Pressure-induced photoluminescence in MnF$_2$ at Room Temperature.

I. Hernández, University of Cantabria, DCITIMAC, Facultad de Ciencias, University of Cantabria, Santander, Spain, hernandi@unican.es
F. Rodríguez*, University of Cantabria, DCITIMAC, Facultad de Ciencias, University of Cantabria, Santander, Spain, rodriguf@unican.es
H. D. Hochheimer, Department. of Physics, Colorado State University, Fort Collins, CO 80523, USA, dieter@lamar.colostate.edu

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$_x$F$_2$) 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 (Rodriguez, 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.
**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 ($m_{\text{spheres}}/m_{\text{sample}} = 10$). 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 $^{4}A_{1g}$, $^{4}E_g$ 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):

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{\hbar \omega}{2kT} \coth \left( \frac{kT}{\hbar \omega} \right) + p_0 e^{-\frac{E_a}{kT}}$$  \hspace{1cm} (1)

\[\text{FIGURE 3.} \] 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 $2 \times 10^8$ 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, $\hbar \omega$ 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$_2$MnF$_5$ 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.](image-url)
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

$$10Dq = KV^{5/3}$$  \hspace{1cm} (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 $E(^4T_{1g}) = A - 10Dq$, (Sugano, 1970) then the expected shift $\Delta E = - \Delta 10Dq$, 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$_6^{4-}$ (Rodriguez, 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 cubical coordination and fourfold tetrahedral coordination Mn$^{2+}$ halides are known to exhibit a green PL due to the smaller crystal-field values ($10Dq \approx 0.5 - 0.6$ 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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References


