

Evaluation of gamma-ray-irradiated, praseodymium-doped aluminum lithium fluorophosphate for scintillator material development

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In this study, we evaluated $20\text{Al}(\text{PO}_3)_3\text{-}80\text{LiF-PrF}_3$ (Pr-doped APLF) glass as a potential scintillator material for laser fusion experiments. A glass was irradiated with gamma (γ)-rays from a cobalt-60 (^{60}Co) source resulting in an absorbed dose of 5.2 kGy. By comparing non-irradiated and irradiated glasses, we found that the structural properties of the Pr-doped APLF glass were not significantly altered by γ -ray exposure. The irradiation did not break any bonds in the fluorophosphate glass nor did it change the valence states or local environment of the Pr ions. These findings suggest that Pr-doped APLF glass retains its structural integrity and scintillation potential even after γ -ray irradiation, making it a promising candidate for use in laser fusion diagnostics.

1 Introduction

Scintillator material development is critical for advancing our laser fusion research at the Osaka University Institute of Laser Engineering (ILE). To achieve controlled fusion reactions, we utilize plasma diagnostic techniques that employ scintillators to detect neutrons generated by the fusion reaction and elastically scattered by the fusion plasma. In this context, we have developed a novel aluminum lithium fluorophosphate glass, $20\text{Al}(\text{PO}_3)_3\text{-}80\text{LiF}_3$ (APLF) as a potential neutron scintillator material. APLF glass boasts a high lithium (Li) content which is essential for distinguishing scattered neutrons from the other high-energy particles and intense background signals. Moreover, APLF glasses doped with rare earth ions such as cerium (Ce) and praseodymium (Pr) exhibit fast scintillation decay times, surpassing those of commercial scintillators such as KG2 (Saint Gobain). For instance, Ce-doped and Pr-doped APLF glasses exhibit decay times of 23.3 and 19.7 ns, respectively, under optical excitation – significantly faster than KG2's 38.8 ns decay time, which is accompanied by a long afterglow or persistence. To advance the development of APLF glasses as neutron scintillators, it is imperative to examine them using various spectroscopic techniques to determine their viability in future fusion reactors.

While rare earth ions typically exhibit a valence or oxidation state of 3+, several studies indicate that these ion dopants can exist with variable oxidation states. However, these studies predominantly focus on bulk single crystals such as silicates, fluorides, and garnets rather than glasses. Changes in oxidation states from 3+ to 2+ and/or 4+ can occur through charge compensation mechanisms depending on the host material, growth conditions, and radiation exposure. In scintillator materials, the presence of variable oxidation states can impact scintillation properties by creating multiple recombination pathways, both radiative and nonradiative.

In this study, we aim evaluate the presence of Pr ions in Pr-doped APLF glasses irradiated with gamma (γ) rays. Fourier transform infrared (FTIR) and x-ray absorption spectroscopies are employed as typical x-ray diffraction measurements are not feasible for the amorphous glasses to assess their structure post-irradiation. Using x-ray absorption spectroscopy, we investigate the oxidation states, local structures, and coordination numbers of Pr ions, thereby elucidating their roles on the scintillation properties of APLF glasses.

2 Experiment

Pr-doped APLF glasses with nominal chemical compositions of $20\text{Al}(\text{PO}_3)_3\text{-}80\text{LiF-PrF}_3$ were prepared by the melt-quenching method as described in Ref. 1. The glasses were cut into pieces measuring $10.7\text{ mm} \times 10.7\text{ mm} \times 1.8\text{ mm}$ pieces and were polished on both sides to an optical finish. Subsequently, γ -ray irradiation was performed at the Rabbit11 facility of the Osaka University Institute of Scientific and Industrial Research (SANKEN). The glasses were irradiated with γ -rays carrying 1.17 and 1.33 MeV energies from Rabbit11's cobalt-60 (^{60}Co) source, which has a radioactivity of $21 \times 10^{12}\text{ Bq}$. The estimated dose rate and total absorbed dose on the glass are 1.36 kGy h^{-1} and 5.2 kGy , respectively. Figure 1 shows the photographs of the non-irradiated and γ -ray-irradiated, Pr-doped APLF glasses.

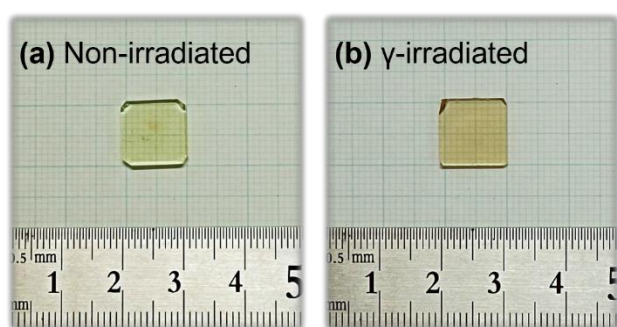


Fig. 1: Photographs of the non-irradiated and γ -ray-irradiated, Pr-doped APLF glasses.

FTIR spectra were first measured using a JASCO FT/IR 6100 spectrophotometer with a single-reflection JASCO ATR-PRO410-S attenuated total reflection (ATR) accessory and a diamond prism. The x-ray absorption near edge structure (XANES) spectra for the Pr LIII edge were then obtained in fluorescence yield mode at the BL-9A beamline of Photon Factory, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The incident x-ray beam had an 10 slit measuring $1.0\text{ mm} \times 1.0\text{ mm}$, and the full width at half maximum of the beam was approximately $500\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$. The energy was calibrated using the chromium (Cr) metal spectrum. A water-cooled Si (111) double-crystal monochromator was used to scan the photon energy from 5460 to 6460 eV. The signals were recorded by a Lytle detector²⁾ with a vanadium (V) filter to reduce elastic scattering. All the experimental XANES data were analyzed using the Athena software.³⁾

3 Results and Discussion

Figure 2 shows the FTIR transmission spectra of both non-irradiated and γ -ray-irradiated, Pr-doped APLF glasses. Given that APLF glass is composed of $\text{Al}(\text{PO}_3)_3$ with substantial amounts of LiF and PrF_3 , multiple components such as the $\text{P}_2(\text{O},\text{F})_7$, $\text{P}(\text{O},\text{F})_4$, $(\text{AlF}_4)^-$, and $(\text{AlF}_6)^{3-}$ groups⁴⁾ contribute to the vibrational spectra, alongside the typical $(\text{PO}_3)^{2-}$ and $(\text{PO}_2)^-$ groups.⁵⁾ The bands at 564 and 668 cm^{-1} can

be attributed to the $(\text{AlF}_4)^-$ and $(\text{AlF}_6)^{3-}$ units, respectively, which are prominent in glass structures with high metal fluoride content. Additionally, bands around 773 and 914 cm^{-1} correspond to the symmetric and asymmetric stretching of the P-O-P bridging oxygen chains. For APLF glass, the P-O-P stretching originates from metaphosphate groups and the pyrophosphate group, $\text{P}_2(\text{O},\text{F})_7$, which is present when metaphosphate chains are shortened and when some oxygen atoms are replaced by fluorine atoms. The band at approximately 1009 cm^{-1} is associated with the symmetric stretching of the $(\text{PO}_3)^{2-}$ terminal group, while the band at approximately 1106 cm^{-1} relates to the asymmetric stretching of the $(\text{PO}_3)^{2-}$ terminal group and the vibrations of some $\text{P}(\text{O},\text{F})_4$ groups, which emerge in glass systems with relatively low $\text{Al}(\text{PO}_3)_3$ content. The 1181 cm^{-1} band is attributed to the O-P-O stretching of the $\text{P}_2(\text{O},\text{F})_7$ group and the symmetric stretching of the $(\text{PO}_2)^-$ terminal group, while the 1244 cm^{-1} band is attributed to the asymmetric stretching of the $(\text{PO}_2)^-$ terminal group. Although the γ -ray-irradiated glass has a slight decrease in transmittance (higher absorption) from 900 to 1250 cm^{-1} , this minor decrease is not significant enough to affect the aforementioned bond groups. Thus, both non-irradiated and γ -ray-irradiated glasses exhibit similar IR absorption bands, indicating that γ -ray irradiation does not alter the structure of Pr-doped APLF glass.

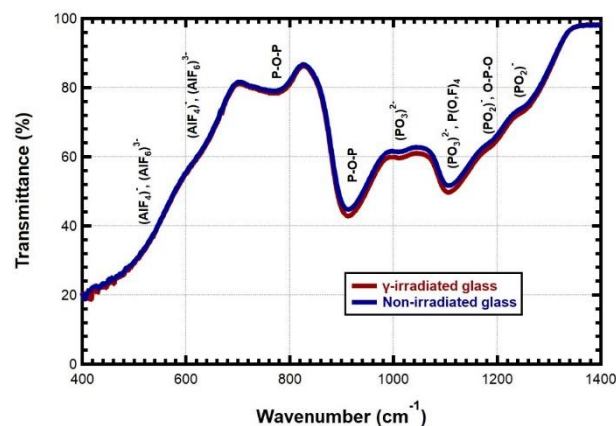


Fig. 2: FTIR transmission spectra of non-irradiated and γ -ray-irradiated, Pr-doped APLF glasses.

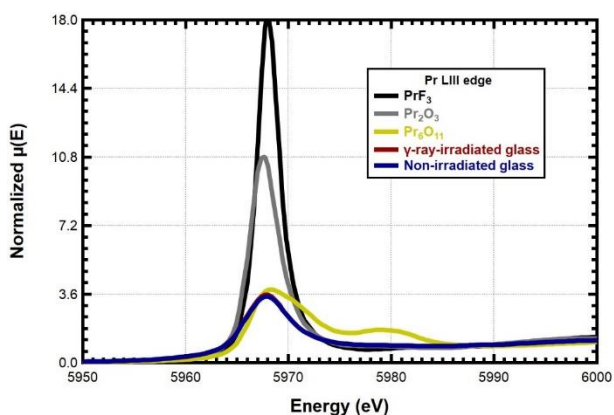


Fig. 3: XANES spectra for the Pr LIII edge of non-irradiated and γ -ray-irradiated, Pr-doped APLF glasses.

Figure 3 shows the XANES spectra for the Pr LIII edge of the non-irradiated and γ -ray-irradiated, Pr-doped APLF glasses, along with PrF_3 , Pr_2O_3 , and Pr_6O_{11} standards for reference. Both glasses exhibit identical spectral line shapes before and after the 5965 eV edge, as well as the same white line intensities. The XANES spectra of the Pr-doped APLF glasses closely match those of the PrF_3 and Pr_2O_3 standards, suggesting that the Pr ions in APLF glasses exist in an environment similar to PrF_3 and Pr_2O_3 , maintaining an oxidation or valence state of +3. In addition, neither the non-irradiated nor the γ -ray-irradiated glasses exhibit any pre-edge peaks, which could indicate asymmetry or disorder around the Pr ions. These results reveal that γ -ray irradiation does not oxidize or reduce Pr ions nor does it distort their arrangement within the APLF glass matrix. These findings demonstrate that the structural integrity and local environment of Pr ions in Pr-doped APLF glass remain unaffected by γ -ray irradiation, supporting its potential use as a scintillator material in laser fusion diagnostics.

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Research Achievements

1. Results are published as K. Shinohara *et al.*, *Jpn. J. Appl. Phys.* **62**, 010613 (2023).

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