18 kbar [9, 10]. The measured lifetime of 16 ms and Raman spectroscopy confirm the occurrence of this phase. However, in $\text{SrF}_2:\text{Mn}^{2+}$ PL can be induced by pressure in the fluorite phase (Fig. 2). The change to the cotunnite is evidenced by the lifetime increase from 7 to 12 ms at 38 kbar and the abrupt energy redshift of 0.11 eV (900 cm^{-1}).

Note that in contrast to the fluorite phase, the PL of $\text{BaF}_2:\text{Mn}^{2+}$ shifts to lower energies 0.15 eV (1200 cm^{-1}) from 48 to 208 kbar pressure in the cotunnite phase. This pressure-induced redshift as well as the redshift jump at the transition pressure in $\text{SrF}_2:\text{Mn}^{2+}$ is likely due to the low-symmetry crystal-field at the Ba or Sr site in the cotunnite phase. The PT splits the first ${}^4\text{T}_{1g}$ state of Mn^{2+} leading to an additional PL redshift associated with the low-lying PL state component.

Figure 3 summarises the results obtained for the whole series. The continuous curves have been calculated through Eq. (1) using values of $\tau_0^{-1} = 2.6\text{ s}^{-1}$ and $\tau_{\text{ED}}^{-1} = 3.5 - 0.016P$ (in units of s^{-1} for P in kbar) for the fluorite phase and $\tau_0^{-1} = 77.5\text{ s}^{-1}$ with $\tau_0^{-1} \gg \tau_{\text{ED}}^{-1}$ for the cotunnite phase. Note that we use the same non-radiative term in both structures. Interestingly, these results 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 related to the crystal volume. Therefore, radiationless processes involved in MnF_8^{6-} are mainly governed by changes of the lattice parameter induced upon replacing Sr for

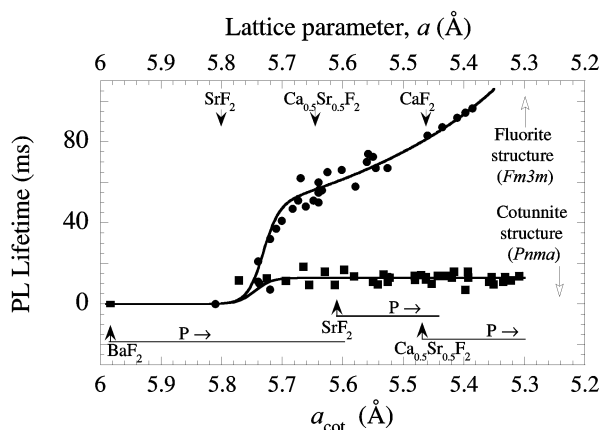


FIGURE 3 Variation of the PL lifetime with the lattice parameter for the whole series, and calculated lifetime for the fluorite and cotunnite phases using Eq. (1) (see text). Experimental data from pressure experiments were renormalised to the lattice parameter through the corresponding equations of state [12, 13]. Parameters a and a_{cot} represent the cubic lattice parameter and the effective lattice parameter in the cotunnite phase, defined as $a_{\text{cot}} = V_{\text{eff}}^{1/3} = (1/2 a \cdot b \cdot c)^{1/3}$ where a , b and c are the orthorhombic lattice parameters. Experimental points: circles and squares correspond to the fluorite and cotunnite structure, respectively.

Ca. The shorter the lattice parameter, the higher the activation energy, thus leading to enhancement of PL quantum yield.

As a salient feature we show that the PL intensity $I(T, P)$ and 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). Furthermore, the radiationless rate is described by thermally activated processes with pre-exponential factor and activation energy depending only on the crystal volume using the *same parameters* in both phases. This noteworthy result suggests that the non-radiative processes rely on the crystal volume irrespective of the local structure around the Mn^{2+} impurity. It confirms a general empirical finding in impurity-related PL materials stating the smaller the host site, the more PL material [11].

In conclusion, PL efficiency along the series as a function of pressure and temperature is mainly related to changes of the multiphonon relaxation rate within the Mn complex through p and E_a independent of the fluorite or cotunnite phase. The PT mainly affects the radiative electric-dipole transition rate, τ_0^{-1} , due to low-symmetry crystal-fields at the impurity site. The volume reduction involved in the fluorite-to-cotunnite PT favours PL recovering even in non-PL materials like $\text{SrF}_2:\text{Mn}^{2+}$ and $\text{BaF}_2:\text{Mn}^{2+}$. This PT can be an attractive way for improving PL. Further work along this line is currently under investigation.

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