



# Crystal growth and scintillation properties of Pr-doped YAlO<sub>3</sub>

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## Abstract

Using the micro-pulling-down method, Pr<sup>3+</sup>-doped YAlO<sub>3</sub> single crystals were grown and their optical and luminescence properties were investigated within 80–300 K. Dominant 5d–4f emission was observed both in radio- and photoluminescence accompanied by weak f–f luminescence at 495 and 620 nm. The 5d–4f emission shows almost no temperature dependence up to 300 K and achieved radioluminescence intensity is more than 15 times higher than that of Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub>. High enough concentration of Pr<sup>3+</sup> in YAlO<sub>3</sub> host can be achieved to observe the onset of concentration quenching in the values and temperature dependence of the photoluminescence decay times.

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## 1. Introduction

Widespread application of fast scintillators based on the efficient and fast 5d–4f luminescence of the Ce<sup>3+</sup> centers, such as Ce<sup>3+</sup>-doped YAlO<sub>3</sub> (YAP), Gd<sub>2</sub>SiO<sub>5</sub>, Y<sub>2</sub>SiO<sub>5</sub>, Lu<sub>2</sub>SiO<sub>5</sub> and (Lu,Y)<sub>2</sub>SiO<sub>5</sub> [1–5], in medical imaging, high-energy physics and industry stimulates the search for new scintillating materials. Recently, allowed 5d–4f transitions of Pr<sup>3+</sup> have become of interest because it can provide a decay time even faster than that of Ce<sup>3+</sup>-doping. However, relative positions of the 4f and 5d levels strongly influence the speed of luminescence response, because the lowest 5d level can relax by multi-phonon emission to nearby lying lower 4f levels. Thus the selection of a host material possessing sufficiently strong crystal field, which shifts the lowest Pr<sup>3+</sup> 5d state below the <sup>1</sup>S<sub>0</sub> state situated round 48,000 cm<sup>-1</sup> becomes important [6]. Trying to find an appropriate host, luminescence properties and scintillation

mechanisms of Pr<sup>3+</sup>-doped LuAlO<sub>3</sub>, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, Y<sub>2</sub>SiO<sub>5</sub> and Lu<sub>2</sub>SiO<sub>5</sub> have been reported recently [7–9].

In this paper we present results on a single crystal growth of Pr-doped YAP using the micro-pulling-down (μ-PD) method and characterization of optical and luminescence properties of grown crystals.

## 2. Experimental

Starting materials were prepared from the stoichiometric mixture of 4N purity Y<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub> and Al<sub>2</sub>O<sub>3</sub> powders. Undoped and Pr-doped YAP square-shaped single crystals were grown by the μ-PD method using an iridium crucible with a die [10]. The crucible was heated inductively at a frequency of 20 kHz. The Czochralski grown YAP was used as a seed. Crystals were grown at the pulling rate 0.05–0.1 mm/min in the N<sub>2</sub> atmosphere.

To identify the obtained phase, powder X-ray diffraction (XRD) analysis was carried out in air at room temperature (RT) with a Rigaku RINT Ultima diffractometer using Cu Kα X-ray source (40 kV, 40 mA).

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Plates of  $4 \times 8 \times 1$  mm were cut and polished for the optical experiments. Absorption spectra at RT were measured by the UV–VIS–NIR spectrophotometer Shimadzu UV-3101PC. Photoluminescence characteristics were measured within 80–300 K using the liquid-nitrogen-bath optical cryostat of Oxford Instruments. The Spectrofluorometer 199S (Edinburgh Instruments) was used for the luminescence experiment. It was equipped with the steady-state hydrogen as well as the pulsed  $\mu$ s xenon and nanosecond hydrogen-filled flashlamps serving as the excitation sources. Single grating emission monochromator and Peltier-cooled TBX-04 detection module (IBH Scotland) working in a photon counting mode were used in the detection part. Spectra were corrected for experimental distortions and deconvolution procedures (Spectra-Solve software of LASTEK) were used to extract true decay times in the situation where the decay curves were distorted due to a finite width of the instrumental response.

### 3. Results and discussion

Parallelepipeds ( $4 \times 4 \times 10$ – $30$  mm) of undoped and Pr-doped (0.1, 0.5, 1 and 5 mol%) YAP single crystals were grown by the  $\mu$ -PD method. They were transparent and crack-free. Powder XRD patterns of ground crystals showed that all studied samples belong to orthorhombic phase, space group Pbnm, with no impurity phase detected.

Optical absorption and luminescence spectra are given in Fig. 1. Pr-doped (1 mol%) sample shows an onset of the 4f–5d transition of  $\text{Pr}^{3+}$  at about 240 nm and weak 4f–4f transitions between 450–500 and around 600 nm (shown in the inset), the amplitude of which is linearly increasing with Pr concentration. Excitation within the 4f–5d<sub>1</sub> absorption band results in the dominant double-peak emission at 254 + 282 nm and weaker line emissions at about 495 nm and 620 nm. As presented in Fig. 1, there

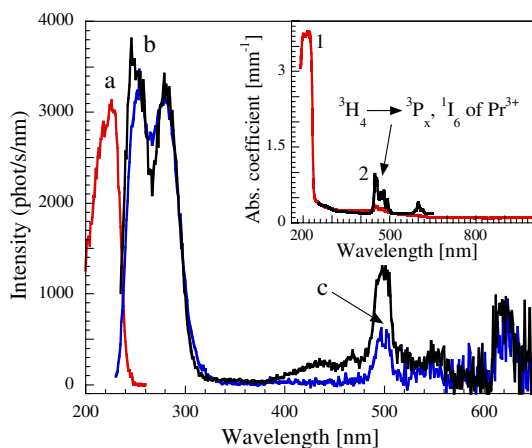


Fig. 1. Excitation (a) and emission (b,c) spectra of Pr-doped YAP (1 mol%) at RT (a,c) and 80 K (b). Emission spectra are mutually comparable in an absolute scale. In the inset the RT absorption spectra of Pr-doped YAP are given,  $\lambda_{\text{ex}} = 227$  nm,  $\lambda_{\text{em}} = 280$  nm. Curves 1 and 2 correspond to the Pr concentration 1 and 5 mol%, respectively.

is almost no change in the dominant emission going from 80 K to 300 K. By contrast, the f–f emission around 495 nm manifests an intensity reduction at higher temperatures. Photoluminescence decay (Fig. 2) within the 5d–4f emission band shows a single exponential course and the decay time of about 7.3 ns at 80 K for both 0.1 and 1 mol% Pr-doped samples. Shorter decay time value of about 6.2 ns was obtained for the 5 mol% Pr-doped sample. With increasing temperature the decay time of the former two samples slightly increases, while for that of the latter slightly decreases. Radioluminescence intensity shows the highest value for 1 mol% Pr-doped sample and is about fifteen times of that of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  for equally shaped samples, see Fig. 3.

Optical absorption within weaker 4f–4f transitions around 450–500 nm shows almost linear increase with Pr concentration up to 5 mol%, which points to high achievable concentrations of  $\text{Pr}^{3+}$  in the crystal using this growth method. Broad and structured emission band below

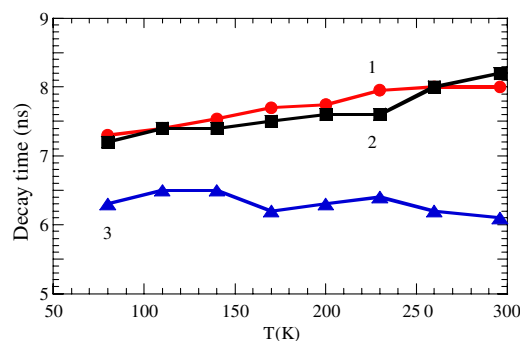


Fig. 2. Temperature dependence of the photoluminescence decay times of the Pr-doped YAP. Curves 1, 2, 3 correspond to: Pr concentration 0.1, 1, 5 mol%,  $\lambda_{\text{ex}} = 223, 227, 231$  nm, and  $\lambda_{\text{em}} = 248, 280, 253$  nm, respectively.

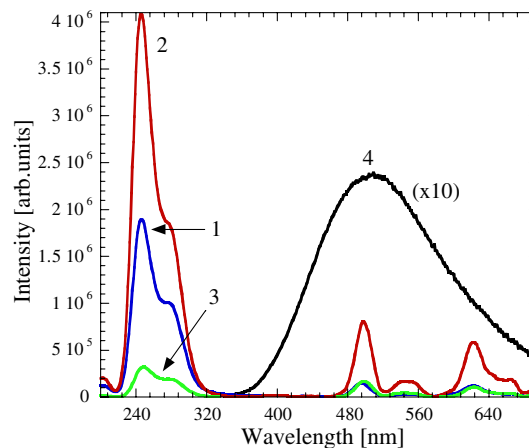


Fig. 3. Radioluminescence spectra (X-ray tube, 40 kV, 15 mA) of Pr-doped YAP at RT. Curves 1, 2 and 3 correspond to the Pr concentration 0.1, 1 and 5 mol%, respectively. The spectra are comparable in an absolute way to the standard  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  sample (curve 4, intensity is multiplied by 10).

300 nm belongs to the radiative transition from the relaxed  $5d_1$  level of  $\text{Pr}^{3+}$  to the ground state  $^3\text{H}_x$  level multiplet. Emission spectral shape and the decay times measured are in complete agreement with e.g., emission of  $\text{Pr}^{3+}$  in  $\text{LuAlO}_3$  [11]. Slight increase of decay times with temperature for lower concentrations is completely analogous to the  $\text{Ce}^{3+}$  luminescence [12], explained by mixing of opposite parity states into 5d or 4f levels with increasing temperature. Rather opposite trend and generally shorter decay time values in the case of 5 mol% Pr-doped sample point to an onset of the concentration quenching over the  $\text{Pr}^{3+}$  ions. This means that one can achieve a sufficient  $\text{Pr}^{3+}$  concentration to efficiently withdraw the absorbed energy in the YAP host lattice, provided no significant competing non-radiative relaxation channels exist. Radioluminescence intensity achieved for 1 mol% Pr-doped sample is very high and comparable with, e.g., the best Pr-doped  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  samples reported elsewhere [13]. Hence, it is not clear why both the Pr-doped YAP and  $\text{LuAlO}_3$  show significantly lower light yield with respect to their Ce-doped counterparts [14,15] when quantum efficiency of both the  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  at RT is about one. Moreover, the ground state of  $\text{Pr}^{3+}$  is about 1.5 eV closer to the top of the valence band, which in the case of the high energy excitation can facilitate the hole capture at  $\text{Pr}^{3+}$ . Possible reason for this phenomenon can be related to a troubled energy transfer from the final relaxed lattice states to  $\text{Pr}^{3+}$  ions, if one does not consider the process of energy capture at  $\text{Pr}^{3+}$  ions as a purely sequential capture of the hole and electron from the valence and conduction bands, respectively. It is well known that at RT the undoped YAP shows an intrinsic luminescence around 300 nm due to an exciton localization around lattice defects [16]. Such emission is resonant with the lowest  $\text{Ce}^{3+}$  4f-5d absorption band, while that of  $\text{Pr}^{3+}$  is too high to interact with such relaxed lattice states. Therefore, a question is whether removing such lattice defects can noticeably improve the scintillation light yield of the Pr-doped YAP, belonging to fastest scintillators based on the 5d-4f transition of  $\text{Ce}^{3+}$  or  $\text{Pr}^{3+}$ .

#### 4. Conclusions

Undoped and Pr-doped (0.1, 0.5, 1 and 5 mol%)  $\text{YAlO}_3$  single crystals were grown by the micro-pulling-down method. Almost linear dependence of the 4f-4f absorption on the Pr concentration points to an easy  $\text{Pr}^{3+}$ -doping into the YAP host as well as a high level of saturated  $\text{Pr}^{3+}$  con-

centration. Moreover, an onset of the concentration quenching observed in the case of 5 mol% Pr-doped sample allows us to conclude that an optimum Pr concentration to efficiently withdraw the absorbed energy in the host lattice is achievable. However, an energy mismatch between the relaxed (defect-related) lattice states and 4f-5d absorption bands of  $\text{Pr}^{3+}$  can be the reason for poor efficiency of final stages of energy transport towards  $\text{Pr}^{3+}$  centres. Even if the steady-state scintillation efficiency is high, the previously reported light yields are noticeably lower with respect to those of both the Ce-doped YAP and  $\text{LuAlO}_3$  scintillators.

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