Assignment of spectroscopic properties in praseodymium-doped and praseodymium/ytterbium-co-doped ternary K_2LaX_5 (X = Cl, Br, I) Halides

J. Cybińska^a, J. Legendziewicz^{a,*}, G. Boulon^b, A. Bensalah^b, G. Meyer^c

^a Institute of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

^b Physics and Chemistry of Luminescent Materials Laboratory, UMR 5620 CNRS, Claude Bernard/Lyon University, 69622 Villeurbanne, France

^c Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

Received 6 January 2005; accepted 10 January 2005

Available online 20 June 2005

Abstract

The potassium lanthanum ternary halides are appropriate host lattices for various luminescent materials including laser devices. The lanthanum ternary halide lattice, co-doped by different lanthanide ions, can exhibit up-conversion emission in a wide spectral range from blue to red. For this purpose (Pr^{3+}) and (Yb^{3+}) ions and also co-doping by other Ln ions are promising systems. In this lecture the excited states dynamics in the praseodymium and praseodymium co-doped by ytterbium ion ternary halides will be discussed basing on the high resolution absorption, emission and emission excitation spectra at 293, 77 and 4 K as well as the decay times of the crystals with different concentrations from 2 mol% to stoichiometric of the optically active ions. Changes of the spectral properties in the range of 4f–5d and 4f–4f transitions are observed for the series of halides (Cl, Br, I).

The differences in emission behavior can be explained by changes of the crystal field strengths, subtle variations of electron–phonon coupling, decrease of the phonon energies and increase of covalency. Some features in the emission vary with excitation energy and in some cases exciton emission and strong re-absorption was detected. Lowering of the emission efficiency in the concentrated systems can be due to the concentration quenching and energy migration to traps. On the other hand, formation of the polymeric chains in the structure is responsible for strong ion–ion interaction, which can promote the up-conversion process. Excitation into 1D_2 of the Pr^{3+} state leads to up-conversion emission from 3P_0 state, whereas 940 nm pumping line used in excitation of $^2F_{5/2}$ level of the Yb^{3+} in $K_2LaCl_5:5\% Pr^{3+}, 2\% Yb^{3+}$ crystal is responsible for both emission from 1D_2 and 3P_0 of Pr^{3+} levels. Non-radiative energy transfers between Pr^{3+} ions and Pr^{3+} – Yb^{3+} ions are observed and up-conversion mechanisms are proposed.

© 2005 Elsevier B.V. All rights reserved.

1. Introduction

The wide band gap materials like fluorides and other halides co-doped by lanthanide ions are important in obtaining valuable insight into many aspects of luminescence centers as well as for wide applications. The development of new phosphors for vacuum ultraviolet (VUV) excitation is an important new challenge in the field of

luminescence materials research. The phosphors excited in the VUV can be used in a new generation of lamps or in gas plasma discharge devices for flat color display panels. Praseodymium and cerium compounds seem to be promising for these purposes. The parity allowed electric dipole transitions in trivalent Ce^{3+} , Pr^{3+} and Nd^{3+} ions make them attractive activating centers in different crystalline hosts which can exhibit intense broad emission useful for fast scintillators and ultraviolet tunable laser devices. This wide emission due to strong coupling between 5d electron of Pr^{3+} ion and lattice phonons of the host is observed if the lowest 5d state

* Corresponding author. Tel.: +48 71 3204 300; fax: +48 71 3282 348.
E-mail address: jl@wchuwr.chem.uni.wroc.pl (J. Legendziewicz).

is located below the $4f^2(^1S_0)$ state. If the 5d states are located at higher energies than the 1S_0 state, the photon cascade emission can be observed after excitation in the 5d bands with quantum yields of more than 100% [1]. This makes interesting investigation of luminescence of Pr^{3+} ions in different host lattices. On the other hand, Yb^{3+} ion spectroscopy have received considerable attention over the past years, too, because of its potential laser emission around 1 μm and also as a sensitizer of the Pr^{3+} emission [10]. The results of the spectroscopic studies in this area were reported mainly by Krupa and Queffelec [2], Meijerink and co-workers [5,8,9], Dorenbos et al. [3,4,6,7], Kaminskii and others [10–16]. Recently, selected optical behaviours [17,18] and simulation of the crystal field effect on the Pr^{3+} ion in ternary chlorides were reported by us [19,20].

In an attempt to further investigations of the influence of the chemical environment on the optical properties and excited state dynamics altered by variation of the halide anions from Cl to Br to I, we have proposed to study either Pr^{3+} -doped or Pr^{3+} – Yb^{3+} co-doped pure lanthanum ternary halides, as well as stoichiometric K_2LnX_5 systems. The goal of the present paper is focused mainly on emission and up-conversion processes in praseodymium and praseodymium co-doped by ytterbium ternary halides.

2. Experimental

2.1. Sample preparation

The K_2LnX_5 and mixed $\text{K}_2(\text{La},\text{Pr})\text{X}_5$; (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$ and $\text{Ln} = \text{Pr}, \text{Yb}$) single crystals were grown by using the Bridgman technique according to the procedure described in [21,22]. The melt was obtained by heating the appropriate amounts of the starting materials (KCl , LaX_3 , PrX_3 and YbCl_3) which were purified prior to the reaction by sublimation in a tantalum ampoule. LaI_3 and PrI_3 were synthesized from the elements. For the crystal growth stoichiometric amounts of the starting materials were sealed in silica ampoules under vacuum. Cooling of the melt was carried out in two steps: first with a rate of 1°/h and then to the room temperature with a rate of 5 °/h. The conditions of the

synthesis for all synthesized ternary halides are given in Table 1. The Pr^{3+} and Yb^{3+} dopant concentration was varied between 2 and 15 mol% of the total rare earth content. In the case of doped samples large crystals up to 1 cm in diameter could be grown.

The samples were found rather moisture-sensitive and were handled under anhydrous conditions. Cutting, sanding and polishing of the crystals were carried out with paraffin oil in a dry box. In this way samples with parallel faces and with thickness of several mm were obtained. Prior to the spectroscopic and magnetic measurements, the X-ray diffraction was used to check the purity and structure of the samples.

2.2. Spectroscopic measurements

2.2.1. Absorption spectra

For the absorption spectra of the $\text{K}_2(\text{La},\text{Pr})\text{X}_5$ (or K_2PrX_5), the single crystals treated as described above were confined between two quartz plates. Orientation of the crystals was random, the spectra were recorded for different concentrations (2, 5, 15 and 100 mol%) at 4 and 293 K with a Carry-Varian 500 Scan spectrometer equipped with an Oxford CF 1204 helium flow cryostat.

2.2.2. Luminescence spectra

The low resolution luminescence spectra excited by a 450 W Oriel xenon lamp in the UV region with wide band excitation at 280, 248 and 308 nm as well as the excitation spectra at 77 and 293 K were recorded between 240 and 750 nm with an Aminco SPF-500 spectrofluorometer with a resolution of 0.1 nm.

The high resolution luminescence spectra with a resolution of 0.01 nm were detected between 470 and 1500 nm by using an Acton Research Corporation Spectra Pro 750 monochromator equipped with a Hamamatsu R 928 photomultiplier as the detector. A 450 W xenon lamp, Nd:YAG laser, EXCIMER laser and an Ar^+ ion laser (457.9 nm) were used as alternative excitation sources. A specially prepared quartz tube was used to assure the best conditions for detection of luminescence at 4, 77 and 293 K. The VUV and UV excitation spectra of the $^3P_0 \rightarrow ^3H_4$ transition (at 494 nm) between 10 and 240 nm as well as the respective emission spectra were obtained by using synchrotron radiation (DESY

Table 1
The conditions of synthesis for ternary halides

	Starting temperature (°C)	Cooling rate (°C/h)	Till temperature (°C)	Cooling rate (°C/h)	End temperature (°C)
K_2PrCl_5	640	1	470	5	20
$\text{K}_2\text{Pr}_x\text{La}_{1-x}\text{Cl}_5$	900	1	700	5	20
K_2PrBr_5	900	1	700	5	20
$\text{K}_2\text{Pr}_x\text{La}_{1-x}\text{Br}_5$	800	1	650	5	20
$\text{K}_2\text{Yb}_x\text{La}_{1-x}\text{Cl}_5$	900	1	700	5	20
$\text{K}_2\text{Yb}_x\text{La}_{1-x}\text{Br}$	840	1.5	390	10	20

synchrotron, Hamburg Synchrotron Radiation Laboratory HASYLAB, Germany).

Luminescence decay time measurements were recorded with a Tektronix Model TDS 3052 digital oscilloscope following selective excitation by Continuum OPO Surelite I (line 460 nm, 8 ns pulse) pumped by the third harmonic of Nd:YAG.

Excitation of the Yb^{3+} fluorescence was performed with a frequency doubled Nd:YAG laser (10 ns, 10 Hz) pumping a Quantel two-amplifier-stage, dye laser containing a mixture of DCM and LD698 and followed by a hydrogen Raman cell shifter to generate a beam in the 920–960 nm range. The specific infrared fluorescence is selected with a Jobin Yvon HRS1 monochromator by using a 600 grooves/mm grating blazed at 1 μm . The signal is detected by a slow North Coast germanium cell, cooled by liquid nitrogen, and sent into a Stanford boxcar averager SRS 250.

2.3. Structural considerations

The non-doped K_2PrCl_5 crystallizes in the orthorhombic centro-symmetric space group Pnma-D_{2h}^{16} (#62, $Z = 4$) with the lattice constants $a = 12.631(8)$, $b = 8.756(3)$, and $c = 7.973(4)$ Å [21]. The other lanthanide halides of the K_2PrX_5 type are isostructural with ternary praseodymium chloride. Moreover, the crystal structures of the mixed $\text{K}_2(\text{La,Ln})\text{X}_5$ single crystals were found to be isotypic with that of the non-doped compounds. All Pr^{3+} ions have identical crystallographic positions. The overall crystal structure of K_2PrCl_5 consists of PrCl_7 polyhedra connected by two common edges to form infinite chains running along the crystallographic b -axis (Fig. 1). The intra-chain $\text{Pr}^{3+}\text{--Pr}^{3+}$ dis-

Fig. 2. The PrCl_7 units of K_2PrCl_5 forming a distorted monocapped trigonal prism as a coordination polyhedron around the Pr^{3+} ion [19,20].

tances are all equal to 4.550 Å. Other $\text{Pr}^{3+}\text{--Pr}^{3+}$ distances are much longer, starting from 6.89 Å. The PrCl_7 cluster forms of a distorted mono-capped trigonal prism (Fig. 2). The point symmetry of the Pr^{3+} site is low, C_s instead of the ideal C_{2v} point symmetry for the mono-capped trigonal prism coordination. The coordination number seven is rather low and together with the rather X^- soft anion from electrostatic point of view, may well decrease the strength of the crystal field around the Ln^{3+} ion in the order Cl, Br, I. The structural data imply that the site symmetry of Pr^{3+} ion should not be higher than C_{2v} . This symmetry was assumed in crystal field (c.f.) calculation [20]. The M-X₇ distances in the coordination polyhedron for praseodymium ternary halides are collected in Table 2.

Fig. 1. Orthorhombic crystal structure of K_2PrCl_5 showing the PrCl_7 units connected by two common edges to form infinite chains along the y -axis [19–21].

Table 2

The M–X₇ distances in the coordination polyhedron for praseodymium ternary halides (in pm) [22]

	K ₂ PrCl ₅	K ₂ PrBr ₅	K ₂ PrI ₅
d(Pr–Pr)	455.0	478.5	513.4
d(Pr–X1)	279.1	296.1	323.2
d(Pr–X2)	278.4	294.9	316.5
d(Pr–X3)	275.2	292.0	316.8
d(Pr–X4), d(Pr–X4') ^a	281.8	297.4	319.0
d(Pr–X4''), d(Pr–X4''')	285.6	302.5	327.0
d(Pr–X)	281.1	297.5	321.2

^a X4: $x, 1/2 - y, z$; X': x, y, z ; X4'': $x, 1/2 + y, z$; X4''': x, y, z .

3. Results and discussion

3.1. Analysis of absorption spectra

Absorption in the UV region is dominated by the parity allowed inter-configurational $4f^2 \rightarrow 4f^1 5d^1$ transitions, very intense even for the crystals at such a low doping level (Figs. 3–5). Parity forbidden transitions within $4f^2$ configuration are observed in the visible and IR regions with weak intensities. The $4f^2 \rightarrow 4f^1 5d^1$ bands are much broader than the $4f^2 \rightarrow 4f^2$ transitions because of the strong coupling between of the 5d electron and the lattice phonons. The energies of the $4f^{N-1} 5d^1$ levels are much more influenced by the crystal field interaction than those of the $4f^N$ levels. This is due to the strong interaction of the 5d electrons with the neighbouring anions in solid state. The $4f^2 \rightarrow 4f^1 5d^1$ spectra in K₂(La,Pr)Cl₅ are composed of four bands located at 220, 245, 263 and 323 nm instead of five components expected for the low point symmetry of the Pr³⁺ site (Cs) [20]. The energies and intensities of the respec-

Fig. 3. Absorption (a, b, d) and reflection (c) spectra of K₂La_{0.95}Pr_{0.05}Cl₅, K₂La_{0.85}Pr_{0.15}Cl₅ and K₂PrCl₅ at 293 and 4 K [20].

tive bands are different from those in the spectrum of the stoichiometric K₂PrCl₅ ternary chloride, in which one band at 250 nm was observed at energies higher than 45,500 cm⁻¹ (220 nm) characterized by a drastic increase in absorption [17].

According to the data reported by Dorenbos et al. for K₂(La,Ce)Cl₅ [6,23], the spread in the $4f^1 \rightarrow 4f^0 5d^1$ transition is equal to 15,128 cm⁻¹ and that for K₂(La,Pr)Cl₅ should be comparable. The first $4f^2 \rightarrow 4f^1 5d^1$ band for

Fig. 4. The UV and VUV synchrotron excitation spectra of the $^3P_0 \rightarrow ^3H_4$ emission (494 nm) (a) and emission spectra excited at 60 nm and 184 nm (b) of the K₂(La_{0.98}Pr_{0.02})Cl₅ single crystal at 8 K.

Fig. 5. (a) Absorption spectra of K_2PrBr_5 and $K_2Pr_xLa_{1-x}Br_5$ at 4 K. The insets show absorption and reflection spectra in UV range for ternary chloride and bromide (a) and shift of the lines corresponding to $^3H_4 \rightarrow ^3P_0$ transition for them (b) [18]. (b) Absorption spectra of K_2PrX_5 crystal in the range of $^3H_4 \rightarrow ^1G_4$ transition and K_2PrI_5 and $K_2Pr_{0.95}La_{0.05}I_5$ in range of $^3H_4 \rightarrow ^1I_6$, 3P_0 transitions at 4 K.

Pr^{3+} in the same matrix could be expected at an energy close to $42,000\text{ cm}^{-1}$ (240 nm) [24], this corresponds to the energy observed for the stoichiometric K_2PrCl_5 crystal (Fig. 3). On the other hand, basing on Andres et al. [25] report on the f–d levels for $K_2LaNdCl_5$ crystal, and keeping in mind the rules formulated by Dorenbos, we should expect the first f–d component at 277 nm in Pr^{3+} -doped crystal. Assuming the component located at 323 nm as the first component of the $4f^2 \rightarrow 4f^15d^1$ transition and the splitting of the $4f^2 \rightarrow 4f^15d^1$ band to be $15,000\text{ cm}^{-1}$, the higher components should be observed at 215 nm ($46,500\text{ cm}^{-1}$). However, other possibilities can be also considered: first two bands are given by impurities and the higher component at $40,000\text{ cm}^{-1}$ (250 nm) is the $4f^2 \rightarrow 4f^15d^1$ one of Pr^{3+} . Thus, the last one could be at $55,100\text{ cm}^{-1}$ (181 nm) and one of former components should be seen at $51,300\text{ cm}^{-1}$ (194 nm). The excitation spectrum of the

$^3P_0 \rightarrow ^3H_4$ emission $\lambda_{det} = 494\text{ nm}$ (Fig. 4) for the $K_2(La_{0.98}Pr_{0.02})Cl_5$ crystal at 8 K was detected with the synchrotron radiation and two components separated of 3800 cm^{-1} at 175 and 190 nm were found [20]. These bands correspond to those calculated basing on the data reported for $K_2(La,Ce)Cl_5$ [6,23,24]. In fact, the f–d transitions in series of praseodymium halides are shifted to the lower energies (see Fig. 5 inset).

On the other hand, the $4f^2$ ground configuration of the Pr^{3+} ion gives rise to 13 $2S+1L_J$ levels (Fig. 5). All of them, except the 1S_0 level, are situated below $25,000\text{ cm}^{-1}$. The electric dipole transitions within the $4f^2$ configuration are strictly forbidden but mixing the $4f^2$ wave functions with those of opposite parity $4f^15d^1$ configuration, [26] lifts this restriction. Thus we can observe very rich spectra for Pr^{3+} from UV to IR region. Transitions of the magnetic dipole origin can be observed, too, but the electric dipole transitions are

dominant in the case of the Pr^{3+} ion. The crystal field effect lifts the $(2J+1)$ degeneracy of the free ion $^{2S+1}L_J$ levels. The $^{2S+1}L_J$ levels of the Pr^{3+} ion are split into Stark components, the number of which for each $^{2S+1}L_J$ level is characterized by the point symmetry of the Pr^{3+} site [27]. For the low point symmetry of Pr^{3+} in $\text{K}_2(\text{La},\text{Pr})\text{X}_5$ host matrices, this degeneracy is almost completely lifted [19,20]. Moreover, even at low temperatures (4 K) where the hot band absorption should be negligible, the number of lines in the absorption spectra was sometimes found greater than the maximum allowed by the quantum number J . For statistical reasons, even at a low doping level ($X_{\text{Pr}} = 0.02$), Pr^{3+} ions are not randomly distributed since the existence of Pr^{3+} pairs linked by X^- ions were found in Figs. 1 and 2 [18–20] and Fig. 5. The additional lines may arise from these pairs since the energies of the single ion energy levels are slightly modified due to the pair forma-

tion [28–32] and pair lines can be assigned basing on known mechanism of cooperative interaction reported earlier [18,20,30–32,36]. On the other hand, the contamination of the surface of single crystals may result in additional lines in the spectra, too, due to the hygroscopic nature of $\text{K}_2(\text{La},\text{Pr})\text{X}_5$ compounds [18,20].

In addition to the electric or magnetic dipole induced transitions, usually weak lines of vibronic origin are frequently observed for the Pr^{3+} ion [30,33–35]. For $\text{K}_2(\text{La},\text{Pr})\text{Cl}_5$ samples, however, this kind of transitions was extremely weak and almost undetectable. They were found only at $^3\text{P}_0 \rightarrow ^3\text{F}_2$ band in emission, see Fig. 6, mainly in $\text{K}_2(\text{La},\text{Pr})\text{Br}_5$ crystals [18] as it will be discussed later. The increase of both covalency and polarizability of ions (Cl, Br, I) leads to increase of vibronic transition probabilities in the ternary halides series [31,37,38].

The absorption spectra of $\text{K}_2(\text{La},\text{Pr})\text{Cl}_5$ between 435 and 2000 nm ($23,000$ and 5000 cm^{-1}) comprises of tran-

Fig. 6. The emission spectra of $\text{K}_2(\text{La}_{0.95}\text{Pr}_{0.05})\text{Cl}_5$, $\text{K}_2(\text{La}_{0.98}\text{Pr}_{0.02})\text{Cl}_5$ single crystals and K_2PrCl_5 powder measured under Ar^+ ion laser excitation ($\lambda = 457.9\text{ nm}$) at 77 and 4 K [18].

sitions from the ground $^3\text{H}_4$ level to the excited $^3\text{F}_{2-4}$, $^1\text{G}_4$, $^1\text{D}_2$, $^3\text{P}_{0-2}$, and $^1\text{I}_6$ levels (Fig. 5a and b). With increasing temperature, interpretation of the absorption spectra of $\text{K}_2(\text{La},\text{Pr})\text{Cl}_5$ was more difficult since the higher Stark components of the $^3\text{H}_4$ level became thermally populated adding both supplementary lines to the spectra and also broadening of the lines. However, based on the splitting of the $^3\text{H}_4$ ground level obtained from the emission spectra recorded at 4 K under Ar^+ ion laser (457.9 nm) excitation, analysis of the crystal field Stark components of the higher $^{2S+1}\text{L}_J$ levels of the Pr^{3+} ion in absorption was possible [19,20]. Assuming the mechanism of cooperative absorption ($^3\text{H}_4 \rightarrow ^3\text{P}_0$ (ion 1) + $^3\text{H}_{4(0-8)}$ (ion 2)) observed earlier in other polymeric or dimeric systems [17,18,30,35,36], the pair components can be selected and the remaining lines should correspond to the transitions to the real Stark components of the respective excited levels. In addition, the energy of $^1\text{S}_0$ level could be detected by using the UV–VUV excitation spectra with synchrotron radiation as described above for K_2LaCl_5 : 2% Pr crystal [19,20].

Basing on the set of the 86 crystal field components selected from absorption and emission spectra, the crystal field calculation was performed for Pr^{3+} in $\text{K}_2(\text{La},\text{Pr})\text{Cl}_5$ matrix [19,20]. The formalism of the phenomenological model used in above calculation and details of the calculations were described by Hölsä et al. [19,20]. The complex energy level schemes of the R^{3+} ions in solid state results from several interactions—both within the $4f^N$ electron configuration and between the R^{3+} ion and its environment [26] and their effects can be parameterised by using phenomenological models.

The effective Hamiltonian H_{FI} comprising these interactions can be written as follows:

$$H_{\text{FI}} = \sum_{k=0}^3 E_k(nf, nf) e^k + \zeta_{4f} A_{\text{SO}} + \alpha L(L+1) + \beta G(G_2) + \gamma G(G_7) + \sum_{k=2,3,4,6,7,8} T^k t_k \quad (1)$$

In which the angular parts e^k , A_{SO} , L , $G(G_2)$, $G(G_7)$, and t_k have their usual meanings [26,39]. Higher-order interactions can be given by the Marvin integrals M^k ($k = 0, 2$, and 4) and P^k ($k = 2, 4$, and 6).

The crystal field Hamiltonian H_{CF} for the R^{3+} ion introduced into an inhomogeneous electrostatic field created by the surrounding charge distribution can be described as follows [26]:

$$H_{\text{CF}} = \sum_k \sum_{q=-k}^{q=k} \left\{ B_q^k \left[C_q^k + (-1)^q C_{-q}^k \right] + i S_q^k \left[C_q^k - (-1)^{-q} C_{-q}^k \right] \right\} \quad (2)$$

in which the parameters B_q^k and S_q^k are the coefficients of the crystal field expansion, i.e. the real and imaginary

functions of the radial distances, respectively. C_q^k 's are tensor operators of rank k closely related to the spherical harmonics. For the Pr^{3+} ion with $4f^2$ electron configuration, only eight free ion parameters are needed to describe the experimental data, because the three body interaction parameters (i.e. the Judd parameters T^k) are not allowed for and the use of the Marvin integrals cannot be involved, since their effect is expected to be restricted mainly to the well-isolated $^1\text{S}_0$ level [19,20]. Moreover, the main low symmetry problem in calculation was avoided by using the higher C_{2v} point symmetry for Pr^{3+} ion site. Thus, the number of c.f. parameters was reduced to nine (the six imaginary terms were excluded). The set of 86 Stark components (out of 91) were used in the calculation and the high quality and reliability of the simulation is reflected in the low esd's of all the parameters [19,20].

Since we expected the crystal field effect on the optical behavior of a series of praseodymium halides, thus basing on crystal field parameters the c.f. strength parameter N_v was calculated according to the formalism described by Auzel and Malta [19,20,41]. The crystal field strength in $\text{K}_2(\text{La},\text{Pr})\text{Cl}_5$ was compared with that for isotypic crystals of $\text{K}_2(\text{Y},\text{Pr})\text{F}_5$ calculated by Min Yin and Krupa et al. [42]. The low value (1730 cm^{-1}) of the crystal field strength parameter N_v correlates well with that for fluoride matrix where stronger crystal field is observed [19,20]. The decrease of the crystal field is well manifested in the splitting of appropriate levels of ternary praseodymium bromides and iodides spectra. Fig. 6 compares splitting of the $^3\text{H}_6$ and $^3\text{F}_2$ levels in the emission spectra of the ternary chloride and iodide. The low value of N_v determined in $\text{K}_2(\text{La},\text{Pr})\text{Cl}_5$ in low coordination number which should favour strong crystal field confirms creation of a rather weak crystal field by chloride ions [19,20]. Comparison of the absorption spectra for three types of ternary halides shows the nephelauxetic effect confirming an increase of the covalency in the order $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ (see Fig. 5b). The crystal field calculation reproduced well the magnetic behaviour of K_2PrCl_5 crystals. The room temperature effective magnetic moment μ_{eff} values observed experimentally ($3.45 \mu_{\text{B}}$) (Fig. 7) and those calculated with the crystal field contribution ($3.57 \mu_{\text{B}}$) [20] agree rather well, and correspond to the theoretical ground level free ion value ($\mu_{\text{eff}} = g_J(J(J+1))^{1/2} = 3.58 \mu_{\text{B}}$ [40]). The experimental behaviour of the inverse susceptibility at low temperature was in fact very well reproduced by using the van Vleck formalism and the wave functions and level energies obtained from the crystal field simulation of the spectral data [19,20]. This indicates the correctness and the high quality of the crystal field simulation of the $4f^2$ energy level scheme in K_2PrCl_5 . The strong anisotropy of the inverse magnetic susceptibility at low temperatures shown by the calculations (see Fig. 9b in [20]) is probably caused by the wave functions and

Fig. 7. Experimental magnetic data plotted as magnetic susceptibilities χ_M , magnetic moment and $1/\chi_M$ (inset) calculated per mol of K_2PrCl_5 versus temperature.

eigenvalues of the (two-three) lowest lying crystal field states of $\infty[PrCl_{4/2}Cl_3]$ chain.

3.2. Analysis of the luminescence spectra

The Ar^+ ion laser line at 457.9 nm excites very effectively the 3P_1 (or 1I_6) level of the Pr^{3+} ion in the K_2LaX_5 host. At low temperature, the excitation energy relaxes in two ways: first, radiative transition as luminescence from the 3P_0 level and second, non-radiative transition, by multiphonon de-excitation or cross-relaxation, to the 1D_2 level which may luminescence, too. Since phonon energy decreases in the order $Cl \rightarrow Br \rightarrow I$ from 235, 146 cm^{-1} to 95 cm^{-1} , some variation in the emission efficiency can be expected. Moreover, the increase of covalency from Cl to I affects the electron–phonon coupling thus—according to theory of vibronic transitions probability—an increase of vibronic components should be observed as it is demonstrated in the range of $^3P_0 \rightarrow ^3F_2$ hypersensitive transitions of Pr^{3+} in ternary bromide emission spectra (see Fig. 6). In fact, the electron–phonon coupling is manifested also by broadening of all electronic transitions in the emission spectra of praseodymium ternary iodides crystals (see Fig. 8).

In the wavelength range between 435 and 1500 nm the luminescence spectrum of Pr^{3+} in the K_2LaX_5 host matrix originates from the $^3P_0 \rightarrow ^3H_{4,5,6}$ and $^3P_0 \rightarrow ^3F_{2,3,4}$ transitions from which the $^3P_0 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3F_2$ transitions dominate (Fig. 6). In the range of 900–1500 nm the $^1I_6 \rightarrow ^1G_4$ and $^3P_0 \rightarrow ^1G_4$ was recorded as well as $^1G_4 \rightarrow ^3H_5$ and $^1D_2 \rightarrow ^1G_4$, one what is not very common [19,20]. This is in accordance to the observation that the electric dipole interaction is the main contribution responsible for the transitions in the Pr^{3+} luminescence spectrum. Very weak emission

from the 1D_2 level was observed in addition to the 3P_0 emission in diluted crystals at 2% in chloride and from 2% to 5% mol concentration in bromide lattice, confirming the phonon assisted cross-relaxation. The more efficient cross-relaxation of 1D_2 emission than for 3P_0 one was confirmed by decay time measurement (see Fig. 9 inset and Table 3). The temperature dependence of the Pr^{3+} luminescence in $K_2(La,Pr)X_5$ is weak.

The concentration quenching of the 3P_0 emission was weak since luminescence could be observed even for the full concentrated K_2PrCl_5 crystal. It can find confirmation also in decay times measurements (Table 3 and Fig. 9), where exponential decays were observed. The decay time versus concentration are collected in Table 3.

As a function of excitation, it means, with the Ar^+ ion laser line at 457.9 nm, the xenon lamp in the UV region, the excimer laser at 308 nm, or the γ -irradiation, there were found some differences in the luminescence spectra. The simplest spectra were obtained when using the Ar^+ ion laser excitation (Fig. 6). Only very weak emission was observed from the 1D_2 level mainly for bromide lattice even with the lowest ($X_{Pr} = 0.02$) dopant concentration. Generally, the 3P_0 level is fed effectively and emission is observed mainly from this level for ternary halides. However, the emission spectra are very sensitive on the energy of excitation. Excitation of 1D_2 level by dye laser 588 nm line leads to 1I_6 , 3P_0 up-conversion emission, except the resonant emission from 1D_2 level (see Fig. 10). Most probably the cooperative level of Pr^{3+} pair is populated at twice higher energy i.e. at 294 nm which falls in f–d transition and complex relaxation process fed 1I_6 and 3P_0 levels in results up-conversion emission from those levels were recorded. This up-conversion emission is dramatically less efficient for ternary iodide systems, and the shape of the fundamental

Fig. 8. Fluorescence spectra of diluted $\text{Pr}^{3+}:\text{K}_2\text{LaX}_5$ crystals at 293 and 77 K excited by 308 nm excimer laser line.

Fig. 9. Decay curves of luminescence recorded for concentrated and diluted crystals upon 460 nm excitation at 77 K of $^3\text{P}_0$ detection and resonance $^1\text{D}_2$ (inset) excitation at 293 K.

Table 3

Luminescence decay data for $\text{K}_2\text{La,PrX}_5$ after excitation using 460 nm line and resonance excitation of $^1\text{D}_2$ level at 293 and 77 K

concentration of Pr^{3+} [mol%]/T [K]	K_2LaCl_5 $^3\text{P}_0$ [μs]	K_2LaCl_5 $^1\text{D}_2$ [μs]	K_2LaBr_5 $^3\text{P}_0$ [μs]
0.02			
293	21.4	63	11.6
77	24		17.6
0.05			
293	5.8		8.8
77	10.5		16.0
0.15			
293	2.7	3.1	7.2
77	10.0		7.1

$^1\text{D}_2$ emission band is significantly different (see Fig. 10 inset). On the other hand, another explanation of the up-conversion $^3\text{P}_0$, $^1\text{I}_6$ emission can be considered, too. If some impurities of Ce^{3+} traces in the crystal occur thus cooperative excitation of $^1\text{D}_2$ of Pr^{3+} pairs can fall into $\text{Ce}^{3+} 4f^1 \rightarrow 4f^0 5d^1$ levels then energy is transferred to $^3\text{P}_J$, $^1\text{I}_6$ of Pr^{3+} levels and emission from those states is observed. Although all starting materials used in our synthesis, KCl , PrX_3 and YbX_3 , have a purity of 99.99% in the spectra some impurities ions were assigned [20]. We finally made effort to determine concentration of these impurities mentioned in discussion of up-conversion using ICP-AES method and Ce^{3+} concentration was less than 10^{-5} mol%, but their fluorescence is strong enough to be considered.

Under the excimer laser excitation, in addition to the emission from the $^3\text{P}_0$ level, a broad band emission was also detected at 375 nm (Fig. 8). The broad band emis-

sion is stronger at room temperature than the emission from the $^3\text{P}_0$ level but the reverse was observed at 77 K for ternary chloride matrix. Quite different effect is observed in ternary bromide lattice. In fact this emission is temperature controlled (see Fig. 8). The origin of this emission is unknown at the moment but it may result from the annihilation of the excitons. The possibility of localised exciton at defects or impurities emission have been considered by Van't Spijker et al. for the Ce^{3+} doped K_2LaCl_5 [6] and Wezel et al. for Pr^{3+} in CsCdBr_3 [8].

We have analysed also the possibility of broad emission from $4f^0 5d^1$ split levels of Ce^{3+} traces. In fact, neither energy of this emission nor splitting of the broad band emission correspond to those reported by Van Loef et al. in appropriate emission spectra of $\text{K}_2(\text{La, Ce})\text{Cl}_5/\text{Br}_5$ crystals [36].

The up-conversion emission spectrum of $\text{K}_2(\text{La, Pr, Yb})\text{Cl}_5$ crystals under 940 nm pumping energy through $^2\text{F}_{5/2}$ level is presented in Fig. 11. Two mechanisms can be responsible for this emission, either the cooperative level of Yb^{3+} pairs is excited at twice higher energy of $^2\text{F}_{5/2}$ state (470 nm) and energy is transferred to $^3\text{P}_0$ level and cross-relaxation feeds $^1\text{D}_2$ state, from which emission occurs or, after excitation of $\text{Yb}^{3+} ^2\text{F}_{5/2}$ excited state energy is transferred to $^1\text{G}_4$ of Pr^{3+} level, then the excited state absorption populates $^3\text{P}_J$, $^1\text{I}_6$ levels and emission from $^3\text{P}_0$ and $^1\text{D}_2$ levels occurs. Fig. 12 presents Dieke diagram where possible mechanisms of up-conversion in $\text{K}_2\text{LaCl}_5:5\% \text{Pr}$, $2\% \text{Yb}$ are proposed. To solve the problem of up-conversion mechanisms, additional studies of the decay rate are needed. These studies will be the object of our future paper.

Fig. 10. Emission spectra of $5\%\text{Pr}^{3+}:\text{K}_2\text{LaX}_5$ excited at 457.9 [18] and 588 nm.

Fig. 11. Up-conversion emission of $\text{K}_2\text{LaCl}_5:5\% \text{Pr}^{3+}$, $2\% \text{Yb}^{3+}$ under 940 nm pumping.

Fig. 12. Dieke diagram presenting up-converting processes in $\text{K}_2\text{LaCl}_5:5\% \text{Pr}^{3+}$, $2\% \text{Yb}^{3+}$ crystal.

4. Conclusion

Comparative studies of the absorption, reflection, emission and excitation spectra for ternary halides were carried out and discussed.

The absorption and excitation spectra of potassium lanthanum praseodymium ternary halides, $\text{K}_2(\text{La},\text{Pr})\text{X}_5$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), single crystals are dominated in the UV region by the parity allowed interconfigurational $4f^2 \rightarrow 4f^1 5d^1$ transitions bands located for chloride at 175, 190, 220, 245, 263 and 323 nm. Since five components are expected for the C_s point symmetry of the Pr^{3+} site the additional bands are given by localized exci-

tons and excitonic emission was observed. More work should be devoted to this aspect. The $^1\text{S}_0$ level could be detected in the UV–VUV excitation spectra [19,20]. The absorption spectra of $\text{K}_2(\text{La},\text{Pr})\text{X}_5$ in the visible and IR regions comprise of the parity forbidden $4f \rightarrow 4f$ transitions from the ground $^3\text{H}_4$ level to the excited $^3\text{H}_6$, $^3\text{F}_{2-4}$, $^1\text{G}_4$, $^1\text{D}_2$, $^3\text{P}_{0-2}$, and $^1\text{I}_6$ levels. The J degeneracy was lifted almost completely in accordance with the low (C_s/C_{2v}) point symmetry appropriate to the Pr^{3+} site. Practically all Stark components were found for these $^{2S+1}\text{L}_J$ levels in K_2LaPrX_5 . The luminescence spectrum of Pr^{3+} in K_2LaX_5 between 435 and 850 nm originates mainly from the $^3\text{P}_0$ level to the $^3\text{H}_{4-6}$ and $^3\text{F}_{2-4}$ levels but the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ and $^3\text{P}_0 \rightarrow ^3\text{F}_2$ transitions dominate. Very weak emission from the $^1\text{D}_2$ level was observed, too, mainly in diluted bromides and iodides crystals. In the range of 900–1500 nm the $^1\text{I}_6 \rightarrow ^1\text{G}_4$, $^3\text{P}_0 \rightarrow ^1\text{G}_4$, $^1\text{G}_4 \rightarrow ^3\text{H}_5$ emission was recorded as well as $^1\text{D}_2 \rightarrow ^1\text{G}_4$ ones in diluted $\text{K}_2(\text{La},\text{Pr})\text{Cl}_5$ [19,20]. The analysis of the luminescence spectra of $\text{K}_2\text{LaX}_5:\text{Pr}^{3+}$ yielded all the Stark levels for the $^3\text{H}_{4,5,6}$ and $^3\text{F}_{2,3,4}$ levels. The low coordination number seven seems to favour a strong crystal field effect, however the crystal field strength parameter ($N_v = 1730 \text{ cm}^{-1}$) [18,19] point at the low contribution of the chloride and other ligands in the crystal field potential. The role of the highest energy of M–L vibration in emission de-excitation process was analysed as well as other factors that affect the emission properties.

The cross-relaxation process was operative in concentrated systems involving mainly $^1\text{D}_2$ level.

Cooperative ion–ion interaction was presented and their role in emission efficiency was analysed. Up-conversion emissions in praseodymium ternary halides

and co-doped by Yb^{3+} ions were detected and their possible mechanisms were proposed.

The strong anisotropy of the inverse magnetic susceptibility at low temperatures is the most probably caused by the wavefunctions and eigenvalues of the (two–three) lowest lying crystal field states of $\infty[\text{PrCl}_{4/2}\text{Cl}_3]$ chain [19,20].

Acknowledgment

Financial support from the KBN, Grant No. 3 T09A 024 26, is gratefully acknowledged.

References

- [1] R.T. Wegh, H. Donker, K.D. Oskam, A. Meijerink, *Science* 283 (1999) 663.
- [2] S.C. Krupa, M. Queffelec, *J. Alloys Compd.* 250 (1997).
- [3] P. Dorenbos, *J. Lumin.* 91 (2000) 91.
- [4] P. Dorenbos, *Phys. Rev. B* 64 (2001) 125117.
- [5] L. van Pieterse, M.F. Reid, R.T. Wegh, S. Soverna, A. Meijerink, *Phys. Rev. B* 65 (2002) 45113.
- [6] J.C. van't Spijker, P. Dorenbos, C.W.E. van Eijk, K. Kramer, H.U. Güdel, *J. Lumin.* 85 (1999) 1.
- [7] A.P. Vink, E. van der Kolk, P. Dorenbos, C.W.E. van Eijk, *J. Alloys Compd.* 341 (2002) 338.
- [8] M. Wenzl, M. Altwein, R. Demirbilek, B. Len, J. Heber, J. Kübler, B. Bleeker, A. Meijerink, *J. Alloys Compd.* 300–301 (2000) 479.
- [9] R.T. Wegh, A. Meijerink, *Phys. Rev. B* 60 (1999) 10820.
- [10] A. Kaminski, in: B. Jeżowska-Trzebiatowska, J. Legendziewicz, W. Stręk (Eds.), *Excited States of Transition Elements*, World Scientific Publishing Co. Pte. Ltd., Singapore, 1989, p. 669.
- [11] A. Brenier, G. Boulon, *J. Lumin.* 82 (1999) 285.
- [12] M. Gaft, R. Reisfeld, G. Panczer, E. Uspensky, B. Varrel, G. Boulon, *Opt. Mater.* 13 (1999) 71.
- [13] L. Laversenne, Y. Goyot, C. Goutaudier, M.Th. Cohen-Adad, G. Boulon, *Opt. Mater.* 16 (2001) 475.
- [14] E. Zych, C. Brecher, *J. Lumin.* 90 (2000) 89.
- [15] K. Horchani, J.G. Gacon, C. Dujardin, N. Garmier, C. Garapon, M. Ferid, M. Trabelsi-Ayedi, *J. Lumin.* 94–95 (2001) 69.
- [16] M. Guzik, T. Aitasalo, W. Szuszkiewicz, J. Hölsä, B. Keller, J. Legendziewicz, *J. Alloys Compd.* 380 (2004) 368.
- [17] J. Cybińska, J. Sokolnicki, J. Legendziewicz, G. Meyer, *J. Alloys Compd.* 341 (2002) 115.
- [18] J. Legendziewicz, J. Cybińska, G. Meyer, *Opt. Mater.* 24 (2003) 197.
- [19] J. Cybińska, J. Hölsä, M. Lastusaari, J. Legendziewicz, G. Meyer, C. Wickleder, *J. Alloys Compd.* 380 (2004) 27.
- [20] J. Cybińska, J. Hölsä, M. Lastusaari, J. Legendziewicz, G. Meyer, C. Wickleder, in press.
- [21] G. Meyer, E. Hüttel, *Z. Anorg. Allg. Chem.* 497 (1983) 191.
- [22] G. Meyer, J. Soose, A. Montz, V. Vitt, Th. Holjes, *Z. Anorg. Allg. Chem.* 521 (1985) 161.
- [23] J.C. van't Spijker, P. Dorenbos, J.T.M. de Haas, C.W.E. van Eijk, H.U. Güdel, K. Krämer, *Radiat. Meas.* 24 (1995) 379.
- [24] P. Dorenbos, *Phys. Rev. B* 62 (2000) 15650.
- [25] H.P. Andres, K. Krämer, H.U. Güdel, *Phys. Rev. B* 54 (1996) 3830.
- [26] B.G. Wybourne, *Spectroscopic Properties of Rare Earths*, Interscience, New York, 1965.
- [27] C. Görller-Walrand, K. Binnemans, *Rationalization of crystal-field parametrization*, in: K.A. Gschneidner Jr., L. Eyring (Eds.), *Handbook Phys. Chem. Rare Earths*, vol. 23, Elsevier, Amsterdam, 1996, Chapter 155.
- [28] E. Antic-Fidancev, J. Hölsä, M. Lastusaari, A. Lupei, *Phys. Rev. B* 64 (2001) 195108.
- [29] J. Hölsä, E. Antic-Fidancev, M. Lastusaari, A. Lupei, *J. Solid State Chem.* 171 (2003) 282.
- [30] J. Legendziewicz, *J. Alloys Compd.* 300–301 (2000) 71.
- [31] J. Legendziewicz, *Acta Phys. Polonica A* 90 (1996) 127.
- [32] L. Macalik, J. Hanuza, J. Sokolnicki, J. Legendziewicz, *J. Appl. Spectrosc.* 62 (5) (1995) 40.
- [33] E. Antic-Fidancev, M. Lemaître-Blaise, P. Porcher, J. Hölsä, *J. Chem. Soc.: Faraday Trans.* 87 (1991) 3625.
- [34] G. Oczko, J. Legendziewicz, J. Hanuza, J. Gliński, L. Macalik, *Acta Phys. Polonica A* 90 (1996) 431.
- [35] J. Legendziewicz, Z. Ciunik, P. Gawryszewska, J. Sokolnicki, *J. Alloys Compd.* 225 (1995) 372.
- [36] M.P. Hehlen, H. Reisen, H.U. Güdel, *Inorg. Chem.* 30 (1991) 2273.
- [37] E.V. Dvan Loef, P. Dorenbos, C.W.E. van Eijk, K.W. Kramer, H.U. Güdel, *Phys. Rev.* 68 (2003) 45108.
- [38] G. Blasse, *Int. Rev. Phys. Chem.* 11 (1992) 71.
- [39] W.T. Carnall, H. Crosswhite, H.M. Crosswhite, J.P. Hessler, N.M. Edelstein, J.G. Conway, G.V. Shalimoff, R. Sarup, *J. Chem. Phys.* 72 (1980) 5089.
- [40] E. Antic-Fidancev, M. Lemaitre-Blaise, P. Caro, *New J. Chem.* 11 (1987) 467.
- [41] F. Auzel, O.L. Malta, *J. Phys. (Fr.)* 44 (1983) 201.
- [42] Min Yin, J.-C. Krupa, E. Antic-Fidancev, V.N. Makhov, N.M. Khaidukov, *J. Lumin.* 101 (2003) 79.