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Pressure effects on the luminescence properties of $CaWO_4:Pr^{3+}$

S. Mahlik [a,*], M. Behrendt [a], M. Grinberg [a], E. Cavalli [b], M. Bettinelli [c]

[a] Institute of Experimental Physics, University of Gdańsk, Wita Stwosza 57, 80-952 Gdańsk, Poland
[b] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parma, Italy
[c] Dipartimento di Biotecnologie, Università di Verona and INSTM, UdR Verona, Verona, Italy

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ABSTRACT

Steady state and time resolved emission measurements of $CaWO_4$ doped with Pr^{3+} have been carried out as a function of hydrostatic pressure in the 1–315 kbar range. The increase of pressure induces several effects: a progressive red shift of the spectral features and a decrement of the decay times of both $^3P_0$ and $^1D_2$ emitting levels, the decrease of the intensity of the $^3P_0$ emission, that is completely quenched at around 100 kbar, and the increase of the $^1D_2$ emission intensity in the 1–120 kbar range followed by a fast decrease at higher pressures. In addition, a variation in the structure of the emission manifolds has been observed in the 80–100 kbar range as a consequence of the tetragonal to monoclinic phase transition of the host lattice induced by pressure. These effects have been accounted for by means of a model that takes into account the role played by a praseodymium trapped exciton in the excited state dynamics of the investigated material.

1. Introduction

$CaWO_4$ and $CaMoO_4$ belong to the family of tungstates and molybdates with the general formula MXO_4 (where M = Mg, Ca, Sr, Cd, etc.; X = W or Mo) having the scheelite or fergusonite structure. These materials have been thoroughly studied for more than fifty years because of their great technological importance [1]. UV/VUV as well as X- or γ-rays excitation of pure $CaWO_4$ results in broadband luminescence with a maximum at about 400 nm that makes this compound suitable for applications as a blue phosphor [2] and scintillator [3,4]. Despite extensive investigations, there are aspects of the mechanisms on the basis of the luminescence of $CaWO_4$ and $CaMoO_4$ that have not yet been fully understood and that still appear to be an open field of investigation [5]. Tungstate and molybdate single crystals activated with luminescent rare earth ions can be grown by the Czochralski (and other) method in order to obtain efficient active media for solid state laser technology [6]. Recent papers dealing with the luminescence of Pr^{3+} in these compounds have evidenced interesting effects having their origin in the interactions between host lattice and doping ions [7,8]. It is therefore our opinion that luminescence measurements as a function of hydrostatic pressure could be of help in order to better understand the nature of these interactions. The information provided by these experiments concerns in fact the effect of the variation (obviously within certain limits) of the structural parameters, namely the lattice parameters, on the energy levels involved in the optical transitions. This paper is focused on $CaWO_4:Pr^{3+}$. Previous studies on the pressure dependence of the Raman lines [9] and that of the absorption edge [10] have evidenced that the spectroscopic properties of pure $CaWO_4$ are affected by a tetragonal (scheelite) to monoclinic (fergusonite) phase transition occurring at about 100 kbar. It will then be interesting to investigate the effect of this phase transition on the praseodymium emission features. The pressure behavior of the Pr^{3+} emission in fact strongly depends on the host characteristics: in the case of $Ca(NbO_3)_2:Pr^{3+}$ [11] and $LiTaO_3:Pr^{3+}$ [12], for instance, the increase of pressure results in the progressive quenching of the emission from the $^3P_0$ state. In systems where no $^3P_0$ emission is observed, like $YVO_4:Pr^{3+}$ [13] and $LiNbO_3:Pr^{3+}$ [14], high pressure induces the quenching of the emission from the $^1D_2$ state. These effects have been accounted for in the frame of a scheme in which the non-radiative depopulation of the emitting level involves a praseodymium trapped exciton (PTE) originating from the photoinduced interaction between host lattice and doping ions. The aim of this paper is the investigation of the excitation mechanisms of $CaWO_4:Pr^{3+}$ crystals, in the frame of the pressure dependence of their luminescence properties, analyzed on the basis of the previously developed models.

2. Experimental

$CaWO_4$ single crystals nominally doped with 0.5 mol% Pr^{3+} were grown by the flux growth method using Na_2WO_4 as a solvent in the 1350–600 °C temperature range [15]. The crystals at ambient pressure have a tetragonal scheelite structure with space group

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[*] Corresponding author.
E-mail address: doksma@univ.gda.pl (S. Mahlik).

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$I4_1/a$ and unit cell parameters $a = 5.243$ and $c = 11.376$ Å [16]. The Pr^{3+} ions occupy the Ca^{2+} sites with 8-fold oxygen coordination (distorted dodecahedron, point group S_4) [17].

The excitation spectra were measured using a Horiba FluoroMax-4P TCSPC spectrofluorimeter. The luminescence was excited at 473 nm by means of a laser diode, analyzed by means of a PGS2 monochromator and detected by a R943-2 photomultiplier working in the photon counting regime.

The experimental setup for the luminescence kinetics and time resolved spectroscopy [18] consists of a PL 2143 A/SS laser pumping a PG 401/SH parametric optical generator that generates 30 ps pulses of tuned wavelength with a frequency of 10 Hz. In our experiments we have used 290 and 473 nm excitation wavelengths. The detection part consists of a 2501S (Bruker Optics) spectrograph and a Hamamatsu model C4334-01 streak camera. The time resolved emission spectra and the luminescence decays were obtained from the streak camera images by integrating over selected time and wavelength intervals, respectively.

The experiments at high pressures were carried out using a Merrill Bassett type diamond anvil cell (DAC) for the measurements upon excitation at 473 nm and a sapphire anvil cell (SAC) for those upon excitation at 290 nm [19]. Poly (dimethylsiloxane) oil was used as the pressure-transmitting medium, and a ruby crystal was used as the pressure detector. All the measurements were carried out at room temperature.

3. Results and discussion

The excitation and emission spectra of $CaWO_4:Pr^{3+}$ recorded at room temperature are presented in Fig. 1. In the emission spectrum measured upon host excitation at 290 nm (Fig. 1a) the sharp emission features of Pr^{3+} are superimposed upon the broad emission of the tungstate group ranging from 380 to 630 nm, whose excitation spectrum (Fig. 1b) constitutes the well known band with a maximum at 270 nm [20], ascribed to the $^1T_2 \leftarrow {}^1A_1$ charge transfer transition of the WO_4^{2-} group. The excitation spectrum of the $^3P_0 \rightarrow {}^3F_2$ transition of Pr^{3+}, shown in Fig. 1c, is composed of the host broadband in the UV region and a manifold of sharp lines peaking at 450, 476, and 488 nm, assigned to the $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, and $^3H_4 \rightarrow {}^3P_0$ absorption transitions of Pr^{3+}, respectively. The emission spectrum measured at 473 nm excitation presents a series of relatively sharp features mainly originating in the $^3P_0$ excited state of Pr^{3+}. The most intense lines with maxima at 488 and 649 nm correspond to the $^3P_0 \rightarrow {}^3H_4$ and $^3P_0 \rightarrow {}^3F_2$ transitions, respectively. The weaker multiplet in the 520–570 nm range is assigned to the $^3P_0 \rightarrow {}^3H_5$ and that in the 590–630 nm range to the $^3P_0 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3H_4$ transitions. The pressure evolution of the Pr^{3+} emission is reported in Fig. 2. The monitored emission region has been limited to the 15,000–17,000 cm^{-1} (580–660 nm) range in order to better evidence the relative behavior of the features originating in the $^3P_0$ and in the $^1D_2$ states. In the ambient pressure spectrum we have also reported the time resolved spectrum measured at 473 nm pulsed excitation with acquisition time in the 10–200 μs range (dashed curve), allowing to isolate the emission from the $^1D_2$ level and to confirm the previous assignment. From Fig. 2a and b it is evident that the increasing pressure induces a red shift of the spectral lines that has been schematized in Fig. 2c. From Fig. 2a it can be observed that:

- in the 1–120 kbar range the red shift of the emission lines varies roughly linearly with the pressure with a slope ranging from −2.13 to −2.65 cm^{-1}/kbar in the case of $^3P_0$, and from −1.28 to −1.75 cm^{-1}/kbar in the case of $^1D_2$;
- the intensity of the $^3P_0$ emission rapidly decreases with pressure and is completely quenched at about 100 kbar;

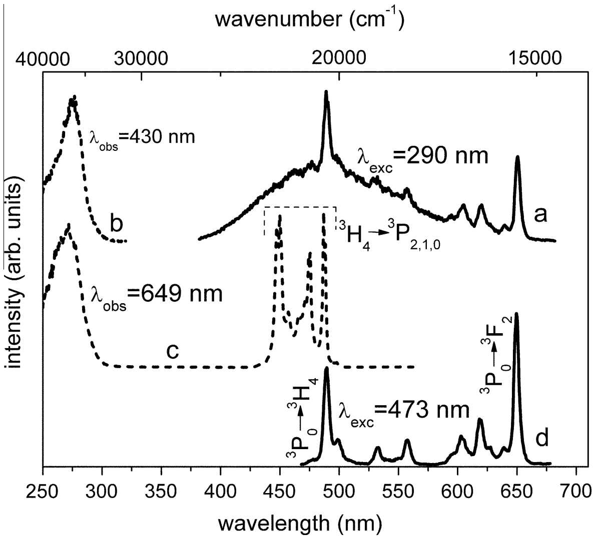

Fig. 1. Excitation (dashed curves) and emission (solid curves) spectra of $CaWO_4:Pr^{3+}$: (a) emission spectrum measured upon host excitation; (b) excitation spectrum of the host broadband luminescence; (c) excitation spectrum of the Pr^{3+} emission; and (d) emission spectrum measured upon Pr^{3+} excitation.

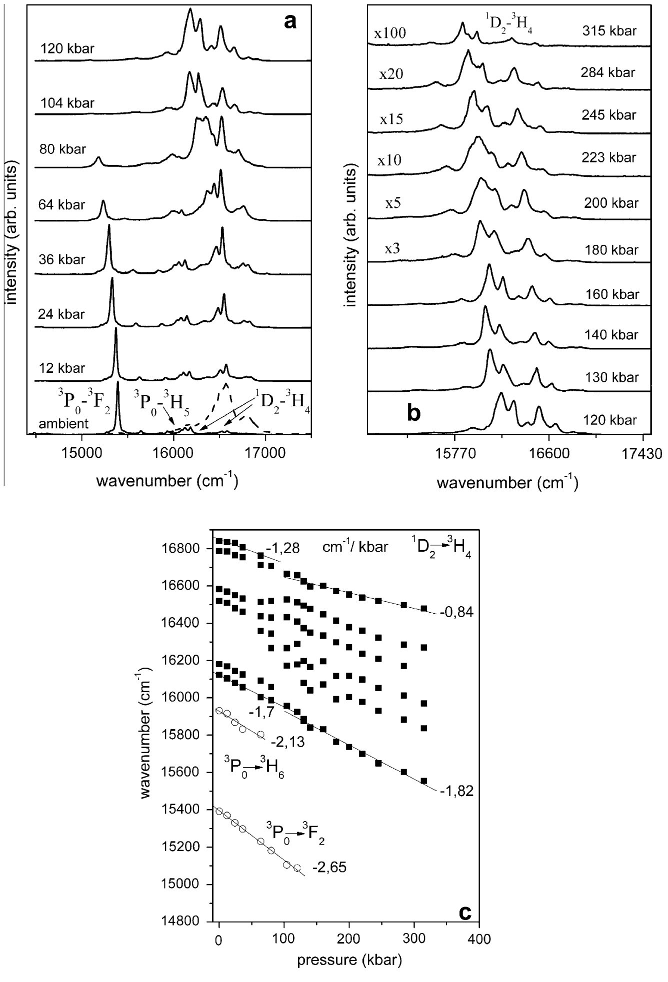

Fig. 2. Pressure dependence of the $CaWO_4:Pr^{3+}$ emission measured upon 473 nm excitation: (a) 1–120 kbar range (dashed line: time resolved spectrum of the $^1D_2$ emission); (b) 120–315 kbar range; and (c) position of the emission peaks versus pressure.