

## High pressure spectroscopy of Pr<sup>3+</sup> doped KLa(MoO<sub>4</sub>)<sub>2</sub> crystal

DANUTA GALANCIAK<sup>1,\*</sup>, WOJCIECH GRYK<sup>2</sup>, MAREK GRINBERG<sup>2</sup>, LUCYNA MACALIK<sup>3</sup>,  
MIROSLAW MAĆZKA<sup>3</sup>

<sup>1</sup>Department of Physics, Kazimierz Wielki University, Weysenhoffa 11, 85-072 Bydgoszcz, Poland

<sup>2</sup>Institute of Experimental Physics, Gdańsk University, Wita Stwosza 57, 80-952 Gdańsk, Poland

<sup>3</sup>Institute for Low Temperature and Structure Research, Polish Academy of Sciences,  
Okólna 2, 50-950 Wrocław, Poland

\*Corresponding author: D. Galanciak, dangal@ukw.edu.pl

Optical properties and electronic structure of Pr<sup>3+</sup> ion in KLa<sub>0.75</sub>Pr<sub>0.25</sub>(MoO<sub>4</sub>)<sub>2</sub> have been investigated. The standard spectroscopy (excitation and photoluminescence spectra) and the high pressure spectroscopy methods have been used. Hydrostatic pressure up to 100 kbar has been applied in diamond anvil cell. The luminescence related to the transitions from the <sup>3</sup>P<sub>0</sub> and <sup>1</sup>D<sub>2</sub> states have been measured at ambient temperature for different pressures. We have found that the pressure shifts of the observed emission lines are negative and equal to 2–3 cm<sup>-1</sup>/kbar. It is due to the changes in Slater and  $\alpha$ ,  $\beta$ ,  $\gamma$  parameters and diminishing of the spin-orbit coupling constant  $\zeta$ .

### 1. Introduction

Interest in praseodymium doped KLa(MoO<sub>4</sub>)<sub>2</sub> crystals is related to potential ability for the generation of the broad spectral range luminescence associated with transitions within  $4f^2$  and between  $5d4f$  and  $4f^2$  electronic configurations of the Pr<sup>3+</sup> ion that can be utilized in lasers, luminophors and scintillators.

In this paper, we present the investigations of praseodymium doped KLa(MoO<sub>4</sub>)<sub>2</sub> crystal (actually the KLa<sub>1-x</sub>Pr<sub>x</sub>(MoO<sub>4</sub>)<sub>2</sub> with  $x = 0.25$ ). This matrix was used in the past as the host for Nd<sup>3+</sup> ions in order to obtain efficient laser active material [1, 2].

The molybdates of lanthanum and praseodymium are isostructural and crystallize as  $\beta$ -phase in monoclinic space group  $P2/n = C_{2h}^4$  with eight molecules per unit cell [3–6]. The lattice parameters are  $a = 10.983 \text{ \AA}$ ,  $b = 12.420 \text{ \AA}$ ,  $c = 10.526 \text{ \AA}$ ,  $\beta = 90.259^\circ$ . The structure consists of isolated MoO<sub>4</sub><sup>2-</sup> tetrahedra and LaO<sub>8</sub> and KO<sub>8</sub> polyhedra. The La–O distances in KLa(MoO<sub>4</sub>)<sub>2</sub> are close to 2.6 Å and those of

La–La are near 4.1 Å. All atoms are in general positions and therefore Pr<sup>3+</sup> ions replacing La<sup>3+</sup> ions occupy the sites of the C<sub>1</sub> symmetry [3–7].

Low temperature absorption and emission spectra of Pr<sup>3+</sup> in KLa(MoO<sub>4</sub>)<sub>2</sub> with concentration of Pr<sup>3+</sup> ions 0.5 and 1 at% have been investigated previously [8, 9]. Thus the basic spectral properties of the Pr<sup>3+</sup> ions are already known. Absorption is a superposition of two distinct bands in the visible region. One of them extends from about 430 nm (23256 cm<sup>-1</sup>) to 500 nm (20000 cm<sup>-1</sup>) and consists of three lines attributed to the transitions from the ground state <sup>3</sup>H<sub>4</sub> to the <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub> and to <sup>3</sup>P<sub>0</sub> states, respectively, where <sup>3</sup>P<sub>0</sub> state is the lowest one. The second band is centered at about 600 nm (16667 cm<sup>-1</sup>) and is associated with the isolated <sup>3</sup>H<sub>4</sub> → <sup>1</sup>D<sub>2</sub> transition [3, 4]. Excitation of the Pr<sup>3+</sup> ion to the <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>0</sub> levels gives rise to the luminescence originating at the <sup>3</sup>P<sub>0</sub> and <sup>1</sup>D<sub>2</sub> states [8, 9].

High pressure causes the decrease of the interatomic distance, thus leads to the increase of interaction of the Pr<sup>3+</sup> ion with surrounding ligands. Therefore, we consider that high pressure is a good tool for investigating the influence of the host on electronic properties of impurity ion. In the case of the localized states, related to the electrons captured on the *f* level of the rare earth ion, it is expected that the pressure influences both the crystal field (described by crystal field parameters) and the inter-electronic interaction (described by Racah integrals, electrostatic interaction parameters and spin-orbit coupling). We focus on the influence of high pressure on photoluminescence spectra of KLa(MoO<sub>4</sub>)<sub>2</sub>:Pr<sup>3+</sup>. We present the ambient pressure luminescence excitation spectra and the luminescence spectra obtained at different pressures. All experiments have been performed at room temperature.

## 2. Experimental methods

Diluted crystals of praseodymium double molybdates were grown by the thermal method developed by BORISOV *et al.* [10] and KLEVSTOV *et al.* [11]. The samples were checked for purity using the X-ray powder diffraction.

Excitation spectra have been measured with 1000 W Xenon Lamp, two SPM 2 (Carl Zeiss Jena) monochromators and the photomultipliers. High pressure has been applied to the sample in the diamond anvill cell of Merrill Basset type. The dimethylsiloxane oil has been used as a pressure medium while ruby (Cr<sup>3+</sup>:Al<sub>2</sub>O<sub>3</sub>) crystal has been employed as a pressure sensor. The high pressure luminescence has been excited by an argon laser of 457.9 nm wavelength. Luminescence has been dispersed by PGS (Carl Zeiss Jena) spectrometer working as monochromator and detected by the photomultiplier working in a photon counting regime. All equipment has been controlled with a PC computer.

## 3. Results and discussion

Excitation spectrum of KLa<sub>1-x</sub>Pr<sub>x</sub>(MoO<sub>4</sub>)<sub>2</sub> with *x* = 0.25 recorded at room temperature for luminescence monitored at 648 nm is presented in Fig. 1. The excitation spectra

obtained for luminescence monitored at other wavelengths are similar. The excitation spectrum is similar to the absorption spectrum. One sees the broad band extended within 450 nm ( $22222 \text{ cm}^{-1}$ ) and 500 nm ( $20000 \text{ cm}^{-1}$ ) corresponding to the transitions from the ground state to excited  $^3P_2$ ,  $^3P_1$  and to  $^3P_0$  states and the band above 250 nm ( $40000 \text{ cm}^{-1}$ ) corresponding to the inter-configurational  $4f^2 \rightarrow 4f5d$  transition.

In Figure 2 the luminescence spectrum recorded at ambient pressure and at room temperature is presented. The spectra consist of the sharp lines related to the transitions from the  $^3P_0$  to the  $^3F_J$  and  $^3H_J$  multiplets. The respective transitions are labelled in the Fig. 2.

One can compare this spectrum to the spectrum obtained for the same material but with smaller concentration ( $x = 0.001$  and  $x = 0.1$ ) of praseodymium ions [8, 9]. The intensity of  $^1D_2 \rightarrow ^3H_4$  transition was comparable to the intensity of  $^3P_0 \rightarrow ^3H_6$  only for low concentrations of doped ions. For our sample, where  $x = 0.25$ , intensity of  $^1D_2 \rightarrow ^3H_4$  transition is very small, nearly negligible. The population of the  $^1D_2$

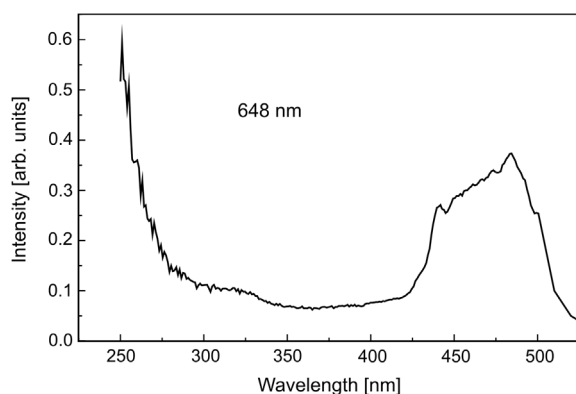


Fig. 1. Excitation spectrum of  $\text{KLa}_{0.75}\text{Pr}_{0.25}(\text{MoO}_4)_2$ ,  $\lambda_{\text{lum}} = 648 \text{ nm}$ .

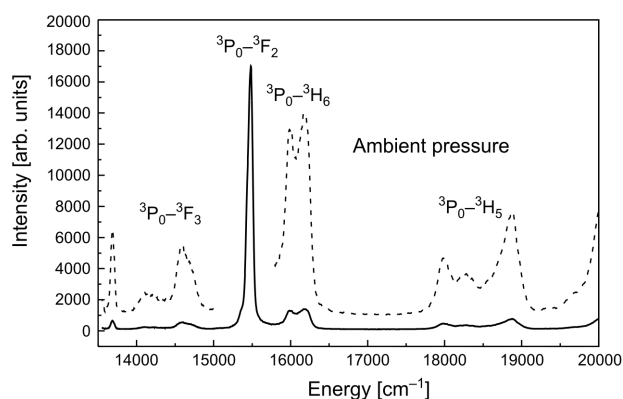


Fig. 2. Ambient pressure and room temperature luminescence spectra of  $\text{KLa}_{0.75}\text{Pr}_{0.25}(\text{MoO}_4)_2$ , excitation  $\lambda = 457.9 \text{ nm}$ . Dashed line – intensities of isolated part of the spectrum are multiplied by factor 10.

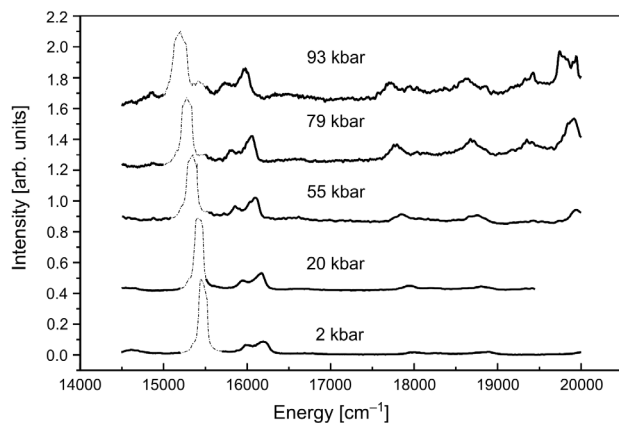


Fig. 3.  $\text{KLa}_{0.75}\text{Pr}_{0.25}(\text{MoO}_4)_2$  luminescence lineshapes for different pressures at room temperature. Dashed line – intensity of those parts is divided by 2.

level is achieved from the  $^3P_0$  state through non-radiative processes. It is possible that with increasing concentration of praseodymium ions non-radiative excitation energy migration and up-conversion processes between ions become more probable than the direct  $^3P_0 \rightarrow ^1D_2$  non-radiative transitions inside the  $\text{Pr}^{3+}$ .

The influence of high pressure on the luminescence properties of the  $\text{KLa}_{0.75}\text{Pr}_{0.25}(\text{MoO}_4)_2$  crystal within the range from 500 nm ( $20000 \text{ cm}^{-1}$ ) to 750 nm ( $13300 \text{ cm}^{-1}$ ) is presented in Fig. 3.

The spectra consist of the sharp lines, labelled in the Fig. 2. One can see two important features that characterize pressure evolution of the spectrum. For all pressures the dominating lines were related to the transition from  $^3P_0$  state. When pressure increases, intensities of  $^3P_0 \rightarrow ^3F_J$  transitions decrease at the expense of  $^3P_0 \rightarrow ^3H_J$  transitions. One can see new transition  $^3P_0 \rightarrow ^3H_4$ , which is visible only for pressure of 55 kbar or above. The effect of weakness of the  $^3P_0 \rightarrow ^3H_4$  lines is artificial and is related to the optical filter used for cutting the laser excitation light. In the higher pressures the  $^3P_0 \rightarrow ^3H_4$  lines are stronger due to the fact that they are shifted to the lower energy where filter dumping is much weaker.

The positions of the individual lines with respect to the pressure are presented in Fig. 4. One can see that all lines shift to the lower energies. All the dependencies have linear character. The pressure shifts for various lines are labelled in Fig. 4. One can notice that pressure coefficients of the spectral lines corresponding to transitions from one level to the crystal field split components of the  $^3H_4$  (or  $^3H_5$  or  $^3H_6$ ) state are very similar. Thus one can conclude that influence of pressure on the crystal field is not large. More significant are changes of Slater parameters, spin orbit coupling and interconfigurational interactions.

Almost all transitions (except one) originate at the  $^3P_0$  state. Thus considering the pressure shifts of the lines one can calculate the energies of the individual states

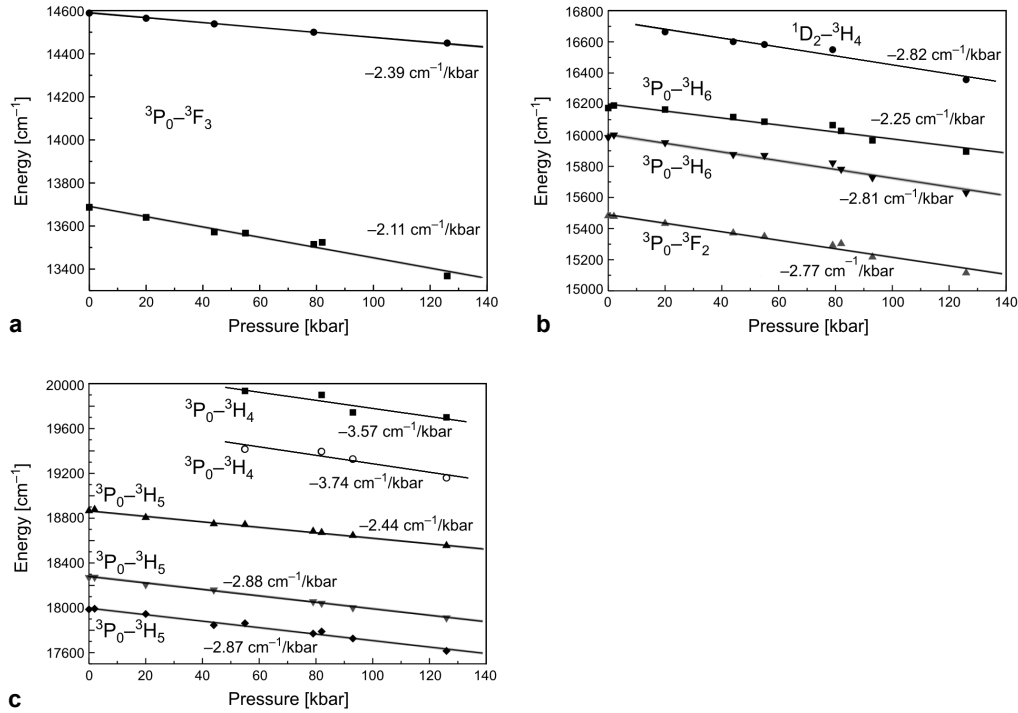


Fig. 4. Energies of the luminescence peaks of  $\text{KLa}_{0.75}\text{Pr}_{0.25}(\text{MoO}_4)_2$  vs. pressure:  ${}^3P_0-{}^3F_3$  (a);  ${}^3P_0-{}^3H_6$ ,  ${}^3P_0-{}^3F_2$ ,  ${}^1D_2-{}^3H_4$ (b);  ${}^3P_0-{}^3H_4$ ,  ${}^3P_0-{}^3H_5$  (c).

and their dependence on pressure. These data are presented in Table 1. We have not considered the effect of crystal field and calculated the centers of gravity of the split states. To obtain the energies listed in Tab. 1 we have considered our data as well as the emission and absorption data presented in paper [9].

To analyze the influence of pressure on the energetic structure of the  $\text{Pr}^{3+}$  in  $\text{KLa}_{0.75}\text{Pr}_{0.25}(\text{MoO}_4)_2$  we have considered following Hamiltonian [12, 13]:

$$H_F = \sum_{i=2,4,6} e_i F_i + H_{s-o} + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7)$$

where  $F_i$  are Slater parameters describing the electron–electron interactions,  $H_{s-o}$  – spin–orbit interaction Hamiltonian parameterized for the  $4f^2$  by the single constant  $\zeta$ . The last three contributions proportional to the constants  $\alpha$ ,  $\beta$  and  $\gamma$  describe the interconfigurational interactions. The  $G(G_2)$  and  $G(R_7)$  are the eigenvalues of Casimirs' operator for the groups  $G_2$  and  $R_7$  used to classify the states of  $f^N$  electronic configuration.

Data collected in Tab. 1 allowed to calculate the quantities of the coefficients listed in Hamiltonian (see the equation above) and their pressure dependence. The respective

T a b l e 1. Ambient pressure energies and pressure shifts of the energy levels of the  $\text{Pr}^{3+}$ .

State	Energy at ambient pressure [ $\text{cm}^{-1}$ ]	Pressure shifts [ $\text{cm}^{-1}/\text{kbar}$ ]
${}^3H_4$	0	0.0
${}^3H_5$	1542	$-1.0 \pm 0.3$
${}^3H_6$	3807	$-1.2 \pm 0.3$
${}^3F_2$	4450	$-0.9 \pm 0.3$
${}^3F_3$	5820	$-1.4 \pm 0.3$
${}^1D_2$	16850	$-2.8 \pm 0.2$
${}^3P_0$	19950	$-3.7 \pm 0.2$

T a b l e 2.  $\text{Pr}^{3+}$  ion Hamiltonian parameters and their pressure changes. In the second column the quantities of the free ion parameters are collected.

Parameter	Free ion [ $\text{cm}^{-1}$ ]	In crystal [ $\text{cm}^{-1}$ ]	Pressure changes [ $\text{cm}^{-1}/\text{kbar}$ ]
$F_2$	318.8	306.78	$-0.04 \pm 0.05$
$F_4$	46.6	50.96	$0.037 \pm 0.05$
$F_6$	4.55	4.8247	$0.0026 \pm 0.003$
$\zeta$	763.4	777.22	$-0.2 \pm 0.06$
$\alpha$	23.5	23.02	$0.01 \pm 0.02$
$\beta$	-600	-605.51	$-0.46 \pm 0.4$
$\gamma$	1552	1536.1	$0.1 \pm 0.9$

data are collected in Tab. 2. The parameters have been fitted using last square method as follows, separately for each pressure. In the first step we have fitted Slater parameters and spin-orbit coupling. Than we have fixed Slater parameters and fitted  $\alpha$ ,  $\beta$ ,  $\gamma$  and again spin-orbit coupling constant. As the initial values the quantities of free ion parameters have been taken. Thus we have obtained the quantities of parameter set for each pressure. The dependences of these quantities on pressure have been calculated by linear fits.

Obtained data are listed in Table 2. One can notice that obtained pressure shifts are charged by quite large errors. This is a result of small number of experimental data. We have not noticed any unambiguous trend in pressure changes of Slater integrals. We have found that  $F_2$  decreases whereas  $F_4$  and  $F_6$  increase with increasing pressure. It allows to conclude that in  $\text{Pr}^{3+}$  in  $\text{KLa}(\text{MoO}_4)_2$  pressure causes an increase of the ratios  $F_4/F_2$  and  $F_6/F_2$ , respectively. We have obtained  $F_4/F_2 = Y = 0.1661 + 1.4 \times 10^{-4} P \text{ kbar}^{-1}$  and  $F_6/F_2 = 0.01572 + 10^{-5} P \text{ kbar}^{-1}$ . For free ion the  $F_4/F_2$  and  $F_6/F_2$  are equal to 0.146 and 0.0144, respectively.

The most evident effect of pressure is decreasing of the spin-orbit coupling constant. This is in accordance to earlier obtained results for  $\text{Pr}^{3+}$  in YAG [14] and

chlorides [15]. An interesting change of the value of parameter  $\gamma$  as a function of pressure has been also noticed. When whole range of pressure is considered the dispersion of calculated values of  $\gamma$  is very large. Therefore one cannot find any specific trends in change of this parameter with pressure.

#### 4. Conclusions

We have investigated the high pressure photoluminescence of the  $\text{KLa}_{1-x}\text{Pr}_x(\text{MoO}_4)_2$  with  $x = 0.25$ . Our results have shown that for the  $\text{Pr}^{3+}$  (the  $4f^2$  electronic configuration) the influence of pressure on the energetic structure of  $\text{Pr}^{3+}$  through magnifying the crystal field strength is quite small. The more important is influence of pressure on the  $4f^2$  inter-electronic interaction and spin-orbit coupling. Analysis of pressure shifts of the  ${}^3P_0 \rightarrow {}^3H_4$ ,  ${}^3P_0 \rightarrow {}^3H_5$  and  ${}^3P_0 \rightarrow {}^3H_6$  transitions has shown that pressure causes decrease of the spin-orbit coupling and the increase of the corresponding ratios of the Slater parameters  $F_4/F_2$  and  $F_6/F_2$ . The  $F_4/F_2$  and  $F_6/F_2$  for free ion is equal to 0.146 and 0.0144, respectively. One notices that interaction with surrounding lattice yields an increase of these ratios. Moreover the pressure, since it causes the increase of electron- lattice coupling, yields additional increase of  $F_4/F_2$  and  $F_6/F_2$ .

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