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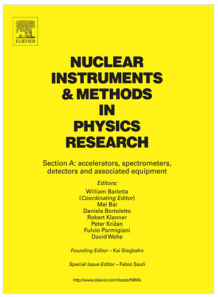

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X-ray Induced Radiation Damage in CLYC(Ce)

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Abstract

The radiation hardness of the ^{6}Li loaded scintillator CLYC(Ce) to X-rays was investigated. Two crystals were studied; one crystal was irradiated with X-rays and one was kept as a control and only exposed to a moderated ^{241}Am-Be source. The control crystal was used as a reference sample for photoluminescence excitation and emission measurements. The exposed crystal was given two doses of X-rays, the first was 2.3 Gy and the second was 118.2 Gy after a 22 week annealing period. The total dose was 120.5 Gy and was found to significantly reduce the light yield of the crystal. Pulse height spectra from the moderated ^{241}Am-Be taken with the irradiated crystal showed a 54% decrease in pulse height and a broadening of the FHWM of the peak from 14.6 % to 44.2%. Analysis of the pulse shapes showed no change to the median decay time to 37% of the scintillator, with values of ~350 ns for the irradiated and control crystal. Photoluminescence excitation and emission measurements revealed a reduction in the relative intensity of the main Ce^{3+} emission with respect to the self-trapped exciton luminescence. This indicated a modification to the Ce^{3+} luminescence center. There was little recovery at room temperature over the course of 22 weeks after the first irradiation. The irradiated crystal was also found to display significant room temperature luminescence after X-ray irradiation with it being measurable up to 120 minutes after the X-ray irradiation.

Keywords: Scintillator; Radiation Damage; Thermal Neutron Detection; Pulse shape discrimination; Afterglow

1. Introduction

New and upgraded neutron scattering facilities such as the European Spallation Source in Sweden [1], J-PARC in Japan [2], the Spallation Neutron Source in the United States [3] and the ISIS pulsed neutron and muon source in the United Kingdom [4] produce high neutron fluxes for materials science. ISIS is a neutron spallation source which is used to generated thermal and epithermal neutrons and muons. There are currently 30 neutron scattering instruments in ISIS which are dedicated to applications including neutron reflectometry, powder and single crystal diffraction, small angle scattering and imaging. Neutron sensitive scintillators such as ZnS:Ag/^{6}LiF and ^{6}Li-glass are currently used on ISIS [5]. These scintillators have disadvantages like long afterglow for ZnS:Ag/^{6}LiF and high sensitivity for the ^{6}Li-glass [4]. Because of these disadvantages, new neutron sensitive scintillators are regularly evaluated to determine their suitability for use at ISIS.

Due to inaccessibility and cost restrictions in neutron scattering instrumentation, instruments are expected to have a lifetime of ~20 years. Radiation hard detectors are therefore required. High neutron fluxes also give rise to high backgrounds of γ-rays. Therefore, damage from both of these

sources of radiation must be evaluated. The group of van Eijk at the Delft University of Technology have performed a thorough, though non-exhaustive, development and characterization of thermal neutron scintillators for multiple applications including spallation neutron sources [6-8].

One of the promising neutron sensitive scintillators is Cerium activated Cs_2LiYCl_6 (CLYC(Ce)) isotopically enriched with ^6Li . CLYC(Ce) is typically used for dual mode γ-ray and neutron detection where the ^6Li is used for thermal neutrons and the $^{35}Cl(n,p)^{35}S$ reaction allows for fast neutron detection. CLYC(Ce) has been shown to have energy resolution in the order of 4-5%, a 1 µs decay time allowing for operation at rates in the order of 100's of kcps, and excellent pulse shape discrimination (PSD) properties [9-13]. PSD arises from the complex decay characteristics of scintillation light in CLYC(Ce) where a γ-ray will induce 3 ns core-valence luminescence in addition to the typical 50 ns and 1000 ns decay components while a neutron event will scintillate with a greater probability of the slower 1000 ns decay. This difference of decay enables PSD, allowing for clear discrimination between neutron events and γ-ray events. The different scintillation mechanisms observed in CLYC(Ce) that gives rise to PSD have been thoroughly studied with substantial data on the decay characteristics and emission wavelengths available [11, 12, 15].

The authors could only find 2 published studies on the radiation hardness of CLYC(Ce). Both studies focused on the suitability to CLYC(Ce) for space radiation environments and using proton beams to characterize radiation hardness. Both studies found that proton irradiation induced the formation of color centers in CLYC(Ce) resulting in a reduction of performance [12,13].

This work presents measurements on X-ray induced changes to the luminescent properties of commercially purchased CLYC(Ce). Suitability of CLYC(Ce) for use in instruments at neutron science facilities where long term stability under significant neutron and γ-ray exposures is assessed.

2. Method

Two 2.54 cm diameter 5 mm thick CLYC(Ce) crystals canned in aluminum with a white reflector and quartz windows were purchased from the same supplier from the same batch so they would be of similar quality. The irradiated crystal was denoted Crystal 1 and the control was denoted Crystal 2. The components of the study were; X-ray irradiations, neutron measurements and luminescence measurements. The crystals were stored in a dark, temperature controlled, dry nitrogen cabinet between irradiations and measurements to investigate room temperature annealing and to ensure there was no optical stimulation of any filled traps.

2.1 X-ray irradiations

Two sets of X-ray irradiations were performed using tungsten anode X-ray sets. The dose was measured using a Radcal Accu-Gold + with the Radcal 10x6-6 6 ionization chamber. The first irradiation was to a dose of 2.3 Gy at 160 kVp, 50 µA for 45 minutes at a source to crystal distance of 10 cm. Crystal 1 was then given a second X-ray irradiation after a 22 week annealing period. This second and final irradiation was to a dose of 118.2 Gy delivered over 10 minutes at 60 kVp 50 mA with a source to crystal distance of 33.5 cm.

2.2 Neutron Measurements

The neutron detection performance was measured using a paraffin moderated ^{241}Am-Be source by monitoring the pulse height of the ^{6}Li neutron capture peak as a function dose and by evaluating the pulse shape discrimination performance. For these measurements the crystals were mounted on a ETL 9902 PMT biased at -900 V with index matching optical grease the signal was integrated for 50 ns and read out by an Acqiris 400 MSps 14-bit digitizer. Pulse shape discrimination was performed by measuring the time for each digitized pulse to reach 37% of its peak amplitude. The neutron detection performance of Crystal 1 was measured after both X-ray irradiations and at 12 weeks into the 22 week annealing period between X-ray irradiations.

2.3 Luminescence Measurements

Both radio- and photoluminescence measurements were performed to study any changes to the luminescent properties of the crystals as a function of dose. The radioluminescence spectrum was acquired using an Ocean Optics USB2000+UV-VIS spectrometer with a fiber coupled f1.0 fused silica lens. It was only measured for Crystal 1 during the first X-ray irradiation in a light tight X-ray set. These measurements were completed within the first 5 minutes of the 45 minute X-ray irradiation which equated to a dose of 0.25 Gy.

Excitation and emission photoluminescence maps were acquired using a Horiba FluoroMax-4 Spectrofluorometer. The excitation and emission photoluminescence maps were acquired after 12 weeks into the 22 week annealing period, and two maps of Crystal 1 were measured following the 2nd irradiation, the first was 2 hours after the final irradiation and the second was 24 hours after the final irradiation. Crystal 2 was also measured for comparison. A long lived room temperature luminescence or afterglow was measured in Crystal 1 immediately following the 2nd irradiation, this was achieved blocking out the excitation source of the spectrofluorometer and was measured 10, 30 and 120 minutes after the irradiation.

3. Results

Both CLYC(Ce) crystals showed the presence of several macro defects in the crystals which included cracks and voids. The volume around the macro defects in crystal 1 developed a blue discoloration after only 2.3 Gy of X-ray irradiation (Fig. 1 top). The bulk of Crystal 1 also developed the same blue discoloration after 120.5 Gy (Fig. 1 bottom).

Figure 1. A photograph of both Commercially bought CLYC(Ce)crystals after the 1st irradiation (top) and the 2nd irradiation (bottom), note the discoloration and the macro-defects.

3.1 Neutron Measurements

Pulse height spectra of the crystals exposed to neutrons and γ-ray from the moderated ^{241}Am-Be after every irradiation are shown in figure 2.The FWHM of the ^{6}Li neutron capture peak of Crystal 1 was significantly broader after irradiation of 2.3 Gy than the control, Crystal 2 (Fig. 2). The FWHM of Crystal 2's ^{6}Li peak was 14.6% compared to Crystal 1's 40.5% after 2.3 Gy and 44.2% after the irradiation of 118.2 Gy or accumulated dose of 120.5 Gy (Table 1). The pulse height of the neutron capture peak also decreased with X-ray irradiation. The peak reduced from 0.3 mV for the control, to 0.175 mV after the first irradiation and 0.138 mV after the final irradiation.

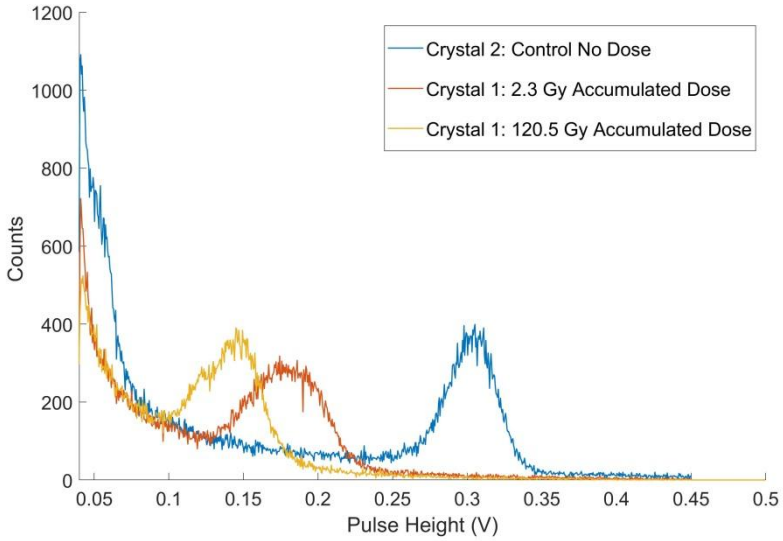

Figure 2. Pulse Height Spectra of the CLYC(Ce) crystals, showing the control crystal and the irradiated crystal after both sets of X-ray irradiation

Figure 3 shows 2D histograms of decay time (defined here as the time it takes for the signal to reduce to 37% of the peak amplitude) versus pulse height for each event in both Crystal 1 after 120.5 Gy and Crystal 2. The median decay time for both crystals was found to be ~350 ns for the neutron events and did not change with irradiation. The broadening in Crystal 1 after 120.5 Gy is attributed to the reduced pulse height. The ratio of γ-ray events in the region from around 75 mV to 150 mV also appear to change. This is a consequence of the lower energy Compton scatter events being lost because of the reduction in the crystal's light output. The pulse height is shown to reduce for both γ-ray and neutron capture events as in the pulse height spectra shown in Figure 2. This reduction in light output by a factor of ~2 in Crystal 1 results in a broadening of the decay time profile of the Compton scattered events. The decay time profile is broadened by a similar factor for both the γ-ray events and thermal neutron events at the same pulse height.

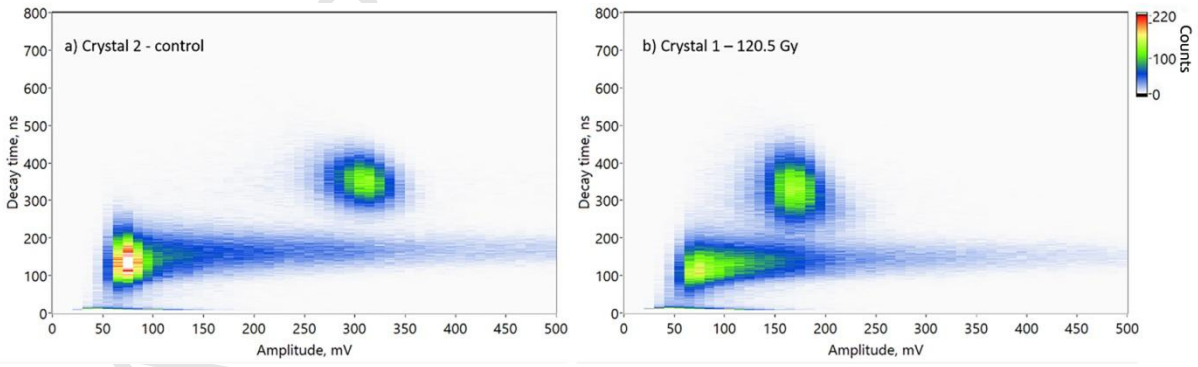

Figure 3. Pulse shape discrimination plots of Crystal 2 (left) and Crystal 1 after exposure to 120.5 Gy of X-ray irradiation.

3.2 Radioluminescence Measurements

The radioluminescence spectrum of Crystal 1 did not show any changes to the emission during irradiation (Fig. 4), however the dose delivered to the crystal was only 0.25 Gy. The emission peaks were found to be at 372 nm and 405 nm with a ratio of 5:3 and match reported values in the literature for the Ce^{3+} emission [9-11, 14, 15].

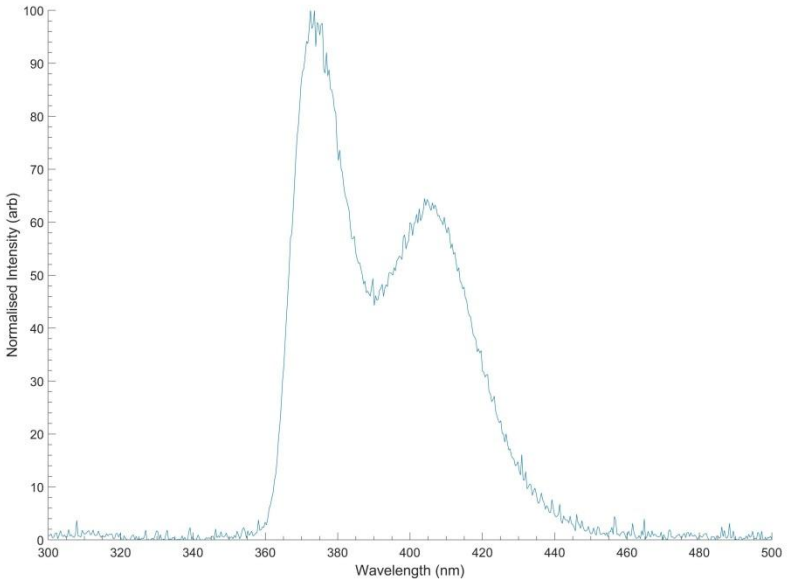

Figure 4. The radioluminescence spectrum of the CLYC(Ce) Crystal 1 prior to irradiation damage.

After the 2nd irradiation of 118.2 Gy, Crystal 1 was found to have developed room temperature luminescence or afterglow which was visible by eye and was still measureable 120 minutes after X-ray irradiation (Fig. 5(a)). The afterglow had the same emission spectrum as the radioluminescence spectrum with peaks at 372 nm and 405 nm along with the same 5:3 peak ratio (Fig. 4 and 5 (b)).

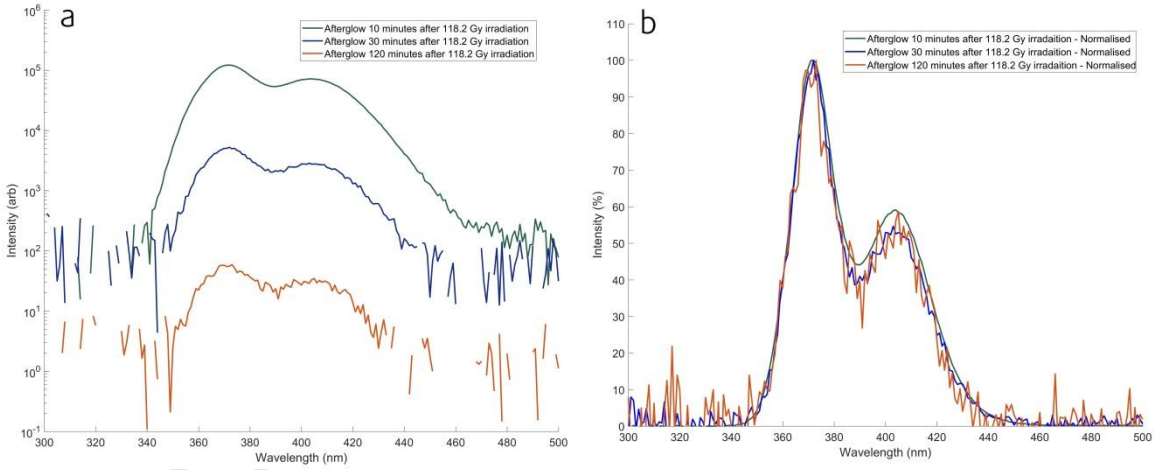

Figure 5. Luminescence spectra of the Afterglow from the X-ray irradiated CLYC(Ce) crystal 10 minutes, 30 minutes and 120 minutes after irradiation with 118.2 Gy. a) Directly comparable intensity on a logarithmic axis and b) intensity normalized to the 372 nm peak.

3.3 Photoluminescence Measurements

The photoluminescence spectrum of Crystal 2 was found to be similar to Crystal 1's radioluminescence spectrum prior to radiation damage. The only difference being the peak ratios, which was 5:3 for the radioluminescence and 5:4 for the photoluminescence. However, after irradiation the photoluminescence spectrum of Crystal 1 was found to differ significantly from Crystal 2 (Fig. 6). The ratio between the 375 nm and 405 nm emissions had changed to 10:9 as opposed to 5:4 in Crystal 2 (Table 1). The relative intensity of the main Ce^{3+} emission lines to other minor emissions changed significantly. The reduction in the intensity of the Ce^{3+} emission resulted in the 340 nm emission, excited by 270 nm light becoming significantly more prominent (circled red in Fig 6. B-D). This reduction in intensity also resulted in the 325 nm and 450 nm emissions being more prominent, effectively broadening the appearance of the main Ce^{3+} emission. The second irradiation of 118.2 Gy caused a further reduction in the intensity of the Ce^{3+} emission with respect to the 340, 325 and 450 nm emissions. It also caused the 370 nm emission in Crystal 1 to be less intense than the 405 nm peak (Fig. 6 c) with a change in the peak ratio from 5:4 to 10:11. Repeating the photoluminescence map after 24 hours showed that there was some recovery in the relative intensity of these minor peaks to the Ce^{3+} emission. The 370 nm peak and the 405 nm peak also showed some recovery to a ratio of 21:20. Table 1 summarizes the results obtained from all of the measurements described above.

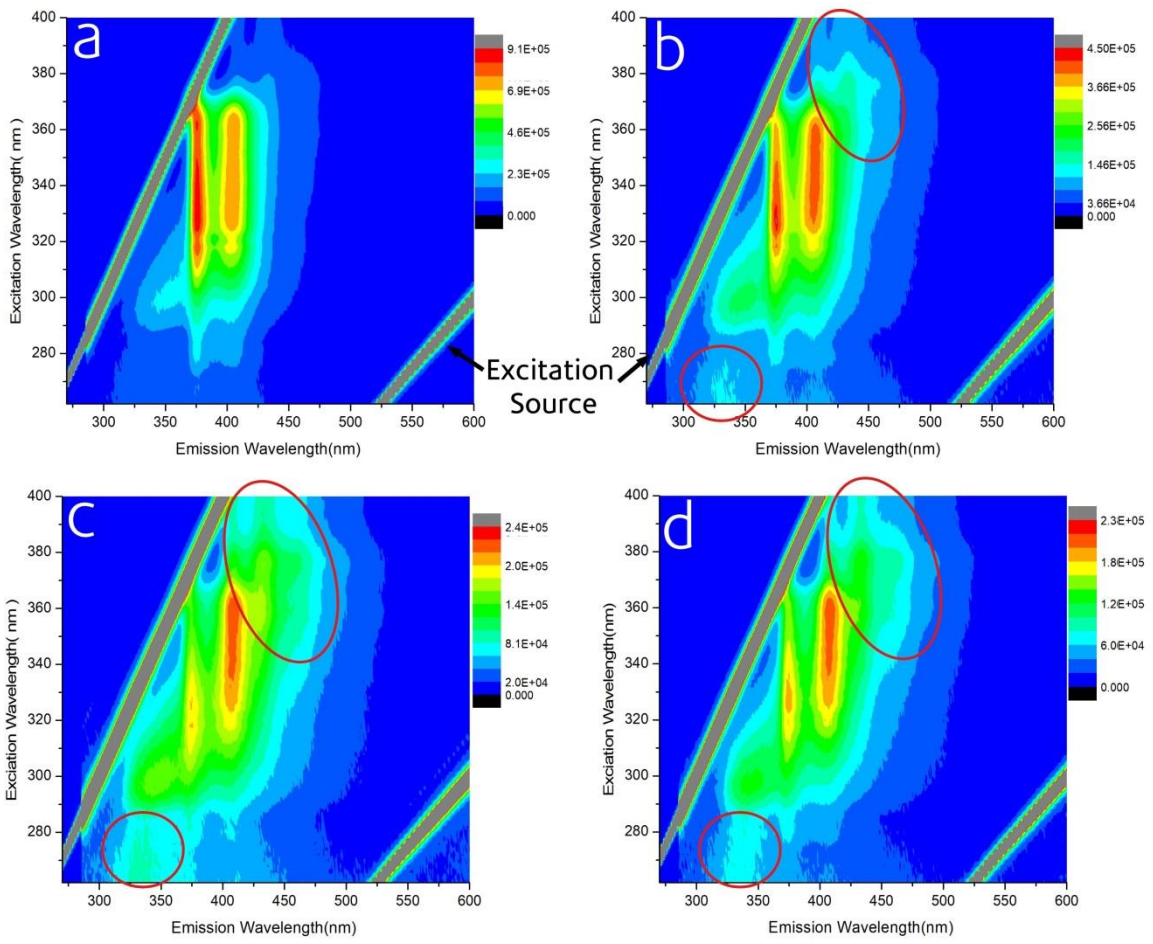

Figure 6. Excitation-Emission photoluminescence maps of Crystal 2 (a), Crystal 1 after the first irradiation of 2.3 Gy (b), 120 minutes after the 2nd irradiation of 118.2 Gy (c), and 24 hours after the

2^{nd} irradiation of 118.2 Gy (d). The regions circled in red become more prominent with X-ray dose. The diagonal lines are the first and second order diffraction lines from the excitation source.

Table 1: A summary of measured performance parameters for the tested CLYC(Ce) crystals

Sample	^{6}Li Peak Height	^{6}Li decay time to 37%	FWHM	Ratio of 375 nm to 405 nm photoluminescence emission (330nm excitation)
Crystal 2 (Control)	0.3 mV	355 ns	14.6%	5:4
Crystal 1 (2.3 Gy dose)	0.175 mV	356 ns	40.5%	10:9
Crystal 1 (120.5 Gy dose) 2 hours after irradiation	Not measured	353 ns	Not Measured	10:11
Crystal 1 (120.5 Gy dose) 24 hours after irradiation	0.138 mV	354 ns	44.2%	21:20

4. Discussion

The commercially purchased CLYC(Ce) crystal showed low tolerance for X-ray irradiation with a dose of 2.3 Gy inducing significant changes to the luminescence properties. The γ-ray dose exposed to the instruments at ISIS is not accurately measured because of the technical challenges it poses. However, off-axis γ-ray monitors placed near the T0 chopper report a dose rate of 0.5 mSv/hour. This is expected to give an underestimate of the dose an instrument would receive resulting in a lifetime of about 4000 hours or less for these CLYC(Ce) crystals. It should be noted that the crystals were purchased in 2015 when CLYC(Ce) was new to the market and developments in the crystal growth could have increased the radiation hardness of these crystals.

Radiation damage in scintillators is a complicated topic with a variety of possible radiation damage mechanisms ranging from the introduction of absorption bands, changes in the scintillation process and/or radiation induced chemical reactions [14]. The initial X-ray radioluminescence spectrum of Crystal 1 before it was heavily irradiated matched the photoluminescence spectrum of Crystal 2, except for a difference in ratio between the 375 nm and 405 nm emission peaks (Table 1). The measured afterglow of Crystal 1 after the 118.2 Gy irradiation also shared the same Ce^{3+} emission peaks and ratio of those peaks as the radioluminescence spectrum. While Crystal 1 did become discolored after the irradiation, it can be concluded from the afterglow spectrum that there was no

self-absorption of the Ce^{3+} emission. The PSD plots show that the decay time to 37% is unaffected by the X-ray irradiation. This leads to the conclusion that the primary scintillation process is still present with no new processes being created. The afterglow would not alter the decay time on the PSD plots as it's much lower than the 37% intensity threshold used. The reduction in the intensity of the Ce^{3+} emission with respect to the other emission lines suggests a formation of a non-radiative recombination pathway. This pathway could be caused by the transformation of the Ce^{3+} to Ce^{4+} which is known to quench Ce^{3+} luminescence [14]. The other peaks which became more prominent with radiation damage have been attributed to STE luminescence [15]. This STE luminescence would not be affected by any radiation induced changes to the oxidation state of the cerium in the crystal. Therefore it is plausible that the Ce^{3+} in the irradiated crystal is being modified by the X-ray irradiation, causing a reduction in light yield. This however does not explain the cause of the very long lived room temperature luminescence. Formation of shallow traps is a possible mechanism of the long lived afterglow which would also support a reduction in scintillation pulse height. Further work to resolve these unanswered questions is needed involving thermoluminescence measurements and techniques such as EPR to probe the valence state of cerium but is beyond the scope of this work.

5. Conclusion

The radiation hardness of CLYC(Ce) to X-ray irradiation was tested using two commercially purchased CLYC(Ce) crystals. One crystal was irradiated and the other was kept as a control. Significant radiation damage was observed after an X-ray dose of 2.3 Gy with only small amounts of recovery at room temperature. A subsequent dose of 118.2 Gy was found to induce further changes in the scintillation properties of the crystal. Radiation damage caused a reduction in pulse height of the ^{6}Li neutron capture peak of CLYC(Ce) but the primary decay time remained unchanged . The ^{6}Li neutron capture peak showed a 54 % reduction in pulse height when compared to the control crystal and broadening of the FWHM of the peak from 14.6 % to 44.2%. Analysis of the luminescent properties of the crystal showed that the irradiated crystal had a long lived room temperature luminescence or afterglow and the photoluminescence measurements showed significant changes to the emission spectrum of the crystal. Further analysis would be required to fully understand these changes and to which could potentially increase the radiation hardness of CLYC(Ce) to X-ray radiation. The associated degradation in the neutron detection performance of the crystal means that, at the present time, they are not suitable for use at facilities such as ISIS due to the requirement to operate for long periods of time in high γ-ray dose environments.

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