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Investigation of high-energetic transitions in some Pr^{3+}-doped fluoride and oxide crystals

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ABSTRACT

The excitation and emission spectra obtained for Pr^{3+}:$YAlO_3$, Pr^{3+}:$LiYF_4$ and $K_5PrLi_2F_{10}$ crystals by means of high-energetic excitation with synchrotron radiation (HASYLAB, DESY Hamburg, Germany) are presented. In the emission spectra broad, overlapping bands in UV range are present. Their positions, bandwidths as well as the short emission decay times suggest, that emission from levels of 4f5d configuration dominate in all of the crystals investigated.

Keywords: Pr^{3+}, optical properties, synchrotron radiation excitation, 5d-4f interconfigurational transitions

1. INTRODUCTION

In recent years an interest in high-energetic intraconfigurational transitions within $4f^n$ electron configuration as well as in interconfiguratinal $4f^n$- $4f^{n-1}5d$ transitions has significantly increased due to expected possible applications. Investigations of the $4f^n$-$4f^n$ transitions follow an old idea of achieving simultaneously more than one emitted photon of luminescence in the visible (VIS) range after excitation with a high energetic photon in the ultraviolet (UV) range [1-3]. Various matrices singly or doubly doped with RE ions (first of all with Pr, Gd, Tm, Tb) have been recently studied [e.g. in ref. 4-7] with hope to find systems where processes of this type (called "cascade emission", "quantum cutting" or "down-conversion") take place with a high quantum efficiency. Such materials could then be used as phosphors for mercury-free UV lamps or other light sources. The interconfigurational $4f^{n-1}5d$ - $4f^n$ transitions are parity-allowed and characterised by short emission lifetimes and broad emission bands of high intensity located in the UV range[8-12]. It is expected that they can be used for tunable solid state lasers, as laser oscillation based on $4f^{n-1}5d$ - $4f^n$ transition was yet realised in Ce^{3+} crystals[13].

For trivalent praseodymium both types of transitions can take place, depending on the host matrix and energetic location of the $^1S_0$ multiplet of the $4f^2$ electron configuration (ca. 46500 cm^{-1}) relative to the states of the 4f5d electron configuration. In some materials the excitation into the $^1S_0$ multiplet brings about a cascade emission due to the two-step intraconfigurational $4f^2$-$4f^2$ transitions: $^1S_0 \rightarrow {}^1I_6$ (ca. 410 nm) followed by $^3P_0 \rightarrow {}^3H_4$ (ca. 485 nm)[1,2,6]. The presence of such a two-photon emission in Pr^{3+}-doped materials is possible only if the $^1S_0$ multiplet is located energetically lower than the lowest state of the 4f5d configuration. It is expected to be observed mainly in fluoride crystals, where the high electronegativity of F^- ion induces a weak crystal field splitting of the 4f5d configuration. The efficiency of this two-photon emission depends strongly on the ion-host interactions (nonradiative relaxation rates) and highly efficient Pr-doped materials for application based on photon cascade emission have not been found yet.

In the majority of the materials investigated so far, the $^1S_0$ multiplet is located within the energetically extended 4f5d states and the high-energetic excitation brings about the emission due to the 4f5d → 4f transitions. Spectroscopic investigations of transitions involving 4f5d levels of Pr^{3+} have been so far carried out for a number of materials (e.g. $Y_3Al_5O_{12}$[12-14], $YAlO_3$[12,15], CaF_2, $LiYF_4$[16,17]) by means of either synchrotron radiation or excited state absorption and two-step excitation techniques or by using the UV excitation lamps. Due to the experimental limitations in the spectral range of high energies, the results obtained are not always consistent, complete and clear. Thus, the comparison of data obtained by various techniques and for various Pr^{3+} materials extends the knowledge about the energy level structure and processes investigated.

In this work we present the spectroscopic results obtained for three single crystals: $YAlO_3$, $LiYF_4$, $K_5PrLi_2F_{10}$ containing Pr^{3+} after high-energetic excitation by synchrotron radiation. The investigation was performed in order to get

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better characterisation of the energy structure of Pr^{3+} ions in $YAlO_3$ and $LiYF_4$ crystals, yet partly investigated [9,12,15] and to determine the position of higher-lying Pr^{3+} energy levels in $K_5PrLi_2F_{10}$ crystal.

2. EXPERIMENTAL

The $YAlO_3:Pr^{3+}$ (YAP) and $LiYF_4:Pr^{3+}$ (YLF) crystals investigated in this work were grown by the Czochralski method and contained 0.75at% and 3at% Pr, respectively. The $K_5PrLi_2F_{10}$ (KPLF) stoichiometric crystal was grown by the Bridgman method[18]. The investigations were carried out at the SUPERLUMI station of HASYLAB (Hamburger Synchrotron Laboratorium) at DESY (Deutsches Elektronen-Synchrotron) synchrotron centre in Hamburg, The experiments were performed at low temperatures (ca. 10K) and at room temperature (RT). The spectral range of the excitation measurements was 50-350 nm (24.7 eV-3.5 eV) with a resolution of the primary monochromator of 0.3 nm. The sensitivity of the set-up used for excitation measurements was corrected by comparison with the sodium salicitate spectrum measured as a standard. The emission spectra were measured in the 200-300 nm and 300-600 nm spectral ranges by using two different monochromators with the resolution of approximately 3nm. The presented emission spectra are not corrected with respect to the sensitivity of the set-up used. The kinetics of the emission decays were measured by standard single-photon counting method. The determination of the decay of the emission is limited by the period between the synchrotron bunches and decay times longer than 200 ns were not possible to be recorded.

3. RESULTS AND DISCUSSION

The optical properties of Pr^{3+} ions in the investigated YAP, YLF and KPLF crystals were previously investigated in spectral ranges of typical spectroscopic methods (e.g. in ref. [19], [20] and [18,21], respectively). In the absorption spectra the narrow bands due to the f-f transitions from the $^3H_4$ multiplet to the multiplets up to the $^3P_2$ are observed (see Fig. 1, energy levels scheme). As an example, the absorption spectrum of the KPLF crystal recorded at RT is presented in Fig. 2.

The positions of the high-lying states, that is of the $^1S_0$ multiplet or states of the 4f5d electron configuration, usually can not be determined from absorption spectra due to either absorption edge of the crystal host or to the too high absorption cross sections of f-d transitions or/and presence of other intense bands (charge transfer, crystal defects, impurities). In the presented absorption spectrum of KPLF the rise of absorption for wavelength lower than 300 nm is probable due to some defects or charge-transfer transition within the host, as it is observed also for the $K_5LaLi_2F_{10}$ crystal[18]. Under excitation into

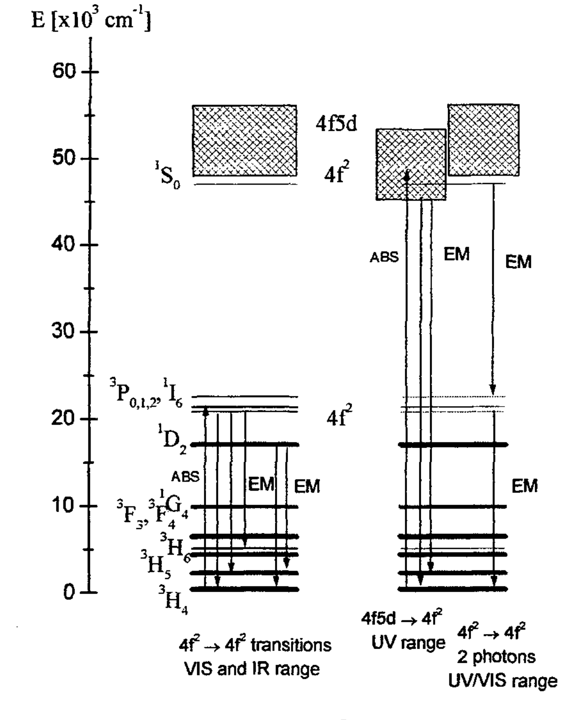

Fig. 1. Energy level scheme of Pr^{3+}-ion

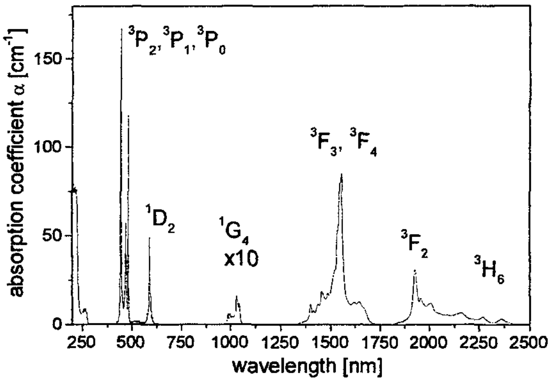

Fig. 2. Absorption spectrum (300K) of the $K_5PrLi_2F_{10}$ crystal

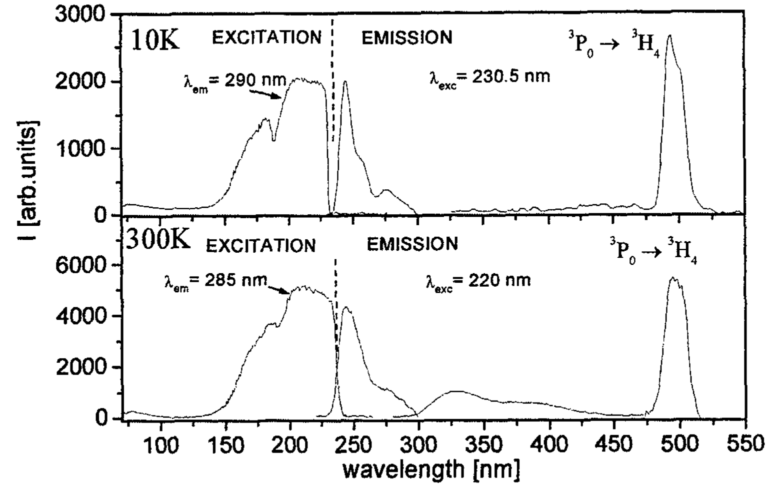

Fig. 3. Excitation and emission spectra of $YAlO_3$ crystal

states of $4f^2$ electron configuration up to the ^3P_J group (up to about 22500cm^{-1}) an emission from the $^3P_0$ or/and from the $^1D_2$ multiplets to the lower-lying multiplets is observed in the blue, green and red spectral ranges. The lifetimes of the luminescent $^3P_0$ multiplet for YAP, YLF and KPLF are at RT about 12 μs[19], 43μs[16] and 0.7μs[20], respectively.

In the Figs. 3-7 the excitation and emission spectra of the Pr^{3+} recorded in a spectral range from 50 nm to 350 nm and from 200 nm up to 600 nm, respectively, are shown. In the excitation spectra dominate the broad slightly structured bands in the range between about 120 nm to about 225 nm. These bands are assigned to the transitions from Pr^{3+} ground state of $4f^2$ configuration ($^3H_4$) to the states of Pr^{3+} 4f5d configuration. Because of the large radial extension of the d-orbitals, transitions involving those states are crystal field sensitive, broad and vibronic in character. In the emission spectra obtained after excitation within the 4f5d states some broad bands in UV and VIS range are present, which are assigned as due to the 5d-4f transitions. The band at about 480 nm is assigned to the $^3P_0 \rightarrow {}^3H_4$ transition. Although this band is not so narrow as expected for 4f-4f transition (due to the low resolution by the measurement), its position practically independent on the crystal host and the long decay time of this emission support this assignment.

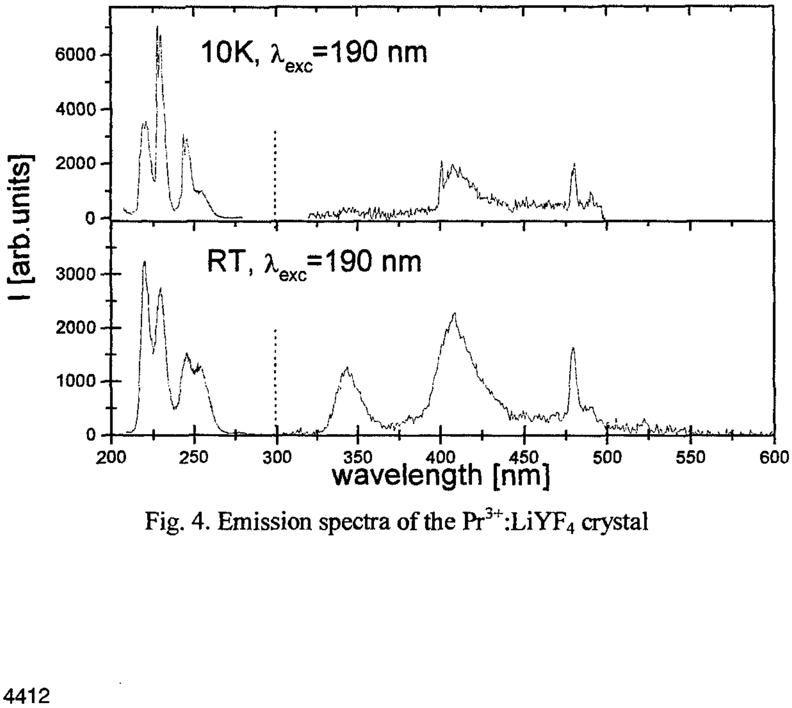

Fig. 4. Emission spectra of the Pr^{3+}:$LiYF_4$ crystal

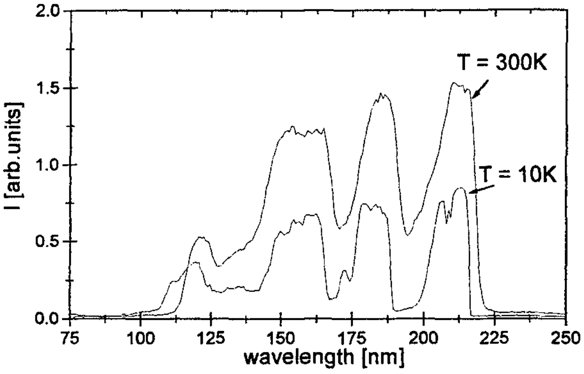

Fig. 5. Excitation spectra of the Pr^{3+}:$LiYF_4$ crystal, λ_{em}=410 nm

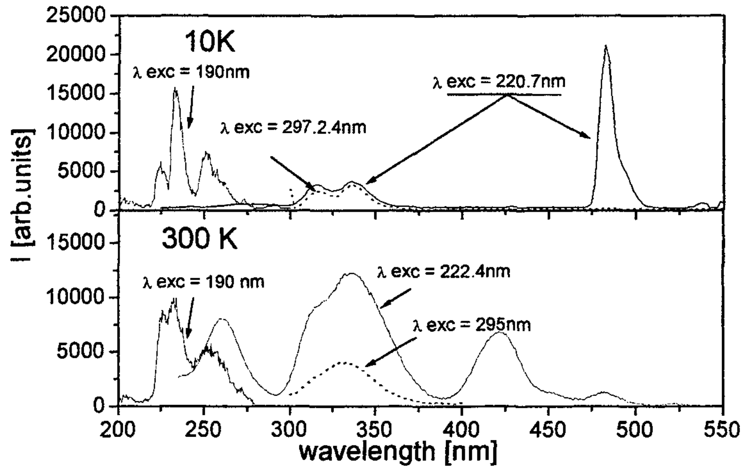

Fig. 6. Emission spectra of the $K_5PrLi_2F_{10}$ crystal

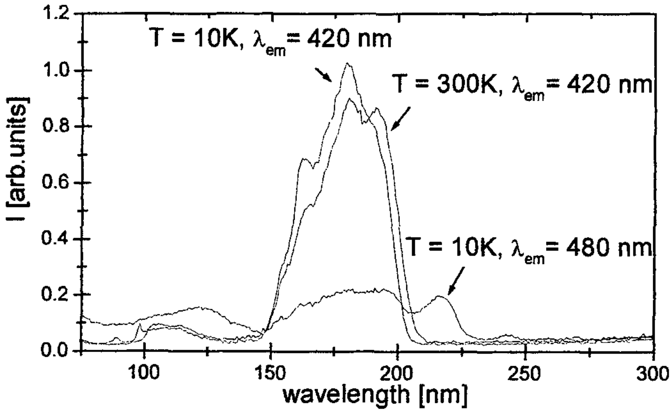

Fig. 7. Excitation spectra of the $K_5PrLi_2F_{10}$ crystal

The mean energies of main absorption and emission transitions observed in the spectra of the crystals investigated are summarised in Table 1. In neither absorption nor emission spectra there are hints for presence of transitions involving the $^{1}S_{0}$ multiplet. The f-f transitions due to the presence of the $^{1}S_{0}$ level would result in a weak and relative sharp peak in an excitation spectrum. However, no such peaks are observed for energies below states of 4f5d configuration in the presented spectra. In the emission spectra the bands due to the emission from $^{1}S_{0}$ multiplet ($^{1}S_{0} \rightarrow {}^{1}I_{6}$) should be located at about 410 nm and have a relative long lifetime. In our emission spectra we observe a strong band around 400 nm in the case of YLF and KPLF crystals and a weak one in the case of YAP crystal. However, these bands are relatively broad, are accompanied by other bands ascribed to the transitions from the 4f5d states, have practically the same decay characteristics and their energetic position can be ascribed to transitions from 4f5d levels to the $^{1}D_{2}$ or $^{3}P_{0}$ multiplets, respectively (see Table 1).Thus, we assume, that for all investigated crystals the $^{1}S_{0}$ level is located above the lowest levels of 4f5d states.

Crystal	Excitation energies/λ [cm^{-1}]/[nm]	Transition	Emission energies /λ [cm^{-1}]/[nm]	Lifetime	Transition
Pr:YAlO$_3$	46 500/ 215	$^{3}H_{4}$ (4f^{2}) → 4f5d (I)	40 780/ 245	7-9 ns	4f5d (I) → $^{3}H_{4}$ (4f^{2})
	55 500/ 180	$^{3}H_{4}$ (4f^{2}) → 4f5d (II)	38 820/ 258	"	4f5d (I) → $^{3}H_{5}$ (4f^{2})
			36 280/ 275	"	4f5d (I) → $^{3}H_{6}$ (4f^{2})
			33 000/ 290	"	4f5d (I) → $^{3}F_{3,4}$ (4f^{2})
			25 640/ 390	"	4f5d (I) → $^{1}D_{2}$ (4f^{2})
			23 530/ 425	"	4f5d (I) → $^{1}D_{2}$ (4f^{2})
			20 400/ 490	long (μs)	$^{3}P_{0}$ (4f^{2}) → $^{3}H_{4}$ (4f^{2})
Pr:YLiF$_4$	46 500/ 215	$^{3}H_{4}$ (4f^{2}) → 4f5d (I)	45 450/ 220.0	17-20 ns	4f5d (I) → $^{3}H_{4}$ (4f^{2})
	48 300/ 207	$^{3}H_{4}$ (4f^{2}) → 4f5d (I)	45 290/ 220.8	"	
	53 700/ 186	$^{3}H_{4}$ (4f^{2}) → 4f5d (I)	43 890/ 227.8	"	4f5d (I) → $^{3}H_{5}$ (4f^{2})
	57 940/ 173	$^{3}H_{4}$ (4f^{2}) → 4f5d (I)	43 515/ 229.8	"	
	61 730/ 162	$^{3}H_{4}$ (4f^{2}) → 4f5d (II)	41 050/ 243.6	"	4f5d (I) → $^{3}H_{6}$,$^{3}F_{2}$ (4f^{2})
	86 960/ 115	excitons/ host	40 683/ 245.8	"	
			39 180/ 255.2	"	4f5d (I) → $^{3}F_{,3,4}$ (4f^{2})
			35 650/ 280	"	4f5d (I) → $^{1}G_{4}$ (4f^{2})
			29 070/ 344	"	4f5d (I) → $^{1}D_{2}$ (4f^{2})
			24 930/ 401	"	4f5d (I) → $^{3}P_{0}$ (4f^{2})
			20 860/ 479	long (μs)	$^{3}P_{0}$ (4f^{2}) → $^{3}H_{4}$ (4f^{2})
K$_5$PrLi$_2$F$_{10}$	41 150/ 243	charge transfer/defects	44 640/ 224	9-11 ns	4f5d (I) → $^{3}H_{4}$ (4f^{2})
	46 300/ 216	charge transfer/defects	43 100/ 232	"	4f5d (I) → $^{3}H_{5}$ (4f^{2})
	52 630/ 190	$^{3}H_{4}$ (4f^{2}) → 4f5d (I)	39 930/ 250	"	4f5d (I) → $^{3}H_{6}$,$^{3}F_{2}$ (4f^{2})
	61 300/ 163	$^{3}H_{4}$ (4f^{2}) → 4f5d (I)	38 460/ 260	"	4f5d (I) → $^{3}F_{3,4}$ (4f^{2})
	64 510/ 163	$^{3}H_{4}$ (4f^{2}) → 4f5d (II)	29 655/ 337	~30 ns	defects/charge transfer
	81 960/ 122	excitons/ host	23 750/ 421	9-11 ns	4f5d (I) → $^{3}P_{0}$ (4f^{2})
			22 200/ 450	"	4f5d (I) → $^{3}P_{2}$ (4f^{2})
			20 800/ 480	long (μs)	$^{3}P_{0}$ (4f^{2}) → $^{3}H_{4}$ (4f^{2})

Table 1. Energies and wavelengths of transitions observed in excitation and emission spectra of the crystals investigated, emission decay times and assignment of transitions observed in the spectra.

The band appearing in the excitation spectra in the high energy region (100-150 nm) is usually characteristic of the transfer of the band to band energy to the luminescent dopant (host-sensitised or exciton luminescence). If the energy corresponds to the fundamental absorption edge of the crystal a photon of this energy can be absorbed by the host and create an electron in the conduction band and a hole in the valence band. The charge carriers can migrate separately within the lattice or together as an exciton till they reach the recombination centre. If the carriers are trapped by the dopant RE ion as a recombination centre, a part of the recombination energy can be emitted in the radiative transition. The host-sensitised luminescence is of significant intensity for some systems only. In the case of crystals investigated by us, the excitation bands at about 120 nm for YLF and for KPLF can by most probably due to the host-sensitisation of emission. The position of this band for YLF is in agreement with the position of fundamental absorption determined also by other techniques[9]. For KLPF the fundamental absorption was not known yet.

4. CONCLUSIONS

We have investigated the transitions involving the 4f5d states of Pr^{3+} ions in $YAlO_3{:}Pr^{3+}$ (YAP), $LiYF_4{:}Pr^{3+}$ (YLF) and $K_5PrLi_2F_{10}$ (KPLF) crystals. In both excitation and emission spectra of the crystals investigated the broad and intense bands due to interconfigurational 4f5d-4f transitions appear, suggesting that the $^1S_0$ multiplet of Pr^{3+} is located above the lowest levels of 4f5d states. Thus, the cascade emission does not take place in those materials. The lifetimes of emission from the 4f5d states are short, of the order of 10 ns for YAP and KPLF and about 20 ns for YLF. This is a desirable feature for possible laser oscillation in this range, as it implies high oscillator strengths and high stimulated emission cross sections.

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