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Spectroscopy of f–f radiative transitions of Yb³⁺ ions in ytterbium doped orthophosphates at ambient and high hydrostatic pressures

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Abstract

Studies of absorption and luminescence spectra, and luminescence decay times of the intrashell f–f transitions of Yb³⁺ ions in bulk orthophosphates at different temperatures and at high hydrostatic pressures are presented. The spectroscopic properties of Y_{0.99}Yb_{0.01}PO₄ crystal with a tetragonal zircon structure and Gd_{0.99}Yb_{0.01}PO₄ and La_{0.95}Yb_{0.05}PO₄ crystals with a monoclinic monazite structure are compared. Experiments at ambient pressure were performed at temperatures from 10 to 295 K whereas measurements at high pressure were performed in a diamond-anvil cell at 10 K with a pressure up to 160 kbar. The results reveal a high thermal and pressure stability of the optical properties of the examined crystals as well as the dependence of Yb³⁺ emission properties on the local symmetry of the site occupied by the ytterbium dopant.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Yb³⁺ rare earth (RE) ion is nowadays attracting a lot of attention as an active dopant ion for solid state laser materials, scintillators or as a structural probe in solids [1]. Due to the development of InGaAs laser diodes emitting near 980 nm, where Yb³⁺ has a strong absorption peak, this ion is now the most promising for use as a non-Nd lasing center in the same range of emission wavelength [2, 3]. The advantages of using Yb³⁺ as a laser emitting center have been emphasized in several review papers [4–6].

Among different host crystals, lanthanide phosphates have gained increasing attention due to their interesting optical and luminescent properties from the point of view of possible applications of these materials in new lighting devices as well as for fundamental studies [7–11]. Apart from being found in nature, they can be relatively easily and cheaply synthesized in

the laboratory by different growth techniques [12] and doped with high concentrations of various RE³⁺ ions.

The comprehensive comparison of numerous laser crystals has been established quite recently by Kaminskii [13], where both other oxides related to orthophosphates and different phosphorus-containing compounds hold a special place. Yb³⁺ ions in these materials present a broad and strong absorption band as well as very intense emission at about 1 μm, with a relatively long emission lifetime [4–6]. However in spite of an intensive search for new solid state lasers and nonlinear laser materials still only a very limited number of papers exist on spectroscopic studies of ytterbium doped orthophosphates. Most of the authors focus on the studies of charge transfer type luminescence of Yb³⁺ ions in these crystals [14–20]. In addition, Becker *et al* measured low-temperature absorption spectra and Zeeman spectra of ytterbium doped YPO₄ and LuPO₄ [21]. Fitting the obtained results to a semiempirical

Hamiltonian they determined crystal field parameters, energy levels and g factor values for Yb^{3+} in these hosts. On the other hand Nakazawa *et al* studied cooperative optical transitions of Yb^{3+} – Yb^{3+} and Gd^{3+} – Yb^{3+} ion pairs in YbPO_4 crystals [22, 23].

In this work we present studies of the absorption, luminescence and luminescence decay times of the intrashell f–f transitions of Yb^{3+} ions in bulk $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$, $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{La}_{0.95}\text{Yb}_{0.05}\text{PO}_4$ orthophosphates at temperatures from 10 to 295 K. The samples differ in the crystal structure and the ytterbium content. High-pressure studies of the luminescence and decay times were performed in a diamond-anvil cell (DAC) up to 160 kbar at 10 K for $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ crystals. Pressure and temperature are basic thermodynamic variables for studying the properties of materials, and using the DAC technique enables us to perform their spectroscopic characterization.

2. Samples and experimental techniques

All the samples used in these studies were prepared by flux growth [8, 12]. This method allows obtaining small needlelike or platelike crystals of good quality.

The pure lanthanide orthophosphates crystallize in two closely related structures: those with the ionic radius of the rare earth cation larger or equal to that of Gd (LaPO_4 to GdPO_4) have the monoclinic monazite structure, while those with the ionic radius of rare earth cation smaller than that of Gd (TbPO_4 to LuPO_4 plus YPO_4 and ScPO_4) have the tetragonal zircon structure [24]. The ytterbium dopant replaces the trivalent cation in its crystal site. In crystals with monoclinic monazite structure ($\text{La}_{0.95}\text{Yb}_{0.05}\text{PO}_4$ and $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ in the present work) Yb^{3+} is surrounded by nine oxygens with C_1 local symmetry, whereas in the crystal with tetragonal zircon structure ($\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ in the present work) Yb^{3+} is surrounded by eight oxygens with D_{2d} local symmetry [25]. The ionic radius of Yb^{3+} is equal to 0.985 Å for coordination number (CN) 8 and 1.042 for CN 9, and the ionic radii of the cations replaced by the ytterbium are equal to 1.019 Å, 1.107 Å and 1.216 Å for Y^{3+} (CN 8), Gd^{3+} (CN 9) and La^{3+} (CN 9), respectively [26]; the value for Gd^{3+} (CN 9) was calculated from bond length–bond strength equations [27].

The optical absorption spectra were measured with a Cary 5000 UV–vis–NIR spectrophotometer. Continuous wave emission spectra were obtained using an Ar-ion laser pumped Ti:sapphire laser as the excitation source. The spectra were measured using a Horiba Jobin-Yvon FHR 1000 monochromator and a cooled linear InGaAs array detector. The high-pressure measurements were performed using a low-temperature diamond-anvil cell (Diacell Products MCDAC-1). Argon was used as a pressure transmitting medium. The DAC was mounted in an Oxford Optistat CF cryostat equipped with a temperature controller for low-temperature measurements. The samples, cut and polished down to a thickness of 20 μm , were loaded into the cell along with a small ruby crystal. The R_1 -line ruby luminescence, excited by the second harmonic of an YAG:Nd laser (532 nm), was used for pressure calibration. The line-width of ruby luminescence

was also used for monitoring hydrostatic conditions in the DAC. Since we did not notice any important increase of this line-width with pressure we believe that the hydrostatic conditions were preserved up to the highest pressure applied to the samples.

The decay kinetics of the luminescence were measured using an SR430 Multichannel Scaler. A large number of decays was collected in order to obtain a good signal-to-noise ratio. The exciting laser beam was chopped by a mechanical chopper with a transient time below 30 μs . The decay times of luminescence were obtained by fitting the decay kinetics with single exponential dependencies.

3. Experimental results and their interpretation

3.1. Absorption and luminescence spectra of Yb^{3+} ions in YPO_4 , GdPO_4 and LaPO_4 crystals at ambient pressure

The energy gap of phosphates is in the range of 7.7–8.7 eV [11, 17, 28] and is wide enough to contain the fundamental and excited energy levels of RE luminescent centers [29]. The energy gaps of YPO_4 , GdPO_4 and LaPO_4 are equal to 8.32 eV, 7.85 eV and 7.75 eV, respectively [20]. The typical transition energies between the ${}^2F_{7/2}$ ground state and the ${}^2F_{5/2}$ excited state levels of Yb^{3+} ions occur around 1.24 eV (10 000 cm^{-1}). In a crystal field of D_{2d} or lower symmetry, as a consequence of the Stark effect, the ${}^2F_{7/2}$ level splits into four, and the ${}^2F_{5/2}$ level into three Kramers doublets [30].

In principle, the electric-dipole transitions between the ${}^2F_{7/2}$ and ${}^2F_{5/2}$ states of Yb^{3+} ion are parity-forbidden and magnetic-dipole transitions should play an important role in the de-excitation of the excited ${}^2F_{5/2}$ state. However, because of some admixture of an opposite parity electronic configuration to the pure 4f state as a result of the interaction of the dopant ion with a non-centrosymmetric crystal field the electric-dipole transitions happen to dominate.

The room-temperature absorption spectra of $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$, $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{La}_{0.95}\text{Yb}_{0.05}\text{PO}_4$ crystals in the IR–vis–UV spectral range are presented in figure 1. The available spectral range on the UV side reached 6.2 eV (about 50 000 cm^{-1}), which is still far from the absorption edge of all the studied host crystals. The absorption edges observed at 45 400 cm^{-1} , 39 300 cm^{-1} and 37 800 cm^{-1} for $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$, $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{La}_{0.95}\text{Yb}_{0.05}\text{PO}_4$ crystals respectively, originate from charge transfer (CT) absorption of the ytterbium dopant. The CT absorption edge energies are in agreement with the observation made by van Pieterse *et al* that in isostructural host lattices these energies decrease with increasing size of cationic site [17, 18].

The lines originating from the $\text{Yb}^{3+} {}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition are shown in the inset of figure 1. They are relatively broad, which could indicate the existence of strong vibronic coupling often observed in Yb^{3+} -doped crystals, or/and some disordering of the crystal structure [31–33]. The lines broadening increases in the crystals, where the differences between the ionic radii of Yb^{3+} and the replaced cation are larger and the lattice relaxation is stronger.

Figure 2 shows the normalized ambient-pressure absorption spectra of $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ crystals

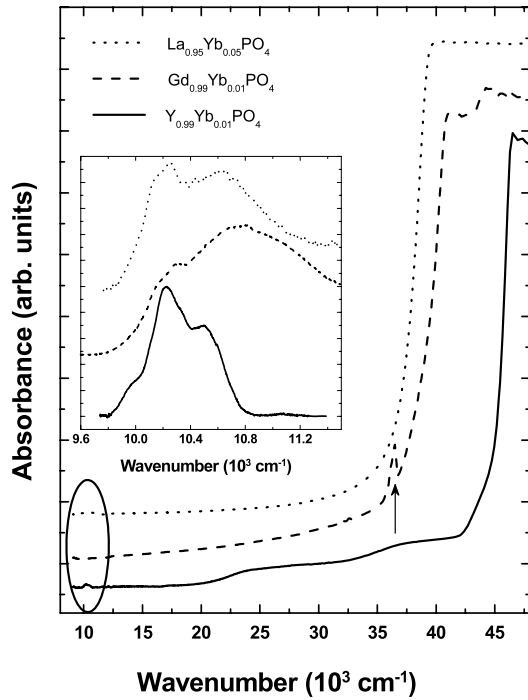


Figure 1. Room-temperature absorption spectra of $Y_{0.99}Yb_{0.01}PO_4$, $Gd_{0.99}Yb_{0.01}PO_4$ and $La_{0.95}Yb_{0.05}PO_4$ crystals. Arrow indicates the gadolinium absorption line. In the inset: expanded spectra in the region of Yb^{3+} absorption. The spectra are shifted along the vertical axis for clarity.

in the region of the Yb^{3+} absorption at temperatures from 10 to 300 K. The main bands of the spectra consist of the three electronic Stark components of the $^2F_{5/2}$ excited level, however the line broadening hampers the assignment of the lines.

In figure 3 normalized ambient-pressure luminescence spectra of $Y_{0.99}Yb_{0.01}PO_4$, $Gd_{0.99}Yb_{0.01}PO_4$ and $La_{0.95}Yb_{0.05}PO_4$ crystals at temperatures from 10 to 300 K are presented, and in figure 4—a comparison of low-temperature luminescence spectra of these crystals is shown. The presence of satellites of several lines is the most probably associated with acoustic-phonon-assisted emission [34] or with the multicenter character of the ytterbium dopant in the orthophosphate host crystals [35].

The luminescence line positions observed in $Y_{0.99}Yb_{0.01}PO_4$ are only partly consistent with the calculations performed by Becker *et al* [21], even taking into account the fact that due to the strong vibronic coupling some of the bands in our absorption and emission spectra can have a vibronic nature. The most likely explanation for this discrepancy is that the small number of Yb^{3+} transitions observed in the experimentally obtained absorption spectra was insufficient to determine uniquely the crystal field and spin orbit parameters. The authors of [21] dealt with this problem by fixing some of the parameters at the values found for Tm^{3+} in YPO_4 ; this can be the source of large uncertainties in the prediction of the Yb^{3+} energy levels scheme.

The spectra of $Gd_{0.99}Yb_{0.01}PO_4$ and $La_{0.95}Yb_{0.05}PO_4$ look similar; this is connected with the same monazite crystal structure of these materials. The small differences in the line positions are connected with different energy level splittings depending on ionic radii and ion distances in the two host crystals. The spectrum of the zircon structure crystal $Y_{0.99}Yb_{0.01}PO_4$ is different, indicating a weaker Stark effect. This observation is consistent with the fact that in the zircon structure Yb^{3+} is surrounded by eight oxygens, whereas in the monazite structure Yb^{3+} is surrounded by nine oxygens [25],

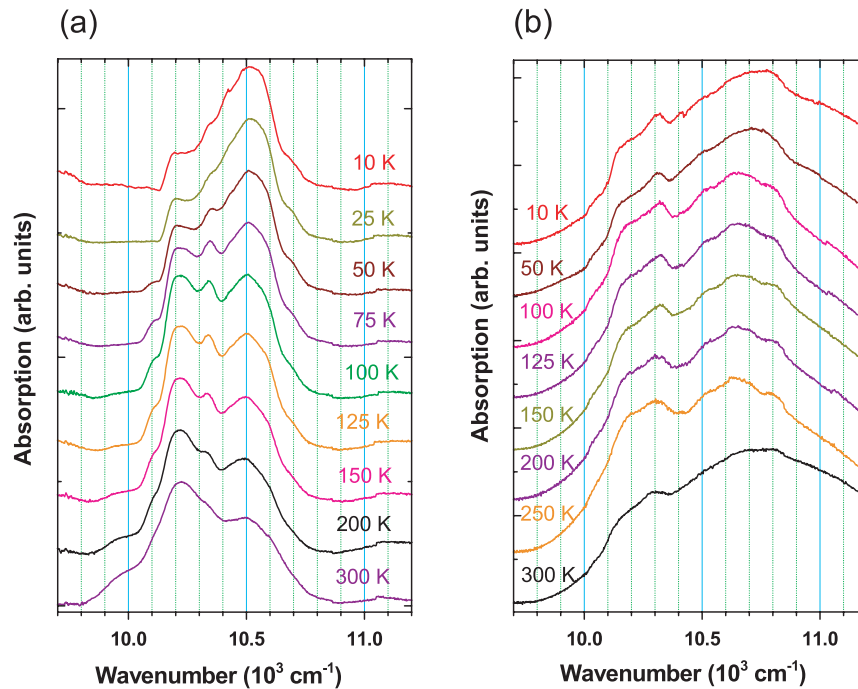


Figure 2. Normalized ambient-pressure absorption spectra of (a) $Y_{0.99}Yb_{0.01}PO_4$ and (b) $Gd_{0.99}Yb_{0.01}PO_4$ crystals at temperatures from 10 to 300 K. The spectra are shifted along the vertical axis for clarity.

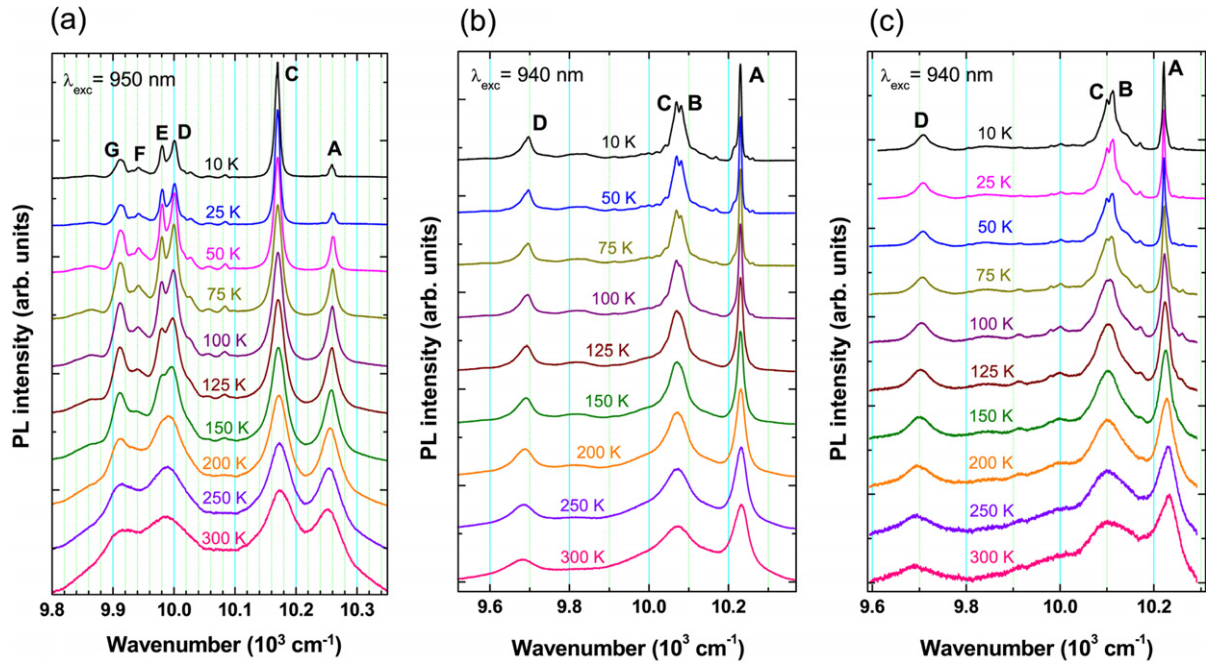


Figure 3. Normalized ambient-pressure photoluminescence spectra of (a) $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$, (b) $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and (c) $\text{La}_{0.95}\text{Yb}_{0.05}\text{PO}_4$ crystals at temperatures from 10 to 300 K.

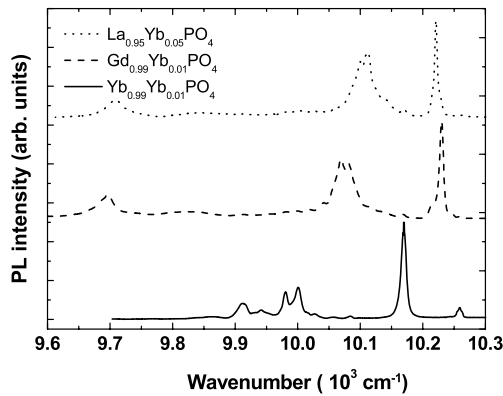


Figure 4. Normalized ambient-pressure PL spectra of $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$, $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{La}_{0.95}\text{Yb}_{0.05}\text{PO}_4$ crystals at temperature 10 K.

so we can expect stronger crystal fields in crystals having the monazite structure.

3.2. Temperature dependence of the decay kinetics of luminescence of Yb^{3+} ions in YPO_4 , GdPO_4 and LaPO_4 crystals at ambient pressure

Decay kinetics measurements as a function of temperature were performed for the two strongest luminescence lines of each studied crystal. The results are presented in figure 5. The measured values of the decay times are consistent with typically observed decay times of the ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ intra-4f-shell emission of Yb^{3+} in ionic materials, which are in the 500–2500 μs range [6, 36–39]. The decay times of the $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{La}_{0.95}\text{Yb}_{0.05}\text{PO}_4$ crystals reveal a

very weak temperature dependence: they are equal to about 820 μs at 20 K and decrease to about 780 μs and 740 μs at room temperature for $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{La}_{0.95}\text{Yb}_{0.05}\text{PO}_4$, respectively. The slightly lower decay time values and the stronger intensity decrease with temperature observed in $\text{La}_{0.95}\text{Yb}_{0.05}\text{PO}_4$ can be connected with a larger ytterbium content giving rise to concentration quenching processes [1].

The results obtained for $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ crystal are slightly surprising. The observed decay times first increase from about 990 up to 1050 μs with temperature increasing from 20 to 75 K, and then decrease to the level of 900 μs at room temperature. The initial increase of the lifetime can tentatively be explained by the presence of fluorescence reabsorption, the so-called self-trapping effect due to resonant ${}^2\text{F}_{5/2} \leftrightarrow {}^2\text{F}_{7/2}$ transitions in Yb^{3+} [1, 40]. This effect has been analyzed by Auzel *et al* and Guyot *et al*, and interpreted by a diffusion process within the Yb^{3+} doping ion subsystem [41, 42]. Increasing of the temperature allows more diffusion and as a result we observe the competition of self-trapping and temperature quenching processes.

The influence of fluorescence reabsorption is visible also as a difference of low-temperature decay times measured at ambient pressure on a bulk sample and on a thin sample loaded into the DAC; the decay times measured on a bulk sample are about 100 μs ($\approx 10\%$) longer for the $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ crystal and about 40 μs ($\approx 5\%$) longer in the $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ crystal (see section 3.3, figure 8).

Apart from this unusual behavior of the decay times for the $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ crystal, both luminescence spectra and the decay times of ytterbium doped orthophosphates reveal a high thermal stability which makes these crystals very promising materials for optical applications.

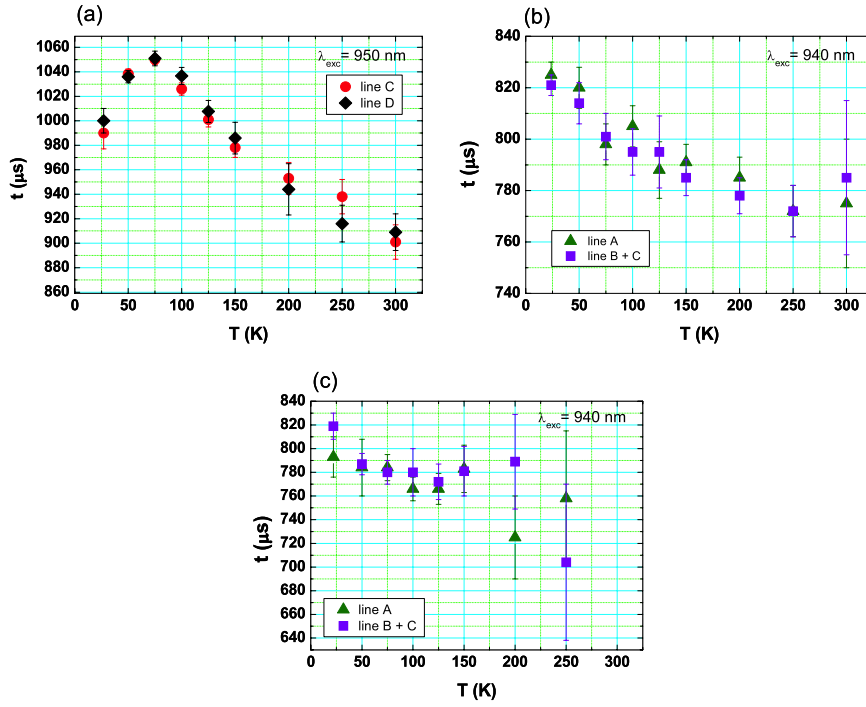


Figure 5. Temperature dependencies of the decay kinetics of luminescence of Yb^{3+} ions in (a) YPO_4 , (b) GdPO_4 and (c) LaPO_4 crystals at ambient pressure. The line descriptions are the same as in figure 3.

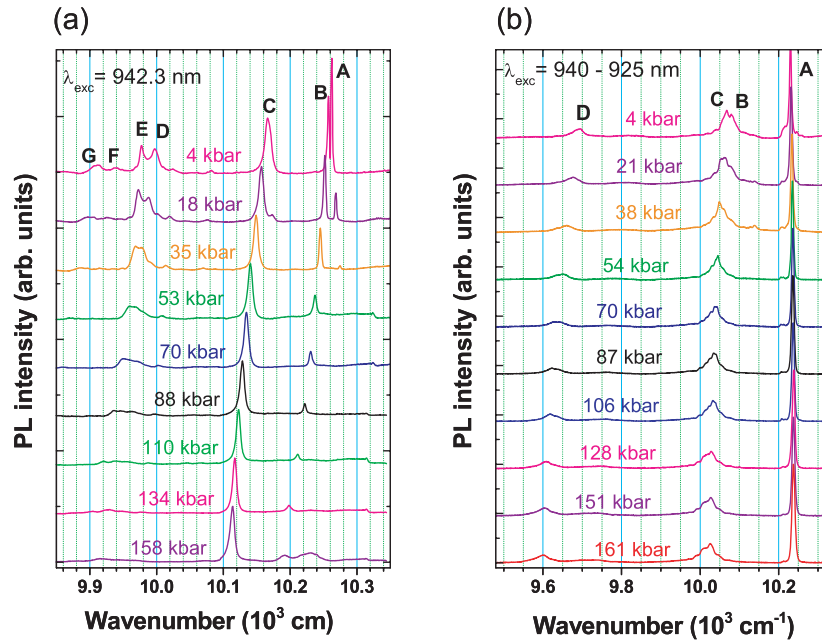


Figure 6. Pressure dependence of the Yb^{3+} luminescence spectra in (a) $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and (b) $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ crystals measured at $T = 10 \text{ K}$. The spectra are shifted along the vertical axis for clarity.

3.3. Pressure dependence of the luminescence spectra of Yb^{3+} ions in YPO_4 and GdPO_4 crystals at low temperature

In the present part of the paper we will present high-pressure studies of only two crystals: $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$. As the GdPO_4 and LaPO_4 have the same crystal structure and the luminescence properties of ytterbium dopant at ambient pressure were found to be

similar in both crystals, we expect to obtain parallel results also at high pressures. On the other hand using $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ crystals with the same ytterbium concentration makes the comparison of their optical properties under pressure more straightforward.

The pressure dependence of the luminescence spectra of Yb^{3+} in $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ at $T = 10 \text{ K}$, in the pressure range up to about 160 kbar is shown in figure 6,

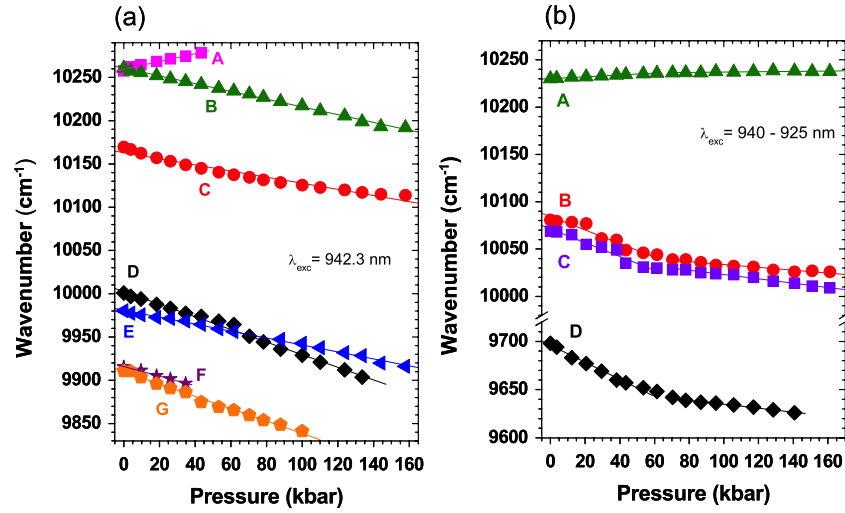


Figure 7. Spectral positions of the major luminescence lines of (a) $Y_{0.99}Yb_{0.01}PO_4$ and (b) $Gd_{0.99}Yb_{0.01}PO_4$ crystals as a function of pressure. The pressure coefficients correspond to the slopes of the linear fits to the data.

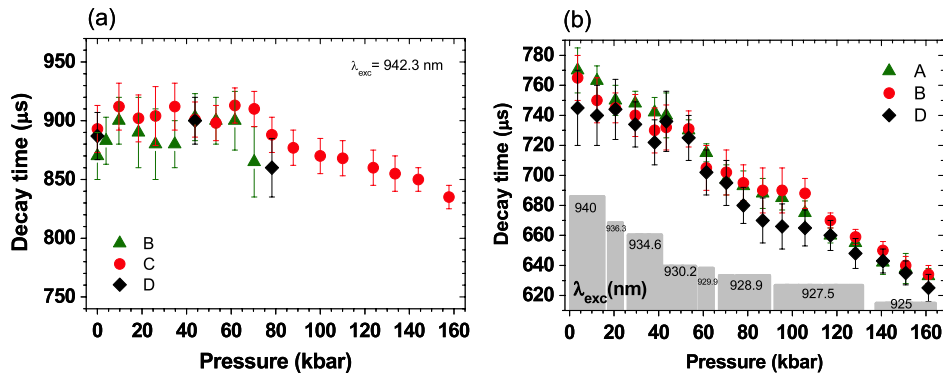


Figure 8. Pressure dependence of the luminescence decay times of Yb^{3+} ions in (a) $Y_{0.99}Yb_{0.01}PO_4$ and (b) $Gd_{0.99}Yb_{0.01}PO_4$ crystals at $T = 10$ K. The excitation wavelength of $Gd_{0.99}Yb_{0.01}PO_4$ was changed to maintain possibly high luminescence intensity. The letters refer to the same line descriptions as in figure 6.

and the spectral positions of the major luminescence lines as a function of pressure are presented in figure 7. One optimum excitation wavelength of the Ti:sapphire laser equal to 942.3 nm (10612 cm^{-1}) has been chosen in the case of $Y_{0.99}Yb_{0.01}PO_4$, whereas the excitation wavelength used for $Gd_{0.99}Yb_{0.01}PO_4$ has been changed gradually from 940 nm (10638 cm^{-1}) to 925 nm (10811 cm^{-1}) with increasing pressure in order to obtain the highest luminescence intensity.

The luminescence spectrum of the $Y_{0.99}Yb_{0.01}PO_4$ crystal measured at the lowest pressure differs slightly from the one at ambient pressure (see figure 3(a)). The line denoted as A in figure 3(a) is split into two lines (denoted as A and B in figure 6(a)) and their intensity is much higher. This effect can be caused by the change in the excitation wavelength, by a different orientation of the polished sample inserted into the DAC or by the influence of the sample size on reabsorption processes. The splitting of the A and B lines increases with pressure, the intensity of the line A decreases and at pressures exceeding 45 kbar it is practically not visible. Moreover line A is the only line of $Y_{0.99}Yb_{0.01}PO_4$ spectrum whose energy shifts to higher energies with increasing pressure; the

Table 1. Spectral positions of the major luminescence lines of Yb^{3+} in $Y_{0.99}Yb_{0.01}PO_4$ at ambient pressure and their pressure coefficients.

Line assignment (see figures 6(a) and 7(a))	Line spectral position E (cm^{-1})	dE/dp ($\text{cm}^{-1}\text{ kbar}^{-1}$)
A	10259 ± 1	0.44 ± 0.03
B	10261 ± 1	-0.45 ± 0.01
C	10163 ± 2	-0.35 ± 0.02
D	10002 ± 2	-0.73 ± 0.02
E	9981 ± 1	-0.40 ± 0.01
F	9916 ± 1	-0.55 ± 0.03
G	9910 ± 2	-0.71 ± 0.02

other lines exhibit shifts toward lower energies. All the luminescence lines shift linearly. The slopes of the linear fits to the experimental data give the pressure coefficient values. The pressure coefficients of the major luminescence lines and their spectral positions at ambient pressure are collected in table 1.

The pressure behavior of the $Gd_{0.99}Yb_{0.01}PO_4$ luminescence is slightly different. The pressure shift of the highest energy luminescence line (denoted as A in figure 6(b)) is also

Table 2. Spectral positions of the major luminescence lines of Yb^{3+} in $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ at ambient pressure and their pressure coefficients.

Line assignment (see figures 6(b) and 7(b))	Line spectral position E (cm^{-1})	dE/dp $p < 55$ kbar ($\text{cm}^{-1} \text{kbar}^{-1}$)	dE/dp $p > 75$ kbar ($\text{cm}^{-1} \text{kbar}^{-1}$)
A	$10\,230 \pm 1$	0.095 ± 0.004	0.018 ± 0.007
B	$10\,084 \pm 3$	-0.71 ± 0.09	-0.15 ± 0.02
C	$10\,071 \pm 3$	-0.73 ± 0.07	-0.23 ± 0.01
D	$9\,696 \pm 2$	-0.88 ± 0.05	-0.20 ± 0.01

positive, and negative for all the other lines. However above about 65 kbar the pressure dependencies of the peak positions of all the luminescence lines flatten out and the values of pressure coefficients decrease. This effect cannot be related to structural changes of GdPO_4 under pressure, because this compound remains stable in the monazite structure in the whole pressure range under investigation [43]. A detailed explanation of this result needs additional studies.

The pressure coefficients of the major luminescence lines in the two pressure ranges (below 55 and over 75 kbar) and their spectral positions at ambient pressure are collected in table 2.

3.4. Pressure dependence of the decay kinetics of Yb^{3+} ions in YPO_4 and GdPO_4 crystals at low temperature

The decay kinetics of the luminescence, recorded for various luminescence transitions, were found to be single exponential (i.e., can be well described by the $I(t) = I_0 \exp(-t/\tau)$ dependence). Pressure dependencies of the luminescence decay times measured at $T = 10$ K are shown in figure 8.

In the $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ crystal the values of the decay times are initially almost constant. Only a very small increase from about $880 \pm 20 \mu\text{s}$ at ambient pressure to about $900 \pm 30 \mu\text{s}$ at 70 kbar is observed. At pressures exceeding 70 kbar the decay times decrease to about $840 \pm 10 \mu\text{s}$ at 160 kbar. This effect is similar to that observed in the ytterbium doped gadolinium gallium garnet crystal ($\text{Gd}_3\text{Ga}_5\text{O}_{12}$), where ytterbium ions are surrounded by eight O^{2-} ions with D_2 point group symmetry [39]. This behavior was explained by the pressure induced changes in the local symmetry of the Yb^{3+} ion environment, i.e. an initial shift toward cubic symmetry up to a certain pressure (in our case: 70 kbar) and then a lowering with further pressure increase. The same symmetry changes were reported also for $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ garnet and gadolinium scandium gallium garnet ($\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$) doped with Nd^{3+} , where the symmetry changes can be easily monitored by the splitting of the quartet $^4\text{F}_{3/2}$ level of neodymium ions [39, 44]. This effect may happen if not all RE-O nearest-neighbor bond lengths are fully equivalent, which is also the case for $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and other crystals with garnet or zircon structure [45]. The second possibility, structural changes of YPO_4 under pressure, can be excluded, because it transforms from zircon to monazite structure only at 197 kbar [43].

This explanation enabled the theoretical model to be elaborated and a quite satisfactory fit to the experimental data to be obtained in the case of the $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Yb}^{3+}$ crystal [38, 39]. The changes of the decay times are connected to the changes of coupling between the 4f and 5d orbitals due

to a decrease of the energy of the $4f^{12}5d^1$ level with pressure, and also to the pressure variation of odd-parity lattice distortion (where the origin of these distortions is structural and is not related to pressure non-hydrostaticity). As a result at lower pressures, where the local symmetry of Yb^{3+} becomes higher and the odd-parity crystal field component decreases, a small initial increase of decay times is observed. At higher pressures the increase of odd-parity crystal field component enhanced by the continuous decrease of the energy of the $4f^{12}5d^1$ level causes a clear decrease of the decay time.

The pressure behavior of the $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ crystal is different: in this case the decay time values decrease monotonically with increasing pressure in the whole measured pressure range. This effect is in turn similar to the one observed for the ytterbium doped lithium niobate crystal (LiNbO_3), where ytterbium ions are surrounded by six oxygens with C_3 point group symmetry [38]. The lower symmetry site results in a higher odd-parity crystal field contribution and shorter decay times. Our results can be explained by a similar effect. The applied pressure causes an increase of the odd-parity crystal field contribution and a decrease of the energy of the $4f^{12}5d^1$ level in the whole pressure range, so that we observe a continuous decrease of the decay time.

4. Summary and conclusions

The study of the influence of temperature and hydrostatic pressure on the radiative intrashell f-f transitions ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$) of Yb^{3+} ions in orthophosphate host crystals $\text{Y}_{0.99}\text{Yb}_{0.01}\text{PO}_4$, $\text{Gd}_{0.99}\text{Yb}_{0.01}\text{PO}_4$ and $\text{La}_{0.95}\text{Yb}_{0.05}\text{PO}_4$ has been presented. We have shown that Yb^{3+} creates thermally stable optically active centers with a weak temperature quenching of the luminescence. The transition energy was found to be only slightly sensitive both to the host crystal and to the pressure induced increase of crystal field strength. In contrast, the probability of the radiative transitions exhibits a distinct dependence on the crystal field strength and on the local symmetry of Yb^{3+} ions. As the longer lifetimes are required to achieve minimum optical pumping in lasing materials, we can tentatively conclude that using host crystals with (i) possible high local symmetry of dopant and (ii) weak crystal field strength is more desirable from the point of view of potential applications of ytterbium in diode pumped lasers.

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