Role of high pressure for understanding luminescent phenomena

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High-pressure techniques make possible to investigate the changes in the electronic properties induced by modifications of the local or crystal structure of the material without changing the chemical composition. The different sensitivity of excited states to crystal-field strength enables energy tuning of the states, which are eventually responsible for the optical properties. It is possible to induce resonance between levels producing exotic effects like upconversion as well as excited state crossover or high-spin to low-spin transitions. Herein, we present selected examples of high-pressure effect for understanding luminescent phenomena or even inducing new ones.

1. Introduction

Spectroscopy deals with the correlation between crystal and local structure, electronic structure and optical properties, upon variation of thermodynamic variables like temperature, pressure, magnetic and electric fields or all at the same time. The advance of high-pressure techniques in spectroscopy labs is related with the design of the diamond anvil cell (DAC). Diamonds present a broad transparency range allowing experiments in an ample wavelength range from short x-ray at synchrotron facilities to far infrared spectroscopy at home labs.

High-pressure allows us to study the effect of volume changes (about 10%) without modification of the chemical composition. So, it is possible to explore pressure effects on different material properties: it induces energy level shifts, structural modifications (local or bulk) or phase transitions and their consequences on electronic properties, changes of color (piezochromism), high-spin to low-spin transitions, and excited state crossover. Making use of the different sensitivities of the state to crystal field strength (electron-ion coupling), the application of an external pressure provides the way to tune the energy of the states responsible of the optical properties (d orbitals in transition metal ions and f in lanthanides) to induce resonance between levels yielding upconversion phenomena, i.e., conversion of low energy radiation in higher energy photons from the emitting ions. Besides, pressure modifies all those processes depending on the interatomic distances like exchange interaction, energy transfer, and cross

relaxation, among others. Finally, it allows us to perform in-situ studies of optical properties of new crystallographic phases, which can solely be induced at high pressures; inaccessible at ambient conditions.

We illustrate, with selected examples, the effect of pressure on optical properties of materials, which have recently been explored by our group.

2. Investigation of the excited state geometry compared to ground state

Ab-initio calculations have predicted a shortening of the Ce–X bond length (X=F, Cl, Br) upon 4f ($^2F_{5/2}$)→5d ($^2T_{2g}$) excitation, whereas 4f ($^2F_{5/2}$)→5d (^2E_g) would show the opposite behavior. This prediction has been proved by high-pressure optical spectroscopy.

Ce^{3+} shows parity-allowed electric-dipole f→d transitions in the UV–vis spectral range. In O_h symmetry, the Ce^{3+} 4f→5d transitions are mainly split into ($^2F_{5/2}+^2F_{7/2}$)→($^2E_g+^2T_{2g}$). The absorption 4f ($^2F_{5/2}$)→5d ($^2T_{2g}$) and emissions ($^2T_{2g}→^2F_{5/2}+^2F_{7/2}$) of $Cs_2NaLuCl_6$: Ce^{3+} as a function of pressure are shown in Fig. 1.

The 4f^1 ($^2F_{5/2}$)→5d^1 ($^2T_{2g}$) band shifts to lower energies with pressure showing a linear dependence (Fig. 1) as E_{abs}^{exp} (f→d)= 29100–530P, with P and E_{abs} expressed in GPa and cm^{-1}, respectively. Similarly, the emission bands behave linearly with pressure with shift rates of –416 ± 10 cm^{-1}/GPa and –415 ± 10 cm^{-1}/GPa (Fig. 6) [1].

Within a single configurational coordinate model, on the assumption that the mode A_{1g} is mainly responsible of the electron–phonon

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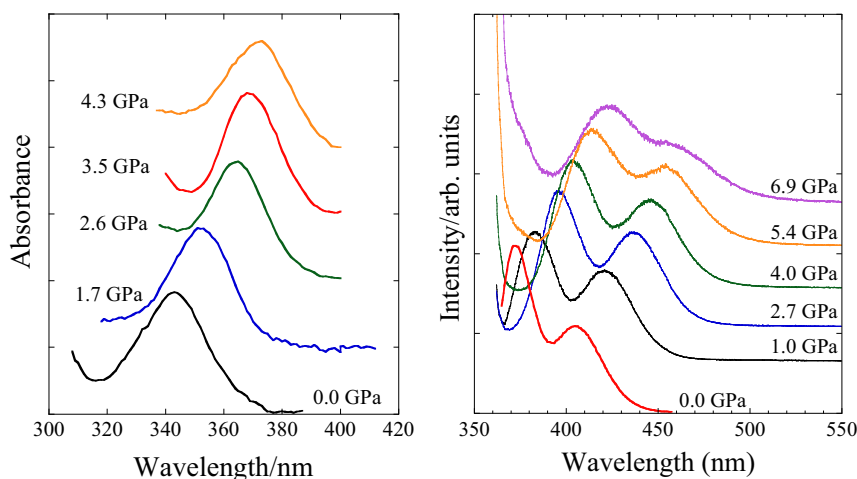E-mail address: valientr@unican.es (R. Valiente).

Fig. 1. Pressure dependence of the $4f^1 \leftrightarrow 5d^1$ transition bands of Ce^{3+}-doped $Cs_2NaLuCl_6$.

coupling and the same vibrational force constants for both ground and excited state, the experimental absorption, E_{abs}^{exp}, and emission energies, E_{em}^{exp}, can be written as (Fig. 2)

$$E_{abs}^{exp} = (E_{ES} - E_{GS})_{Q_0(P)} = E_{abs} + AQ_0(P)$$

$$E_{em}^{exp} = (E_{ES} - E_{GS})_{Q_1(P)} = E_{abs} + AQ_1(P)$$

where E_{abs} represents the Franck–Condon absorption energy and Q_0 and Q_1 represents the normal coordinate at the equilibrium geometry in the ground (GS) and excited (ES) states, respectively. There are two possible scenarios: (a) ES bond distances are larger than GS distances, $Q_1 > Q_0$: $A = (\partial E_{abs}/\partial Q)_{Q_0} < 0$ then $(\partial E/\partial P) > 0$. (b) ES is compressed compared to GS, $Q_1 < Q_0$: $A > 0$ and $(\partial E/\partial P) < 0$. The pressure shift of absorption and emission bands: $(\partial E_i^{exp}/\partial P) = A(\partial Q_i/\partial P)$.

Given that this pressure energy shift is negative in absorption, and $(\partial Q_i/\partial P) < 0$, due to volume compression, then $A < 0$, and, therefore, the excited state is compressed compared to the ground state (Fig. 2). This can be generalized to other rare earth in octahedral symmetry, where the first transition corresponds to $f \to d$ (T_{2g}) crystal field level. Since the equilibrium metal–ligand distance is mainly governed by the external 6s and 6p shells the transition from the internal 4f electron to d (T_{2g}) bonding state would give rise to a compression of the excited state. The opposite should be expected if the transition is to the non-bonding d (E_g) excited state.

3. Pressure-induced excited state crossover

Cr^{3+}-doped $LiCaAlF_6$ presents a crystal-field (CF) strength that is very close to the ^2E–$^4T_2$ excited-state crossover (ESCO) in the Tanabe–Sugano diagram for d^3 ions (Fig. 3). These excited states exhibit different photoluminescence (PL) ; the spin-allowed $^4T_2 \to {}^4A_2$ transition is strongly coupled to the lattice providing short-lived broadband PL, while the spin-forbidden $^2E \to {}^4A_2$ transition (spin-flip) is weakly coupled to the lattice, giving rise to long-lived narrow-line emission. At ambient conditions, the PL-excited state of Cr^{3+} in fluorides lies below the ESCO leading to a $^4T_2 \to {}^4A_2$ broadband emission. Pressure increases CF towards the ESCO providing ideal conditions for drastic PL transformations at pressures well above the ESCO (Fig. 3).

Room temperature (RT) high pressure requires to place the emitting state $^4T_2$ broadband PL far above the ^2E emitting state narrow-line PL in order to get ^2E mostly populated. The change from a broadband emission to a ruby-like emission is accompanied by a dramatic change of the corresponding lifetime (Fig. 4) [2,3].
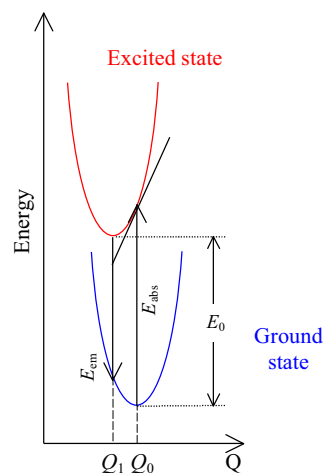

Fig. 2. Configurational coordinate model in the harmonic approximation for a compressed electronic excited state compared to the ground state ($Q_1 < Q_0$).

4. Effect on energy transfer processes

Energy transfer probability between donor and acceptor, P_{DA}, is given by Fermi's golden rule

$$P_{DA} = \frac{2\pi}{\hbar}|D^*A|H_{DA}|DA^*|^2 \int g_A(E)g_D(E)dE \qquad (1)$$

where H_{DA} represents the physical interaction (multipolar or exchange) leading to the energy transfer. $g_D(E)$ and $g_A(E)$ are the normalized line shape functions for $D^* \to D$ emission and $A \to A^*$ absorption transitions, respectively. The last factor in Eq. (1) is the so-called spectral overlap integral. It represents both the energy conservation and the effective density of states. This proportionality was experimentally proved by measuring the emission intensity of Eu^{3+} emission as a function of the overlap between emission of Pt^{2+} and absorption of Eu^{3+} [4]. The effect of pressure is schematically plotted in Fig. 5. The experiments took advantage on the different sensitivity of d–d and f–f transitions with pressure.

5. Pressure-induced enhancement of upconversion luminescence

In appropriate host lattices and at low temperatures Ni^{2+} shows luminescence from two excited states. Therefore, Ni^{2+} fulfills the