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LUMINESCENCE AND LIFETIMES OF Pr^{3+} EXCITED STATES IN $\text{KLa}_{1-x}\text{Pr}_x(\text{MoO}_4)_2$ AND $\text{KLa}_{1-x}\text{Pr}_x(\text{WO}_4)_2$ CRYSTALS

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Single crystals of double molybdates and tungstates of the formula $\text{KLa}_{1-x}\text{Pr}_x(\text{MO}_4)_2$ ($\text{M} = \text{Mo}, \text{W}$) with a concentration of Pr^{3+} ions ranging from $x = 0.1$ to $x = 0.005$ have been prepared. Their electronic absorption and emission spectra have been measured and discussed as well as related to their crystal structures. Both the multiphonon relaxation and cross relaxation contribute to the decay of the $^3\text{P}_0$ level of Pr^{3+} in these two matrices.

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1. Introduction

Interest in praseodymium doped crystals is related to potential laser operation associated with transitions within the $4f^2$ configuration of Pr^{3+} . The $^1\text{G}_4$ – $^3\text{H}_5$ transition at about $1.33 \mu\text{m}$ matches well the transmission window of optical fibres and may be involved in amplification of light in telecommunication systems. Other laser channels involving the $^3\text{P}_0$ – $^3\text{H}_4$ transition at about 480 nm [1], and the $^3\text{P}_0$ – $^3\text{H}_6$ transition at about 640 nm [2–5] are particularly important since the emission is in the visible. Major shortcoming of Pr^{3+} lasers is related to the pumping efficiency. The wavelength of the $^3\text{H}_4$ – $^1\text{G}_4$ matches perfectly the emission of the InGaAs laser diodes but its intensity is very low in virtually all compounds. Considerably more intense absorption bands corresponding to transitions to the $^3\text{P}_2$, $^3\text{P}_1$, $^3\text{P}_0$ levels make it possible to populate the metastable $^3\text{P}_0$ level, however laser diodes operating in the blue region of the spectrum are not yet available. Nevertheless, taking into account the progress in the field of semiconductor lasers one can expect that the design of efficient all-solid state praseodymium lasers will be feasible in the near future. With the view of finding an activator-host combination

which would be promising as a low threshold laser, in this paper we investigate the praseodymium doped $\text{KLa}(\text{MoO}_4)_2$ and $\text{KLa}(\text{WO}_4)_2$ crystals. The two matrices were used in the past as hosts for Nd^{3+} ions in order to obtain efficient laser active materials [6, 7]. The main goal of the present study was to get knowledge on the excitation and relaxation of the 3P_0 and 1D_2 levels of praseodymium.

2. Experimental

Electronic absorption spectra were measured at room temperature and at 5 K with a Varian Model 2300 Absorption Spectrophotometer. Emission spectra were excited by the 488 and 476 nm line of an argon ion laser, dispersed with a 1 m double grating monochromator and detected with a photomultiplier with the S20 spectral response. The resulting signal was averaged by a boxcar integrator and stored in a IBM computer. Absorption and emission spectra were recorded with spectral resolution of 0.2 nm and 0.05 nm, respectively. Luminescence lifetimes were measured using an apparatus consisting of a tunable dye laser pumped by a nitrogen laser, a grating monochromator and photomultiplier connected to a boxcar integrator. Dye laser emission was tuned to excite the 3P_1 level at about 20800 cm^{-1} . The emission spectra and lifetimes were recorded at room temperature and at 77 K.

3. Crystal structure

The molybdates of lanthanum and praseodymium are isostructural and crystallize as the β -phase in the monoclinic space group $P2_1/n = C_{2h}^4$ with eight molecules per unit cell. The lattice parameters are $a = 10.983\text{ \AA}$, $b = 12.420\text{ \AA}$, $c = 11.019\text{ \AA}$, $\beta = 90.259^\circ$ for $\text{KLa}(\text{MoO}_4)_2$ and $a = 10.606\text{ \AA}$, $b = 11.726\text{ \AA}$, $c = 10.526\text{ \AA}$, $\beta = 90.223^\circ$ for $\text{KPr}(\text{MoO}_4)_2$. The structure of the unit cell is a modification of scheelite, their dimensions, however, are four times greater than those for CaWO_4 . The structure consists of isolated MoO_4^{2-} tetrahedra and LnO_8 and KO_8 polyhedra. The Ln–O distances in $\text{KLa}(\text{MoO}_4)_2$ are close to 2.6 \AA and those of La–La are near to 4.1 \AA . All atoms are in general positions and therefore Pr^{3+} ions replacing La^{3+} ions occupy the sites of the C_1 symmetry.

The $\text{KLa}(\text{WO}_4)_2$ and $\text{KPr}(\text{WO}_4)_2$ tungstates also crystallize as the β -modification and are isostructural with the molybdates described above. Their unit cell parameters are: $a = 10.968\text{ \AA}$, $b = 12.115\text{ \AA}$, $c = 10.890\text{ \AA}$, $\beta = 90.612^\circ$ and $a = 10.835\text{ \AA}$, $b = 12.088\text{ \AA}$, $c = 10.826\text{ \AA}$, $\beta = 89.991^\circ$, respectively. The symmetry of the mixed crystals with substituted Pr^{3+} ions is the same as for molybdates with similar La–O and La–La distances. All these structures are of scheelite type with the statistical distribution of K^+ and Ln^{3+} ions replacing Ca^{2+} sites in CaWO_4 . In the praseodymium tungstates the subunits of $\text{W}_4\text{O}_{16}^{8-}$ are separated by a sandwich layer structure composed of periodical repeated LnO_8 and KO_{12} polyhedra.

4. Results and discussion

At room temperature two distinct absorption bands appear in the visible region. One of them ranges from about 430 nm to 500 nm and consists of three lines overlapping partially each other. These lines correspond to transitions from the ground state to the 3P_2 , 3P_1 and 3P_0 levels with the 3P_0 level as the lowest one. The second band centred at about 600 nm is associated with the isolated

$^3H_4-^1D_2$ transition [8]. At 5 K the lines in the blue region become resolved and the unsplit 3P_0 level can be located (Fig. 1). In both matrices the line associated

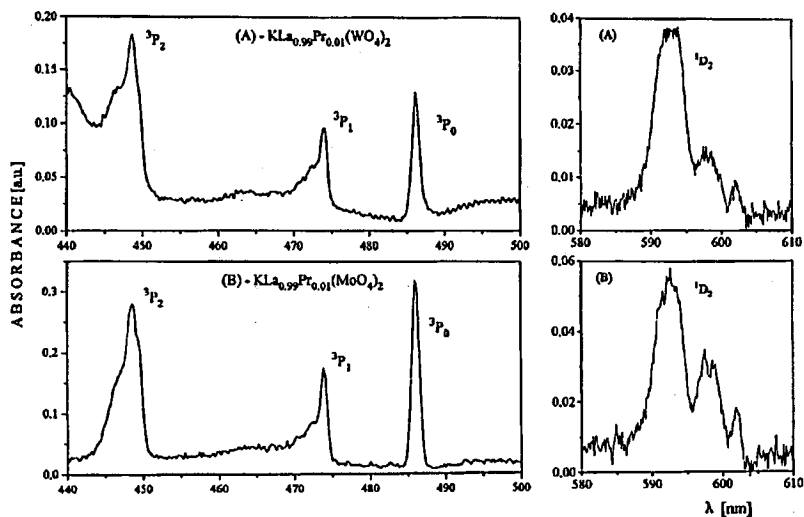


Fig. 1. Absorption spectra of diluted double molybdates and tungstates crystals recorded at 5 K. All transitions are from the ground 3H_4 multiplet to the multiplets indicated.

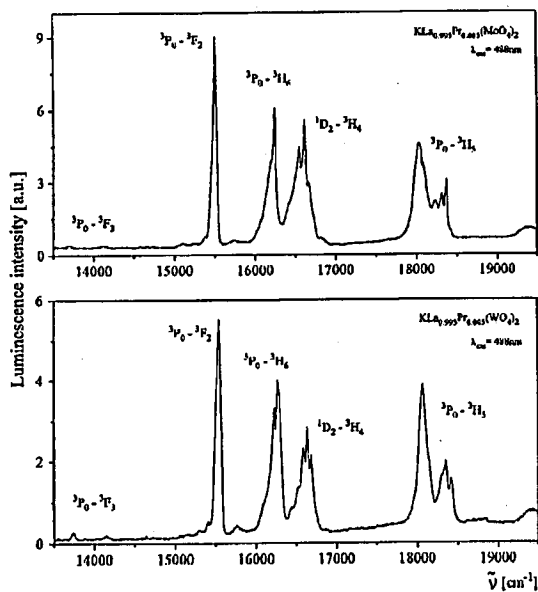


Fig. 2. Luminescence spectra of $\text{KLa}_{1-x}\text{Pr}_x(\text{Mo/WO}_4)_2$ crystals with $x = 0.005$ recorded at 77 K.

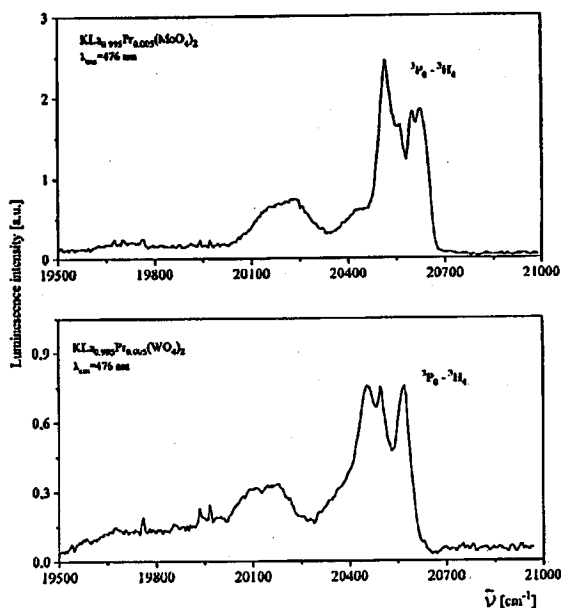


Fig. 3. 3P_0 - 3H_4 luminescence spectra of $\text{KLa}_{1-x}\text{Pr}_x(\text{Mo/WO}_4)_2$ crystals with $x = 0.005$ recorded at 77 K.

with the ${}^3H_4(1)$ - 3P_0 transition is centred at 486 nm. It may be approximated by the Gauss bandshape having full width at half maximum (FWHM) of 1 nm for $\text{KLa}(\text{MoO}_4)_2$ and 1.16 nm for $\text{KLa}(\text{WO}_4)_2$. It appears that in these structures the Pr^{3+} ions occupy a single site in a strongly distorted crystal field as indicated by the significant bandwidth of inhomogeneously broadened absorption lines.

Excitation of the 3P_2 , 3P_1 and 3P_0 levels gives rise to luminescence originating on the 3P_0 and 1D_2 and ending on multiplets of the 3F and 3H terms. In Fig. 2 the luminescence spectra recorded at 77 K in the 15500–19500 cm^{-1} region for $\text{KLa}_{0.995}\text{Pr}_{0.005}(\text{MoO}_4)_2$ and $\text{KLa}_{0.995}\text{Pr}_{0.005}(\text{WO}_4)_2$ are compared and in Fig. 3 the details of the band associated with the 3P_0 - 3H_4 transition in both crystals are shown. The emission spectra of these compounds are very similar indicating comparable branching ratios for the 3P_0 radiative decay. The branching ratio for the 3P_0 - 3F_2 transition is lower than those corresponding to the 3P_0 - 3H_4 , 3H_5 and 3H_6 transitions, however its stimulated emission cross section is the highest owing to a small bandwidth. The occurrence of the band associated with the 1D_2 - 3H_4 transition, when the 3P_0 level is excited, is an evidence that the quantum efficiency of the 3P_0 level is inferior to unity. In principle two processes may be involved in the population built up on the 1D_2 level. One of them is a cross-relaxation process in which the 3P_0 excitation is removed and the 1D_2 becomes populated. The second one is an intracentre multiphonon relaxation bridging the 3P_0 and 1D_2 levels. The relative contribution of these processes is difficult to assess because the selfquenching concerns both luminescence levels. Strong 1D_2 - 3H_4 luminescence in our diluted samples ($x = 0.005$) indicates that multiphonon relaxation may be an

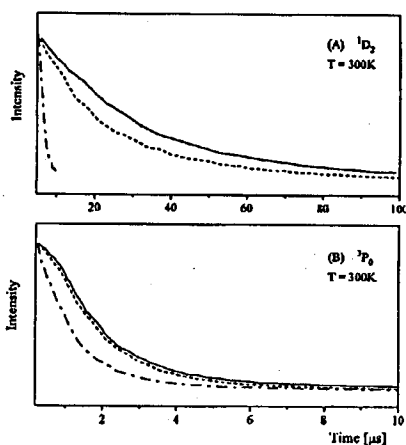


Fig. 4. The luminescence decay curves for the 1D_2 (A) and 3P_0 (B) emission at room temperature for several Pr^{3+} concentrations in $\text{KLa}(\text{MoO}_4)_2$ crystals: — $\text{KLa}_{0.995}\text{Pr}_{0.005}(\text{MoO}_4)_2$, --- $\text{KLa}_{0.99}\text{Pr}_{0.01}(\text{MoO}_4)_2$, - · - · - $\text{KLa}_{0.9}\text{Pr}_{0.1}(\text{MoO}_4)_2$.

important way of the 3P_0 decay. The 3P_0 – 1D_2 energy gap of about 3300 cm^{-1} may be covered by a simultaneous emission of four high energy phonons associated with Mo–O stretching vibrations [9]. With increasing Pr^{3+} concentration the emission originating on the 1D_2 level decreases and becomes negligibly small when $x > 0.1$. In Fig. 4 luminescence decay curves for the 3P_0 and 1D_2 emission at room temperature are shown for several Pr^{3+} concentrations in $\text{KLa}(\text{MoO}_4)_2$ crystals. At room temperature the 1D_2 lifetime of $32\text{ }\mu\text{s}$ for $x = 0.005$ drops to $23\text{ }\mu\text{s}$ for $x = 0.01$ and to $1.5\text{ }\mu\text{s}$ when $x = 0.1$ and at 77 K the 1D_2 lifetime is reduced from $38\text{ }\mu\text{s}$ to $28\text{ }\mu\text{s}$ when x changes from 0.005 to 0.01 . The 3P_0 lifetime is considerably less influenced by increasing Pr^{3+} concentration since the lifetime at room temperature is reduced from $1.6\text{ }\mu\text{s}$ for $x = 0.005$ to $1.5\text{ }\mu\text{s}$ for $x = 0.01$ and to $1\text{ }\mu\text{s}$ when $x = 0.1$. At 77 K the situation is similar: the 3P_0 lifetime of $1.8\text{ }\mu\text{s}$ for $x = 0.005$ drops to $1.55\text{ }\mu\text{s}$ for $x = 0.01$ and to $1.25\text{ }\mu\text{s}$ when $x = 0.1$. The cross-relaxation processes involve the emission of phonons as indicated by longer 1D_2 and 3P_0 lifetimes at 77 K . The behaviour of $\text{KLa}_{1-x}\text{Pr}_x(\text{WO}_4)_2$ crystals is qualitatively similar except that the corresponding lifetimes are higher by a factor of 2 implying lower radiative transition rates.

Concluding, a room temperature laser action associated with the 3P_0 – 3F_2 transition should be possible in both crystals provided that the Pr^{3+} concentration is kept small.

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