Luminescence of Ce-doped aluminophosphate glasses

M. W. Kielty¹ · L. Pan¹ · M. A. Dettmann² · V. Herrig² · U. Akgun² · L. G. Jacobsohn^{1,3}

Received: 30 January 2019 / Accepted: 8 April 2019 © Springer Science+Business Media, LLC, part of Springer Nature 2019

Abstract



The effects of BaO network modifier on the structure, optical properties and luminescence of Ce-doped aluminophosphate glasses were investigated. Glasses were prepared by the melt quenching method in air with different chemical compositions: 50 or 60 mol% P_2O_5+5 , 15 or 25 mol% SiO_2+4-19 mol% BaO+15 mol% Al_2O_3+1-6 mol% Ce_2O_3 such the total summed up to 100 mol%. Density was determined to be within 2.7–3.0 g/cm³, while the index of refraction was estimated using the Gladstone-Dale relation using the experimentally-obtained density values to be around 1.48. For each glass series, Raman spectra varied according to the BaO and/or Ce_2O_3 content. For 1 mol% Ce-doped glasses, the ultraviolet (UV) transparency cutoff was within 317–328 nm, with the cutoff wavelength increasing to 367–373 nm for 6 mol% doped glasses. Scintillation was characterized by radioluminescence (RL) measurements under X-ray excitation, and luminescence by photoluminescence emission (PL), excitation, and fluorescence lifetime measurements. PL and RL results showed a broad band centered around 3.3–3.6 eV with a fluorescence lifetime of about 30 ns. The highest RL output was observed from the $60P_2O_5 \cdot 14BaO \cdot 5SiO_2 \cdot 15Al_2O_3 \cdot 6Ce_2O_3$ glass.

1 Introduction

Scintillators are luminescent materials used for the detection and measurement of ionizing radiation, finding application in many fields, including medical imaging, oil exploration, security, and science. In particular, glass scintillators find application in neutron and gamma detection, oil logging, X-ray imaging, and radiation detection in chemically corrosive environments. There is an increasing interest in developing glass scintillators since they offer distinct advantages such as low cost of production, large area and volume, and the ability to tailor size and shape for the required application. Ce³⁺ is commonly used as the activator though the host strongly affects its luminescent characteristics [1]. The luminescence of Ce³⁺ in glasses is an active research topic [2–7], but it has not been investigated in detail in aluminophosphate glasses. This work aims at investigating the

L. G. Jacobsohn luiz@clemson.edu

² Physics Department, Coe College, Cedar Rapids, IA, USA

optical properties, the structure, and the luminescence of Ce-doped aluminophosphate glasses containing BaO.

2 Experimental procedures

Glasses were prepared by the melt quenching method in air using oversized alumina crucibles to avoid boiling over. Two series of glasses were prepared according to the amount of phosphate precursor, 50 and 60 mol%. The amount of precursors used reflected the correct molar ratios for each sample according to the batch procedure described in [8], together with thorough mixing of the precursors for 5-7 min to ensure homogeneity of the melt. 7-25 g batches were produced with the following starting materials: ammonium phosphate dibasic ((NH₄)₂HPO₄, Alfa Aesar, 98%), barium oxide (BaO, Strem Chemicals, $\geq 99.5\%$), silicon dioxide (SiO₂, BeanTown Chemical, \geq 99.9%), aluminum oxide, (Al₂O₃, activated, neutral, gamma-phase, Sigma-Aldrich, 99.9%), and cerium chloride (CeCl₃, anhydrous, Acros Organics, \geq 99.9%). The series of phosphate glasses with 1 mol% Ce₂O₃ were calcined at 300 °C for 60 min, followed by an additional annealing at 1000 °C for 30 min. Samples were naturally cooled to room temperature following each melt. In the series of phosphate glasses with higher Ce_2O_3 contents, 3 and 6 mol%, only the later annealing was used.

¹ Department of Materials Science and Engineering, Clemson University, Clemson, SC, USA

³ Center for Nuclear Environmental Engineering Sciences and Radioactive Waste Management (NEESRWM), Clemson University, Anderson, SC, USA

Following the melt at 1000 °C and cooling to room temperature, samples were weighed to compare the experimental weight loss to the predicted the weight loss due to the release of volatile species during the melt, specifically Cl_2 and NH_3 . All samples underwent a final melt at 1400 °C for 15 min, poured into a steel mold, and air quenched with natural cooling down to room temperature. Table 1 summarizes the glass compositions investigated in this work as a function of decreasing BaO content, for each phosphate series. Given the glasses preparation in air, the conversion of some Ce^{3+} to Ce^{4+} is expected to occur (see, e.g., [9]).

Density measurements were made using a Quantachrome Micro-Ultrapycnometer 1000. Density values reported in this work corresponded to the average of multiple measurements for each sample. The index of refraction was estimated for each composition, including the activator content, by means of the Gladstone–Dale relation [10, 11] using the experimentally-determined density as input.

Raman scattering spectroscopy was executed with a Horiba LabRAM HR Evolution Raman microscope equipped with a 800 mm focal length spectrograph and an air-cooled (-60 °C) back-illuminated deep-depleted 1024×256 pixels CCD detector using a 100 mW 532 nm laser, 50% neutral density filter, and a $\times 5$ magnification objective. 600 and 1800 groves/mm diffraction gratings were used for the acquisition of low resolution (broad spectral range) and high resolution (narrow spectral range) measurements, respectively. Spectra were obtained with 10 s long scans. Background subtraction was executed by means of linear segments between ca. 200–850 and 850–1400 cm⁻¹.

Optical transmission spectra were collected using a Perkin Elmer Lambda 900 UV/Vis/NIR spectrometer.

Photoluminescence emission (PL) and excitation (PLE) measurements were executed using an Edinburgh Instruments FLS-1000 spectrofluorometer equipped with a 450 W Xe lamp and dual monochromators for emission and excitation. Excitation and emission monitoring wavelengths varied for each sample and were within 3.78–4.04 eV (307–328 nm), and 2.98–3.54 eV (350–416 nm), respectively, while excitation and emission bandwidths were fixed

at 0.5 nm. The number of detected photons was automatically corrected by the instrument's software for the background and spectral differences in excitation intensity and detection sensitivity. Fluorescence lifetime was executed with a picosecond pulsed LED EPLED-310 emitting at 317.0 nm (9.6 nm FWHM bandwidth, 915.6 ps pulse width at 10 MHz). The detection wavelength varied for each sample, being within 350 and 416 nm (2–5 nm bandwidth), while EPLED repetition rate was fixed at 0.1 MHz.

Radioluminescence (RL) measurements were executed using a customer-designed Freiberg Instruments Lexsyg Research spectrofluorometer equipped with a Varian Medical Systems VF-50J X-ray tube with a tungsten target coupled with an ionization chamber for irradiation dose monitoring. The light emitted by the sample was collected by a lens and converged into an optical fiber connected to an Andor Technology Shamrock 163 spectrograph coupled to an Andor Technology DU920P-BU Newton CCD camera. RL measurements were executed under continuous X-ray irradiation (40 kV, 1 mA) at room temperature. Powders filled ca. 8 mm diameter 1 mm deep cups thus allowing for relative RL intensity comparison between different samples. Results were not corrected for the spectral sensitivity of the system.

3 Results and discussion

Density was determined to be between 2.7 and 3.0 g/cm³ for all glasses, as shown in Table 1, in agreement with other works on similar glasses [4, 12]. These density values are about 10% higher than those of commercial Ce-doped lithium silicate glass scintillators [e.g., 13]. The variation of the density was remarkably small given the large variation of the BaO content from 4 or 9 to 19 mol%, depending on the P_2O_5 content, either 50 or 60 mol%, respectively.

Phosphate glasses are composed of PO_4 tetrahedra that are bonded to other tetrahedra through three of its corners by P–O–P bonds. The connectivity of the glass network is mostly determined by the average number of tetrahedra

Table 1Glass label, chemicalcomposition, density, index ofrefraction calculated using theGladstone–Dale relation, opticaltransmission cutoff wavelengthand corresponding cutoff energy

| Glass # | Molar fraction (%) | | | | | Density | n | $\lambda_{cutoff}(nm)$ | $E_{cutoff}\left(eV\right)$ |
|---------|--------------------|-----|------------------|-----------|--------------------------------|----------------------|------|------------------------|-----------------------------|
| | P_2O_5 | BaO | SiO ₂ | Al_2O_3 | Ce ₂ O ₃ | (g/cm ³) | | | |
| 4 | 50 | 19 | 15 | 15 | 1 | 2.8 | 1.47 | 321 | 3.86 |
| 3 | 50 | 9 | 25 | 15 | 1 | 2.7 | 1.47 | 328 | 3.78 |
| 3A | 50 | 7 | 25 | 15 | 3 | 2.7 | 1.48 | 342 | 3.63 |
| 3B | 50 | 4 | 25 | 15 | 6 | 2.7 | 1.48 | 373 | 3.32 |
| 1 | 60 | 19 | 5 | 15 | 1 | 2.9 | 1.48 | 317 | 3.91 |
| 1A | 60 | 17 | 5 | 15 | 3 | 3.0 | 1.49 | 362 | 3.43 |
| 1B | 60 | 14 | 5 | 15 | 6 | 3.0 | 1.50 | 367 | 3.38 |
| 2 | 60 | 9 | 15 | 15 | 1 | 2.8 | 1.49 | 318 | 3.90 |

connected to a given tetrahedron, with O^{i} indicating that there are *i* bridging oxygens per tetrahedron. The incorporation of network modifiers such as Zn, Ca, Sr, and Ba in phosphate glasses tends to decrease the connectivity of the network, leading to the formation of Q^2 tetrahedra at the expense of Q³ tetrahedra [14 and references therein]. The incorporation of Al₂O₃ changes the structure of phosphate glasses forming a mixed aluminophosphate network. In the 32MgO·16Al₂O₃·52P₂O₅ glass, three Raman bands at 334, 605, and 723 cm^{-1} were identified below 1000 cm^{-1} and four bands between 800 and 1500 cm⁻¹ through spectral analysis at 1040, 1165, 1205, and 1305 cm⁻¹. The bands at about 723, 1040, 1165, 1205, and 1305 cm⁻¹ were identified as P–O–P bending, $-PO_3^{2-}$ terminal groups, symmetric PO₂ stretching, asymmetric PO₂ stretching, and P=O stretching, respectively. Addition of SiO₂ into this glass changed the position of these bands by no more than 25 cm^{-1} [15]. In a series of Na₂O·P₂O₅·Al₂O₃ glasses, the bands near 300 cm⁻¹ were assigned to the rocking motion of the phosphate tetrahedra or to the motions of the alkali modifier, and the bands within 430-650 cm⁻¹ to Al³⁺ octahedra. Further, no evidence that SiO₂ was incorporated into the phosphate or aluminophosphate networks was found, and that the major Raman manifestation of SiO₂ addition into the glasses was the intensification of a band at 468 cm^{-1} [16].

The Raman spectra of all glasses investigated in this work were similar, presenting vibrational bands within $200-650 \text{ cm}^{-1}$, a relatively narrow intense band at 711–732 cm⁻¹, and bands within 850–1400 cm⁻¹ that dominated the spectra. These bands are in agreement with the description of the aluminophosphate glasses incorporated with SiO₂ given above. Selected normalized spectra are presented in Fig. 1 where the contribution to the Raman spectra due to the incorporation of SiO₂ could be identified through the relative increase of the intensity of the bands at ca. 470 (in agreement with [16]) and 605 cm^{-1} between glasses with 5 (glass #1) and 15 (glass #2) SiO₂ mol% (Fig. 1a and inset), and 15 (glass #4) and 25 (glass #3) mol% SiO₂ (Fig. 1b). The progressive incorporation of SiO₂ also led to a shift of the 711–732 cm⁻¹ band to higher wavenumbers, in agreement with [15]. Figure 2 compares the normalized Raman spectra of glasses #1 to 4 (Fig. 2a), the #1 glass series (Fig. 2b), and the #3 glass series (Fig. 2c) in the $850-1400 \text{ cm}^{-1}$ region. Two major differences were observed, the variation of the peak position of the most intense band at about 1200 cm⁻¹, and the relative intensity variation within ca. $1250-1400 \text{ cm}^{-1}$, while the relative intensity of the 900–1050 cm^{-1} band remained constant for all glasses. These variations did not follow the incorporation of SiO₂ in a systematic way (cf. Figure 2a-c). On the other hand, the shift of the $\sim 1200 \text{ cm}^{-1}$ band to higher frequencies and the increase of the relative intensity of the ca. $1250-1400 \text{ cm}^{-1}$ band correlated with the increase of the BaO content and/or



Fig. 1 Normalized Raman spectra of selected glasses: (A) 60 mol% P_2O_5 (#1 $(60P_2O_5 \cdot 19BaO \cdot 5SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3),$ $(60P_2O_5 \cdot 9BaO \cdot 15SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3),$ #2 and #1B $(60P_2O_5 \cdot 14BaO \cdot 5SiO_2 \cdot 15Al_2O_3 \cdot 6Ce_2O_3))$, and (B) 50 mol% P_2O_5 (#3 (50 P_2O_5 ·9BaO·25SiO_2·15Al_2O_3·1Ce_2O_3), and #4 (50P₂O₅·19BaO·15SiO₂·15Al₂O₃·1Ce₂O₃)) obtained with 600 groves/ mm diffraction grating

decrease of the Ce_2O_3 content within each of the #1 and #3 glass series (Fig. 2b and c, respectively).

The optical transmission results are presented in Fig. 3, highlighting the transmission cutoff wavelength. Comparison of the cutoff values of glasses #3 and 4 from the 50 mol% P_2O_5 series, and of glasses #1 and 2 from the 60 mol% P_2O_5 series (cf. Table 1), all of them with 1 mol% Ce_2O_3 , showed that the SiO₂ and BaO contents had no major role in determining the cutoff wavelength of the glasses. On the other hand, the cutoff wavelength increased with the Ce_2O_3 content, from 317 to 373 nm, as shown in Fig. 4 for the two P_2O_5 series, in agreement with previous reports that showed Ce^{3+} to have a strong effect on the UV transparency of glasses [3, 4].

The index of refraction was estimated to be within 1.47 and 1.50 using the Gladstone–Dale equation and the experimental density values, as shown in Table 1, in agreement with the measured values of the index of refraction of similar glasses [4]. The small variation of the density (cf. Table 1) together with the weaker contribution of BaO (k=0.128) in the calculation of the index of refraction in comparison to the contribution of P₂O₃ (k=0.315), Al₂O₃ (k=0.207), and SiO₂ (k=0.208), where k is the refractive coefficient of the binary oxide (the so called 'Gladstone–Dale constant') [10, 11], explained the small variation of the index of refraction found in these glasses.

The scintillation was evaluated by means of RL measurements. RL spectra are shown in Fig. 5 together with



Fig. 2 High resolution (1800 groves/mm diffraction grating) normalized Raman spectra: (A) glasses #1 ($60P_2O_5 \cdot 19BaO \cdot 5SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), #2 ($60P_2O_5 \cdot 9BaO \cdot 15SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), #3 ($50P_2O_5 \cdot 9BaO \cdot 25SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), and #4 ($50P_2O_5 \cdot 19BaO \cdot 15SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), (B) glass #1 series (#1 ($60P_2O_5 \cdot 19BaO \cdot 5SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), #1A ($60P_2O_5 \cdot 17BaO \cdot 5SiO_2 \cdot 15Al_2O_3 \cdot 3Ce_2O_3$), and #1B ($60P_2O_5 \cdot 14BaO \cdot 5SiO_2 \cdot 15Al_2O_3 \cdot 3Ce_2O_3$), and (C) glass #3 series (#3 ($50P_2O_5 \cdot 9BaO \cdot 25SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), #3A ($50P_2O_5 \cdot 7BaO \cdot 25SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), series

the optical transmission cutoff energy of each glass (dotted lines). Glasses with the lowest cerium content, 1 mol%, presented a weaker band at 1.86 eV and the main band centered at 3.65 eV, while glasses with 3 or 6 mol% Ce₂O₃ presented a weaker band at 1.71–1.78 eV (henceforth 1.7 eV) and the main band centered at 3.31–3.44 eV. In the Ce₂O₃-richer glasses, the main band progressively started at lower energies than in the 1 mol% Ce₂O₃ glasses, and the cutoff energy was at about the maximum of the main band. Consequently, the shape of the main band was affected by the optical transmission of the glasses precluding reliable spectral analysis and possibly affecting the determination





Fig. 4 Optical transmission cutoff wavelength as a function of the Ce₂O₃ content of the glasses from the series with 50 mol% P₂O₅ (#3 (50P₂O₅·9BaO·25SiO₂·15Al₂O₃·1Ce₂O₃), #3A (50P₂O₅·7BaO·25SiO₂·15Al₂O₃·3Ce₂O₃), #3B (50P₂O₅·4BaO·25SiO₂·15Al₂O₃·6Ce₂O₃), and #4 (50P₂O₅·19BaO·15SiO₂·15Al₂O₃·1Ce₂O₃)) and 60 mol% P₂O₅ (#1 (60P₂O₅·19BaO·5SiO₂·15Al₂O₃·1Ce₂O₃), #1A (60P₂O₅·17BaO·5SiO₂·15Al₂O₃·3Ce₂O₃), #1B (60P₂O₅·14BaO·5SiO₂·15Al₂O₃·1Ce₂O₃))

of the peak position. The 1.7 eV band was assigned to Fe^{3+} substitutional impurities in silica, perhaps from the steel mold, due to the similarity with the 1.75 eV emission from Fe^{3+} in quartz [17]. The 1.86 eV band was assigned



Fig. 5 RL spectra together with optical transmission cutoff energy (dotted lines). The composition of the glasses is as follows: #1 $(60P_2O_5\cdot19BaO\cdot5SiO_2\cdot15Al_2O_3\cdot1Ce_2O_3)$, #1A $(60P_2O_5\cdot17BaO\cdot5SiO_2\cdot15Al_2O_3\cdot3Ce_2O_3)$, #1B $(60P_2O_5\cdot14BaO\cdot5SiO_2\cdot15Al_2O_3\cdot6Ce_2O_3)$, #2 $(60P_2O_5\cdot9BaO\cdot15SiO_2\cdot15Al_2O_3\cdot1Ce_2O_3)$, #3 $(50P_2O_5\cdot9BaO\cdot25SiO_2\cdot15Al_2O_3\cdot1Ce_2O_3)$, #3 $(50P_2O_5\cdot7BaO\cdot25SiO_2\cdot15Al_2O_3\cdot3Ce_2O_3)$, #3 $(50P_2O_5\cdot7BaO\cdot25SiO_2\cdot15Al_2O_3\cdot3Ce_2O_3)$, and #3B $(50P_2O_5\cdot4BaO\cdot25SiO_2\cdot15Al_2O_3\cdot6Ce_2O_3)$

to non-bridging oxygen hole centers (NBOHC) in silica known to luminesce at 1.85–1.95 eV [18]. The luminescence of Ce³⁺ is due to the $5d^1 \rightarrow 4f$ parity allowed transition with fast decay time of tens of nanoseconds. However, since the $5d^{1}$ level lacks shielding from outer electrons, the $5d^1 \rightarrow 4f$ transition is greatly affected by the chemical and structural arrangement surrounding the Ce³⁺ ions [1]. To the best of our knowledge, Ce³⁺ luminescence has not been investigated in aluminophosphate glasses similar to those in this work so we refer to the results on available phosphate and aluminophosphate glasses. Ce³⁺ emission in the $60P_2O_5 \cdot 35BaO \cdot 5Gd_2O_3 \cdot 0.5Ce_2O_3$ [5] and $55.5P_2O_5 \cdot 19.5BaO \cdot 15BaF_2 \cdot 8Al_2O_3 \cdot 1Gd_2O_3 \cdot 1Ce_2O_3$ [19] glasses was reported at around 3.65 eV, in aluminophosphate glasses with no modifiers at around 3.8 eV [20], in $75P_2O_5 \cdot 17La_2O_3 \cdot 3Al_2O_3 \cdot 2ZnO \cdot 3K_2O$ at about 3.82 eV [21], and in calcium metaphosphate glasses between 3.58



and 3.88 eV [22]. While slightly higher, these peak values are compatible with the spectral region of the main emission band reported in this work supporting the interpretation that the main band corresponds to the emission of Ce^{3+} . The integrated RL intensity of the main band is presented in Fig. 6 as a function of the Ce_2O_3 content for both P_2O_5 series of glasses showing a progressive increase for higher Ce_2O_3 contents. RL enhancement is understood as a competition between the increase of the number of Ce^{3+} ions combined with the progressive enhancement of the Ce^{3+} emission at lower energies against the decrease of the cutoff energy for higher Ce_2O_3 concentrations. It is noted that the expected formation of Ce^{4+} at the expense of Ce^{3+} during the synthesis of the glasses will affect these results.

Additional insight into the main band was obtained by means of PL/PLE and fluorescence lifetime measurements reported in Figs. 7 and 8, respectively. Figure 7 shows the normalized PL and PLE spectra (continuous lines), together with the transparency cutoff energy (dotted lines). The PL spectra of the 1 mol% Ce₂O₃ doped glasses (black continuous lines) was peaked around 3.50-3.55 eV with the peak position progressively shifting to lower energies for higher Ce₂O₃ concentrations. While the shape and PL peak position could have been affected by the optical transmission of the glasses, these results clearly showed that higher Ce₂O₃ concentrations led to stronger PL at lower energies. These



Fig. 7 Normalized PL and PLE spectra of the glasses together with the transparency cutoff energy (dotted lines). The composition of the glasses is as follows: #1 ($60P_2O_5 \cdot 19BaO \cdot 5SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), #1A ($60P_2O_5 \cdot 17BaO \cdot 5SiO_2 \cdot 15Al_2O_3 \cdot 3Ce_2O_3$), #1B ($60P_2O_5 \cdot 17BaO \cdot 5SiO_2 \cdot 15Al_2O_3 \cdot 3Ce_2O_3$), #1B ($60P_2O_5 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), #3 ($50P_2O_5 \cdot 9BaO \cdot 25SiO_2 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), #3A ($50P_2O_5 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), #3A ($50P_2O_5 \cdot 15Al_2O_3 \cdot 1Ce_2O_3$), #3B ($50P_2O_5 \cdot 4BaO \cdot 25SiO_2 \cdot 15Al_2O_3 \cdot 3Ce_2O_3$), #3B ($50P_2O_5 \cdot 4BaO \cdot 25SiO_2 \cdot 15Al_2O_3 \cdot 3Ce_2O_3$), #3B ($50P_2O_5 \cdot 4BaO \cdot 25SiO_2 \cdot 15Al_2O_3 \cdot 3Ce_2O_3$), The numerical values correspond to the PL excitation and PLE emission monitoring energies in eV according to the color code

results are in agreement with RL results that showed luminescence enhancement at lower energies and help explain the increase of RL output for higher Ce_2O_3 concentrations. The PLE spectra of the 1 mol% Ce_2O_3 doped glasses presented a well-defined peak at about 3.80–3.85 eV, while glasses with higher Ce_2O_3 concentrations presented flat PLE spectra. These results could be understood by the progressive shift of the cutoff energy to lower energies. The PLE band of the glasses with 3 and 6 mol% Ce_2O_3 was completely immersed in the fundamental absorption of the host, and only the few



Fig. 8 Fluorescence lifetime decay curves (symbols) and corresponding best fit (lines). The composition of the glasses is as follows: #1 ($60P_2O_5$ ·19BaO·5SiO_2·15Al_2O_3·1Ce_2O_3), #1A ($60P_2O_5$ ·17BaO·5SiO_2·15Al_2O_3·3Ce_2O_3), #1B ($60P_2O_5$ ·14BaO·5SiO_2·15Al_2O_3·6Ce_2O_3), #2 ($60P_2O_5$ ·9BaO·15SiO_2·15Al_2O_3·1Ce_2O_3), #3 ($50P_2O_5$ ·9BaO·25SiO_2·15Al_2O_3·1Ce_2O_3), #3A ($50P_2O_5$ ·7BaO·25SiO_2·15Al_2O_3·3Ce_2O_3), #3B ($50P_2O_5$ ·4BaO·25SiO_2·15Al_2O_3·1Ce_2O_3), #3A ($50P_2O_5$ ·19BaO·15SiO_2·15Al_2O_3·1Ce_2O_3) ($5Al_2O_3\cdot6Ce_2O_3$), #3B ($50P_2O_5\cdot4BaO\cdot25SiO_2\cdot15Al_2O_3\cdot1Ce_2O_3$)

Ce³⁺ ions close to the surface of the samples contributing to photoluminescence.

Fluorescence lifetime results (solid circles) are presented in Fig. 8, together with best fitting using two exponential functions (continuous lines). The results were consistent with the reported lifetime decay of Ce^{3+} in phosphate glasses [19, 20, 22]. The decays were dominated by the fast lifetime component that ranged from 28 to 31 ns for the 1 mol% Ce_2O_3 glasses, and slightly increased for higher Ce concentrations (30–31 ns for 3 mol% Ce_2O_3 , and 30–35 ns for 6 mol% Ce_2O_3). A small, less that 0.5%, contribution of a long time component (lifetimes from ca. 600–1400 ns) was also observed.

4 Conclusions

An investigation of the structure, optical properties and luminescence of Ce-doped BaO-containing aluminophosphate glasses was executed. The density was found to be insensitive to the BaO content, while the Ce₂O₃ content controlled the UV transparency threshold. Within each glass series, Raman spectra varied according to the changes of BaO and Ce₂O₃ contents. Luminescence was dominated by Ce³⁺ emission and presented a fast luminescence decay time of about 30 ns. Increased RL output was observed for higher Ce₂O₃ concentrations, particularly for the 60 mol% P₂O₅ series, and was attributed to the higher number of Ce³⁺ ions and the enhancement of luminescence at lower energies, with glass #1B (60P₂O₅·14BaO·5SiO₂·15Al₂O₃·6Ce₂O₃) yielding the best scintillation (RL) results.

Acknowledgements This material is based upon work supported by the National Science Foundation under Grants Nos. 1653016 and 1746230.

References

- 1. P. Dorenbos, J. Lumin. **91**, 155 (2000)
- I.J. Tillman, M.A. Dettman, V.V. Herrig, Z.L. Thune, A.J. Zieser, S.F. Michalek, M.O. Been, M.M. Martinez-Szewczyk, H.J. Koster, C.J. Wilkinson, M.W. Kielty, L.G. Jacobsohn, U. Akgun, Opt. Mater. 68, 58 (2017)
- M.W. Kielty, M. Dettmann, V. Herrig, M.G. Chapman, M.R. Marchewka, A.A. Trofimov, U. Akgun, L.G. Jacobsohn, J. Non-Cryst. Solids 471, 357 (2017)
- 4. J.L. Rygel, C.G. Pantano, J. Non-Cryst. Solids 355, 2622 (2009)

- J. Bei, G. Qian, X. Liang, S. Yuan, Y. Yang, G. Chen, Mater. Res. Bull. 42, 1195 (2007)
- M. Rodová, A. Cihlar, K. Knizek, K. Nitsch, N. Solovieva, Rad. Meas. 38, 489 (2004)
- J. Jiang, G. Zhang, M. Poulain, J. Alloys Cmpds. 275–277, 733 (1998)
- 8. J.E. Shelby, *Introduction to Glass Science and Technology*, 2nd edn. (The Royal Society of Chemistry, Cambridge, 2005)
- A. Herrmann, H.A. Othman, A.A. Assadi, M. Tiegel, S. Kuhn, C. Rüssel, Opt. Mater. Exp. 5, 720 (2015)
- 10. J.A. Mandarino, Can. Mineral. **14**, 498 (1976)
- 11. J.A. Mandarino, Can. Mineral. 19, 441 (1981)
- A. Aldaadaa, M. Al Qaysi, G. Georgiou, R.M.A. Leeson, J.C. Knowles, J. Biomater. Appl. 33, 271 (2018)
- http://www.crystals.saint-gobain.com/products/lithium-glass -scintillators; and http://www.scintacor.com/wp-content/uploa ds/2015/09/GlassScintillators.pdf
- 14. R.K. Brow, J. Non-Cryst. Solids 263&264, 1 (2000)
- P.H. Larsen, F.W. Poulsen, R.W. Berg, J. Non-Cryst. Solids 244, 16 (1999)
- 16. D.R. Tallant, C. Nelson, Phys. Chem. Glasses 27, 75 (1986)
- 17. J. Götze, M. Plötze, D. Habermann, Mineral. Petrol. **71**, 225 (2001)
- 18. L. Skuja, J. Non-Cryst. Solids 239, 16 (1998)
- Y. Yao, L. Liu, Y. Zhang, D. Chen, Y. Fang, G. Zhao, Opt. Mater. 51, 94 (2016)
- H. Masai, K. Shinozaki, G. Okada, N. Kawaguchi, T. Ina, T. Yanagida, J. Lumin. 195, 413 (2018)
- 21. Q. Changhong, G. Fuxi, A. Xilin, J. Non-Cryst. Solids **80**, 440 (1986)
- 22. G.K. Das Mohapatra, Phys. Chem. Glasses 39, 50 (1998)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.