

# Spectroscopic study of Praseodymium and Cerium co-doped APLF glass as improved neutron scintillator

Marilou Cadatal-Raduban<sup>1</sup>, John A. Harrison<sup>1</sup>, Melvin John F. Empizo<sup>2</sup>, Takahiro Murata<sup>3</sup>, Yuki Minami<sup>2</sup>, Keisuke Kawano<sup>2</sup>, Kohei Yamanoi<sup>2</sup>, Toshihiko Shimizu<sup>2</sup>, Nobuhiko Sarukura<sup>2</sup>, Malgorzata Guzik<sup>4</sup>, Yannick Guyot<sup>5</sup>, and Georges Boulon<sup>5</sup>

<sup>1</sup>Institute of Natural and Mathematical Sciences, Albany, Auckland 0632 New Zealand, <sup>2</sup>Institute of Laser Engineering, Osaka University, 2-6 Yamadaoka, Suita, Osaka 565-0871 Japan, <sup>3</sup>Faculty of Education, Kumamoto University, 2-40-1 Kurokami, Chuo-ku, Kumamoto 860-8555 Japan, <sup>4</sup>Faculty of Chemistry, University of Wroclaw, ul. Joliot-Curie 14, Wroclaw 50-383 Poland, <sup>5</sup>Univ Lyon, Université Claude Bernard Lyon1, CNRS, Institut Lumière Matière, Villeurbanne 69622 France

## INTRODUCTION

Efficient detection of scattered neutrons is crucial for realizing the potential of inertial confinement fusion as a sustainable energy source. The efficiency of the nuclear fusion event is derived from the plasma areal density that can be measured using several methods, the most desirable of which is down-scattered neutron diagnostics. Therefore, a scintillator having a response time of less than 20 ns and high quantum efficiency for the scattered neutrons is needed. Lanthanide ions, known for their wide emission bands in the vacuum ultraviolet and ultraviolet regions, have been used as activator dopants in APLF [1]. The fluorescence band of optically-activated lanthanides translates to shorter lifetime in the order of  $\lambda^3$  [2], which could satisfy one of the above-mentioned criteria for an efficient scintillator. Lanthanide ions singly-doped with APLF yield faster response times than either Ce-doped lithium silicate glasses or the glass scintillator GS2 where decay lifetimes range from 50 to 70ns [3]. The decay time profiles of singly-doped APLF vary depending on the concentration and species of the activator ions, which are 4-6.6 ns with  $\text{Nd}^{3+}$  [4], 5.8-31ns with  $\text{Er}^{3+}$  [4], 16-19.3ns with  $\text{Pr}^{3+}$  [5], and 23.3-40 ns with  $\text{Ce}^{3+}$  [6] with radioactive, optical, or x-ray excitation. However, there is a usual tradeoff between short decay time and therefore fast response and emission intensity, which can result to very fast detector but with poor light throughput. Therefore, this project investigates the effects of codoping APLF with  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  ions. We evaluate the optical characteristics based on photoluminescence excitation (PLE), photoluminescence spectroscopy (PL), and time-resolved photoluminescence (TRPL) analyses for fixed  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  concentration ratio in the host glass. We selected  $\text{Ce}^{3+}$  as co-activator due to its high fluorescence yield [7] and  $\text{Pr}^{3+}$  dopant for its short decay

time [5]. Singly-doped APLFs with either  $\text{Ce}^{3+}$  or  $\text{Pr}^{3+}$  have been recently shown to be capable of discriminating down-scattered neutrons against background X-rays, primary neutrons, and gamma signals in inertial confinement fusion investigations [8]. Although codoping of lanthanides with other host materials has been reported for phosphor displays in the visible to near infrared [7], this study focuses on the spectral and temporal responses in the UV region. Some of the expected  $4f5d \rightarrow 4f$  transitions of  $\text{Pr}^{3+}$  fall below 200nm so the optical characterizations of singly-doped  $\text{Pr}^{3+}$  or  $\text{Ce}^{3+}$  APLF and codoped APLF were also examined using the spectroscopy beamline (BL7B) of the Institute of Molecular Science (IMS, Japan) Ultraviolet Synchrotron Orbital Radiation (UVSOR) facility. It is shown that in comparison to singly-doped APLF, codoping can provide 4 times improvement in response time due to  $\text{Pr}^{3+}$  luminescence. The fast response time is attributed to a fast energy transfer from the  $4f5d$  level of  $\text{Pr}^{3+}$  and the  $5d$  level of  $\text{Ce}^{3+}$ . With four times improvement in response time, this material may enable very fast detection of secondary neutrons in inertial confinement fusion.

## EXPERIMENT

Two singly-doped and one codoped  $20\text{Al}(\text{PO}_3)_3\text{-}80\text{LiF} + x\text{PrF}_3 + y\text{CeF}_3$  ( $x=0, 1; y=0, 0.5$ ) samples were prepared by the melt-quenching method described in [2]. Namely, these were: APLF+1Pr0Ce, APLF+0Pr1Ce, and APLF+1Pr0.5Ce. The precursor materials consisted of high-purity aluminum metaphosphate ( $\text{Al}(\text{PO}_3)_3$ ), lithium fluoride (LiF), 6Li-enriched LiF, praseodymium fluoride ( $\text{PrF}_3$ ) and cerium fluoride ( $\text{CeF}_3$ ) powders. All the starting materials were mixed in a glassy carbon crucible and were melted for 0.5h at  $1100^\circ\text{C}$  in nitrogen atmosphere. The glass melts were cooled to  $400^\circ\text{C}$  and were

subsequently annealed near the glass transition temperature. The glasses were cooled down to room temperature, and finally were cut into 22 mm diameter  $\times$  6 mm thickness disks and polished on both sides to an optical finish.

The spectral properties of APLF+1Pr0Ce, APLF+0Pr1Ce, and APLF+1Pr0.5Ce were characterized using PLE and PL measurements under 200nm excitation at the IMS-UVSOR facility. The PL spectra were also measured under 217nm excitation using the fourth harmonics of Ti-sapphire regenerative amplifier at room temperature. The photoluminescence lifetime was measured with the same excitation at 1kHz repetition rate and 100fs laser pulse duration focused on the APLF glass surface. The luminescence was collected and focused onto an imaging spectrograph with streak camera and digital CCD camera attachments.

## RESULTS AND DISCUSSIONS

The spectral characteristics were evaluated for singly-doped and codoped samples. Figure 1 shows the PL spectra under 217nm excitation for singly-doped and codoped APLF glasses. Two distinct luminescence peaks are attributable to each dopant emissions. The asymmetric luminescence band from 220 to 285nm corresponds to the  $4f5d \rightarrow 4f$  transition of  $\text{Pr}^{3+}$ . The luminescence intensity at 238nm is more intense than at 260nm for both APLF80+1Pr0Ce and APLF80+1Pr0.5Ce samples. The luminescence peak at 337nm is ascribed to the  $5d \rightarrow 4f$   $\text{Ce}^{3+}$  transition. From PL spectra, we can discriminate the respective luminescence of each activated ion and measure the respective response times.

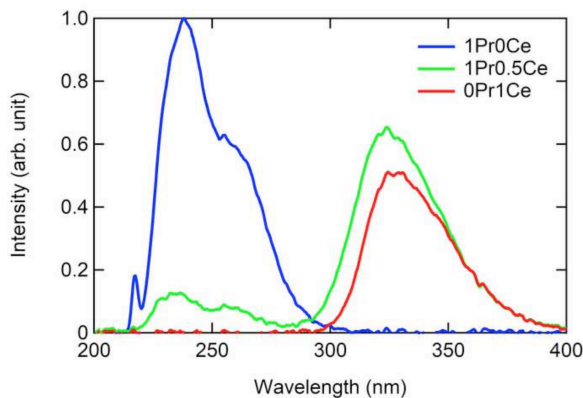


Fig. 1. PL spectra of APLF+1Pr0Ce, APLF+0Pr1Ce, and APLF+1Pr0.5Ce under 217 nm excitation.

Figure 2 shows the streak camera images of the fluorescence for singly-doped and codoped APLF samples under 217nm excitation. A single exponential function was used for fitting each respective decay profiles. The fluorescence decay time is 17.7ns for APLF80+1Pr0Ce and 30.6ns for APLF80+0Pr1Ce luminescence. With codoping, the luminescence lifetime of  $\text{Pr}^{3+}$  around 270 nm is improved to 5.5ns. This

response time is four times (4x) shorter than the APLF80+1Pr0Ce sample and the 19.6ns lifetime previously obtained of APLF+Pr3+ [5] under similar concentration, optical excitation, and temperature condition. For the  $\text{Ce}^{3+}$  luminescence, the decay time has somewhat broadened to 35ns but the emission intensity was increased. From the luminescence observations, we can infer that the 5d energy level of  $\text{Ce}^{3+}$  is the more efficient at light-emitting state than the 4f5d levels of  $\text{Pr}^{3+}$  in codoped APLF supporting the possibility of energy transfer between the two excited levels. Measurements are underway to investigate further the transfer mechanism and co-activation process brought by codoping.

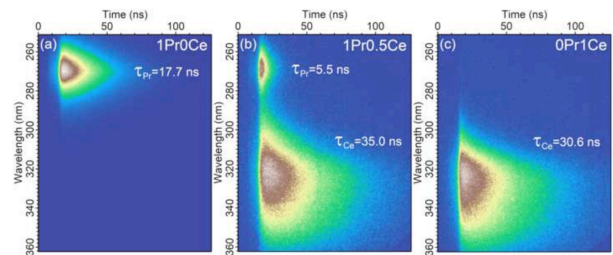


Fig. 2. Streak camera images of photoluminescence around 270 and 330 nm of (a) APLF+1Pr0Ce, (b) APLF+0Pr1Ce, and (c) APLF+1Pr0.5Ce under 217nm excitation. The fluorescence decay times of singly-doped APLF are 17.7ns for  $\text{Pr}^{3+}$  and 30.6ns for  $\text{Ce}^{3+}$  luminescence. The luminescence lifetime of  $\text{Pr}^{3+}$  is 5.5ns and of  $\text{Ce}^{3+}$  is 35ns for codoped APLF.

## CONCLUSIONS

In summary, we have investigated the spectral properties of  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  codoped APLF glass. We were able to discriminate the luminescence band from each ion and achieved 5.5ns decay time in  $\text{Pr}^{3+}$  luminescence. This is four times improvement of singly-doped APLF.  $\text{Ce}^{3+}$  was found to be the more efficient light-emitting state than  $\text{Pr}^{3+}$  in codoped APLF. Fast response time in  $\text{Pr}^{3+}$  and increased emission intensity of  $\text{Ce}^{3+}$  is attributed to a fast energy exchange from the 4f5d level of  $\text{Pr}^{3+}$  and the 5d level of  $\text{Ce}^{3+}$ . The energy transfer mechanism and co-activation needs further investigation, but with four times improvement in response time, codoped APLF may find application as a fast scintillator for inertial confinement fusion.

## ACKNOWLEDGEMENTS

This work was supported by the Osaka University Institute of Laser Engineering (ILE) through the Collaborative Research Program Grant No. 2018B1-RADUBAN, by the Japan Society for the Promotion of Science (JSPS) through the Grants-in-Aid for Scientific Research (KAKENHI) Grant No. 16K06725, and by the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) through the Program for Creation of Research Platforms

and Sharing of Advanced Research Facilities (Photon Beam Platform).

## REFERENCES

- [1] K. Watanabe, Y. Arikawa, K. Yamanoi, M. Cadatal-Raduban, T. Nagai, M. Kouno, K. Sakai, T. Nakazato, T. Shimizu, N. Sarukura, M. Nakai, T. Norimatsu, H. Azechi, A. Yoshikawa, T. Murata, S. Fujino, H. Yoshida, N. Izumi, N. Satoh, H. Kan, *J. Cryst. Growth* 362, (2013) 288-290.
- [2] T. Murata, S. Fujino, H. Yoshida, Y. Arikawa, T. Nakazato, T. Shimizu, N. Sarukura, M. Nakai, T. Norimatsu, H. Azechi, K. Kamada, Y. Usuki, T. Suyama, A. Yoshikawa, N. Sato, and H. Kan, *IEEE Trans. Nucl. Sci.* 57, 3 (2010) 1426-1429.
- [3] D.C. Wilson, W.C. Mead, L. Disdier, M. Houry, J.L. Bourgade, and T.J. Murphy, *Nucl. Instrum. Methods Phys. Res. A Accel. Spectrom. Detect. Assoc. Equip.*, 488, (2002) 400–409.
- [4] K. Yamanoi, T. Murata, Y. Arikawa, T. Nakazato, M. Cadatal-Raduban, T. Shimizu, N. Sarukura, M. Nakai, T. Norimatsu, H. Nishimura, H. Azechi, S. Fujino, H. Yoshida, A. Yoshikawa, N. Satoh, and H. Kan, *Opt.Mater.* 35, (2013) 1962–1964.
- [5] M.J.F. Empizo, M. Cadatal-Raduban, T. Murata, Y. Minami, K. Kawano, K. Yamanoi, T. Shimizu, N. Sarukura, M. Guzik, Y. Guyot, Georges Boulon, *J. Lumin.* 193, (2018) 13-21.
- [6] K. Yamanoi, T. Murata, T. Yanagida, Y. Fujimoto, M.J.F. Empizo, K. Iwano, Y. Iwasa, R. Arita, Y. Minami, Y. Arikawa, T. Shimizu, N. Sarukura, T. Norimatsu, H. Azechi, S. Fujino, H. Yoshida, N. Satoh, and H. Kan, *Sensors Mater.* 27, 3 (2015) 229–235.
- [7] R. Guan, L. Cao, Y. You, and Y. Cao, *J. Nanomater.* 2015, (2015) 549208.
- [8] Y. Arikawa, K. Yamanoi, T. Nakazato, E.S. Estacio, T. Shimizu, N. Sarukura, M. Nakai, H. Hosoda, T. Norimatsu, Y. Hironaka, H. Azechi, N. Izumi, T. Murata, S. Fujino, H. Yoshida, K. Kamada, Y. Usuki, T. Suyama, A. Yoshikawa, N. Satoh, and H. Kan, *Rev. Sci. Instrum.* 81, (2010) 10D303.