Synchrotron Radiation Study of Interconfigurational $5d$-$4f$ Luminescence of Pr^{3+} in $KLuP_2O_7$

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The double phosphate $KLuP_2O_7$ doped with Pr^{3+} ions was prepared by solid-state reaction. The material obtained was characterized by powder X-ray diffraction. The luminescence spectroscopy and the excited state dynamics of this material were studied upon excitation with VUV synchrotron radiation. The $5d$-$4f$ emission of Pr^{3+} upon both direct and band gap excitation was detected and assigned. The decay kinetics of the Pr^{3+} $5d$-$4f$ emission is characterized by a decay time of about 20 ns and is nearly temperature independent within the range $8 - 300$ K. Both dynamics and energy transfer peculiarities revealed in the study suggested good potentials for application of $KLuP_2O_7$:Pr^{3+} as a fast scintillator material.

Key words: Pr^{3+}, $5d$-$4f$ Luminescence, $KLuP_2O_7$, VUV Spectroscopy, Synchrotron Radiation, Scintillator

Introduction

Luminescent materials doped with Pr^{3+} ions are being actively investigated, as they can show electric dipole allowed interconfigurational $5d$-$4f$ optical transitions located in the UV and visible spectral regions. These optical features find numerous applications in important technological fields, such as the development of fast scintillators for detection of ionizing radiation (X-rays and γ-rays) [1]. Compared to Ce^{3+} $5d$-$4f$ emission, the $5d$-$4f$ emission of Pr^{3+} is located at shorter wavelengths and characterized by shorter decay times (less than 30 ns). The latter is beneficial for many applications requiring time-correlated registration of photons or working at higher count rate, *e. g.* PET scanners. Our search for new materials exhibiting efficient $5d$-$4f$ luminescence of the Pr^{3+} ion [2, 3] has led us to the synthesis and the spectroscopic investigation of the double phosphate $KLuP_2O_7$ doped with this ion. This host is characterized by a high effective atomic number of ~ 52.3, similar to that of $Lu_3Al_5O_{12}$, and potentially advantageous for γ-ray scintillators.

Due to the wide band gap and the suitability for doping with rare-earth activators, the optical properties of several alkali rare-earth phosphates belonging to the A_2O-RE_2O_3-P_2O_5 (A = alkali metal ion, RE = rare-earth metal) system have been recently investigated under vacuum ultraviolet (VUV) and X-ray radiation to demonstrate the potential as scintillating materials [4, 5]. Some room temperature luminescence properties of Ce^{3+}- and Pr^{3+}-doped $KLuP_2O_7$ have been studied in [6, 7]. Particularly, it was shown that Ce^{3+}-doped $KLuP_2O_7$ produces efficient and fast d-f emission upon X-ray excitation with a lifetime of the dominating decay component of about 27 ns [6]. The results obtained for Pr^{3+}-doped $KLuP_2O_7$ [7] included intracenter ($4f$-$5d$) excited emission and excitation spectra recorded down to about 140 nm. To the best of our knowledge, time-resolved VUV spectroscopy and excited state dynamics under excitation with synchrotron radiation (SR) of Pr^{3+}-doped $KLuP_2O_7$ has not been reported in the literature so far. Moreover, this promising material is lacking a low-temperature study that would help to establish the nature of host-to-impurity energy transfer.

In this contribution we present and analyze time-resolved emission and excitation spectra as well as luminescence decay curves measured at room and liquid helium temperature upon selective excitation with SR in the UV/VUV region (down to about 61 nm). In addition, the prospective applications of this luminescent material are discussed.

Experimental Section

Powder crystalline materials having a stoichiometry KLu$_{0.99}$Pr$_{0.01}$P$_2$O$_7$ (*i. e.* containing 1 mol % Pr^{3+} substituting for Lu^{3+}) were obtained by solid-state reaction from high purity KNO$_3$, (NH$_4$)$_2$HPO$_4$, Lu$_2$O$_3$, and Pr$_6$O$_{11}$ (the last two reagents 4N). Appropriate amounts of the reagents were mixed and heat treated in a horizontal furnace in air for 1 h at 400 °C and 24 h at 750 °C with intermediate regrinding.

Powder X-ray diffraction patterns were measured with a Thermo ARL X′TRA powder diffractometer, operating in the Bragg-Brentano geometry and equipped with a Cu anode X-ray source (K_α, $\lambda = 1.5418$ Å) with a Peltier Si(Li) cooled solid-state detector. The powder patterns were collected with a scan rate of 0.4° s^{-1} and an exposure time of 0.72 s in the $2\theta = 5 - 90°$ range. The phase identification was performed with the PDF-4+ 2011 database supplied by the International Centre for Diffraction Data (ICDD). Polycrystalline samples were ground in a mortar and then put in a low background sample holder for data collection.

All the diffraction peaks in the powder patterns of Pr^{3+}-doped KLuP$_2$O$_7$ (Fig. 1) are compatible with ICDD data on KLuP$_2$O$_7$ (PDF Card No. 01-076-7386). No other phases were detected, indicating that the synthesized sample is a single phase. This compound crystallizes in a monoclinic structure belonging to space group $P2_1/c$ (no. 14) [6]. The crys-
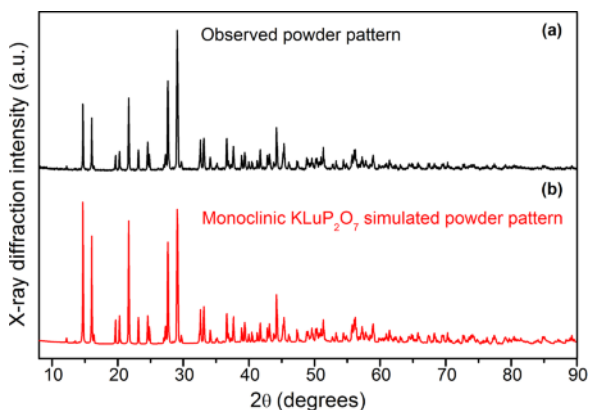

Fig. 1 (color online). Experimental powder pattern of the KLuP$_2$O$_7$:1 % Pr^{3+} powders (a) and simulated pattern of KLuP$_2$O$_7$ (PDF card no. 01-076-7386) (b).

talline structure of KLuP$_2$O$_7$ offers only one site for Lu^{3+} (or Pr^{3+}) with a coordination number of 6 of point symmetry C_1. In addition, we observed a small expansion of the cell volume as a consequence of substitution of Lu^{3+} ion (ionic radius 0.861 Å, in six-fold coordination [8]) by the larger Pr^{3+} ion (0.99 Å, in six-fold coordination [8]). The cell volume of the Pr^{3+}-doped sample and the undoped one are 666.45(1) Å^3 and 665.94(1) Å^3 (PDF Card No. 01-076-7386 and [6]), respectively.

Time-resolved VUV spectroscopic measurements were carried out at the SUPERLUMI station of HASYLAB (Hamburg, Germany) using SR from the DORIS III storage ring as excitation source. For the selective excitation and measurements of excitation spectra in the range of 3.7 – 20.4 eV a 2 m monochromator in McPherson mounting with a resolution of 3.2 Å was used. The detection of the luminescence was performed with a 0.3 m ARC SpectraPro-308i monochromator equipped with a high-speed R3809U-50S (Hamamatsu) microchannel plate (MCP) detector. The time-resolved spectra were recorded within two time gates (TG): 2 – 11 ns (fast TG) and 50 – 71 ns (slow TG) relative to the beginning of the SR pulse. The time-integrated spectra were recorded counting the emission signal within the whole time period of 96 ns available between SR pulses at 10 bunch mode of the storage ring. The measurements were performed in an ultrahigh vacuum chamber ($\sim 10^{-9}$ mbar) in the temperature range 8 – 300 K. The excitation spectra were corrected for the wavelength-dependent variation of the SR intensity using the sodium salicylate signal. A background signal corresponding to the dark count of the MCP detector was subtracted from the original spectra and decay curves.

Results and Discussion

Fig. 2 shows emission spectra of KLuP$_2$O$_7$:Pr^{3+} recorded upon SR excitation at $T = 300$ K. The time-resolved and time-integrated spectra obtained upon direct intra-center excitation at 210 nm (5.9 eV) (Fig. 2a) are presented by a broad band located in the UV spectral region (225 – 350 nm). This band is well pronounced in the fast time gated spectrum, and it is assigned to the parity-allowed 5*d*-4*f* transitions from the lowest excited state of the $4f^15d^1$ configuration to the multiplets belonging to the $4f^2$ ground configuration of Pr^{3+}. No emission features associated with $4f$-$4f$ transitions from the $^3P_0$ and $^1D_2$ levels which are expected to be located around 490 and 600 – 650 nm, respectively, are observed. Fig. 2b presents room-temperature time-integrated and time-resolved emission spectra recorded upon excitation at 90 nm (13.8 eV) that corresponds to excitation across
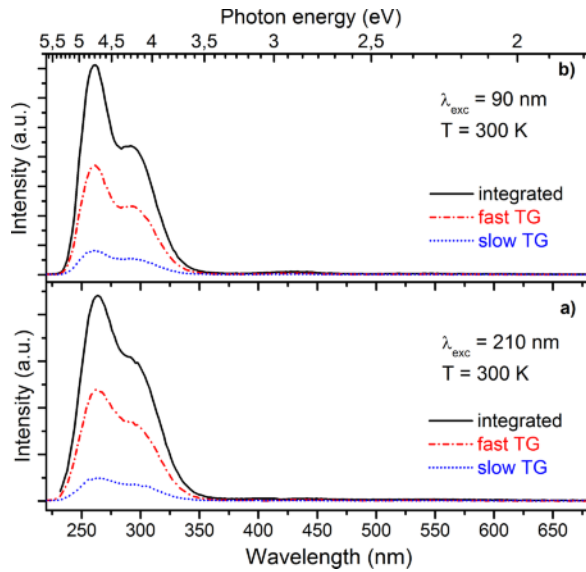
Fig. 2 (color online). Time-integrated and time-resolved emission spectra of KLuP$_2$O$_7$:Pr^{3+} powders recorded upon selective excitation at 210 nm (a) and 90 nm (b) at 300 K.

Fig. 3 (color online). Time-integrated and time-resolved excitation spectra monitoring 5*d*-4*f* emission of Pr^{3+} in KLuP$_2$O$_7$:Pr^{3+} powders at $T = 300$ K (a) and $T = 8$ K (b).

the band gap. The latter is located around 7.7 eV ($\sim$ 160 nm) in many phosphates of the type *ARE*P$_2$O$_7$ (*RE* = Y, Lu) [9] and for other complex phosphates does not exceed 9.3 eV (see [2] and references therein). The spectra show profiles quite similar to that observed upon direct intra-center excitation, indicating a fast and efficient energy transfer from the host to the impurity.

Time-integrated and time-resolved excitation spectra recorded for Pr^{3+} 5*d*-4*f* emission measured at 300 and 8 K are shown in Fig. 3a and 3b, respectively. The intra-center Pr^{3+} 4*f*-5*d* transitions to the crystal field components belonging to the 4$f^1$5d^1 configuration are observed as an unresolved band in the UV region between 200 and 250 nm (5 – 6.4 eV) that is in agreement with the KLuP$_2$O$_7$:Pr^{3+} excitation spectrum [7]. The lowest energetic maximum in this band that is most pronounced at low temperature is located around 230 nm (5.39 eV). This is consistent with the position (231 nm) predicted with the Dorenbos model [10], using the data on the energy of 4*f*-5*d* transitions for Ce^{3+} in the same host [7]. The time-integrated excitation spectrum recorded at $T = 8$ K shows a relatively broad excitation feature centered at 175 nm and most pronounced in the slow time gated spectrum. This weak band can be attributed to the defect absorption.
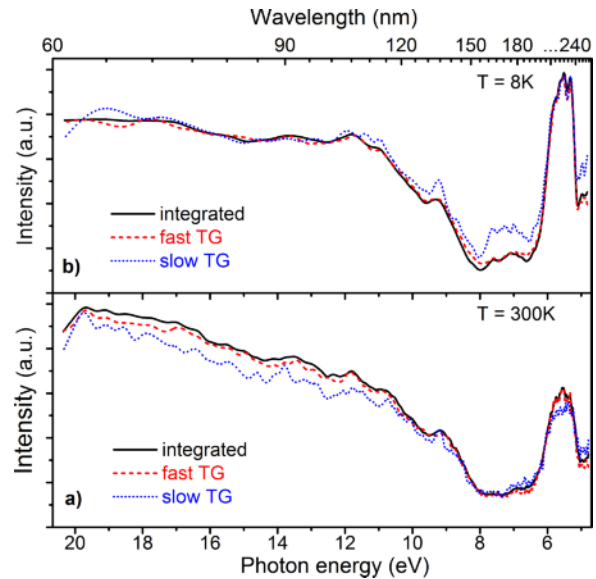
A gradual rise of the excitation spectra observed below 159 nm (> 7.8 eV) and 155 nm (> 8 eV) at $T = 300$ and 8 K, respectively, is likely to be connected with a beginning of the fundamental absorption of the host that correlates with the band gap energies reported for similar double phosphates in Ref. [9]. An absence of an excitonic peak suggests that the host-to-impurity energy transfer mechanism is dominated by a recombination mechanism.

The decay curves of the Pr^{3+} 5*d*-4*f* emission measured at 8 and 300 K upon both intra-center and band gap excitations are presented in Fig. 4. Upon direct excitation into the 4$f^1$5d^1 states at 210 nm (5.9 eV) the decay curves are single exponential with a lifetime of about 20 ns both at 8 and 300 K (Fig. 4a and 4b) that suggests the absence of any intra-center quenching mechanisms up to $T = 300$ K. This value is very close to the radiative lifetime [11], and this fact, together with the absence of temperature dependence, indicates clearly that non-radiative quenching processes are not operative in the material under investigation. On the other hand, the decay curves obtained upon band gap excitation (Fig. 4a and 4b) demonstrate the existence of an additional faster decay component with lifetime $\tau_1 = 4 - 5$ ns with fraction values of about $13 - 14$ % for the total decay process. The presence of a faster decay
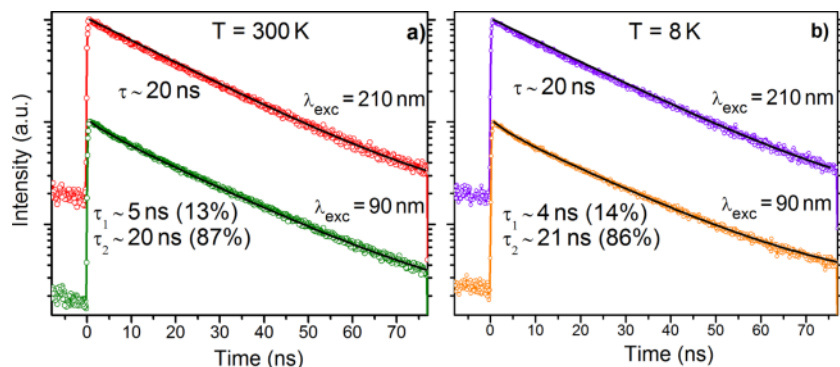
Fig. 4 (color online). Decay curves recorded monitoring 5*d*-4*f* emission of Pr^{3+} at 300 nm upon intra-center excitation at 210 nm and host excitation at 90 nm at $T = 300$ K (a) and $T = 8$ K (b).

component can be tentatively explained as a result of surface quenching. The latter comes from the fact that VUV photons with an energy exceeding the band gap are absorbed in a very thin (submicron) layer of the sample due to very high host absorption. As a result some parts of the electronic excitations transfer their energy to Pr^{3+} ions localized in the vicinity of surface-related defects which may play a role as quenching centers. We note that a somewhat similar effect was observed in the decay curves recorded for KLuP$_2$O$_7$ powders doped with Ce^{3+} upon X-ray excitation [6]. It may thus be concluded that host-to-Pr^{3+} energy transfer is characterized by very fast dynamics that seem to be independent of excitation energy across the range from the beginning of fundamental absorption to the upper limit of the measurement (20.4 eV). The latter is particularly suggested by the fact that the fast and slow time gated excitation spectra closely follow the time-integrated ones in this energy range at both $T = 8$ and 300 K. In addition, it is worth noting that the Pr^{3+} 5*d*-4*f* emission decay curves do not reveal any significant rise time within the time resolution capabilities of the setup (better than 1 ns). This indicates that excited Pr^{3+} 4*f*^{1}5*d*^{1} states do not experience any thermally assisted population of the emitting level that is typically connected with delocalization of electrons from shallow traps (see [12] for example). Overall, the results of the study of dynamic and time-resolved VUV spec-

troscopic properties of KLuP$_2$O$_7$ doped with Pr^{3+} revealed its potentials for fast scintillator applications. Obviously, additional experimental studies of scintillation properties such as energy resolution, light yield and decay time upon excitation with pulsed X- or γ-ray sources are required to establish the scintillation performance of the material.

Conclusions

In summary, KLuP$_2$O$_7$ doped with Pr^{3+} ions has been synthesized by solid-state reaction. The time-resolved VUV luminescence spectroscopic properties of the material have been studied using synchrotron radiation. Upon both direct intra-center and band gap VUV excitation the emission of KLuP$_2$O$_7$:Pr^{3+} is dominated by Pr^{3+} 5*d*-4*f* interconfigurational radiative transitions with a lifetime of approximately 20 ns. The lifetime is found to be temperature independent within the range 8 – 300 K, and no build-up of the luminescence at short time scale is observed. The VUV excitation spectra clearly demonstrated high efficiency of host-to-Pr^{3+} energy transfer in KLuP$_2$O$_7$:Pr^{3+}. Due to the efficient and fast host-to-impurity energy transfer along with the good chemical stability of the matrix, KLuP$_2$O$_7$:Pr^{3+} may provide a new interesting addition to the arsenal of available dense scintillators for detection of γ-rays.

[1] C. Ronda, J. Gondek, E. Goirand, T. Jüstel, M. Bettinelli, A. Meijerink, *Mater. Res. Soc. Symp. Proc.* **2009**, *1111*, 175.

[2] K. Ivanovskikh, A. Meijerink, C. Ronda, F. Piccinelli, A. Speghini, M. Bettinelli, *Opt. Mater.* **2011**, *34*, 419.

[3] M. Trevisani, K. V. Ivanovskikh, F. Piccinelli, A. Speghini, M. Bettinelli, *J. Phys.: Condens. Matter* **2012**, *24*, 385502 (see also 489501).

[4] D. Wisniewski, A. J. Wojtowicz, W. Drozdowski, J. M. Farmer, L. A. Boatner, *Cryst. Res. Technol.* **2003**, *38*, 275.

[5] M. Kloss, B. Finke, L. Schwarz, D. Haberland, *J. Lumin.* **1997**, *72 – 74*, 684.

[6] J.-L. Yuan, H. Zhang, H.-H. Chen, X.-X. Yang, J.-T. Zhao, M. Gu, *J. Solid State Chem.* **2007**, *180*, 3381.

[7] J. L. Yuan, X. J. Wang, D. B. Xiong, C. J. Duan, J. T. Zhao, Y. B. Fu, G. B. Zhang, C. S. Shi, *J. Lumin.* **2007**, *126*, 130.

[8] R. D. Shannon, C. T. Prewitt, *Acta Crystallogr.* **1969**, *B25*, 925.

[9] L. Schwarz, B. Finke, M. Kloss, A. Rohmann, U. Sasum, D. Haberland, *J. Lumin.* **1997**, *72 – 74*, 257.

[10] P. Dorenbos, *J. Lumin.* **2000**, *91*, 155.

[11] A. Zych, M. de Lange, C. De Mello Donegá, A. Meijerink, *J. Appl. Phys.* **2012**, *112*, 013536.

[12] J. Glodo, A. J. Wojtowicz, *Proc. SPIE* **2001**, *4412*, 216.