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# Crystal growth and spectroscopic properties of praseodymium and cerium co-doped $Y_2SiO_5$

Lihe Zheng<sup>a,b</sup>, Radosław Lisiecki<sup>c,\*</sup>, Witold Ryba-Romanowski<sup>c</sup>, Gérard Aka<sup>b</sup>, Juqing Di<sup>d</sup>, Dongzhen Li<sup>d</sup>, Xiaodong Xu<sup>a,\*\*</sup>, Jun Xu<sup>a,\*\*</sup>

<sup>a</sup> Shanghai Institute of Ceramics, Chinese Academy of Sciences, 588 Heshuo Road, Shanghai 201899, China

<sup>b</sup> Laboratoire de Chimie de la Matière Condensée de Paris, ENSCP, 11 Rue P. et M. Curie, 75231 Paris Cedex 5, France

<sup>c</sup> Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland

<sup>d</sup> Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Science, 390 Qinghe Road, Shanghai 201800, China

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## ABSTRACT

Praseodymium and cerium co-doped yttrium silicate (Pr,Ce:YSO) crystal with high optical quality was grown by the Czochralski method. The segregation coefficient of  $Pr^{3+}$  and  $Ce^{3+}$  is measured to be 0.547 and 0.136, respectively. The polarized absorption bands centered at 268 nm, 299 nm and 356 nm were assigned to  $4f$  ( $^2F_{5/2}$ )  $\rightarrow$   $5d$  inter-configuration transitions of  $Ce^{3+}$ , while bands centered at 220 nm and 250 nm were assigned to  $4f^n-4f^{n-1}5d$  transitions of  $Pr^{3+}$ . The VUV–UV excitation spectra for monitoring  $Pr^{3+}$  emissions centered at 610 nm ( $^1D_2 \rightarrow ^3H_4$ ) and 489 nm ( $^3P_0 \rightarrow ^3H_4$ ), as well as  $Ce^{3+}$  emission centered at 450 nm were recorded at  $T=8$  K in the range of 100 nm–320 nm. Polarized excitation spectra for  $Ce^{3+}$  emission centered at 424 nm and  $Pr^{3+}$  emission centered at 611 nm were recorded at  $T=300$  K. Polarized emission spectra were obtained upon excitation at 365 nm and 456 nm at  $T=300$  K. Lifetimes were estimated to be 170  $\mu$ s for  $Pr^{3+}$  ( $^1D_2$ ), 3  $\mu$ s for  $Pr^{3+}$  ( $^3P_0$ ) and 39 ns for  $Ce^{3+}$  ( $^5d_1$ ).

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## 1. Introduction

Interests in rare-earth ions doped crystals exhibiting broad and intense  $4f^{n-1}5d \rightarrow 4f^n$  emission are stimulated by potential application in environmental sciences, medicine, photolithography, material processing, density optical storage, UV solid-state lasers and quantum computing [1–3]. Yttrium silicate ( $Y_2SiO_5$ , YSO) crystal is well-known host material by accommodating appreciable amounts of rare earth ions. Ce:YSO have been investigated in numerous papers for scintillation applications [4–5]. Compared with  $Ce^{3+}$  ions, the  $5d-4f$  energy transition of  $Pr^{3+}$  in YSO is blue-shifted and the excitation energy transfer between  $Pr^{3+}$  and  $Ce^{3+}$  may enhance the luminescence intensity in blue spectral range [6–8]. On the other hand, Pr:YSO was considered for the initial qubit experiments [9–13]. Yan et al. reported the incorporation of a low concentration of readout ions  $Ce^{3+}$  serving as a sensor for reading out the state of the nearby qubit of  $Pr^{3+}$  through the interaction between the qubit and readout ion [14].

In this paper, we concentrate on VUV–UV–Vis spectroscopic properties of praseodymium and cerium co-doped yttrium silicate (Pr,Ce:YSO) crystal. The intention of this paper is to get insights into the excitation and relaxation process of excited states which are relevant to luminescence phenomena in Pr,Ce:YSO with low concentration of 0.05 at% for  $Pr^{3+}$  and 0.088 at% for  $Ce^{3+}$ . Accordingly, the excitation and emission spectra, together with relaxation dynamic were investigated.

## 2. Experimental

### 2.1. Crystal growth

The Pr,Ce:YSO crystal was grown by the Czochralski method from an inductively heated iridium crucible. The Pr and Ce concentration in the melt was 0.05 at% and 0.088 at% with respect to Y, respectively. The starting materials were  $SiO_2$ ,  $Y_2O_3$ ,  $Pr_6O_{11}$  and  $CeO_2$  powders with purity higher than 99.99%. The powders were weighed, mixed and pressed into tablets before sintered at 1400 °C for 24 h. The total weight of raw materials was 330 g.

Nitrogen with purity of 5 N was used as growth atmosphere. The Pr:YSO crystal oriented along (010) with diameter of 4.5 mm and length of 30 mm was used as a seed. The pulling rate was set to 1–5 mm  $h^{-1}$  and the rotation rate of the seed was set to 10–30 rpm. After pulling off from the melting, the crystal was

\* Corresponding author at: Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland.

\*\* Corresponding authors at: Shanghai Institute of Ceramics, Chinese Academy of Sciences, 588 Heshuo Road, Shanghai 201899, China. Tel.: +86 (0)21 69987573.

E-mail addresses: [zhenglihe@gmail.com](mailto:zhenglihe@gmail.com) (L. Zheng).

[R.Lisiecki@int.pan.wroc.pl](mailto:R.Lisiecki@int.pan.wroc.pl) (R. Lisiecki), [xdxu79@mail.sic.ac.cn](mailto:xdxu79@mail.sic.ac.cn) (X. Xu).

[xujun@mail.shcnc.ac.cn](mailto:xujun@mail.shcnc.ac.cn) (J. Xu).

cooled to room temperature in 40 h. Fig. 1 shows the obtained Pr,Ce:YSO crystal boule with diameter of 32 mm and length of 65 mm.

## 2.2. ICP-AES and XRD measurement

The segregation coefficient of Pr and Ce in the YSO crystal was calculated according to the measured concentrations of Pr, Ce and Y atoms at the starting position attached to the grown Pr,Ce:YSO crystal using the inductively coupled plasma atomic emission spectrometer (ICP-AES) method. The segregation coefficient  $k_m$  was calculated according to Eq. (1), where  $C_t$  stands for the concentration of Pr or Ce close to seed crystal, and  $C_0$  stands for the initial concentration of Pr or Ce in the melt.

$$k_m = C_t / C_0 \quad (1)$$

The segregation coefficient of Pr and Ce ion in Pr,Ce:YSO crystal is accordingly calculated to be 0.547 and 0.136, respectively.

The sample for XRD measurement was cut adjacent to the seed crystal position and then ground to fine powder in an agate mortar. The crystal structure was examined by D/MAX 2550V powder X-ray diffractometer (XRD, Cu target,  $K_{\alpha}$ ). Fig. 2 shows the powder XRD pattern of as-grown Pr,Ce:YSO crystal which is in good agreement with the YSO structure phase of monoclinic system with a space group  $C2/m$  shown in PDF #36-1476 [15].

## 2.3. Spectroscopic measurement

Excitation spectra and decay curves of luminescence in vacuum-ultraviolet VUV were acquired using experimental set-up available



Fig. 1. As-grown Pr, Ce:YSO crystal.

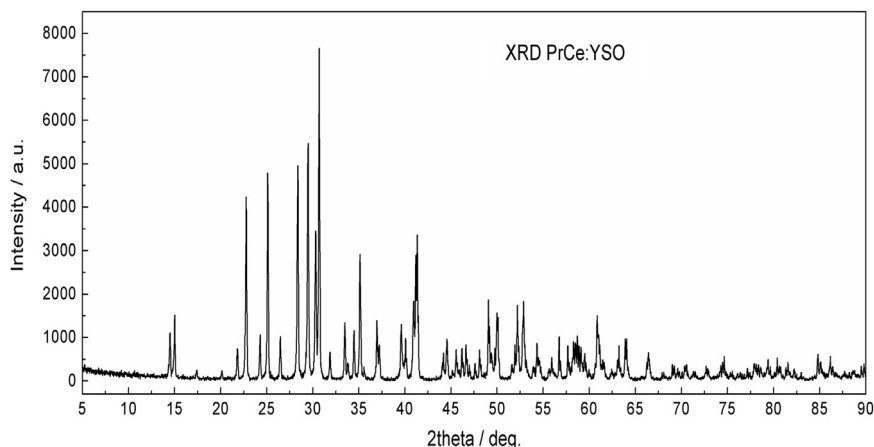


Fig. 2. Powder XRD pattern for as-grown Pr,Ce:YSO crystal.

at the SUPERLUMI station of Hamburger Synchrotron Strahlungslabor (HASYLAB) at Deutsches Elektronen-Synchrotron (DESY). Excitation spectra were scanned within spectral region of 100 nm–300 nm with the primary 2 m McPherson monochromator when monitoring luminescence intensity with a secondary ARC monochromator coupled to a Hamamatsu R6358P photomultiplier and a PMT detector. The spectra were corrected for the incident photon flux using a reference sodium salicylate (NaSal) sample. The quantum efficiency of NaSal is constant in wide VUV–UV wavelength range. To record low-temperature spectra at 8 K, the sample was placed in a cold-finger liquid-helium cryostat (Cryovac GmbH). The emission spectra excited in the VUV region were monitored with a CCD camera. Polarized absorption spectra in the UV-Vis–NIR region were measured at room temperature with a Varian model 5 spectrophotometer where the resolution was 0.2 nm in the near-infrared region and 0.1 nm in UV-Vis. Luminescence and excitation spectra in UV-Vis were acquired with a Dongwoo Optron system containing a DM 711 emission monochromator and a DM 158i excitation monochromator with 750 mm and 150 mm focal length, respectively. The excitation source was an ozone-free Xenon lamp DL180-Xe and the luminescence was detected with a Hamamatsu R-955 photomultiplier. To record luminescence decay curves, a Surelite OPO pumped by a third harmonic of a Nd:YAG laser was used as an excitation source. Luminescence was dispersed by a grating monochromator and detected with a photomultiplier connected to a Tektronix TDS 3052 oscilloscope.

## 3. Results and discussion

Fig. 3 displays survey on polarized absorption spectra of Pr,Ce:YSO crystal recorded at 300 K with electric  $E$  vector of incident light parallel to  $a$ ,  $b$  and  $c$  crystallographic axes. The absorption spectra are spanned within 200 nm–2500 nm. It can be seen that the absorption bands of active ions appear in the UV region. Owing to small concentration of  $Pr^{3+}$  ions, considerably weaker  $f$ – $f$  transition within  $4f^2$  electronic configuration of Pr in Vis–NIR range are hardly observed in this spectrum. The inset shows in detail the absorption spectrum in UV region. The absorption bands peaked at 299 nm and 356 nm can be undoubtedly assigned to  $4f$  ( $^2F_{5/2}$ )  $\rightarrow$   $5d$  inter-configuration transitions of  $Ce^{3+}$  in YSO. A less apparent absorption in the form of shoulder around 268 nm may be due to  $Ce^{3+}$  transition, too. Since the  $5d$  electrons are located on outer-most orbits, the spectral broadening of absorption bands is quite effective. For comparison, the three absorption bands of  $Ce^{3+}$  within 250 nm–380 nm have also been observed in LYSO [16]. The absorption bands around 220 nm and 250 nm in Fig. 3 can be

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