# Pressure-induced photoluminescence in $MnF_2$ at Room Temperature.

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## Summary

This work investigates the photoluminescence (PL) processes in $MnF_2$ as a function of pressure and temperature. The aim is to understand the competition between radiative and non-radiative processes yielding PL quenching at room temperature, and how to modify them by applying pressure or reducing the $MnF_2$ particle size. As salient feature, we have transformed non-PL $MnF_2$ into PL at room temperature above 14.7 GPa. The two observed PL bands at 2.34 and 1.87 eV are assigned to $Mn^{2+}$ emissions in the cotunnite high-pressure phase. Their pressure shift and lifetime suggest that PL takes place from two $Mn^{2+}$ sites of different symmetry. The high-pressure structure seems to reduce the exciton transfer thus favouring trap PL. The microscopic origin of the two pressure-induced emissions is analysed.

## Introduction

PL and non-radiative processes yielding PL quenching in $Mn^{2+}$-doped fluorite crystals ($Ca_{1-x}Sr_xF_2$) mainly depend on the host site volume. The smaller the volume, the higher the PL efficiency (Rodriguez, 2003). Following this idea, we were able to induce PL at room temperature (RT) in the non-PL $Mn^{2+}$-doped $SrF_2$ and $BaF_2$ by applying pressure (Hernández, 2003). Furthermore we demonstrated the general trend observed in impurity-related PL in materials by which PL is favoured in smaller host sites.

On the other hand, the PL mechanism is quite different in concentrated materials such as $MnF_2$ (rutile-type structure) whose PL for $T > 10$ K is dominated by $Mn^{2+}$-perturbed sites (traps) after excitation migration. In this system, PL occurs only at low temperatures given that is quenched for $T > 120$ K (Holloway, 1963). Increase of quenching temperature can be achieved either decreasing the Mn-Mn transfer probability or reducing the concentration of non-PL impurities to which the $Mn^{2+}$-excitation is transferred (Rodríguez, 1985; Henderson, 1989). In the former case, structural changes leading to modifications of local structure, superexchange pathway or non-equivalent $Mn^{2+}$ neighbours can modify the transfer probability thus enhancing the intrinsic $Mn^{2+}$ PL. The suppression of non-PL impurities from $MnF_2$ can also increase the quenching temperature even though exciton migration occurs.

In this work we investigate whether structural changes in $MnF_2$ induced by pressure or suppression of non-PL impurities through $MnF_2$ nanoparticles can efficiently enhance PL processes. In particular, we explore the possibilities to get room-temperature PL in $MnF_2$ following the two proposed strategies. Throughout this work we demonstrate that non-PL $MnF_2$ can be transformed into PL $MnF_2$ by pressure. This new pressure-induced phenomenon correlates with the corresponding structural transition sequence from rutile to cotunnite undergone by $MnF_2$ with pressure (Tonkov, 1992) as it is illustrated in Fig. 1.

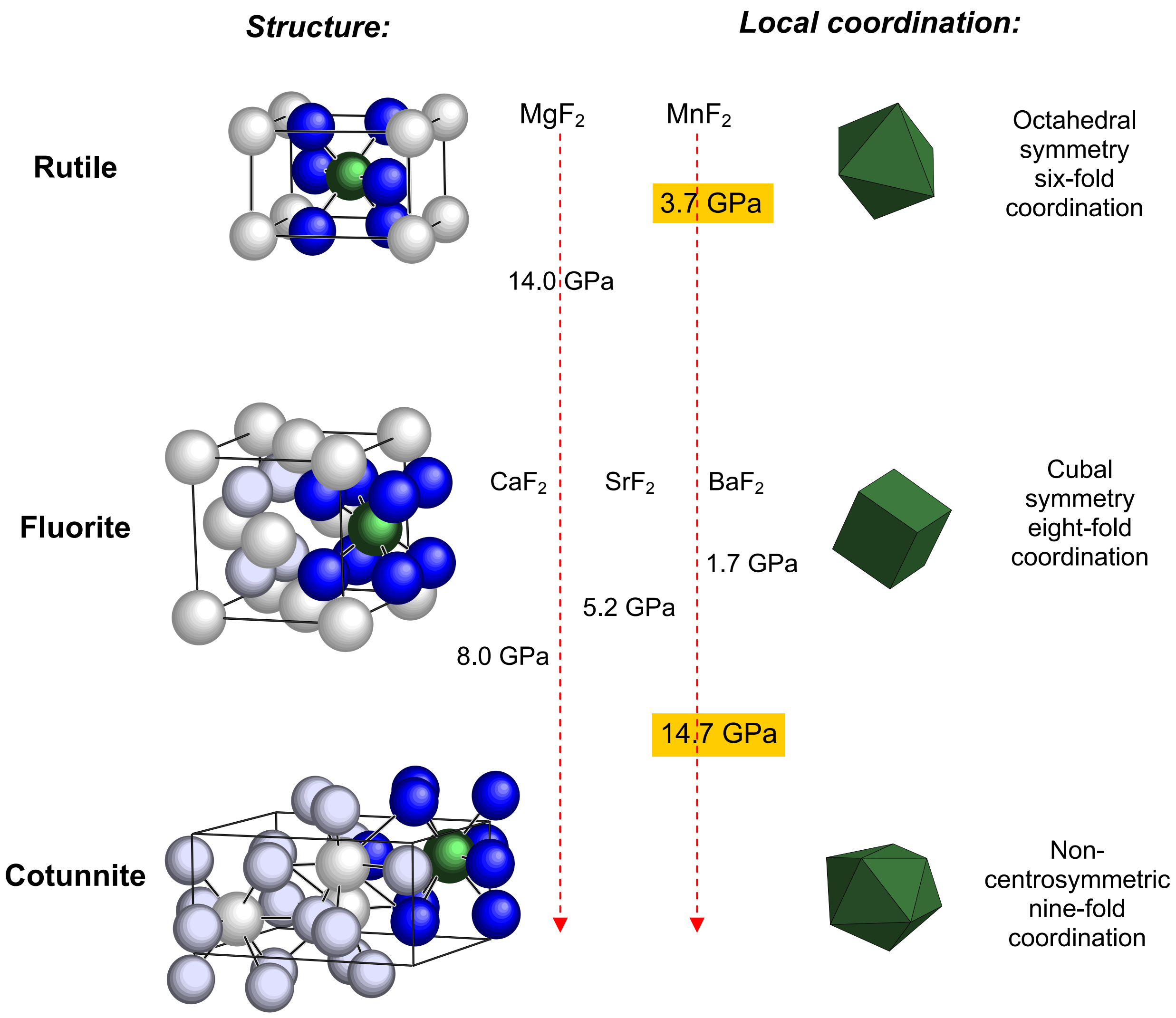

**FIGURE 1**. Evolution of the $MF_2$ crystal structure with pressure. The phase-transition pressure is indicated for different compounds (M = Mn, Ca, Sr, Ba) having fluorite-, rutile- or cotunnite-type structure at room temperature. The structural transformations involve changes of symmetry and coordination number around the cation $M^{2+}$ upon increasing pressure.

## Experimental Method

$MnF_2$ crystals 99% (Alfa Aesar) were used for pressure spectroscopy and as starting materials to transform in nanoparticles and $MnF_2$ single crystal samples were grown by Bridgman technique as described elsewhere (Rodríguez, 1985). $MnF_2$ nanoparticles were obtained from the bulk by milling using a Retsch PM 400/2 planetary balls mill with tungsten carbide spheres ($m_{spheres}/m_{sample}$ = 10). This method provided different $MnF_2$ particle sizes ranging from 1000 to aprox. 7 nm depending on the milling time; 7 nm particles were obtained for 175 milling hours. The crystal structure was checked by X-ray diffraction and the particle size was determined from the Bragg peak broadening through the Scherrer relation (Cullity, 1978)

Optical absorption (OA) and PL spectra as well as lifetime measurements at ambient pressure were obtained using a Perkin-Elmer Lambda 9 spectrophotometer, a ISA Fluoromax-2 fluorometer and a Chromex 500IS monochromator with a Tektronix

2430A oscilloscope, respectively. For lifetime measurements, the $Mn^{2+}$ was excited with the 407 nm line of a Coherent I-302-K Krypton ion laser, which was modulated by a Newport 35085-3 acousto-optic modulator. Time resolved emission spectra in the 407-700 nm were obtained using a Vibrant B 355 II OPO laser. Experiments in the 10-300 K range were accomplished through a Scientific Instruments 202 closed-circuit cryostat and an APD-K controller. Hydrostatic pressure experiments were performed in a Diamond Anvil Cell (DAC; High Pressure Diamond Optics, Inc.). A mixture ethanol-methanol-water 16:3:1 was used as pressure transmitter and the pressure was calibrated through the Ruby PL. The OA of $MnF_2$ nanoparticles at ambient pressure consists the characteristic crystal-field peaks of $Mn^{2+}$ in an octahedral environment of $F^-$ : $MnF_6^{4-}$ unit (Rodríguez, 1986) on an important Raleigh background. PL spectroscopy was accomplished by excitation into the $^4A_{1g}$, $^4E_g$ excited state of $Mn^{2+}$ ($O_h$) located at 400 nm. Due to the extremely low PL quantum yield and lifetime of several crystals of the series, we employed a high-sensitivity PL setup for measuring the PL lifetime and time resolved spectroscopy under pressure (Hernández, 2003).

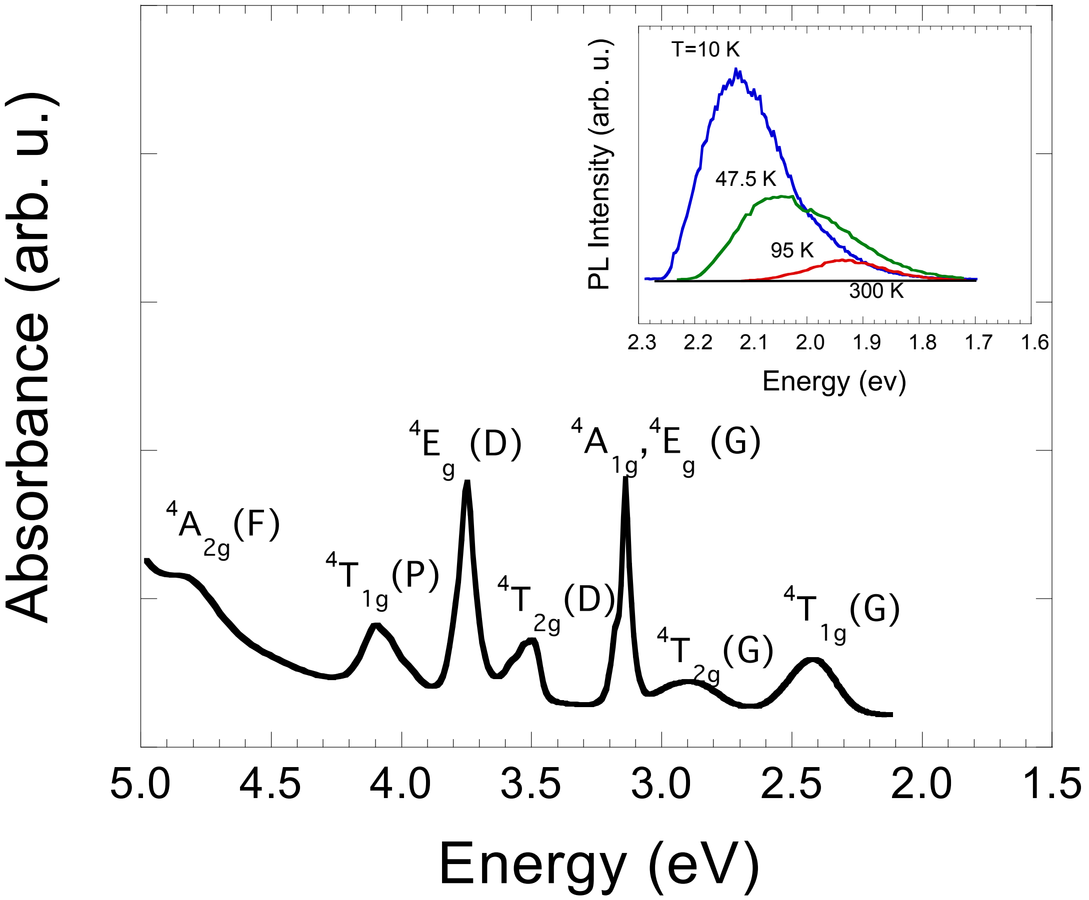

**FIGURE 2**. Optical Absorption spectrum of $MnF_2$ single crystal and corresponding PL emission of its powder as a function of temperature. The peak assignment on the basis of a $MnF_6^{4-}$ unit of $O_h$ symmetry is indicated. Note that above 120 K the PL disappears by exciton transfer to non-PL impurities.

## Results and Discussion

Fig. 2 shows the OA spectrum of single crystals of $MnF_2$ at ambient conditions, and the corresponding PL at different temperatures. The peak assignment corresponds to crystal-field transitions from the electronic ground state, $^6A_{1g}$, to different spin-quartet excited states, $^4\Gamma$, within the $O_h$ $MnF_6^{4-}$ structural unit. The $MnF_2$ PL is associated with the $^4T_{1g} \rightarrow {}^6A_{1g}$ transition and is induced under excitation into any OA peak although PL only occurs at low temperatures (T < 120 K). The PL band shifts toward lower energies with increasing temperature due to the thermal activation of deeper $Mn^{2+}$ traps. Note that the PL intensity decreases progressively from low temperature and disappears completely for T > 120 K as illustrated in Fig. 3. The PL decrease correlates with the lifetime decrease associated with an increase of the transfer rate from the $Mn^{2+}$ exciton to unavoidable non-radiative impurities. The temperature variation of the lifetime is well described by the equation (Di Bartolo, 1968; Hernández, 2003):

$$\tau^{-1} = \tau_0^{-1} + \tau_{ED}^{-1} Coth \frac{\hbar\omega}{2KT} + p_0 e^{\frac{-E_a}{KT}} \qquad (1)$$

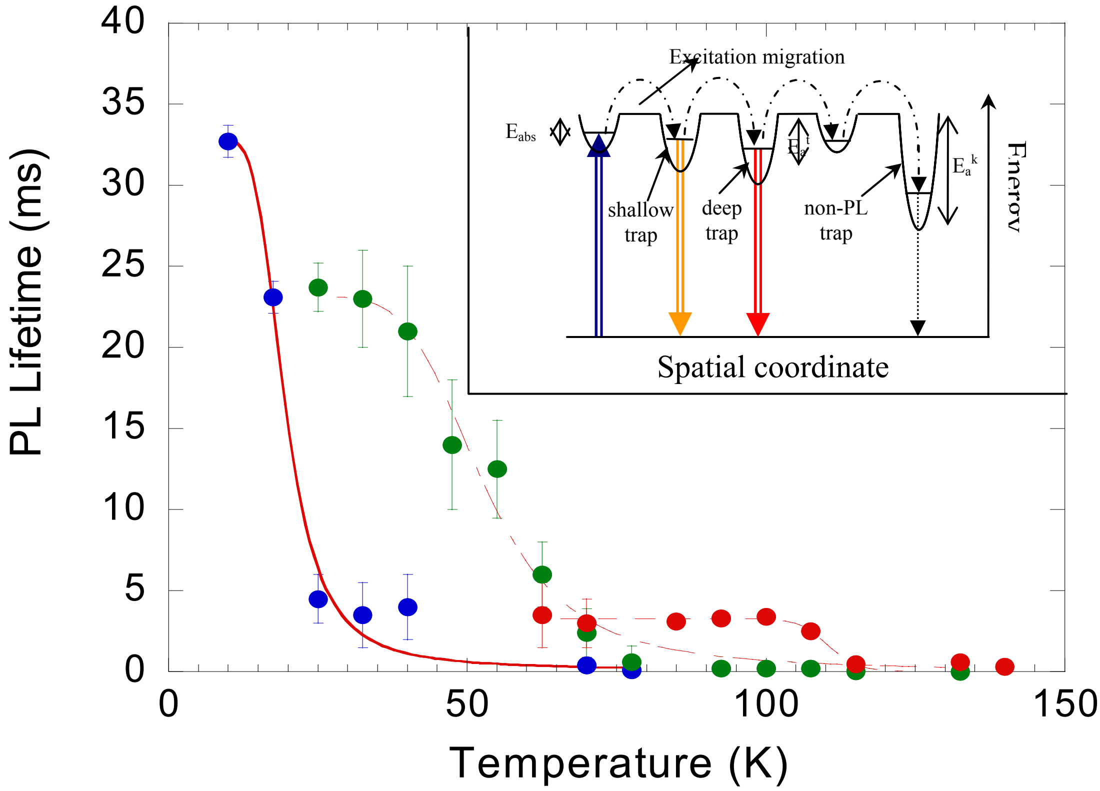

**FIGURE 3**. Variation of the PL lifetime of $MnF_2$ with temperature. The curves correspond to the fit of experimental data to Eq. (1). The fit parameters are $\tau_0^{-1}$ = 0.03, 0.43 and 0.30 $s^{-1}$, $p_0$ = 0.02, 0.06 and $2\text{x}10^6$ $s^{-1}$ and $E_a$ =0.0015, 0.033 and 0.215 eV, respectively (see text). The energy level scheme illustrates the exciton migration and its localization in excitation traps and non-PL impurities.

where $\tau^{-1}$ is the PL lifetime, $\tau_0^{-1}$, the $^4T_{1g} \rightarrow {}^6A_{1g}$ radiative transition probability due to non-centrosymmetric static distortions of the crystal field and exchange interactions between Mn neighbours, $\tau_{ED}^{-1}$, the transition probability by the electric-dipole vibronic mechanism, $\omega$ is the frequency of the assisting phonon, $p_0$ is the pre-exponential factor of the thermally activated non-radiative process and $E_a$ is the corresponding activation energy. Although the nature of non-PL impurities responsible for the PL quenching still remains unknown, the presence of small traces of $Mn^{3+}$ (< 1 ppm) could partially account for the PL loss at RT in $MnF_2$. This proposition is based i) on the non-PL nature of $Mn^{3+}$ in fluorides at RT, at variance with $Mn^{2+}$ which shows an PL quantum yield close to 1 (Rodriguez, 1991; Aguado, 2002). ii) The absorption spectrum of $MnF_6^{3-}$ obtained either in $NaMnF_4$ or $Na_2MnF_5$ or other isomorphous fluorides fully overlaps with the relaxed excited state, $^4T_{1g}$, of $Mn^{2+}$ thus achieving requirements for energy transfer from $Mn^{2+}$ to non-PL $Mn^{3+}$ (Rodriguez, 1994; Aguado, 2002). Although the presence of $Mn^{3+}$ in $MnF_2$ was not detected by OA, what limits $Mn^{3+}$ concentration to a maximum of 10 ppm, its presence cannot be ruled out as an effective charge compensator for unavoidable $O^{2-}$ impurities.

Different PL traps have been observed in $MnF_2$ using high-resolution spectroscopy (doping) (Greene 1968; Wilson, 1979) and time dependent studies (Tsuboi, 1991). Shallow traps mainly correspond to perturbed by neighbouring $Zn^{2+}$, $Mg^{2+}$ and $Ca^{2+}$ impurities whose activation energies are 0.008, 0.010, and 0.037 eV, respectively $Mn^{2+}$ ions. These traps account for the broad PL band peaking at 2.25 and 2.14 eV (550 and 580 nm) whereas thermal-shifted band at 2.05 (605 nm) was identified to an oxygen perturbed $Mn^{2+}$ with an activation energy of 0.15 eV (Rodríguez, 1985). These traps were the ultimate PL $Mn^{2+}$ centres prior to thermal quenching above 120 K.

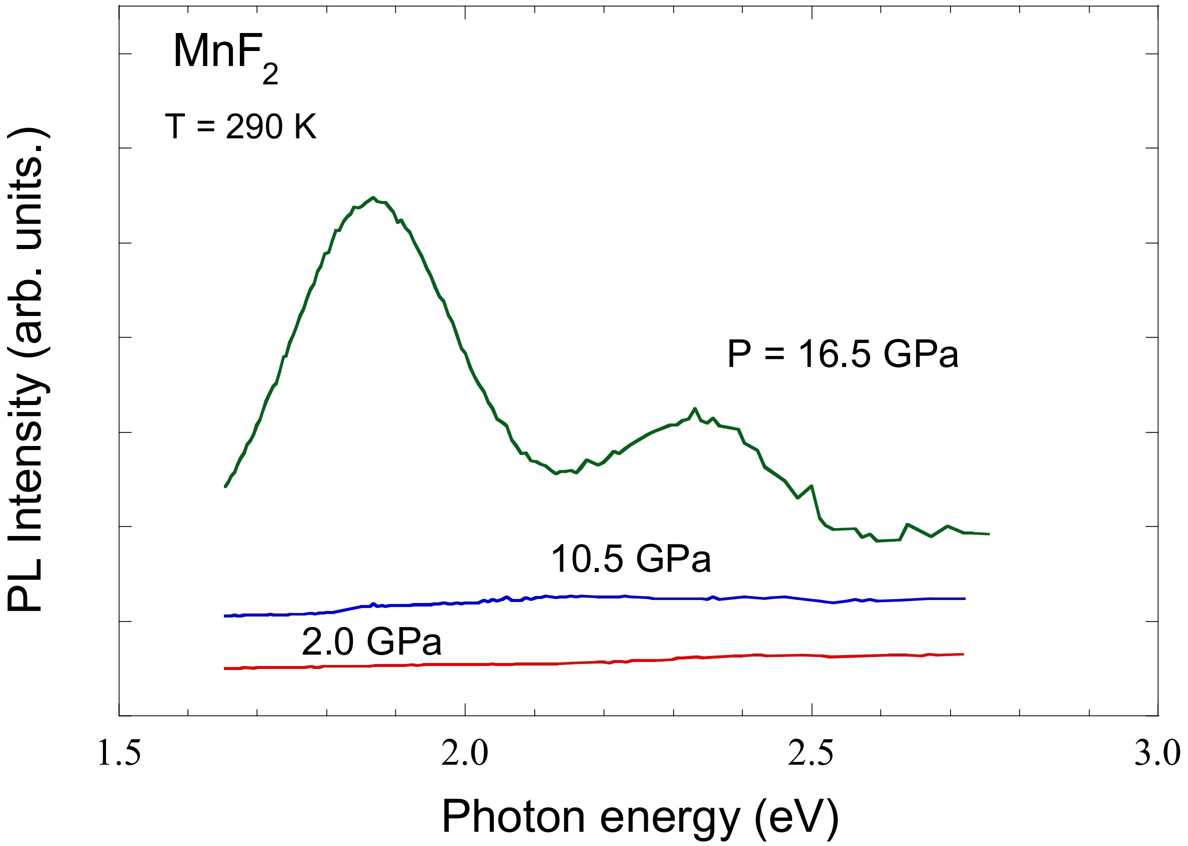

**FIGURE 4**. Variation of the PL spectrum of $MnF_2$ as a function of pressure at room temperature. Note the rising of PL above 14.7 GPa. The crystal is in the fluorite-type structure in the 3.7 – 14.7 GPa range and in cotunnite-type from 14.7 GPa.

The time-dependence thermal study shown in Fig. 3 for powder indicate that PL can be described in terms of three different decays. The corresponding $\tau(T)$ curves follow Eq. (1). The measured activation energy for each component is 0.0015, 0.033 and 0.215 eV, respectively. Note that the first two values resemble the activation energies associated with shallow traps and are responsible for the broad band PL at low temperatures. However we observe a deep trap which still luminesces above 150 K and is responsible for the PL band at 1.97 (630 nm). This PL has been also detected (Flaherty, 1973) but its nature still remains unknown. The measured activation energy, $E_a$ = 0.30 eV coincides with the band shift experienced by the PL in the 10 - 150 K range. The origin of this PL as due to oxygen-perturbed Mn traps is currently under investigation.

Figure 4 shows the emission spectrum of $MnF_2$ as a function of pressure at RT. Note that PL appears for P > 14.7 GPa. The spectrum consists of two emission bands peaking at 2.34 and 1.87 eV which are likely associated with differently perturbed $Mn^{2+}$ sites (i.e. shallow and deep traps, respectively), according to level scheme for transfer given in the inset. This assignment is based on the PL lifetimes measured for both bands of 0.16 and 1.18 ms, respectively.

Shallower $Mn^{2+}$ traps have smaller activation energies for energy transfer than deep traps, i.e. 0.0015 and 0.033 eV versus 0.215 eV for bands in bulk $MnF_2$ at ambient pressure, respectively. Therefore, a shorter PL lifetime is expected for the 2.34 eV emission band at 15 GPa. The PL time dependence, I(t), and the corresponding pressure shifts are shown in Fig. 5. The redshift of about 0.1 eV from 15 to 25 GPa

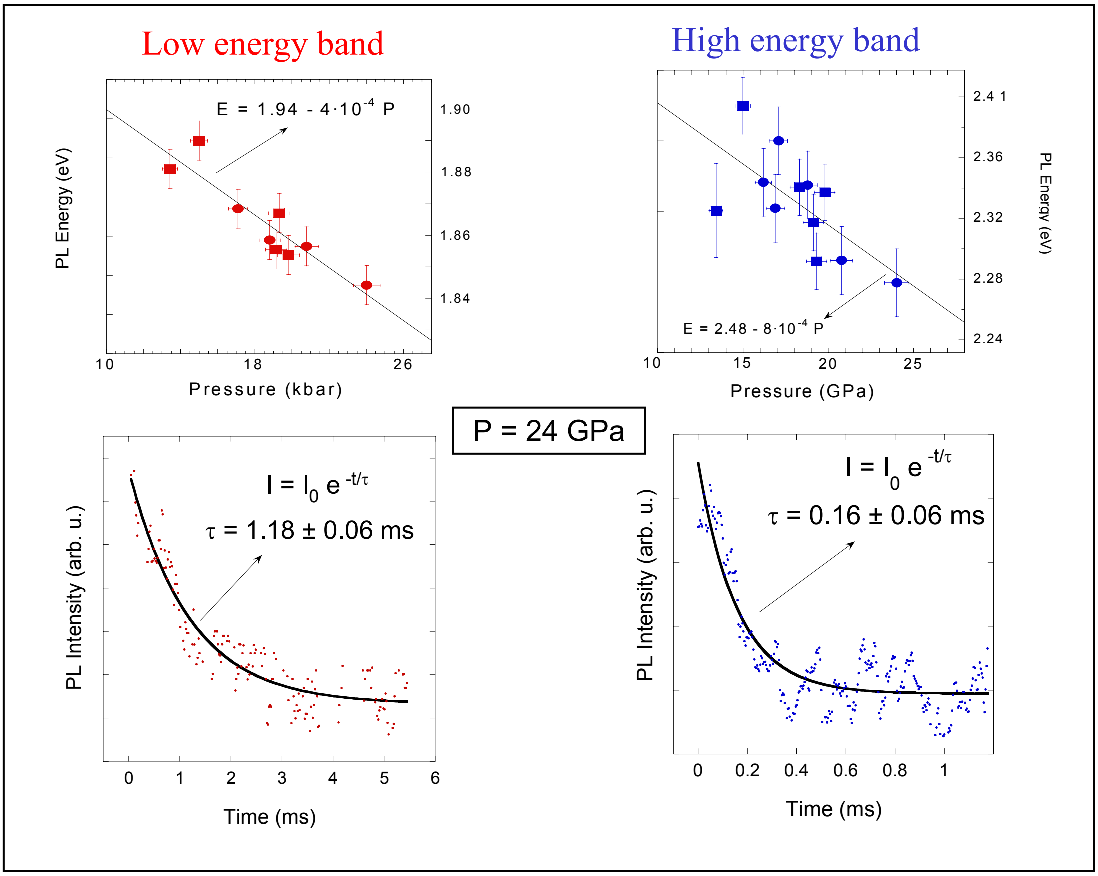

**FIGURE 5**. Variation of the emission band energy with pressure for the two PL bands at room temperature. The PL time dependence of each band at 24 GPa is shown below. The PL follows an exponential behaviour with associated lifetimes of 1.18 and 0.16 ms for the low- and high-energy bands, respectively.

found for the two PL bands agrees with expectations for $Mn^{2+}$ on the basis of an increase of the crystal-field, 10Dq, by pressure. On the assumption that 10Dq depends on volume as

$$10Dq = K\ V^{-5/3} \qquad (2)$$

according to crystal-field theory and experiments (Zahner, 1961; Drickamer, 1973; Rodriguez, 1986; Moreno, 1992), and given that the first $^4T_{1g}$ excited state depends on 10Dq as $E(^4T_{1g}) \approx A - 10Dq$, (Sugano, 1970) then the expected shift $\Delta E \approx -\Delta 10Dq$, would be of 0.1 eV using a Murnaghan equation of state of $MnF_2$ with $B_0 = 94$ GPa, and $B' = 4$ (Knittle, 1995), and 10Dq = 1 eV. Actually, 10Dq = 0.93 eV at RT for octahedral $MnF_6^{4-}$ (Rodríguez, 1986), and 10Dq = 0.50 eV for cubal $MnF_8^{6-}$ in $CaF_2$ (Hernández, 2003), thus 10Dq would increase to 1.13 and 0.6 eV at 15 GPa following Eq. 2 and the EOS of $MnF_2$ and $CaF_2$, respectively (Knittle, 1995; Ross, 1993). Therefore the PL pressure shifts are characteristic of $Mn^{2+}$ in either coordination. It must be pointed out that pressure-induced PL occurs in a range of pressures where the $MnF_2$ is no longer rutile but cotunnite ($P > 14.7$ GPa). It means that PL cannot be associated to $MnF_6^{4-}$ units in hexahedral coordination but $MnF_9^{7-}$ according to the scheme of Fig. 1. The high energy PL band peaking at 2.34 eV (green emission) confirms this point. Actually, eightfold cubal coordination and fourfold tetrahedral coordination $Mn^{2+}$ halides are known to exhibit a green PL due to the smaller crystal-field values (10Dq ~ 0.5 - 0.6 eV) attained for such coordinations in comparison to sixfold octahedral coordination (Lever, 1984). Besides green emission, another red PL at 1.87 eV (660 nm)is also observed, which is probably associated with deeper traps.

The associated lifetime of 1.18 ms is about an order of magnitude longer than the green PL lifetime thus suggesting the presence of another non-equivalent $Mn^{2+}$ site in the high pressure phase. The values of the PL energy and lifetime likely indicate that $Mn^{2+}$ emission takes place at low symmetry sites and transfer from the high-energy site is involved. A similar phenomenon has also been observed in $Mn^{2+}$-doped $CaF_2$ and $SrF_2$, whose PL in the high pressure cotunnite phase revealed an increase of the radiative transition rate due to non-centrosymmetric distortions of the crystal field (Hernández, 2003). The presence of such low symmetry distortions shortens the radiative lifetime. In addition the non-cubic crystal field splits the cubic $^4T_{1g}$ emitting state into two states of E + A symmetry in the case of an axial distortion. Depending on the axial crystal-field strength, the low lying emitting state may be depressed with respect to the cubic $^4T_{1g}$ state shifting the PL emission to lower energies.

Preliminary experiments carried out in $MnF_2$ nanoparticles indicate interestingly that reduction of the $MnF_2$ volume to particle sizes of 10-20 nm enhances the $Mn^{2+}$ PL at 1.97 (630 nm) at expenses of the PL at 2.14 (580 nm). We have observed an increase of water molecule concentration with particle size reduction in the investigated samples as inferred from FTIR spectroscopy.

## Conclusions

The present results reveal that pressure is an efficient tool to reduce the exciton migration in $MnF_2$ thus increasing PL efficiency. Actually we observed $Mn^{2+}$ PL at room temperature in $MnF_2$ above 14.7 GPa (cotunnite phase). We have found two PL bands at 2.34 and 1.87 eV, both corresponding to $Mn^{2+}$ at low symmetry sites of ninefold coordination geometries and probably associated with $Mn^{2+}$ traps observed at ambient pressure and low temperatures. The two bands redshift with pressure according to expectations on the basis of the crystal-field dependence of the $^4T_{1g}$ emitting state of $Mn^{2+}$. At this stage we have not observed PL at ambient conditions after pressure release since $MnF_2$ recovers the non-PL rutile phase for $P < 13$ GPa. In fact, we can infer that the process of exciton migration and transfer to non-PL traps is recovered in the $\alpha$-$PbO_2$ (Tonkov, 1992) phase in downstroke. Interestingly, the present findings open new ways of achieving PL based on concentrated materials containing transition metal ions, particularly, in those cases where phase transformations show large hysteresis.

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