



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Beta Radiation Hardness of GYGAG(Ce) Transparent Ceramic Scintillators

J. T. Jarrell, N. J. Cherepy, Z. M. Seeley, J. W. Murphy,
E. L. Swanberg, L. F. Voss, C. D. Frye, M. A. Stoyer, R.
A. Henderson, S. P. O'Neal, R. J. Nikolic

July 14, 2021

Institute of Electrical and Electronics Engineers Transactions
on Nuclear Science

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Beta Radiation Hardness of GYGAG(Ce) Transparent Ceramic Scintillators

J. T. Jarrell, *Member, IEEE*, N. J. Cherepy, *Senior Member, IEEE*, Z. M. Seeley, J. W. Murphy, *Member, IEEE*, E. L. Swanberg, L. F. Voss, *Member, IEEE*, C. D. Frye, *Member, IEEE*, M. A. Stoyer, R. A. Henderson, S. P. O'Neal, *Member, IEEE*, R. J. Nikolic

Abstract— GYGAG(Ce) transparent ceramic garnet scintillators were irradiated with electrons from 0.5 MeV to 2 MeV with fluences from 10^{16} e/cm² to 10^{19} e/cm², corresponding to doses from 0.3 to 310 Gigarad. Absorption spectra were measured before and after irradiations. Light yields from alpha, beta and gamma excitations were measured before and after irradiation and compared to pre-irradiation values to gain a deeper understanding of how electron irradiations can affect light yield, as well as defects generated in both the surface and bulk. Within experimental error no degradation in light yield was observed for the electron-irradiated samples, as measured via beta or gamma excitation, with minimal degradation observed via alpha excitation. A small increase in optical absorption near the wavelength of emission was observed following the largest dose irradiation. These results suggest that GYGAG(Ce) is radiation hard to electron irradiation up to 10^{19} e/cm² and doses up to 310 Gigarad. This robustness to irradiation indicates that transparent ceramic garnets may prove useful for applications such as scintillation-based nuclear batteries by allowing for higher energy beta emitters, increased power densities, and enabling long service lifetimes.

Index Terms—Alpha particles, beta particles, garnets, nuclear batteries, radiation hardness, transparent ceramics, scintillators, thermal annealing

I. INTRODUCTION

Radiation-hard scintillators have applications in many areas of scientific endeavor including the development of scintillator-based nuclear batteries [1]. The superior radiation hardness of ceramic scintillators is not unexpected when compared to organic and single crystal scintillating materials. The radiation hardness of ceramic scintillators to damage from proton and gamma radiation has been explored extensively [2]. Gd_{1.5}Y_{1.5}Ga_{2.2}Al_{2.8}O₁₂(Ce), or GYGAG(Ce), is a recently developed transparent polycrystalline ceramic scintillator which has demonstrated excellent radiation hardness, with no measurable darkening at an exposure of 53 Megarad (9 MeV bremsstrahlung) [3]. The formation of color centers in a scintillating material from high dose ionizing radiation exposure can be a concern if it decreases transparency and effective light yield. The radiation tolerance of related ceramic scintillators such as Y₃Al₅O₁₂(Ce), YAG:Ce, have previously

been studied by relative scintillation efficiency measurements for 3 MeV proton and helium irradiation. Ceramic YAG:Ce samples retained approximately 50% of the initial light yield after 3 MeV helium ion irradiation to a fluence of 10^{14} /cm² [3][4]. High energy proton irradiation effects have been studied for Bi₄Ge₃O₁₂, Lu₃Al₅O₁₂, and Lu_{2(1-x)}Y_{2x}SiO₅ (BGO, LuAG, and LYSO) scintillators by optical transmission studies at fluences on the order of 10^{14} /cm² at 800 MeV and 24 GeV,¹ respectively. In these experiments, BGO and LYSO scintillators demonstrate near total loss of transmittance, while LuAG demonstrated minimal (<1%) degradation in transmittance [5-7]. Neutron-induced damage has been measured for similar applications for single crystal scintillators such as LYSO showing similar radiation hardness to proton irradiation [7]. However, comparatively little work has been done on the effects of beta particle radiation on ceramic scintillating materials. Damage effects from beta particle radiation in the energy range of a few 100 keV to a few MeV are of interest for indirect conversion nuclear batteries, where the conversion of the energy of the radiation to electricity occurs through a multi-step process and the effects of beta radiation on scintillator light yield and transmission is of special interest [8]. The degradation of the converting material and isotope half-life largely determines the decrease in power output over time for indirect conversion nuclear batteries [9-11].

Radiation damage effects for beta and gamma irradiation typically manifest as a darkening of the scintillator due to the formation of color centers in the volume. By heating the scintillating material, some amount of diffusion of defects can be annealed out of the material due to thermal activation of diffusion. For beta and gamma irradiation, this consists of the removal of color centers by supplying sufficient thermal energy to the trapped charge, recombination of vacancy and interstitial defect pairs, and the formation of neutral defect complexes [10]. It is theorized that the polycrystalline microstructure of ceramic scintillators aids in the damage recovery by providing defect sinks and facilitating oxygen diffusion at the grain boundaries [11].

Manuscript received July 26, 2021; revised September 15, 2021; accepted XX XX,XXXX. Date of publication XX XX, XXXX; date of current version XX XX, XXXX. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344, LLNL-JRNL-824518-DRAFT. J.T. Jarrell,

N.J. Cherepy, Z.M. Seeley, J.W. Murphy, E. L. Swanberg, L. F. Voss, C. D. Frye, M. A. Stoyer, R. A. Henderson, S.P. O'Neal, and R.J. Nikolic are with Lawrence Livermore National Laboratory, Livermore, CA 94550 USA (e-mail: jarrell2@llnl.gov).

II. METHODS

A. Transparent Scintillator Sample Preparation

To explore the effects of electron irradiation on the transparent ceramic GYGAG(Ce), $\text{Gd}_{1.5}\text{Y}_{1.5}\text{Ga}_{2.2}\text{Al}_{2.8}\text{O}_{12}$ (Ce), scintillators, samples of approximately 18 mm diameter and 5 mm thickness were formed using the process described by Cherepy, et. al [12]. The scintillator thickness was chosen to ensure that it was greater than the range in the GYGAG(Ce) of the highest energy electrons used in the experiment, approximately 2 mm for 2 MeV electrons. The range of the 5.3 MeV alpha particles from the ^{210}Po source used to characterize the samples after irradiation was far less than the thickness of the samples, at approximately 10 μm .

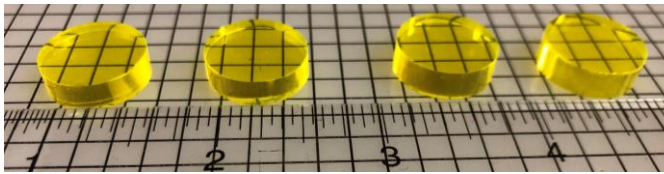


Fig. 1. Several of the transparent ceramic GYGAG(Ce) samples used in the electron irradiation experiment, prior to irradiation.

B. GYGAG(Ce) Response to Electron Irradiation

An initial GYGAG(Ce) electron irradiation was performed at the National Institute for Standards and Technology (NIST), followed by a series of electron irradiations at IBA Industrial. The NIST irradiation was performed using a Van de Graaff electron accelerator to a fluence of 2×10^{16} e/cm^2 with 1 MeV electrons at a flux of 2×10^{12} $\text{e}/\text{cm}^2\text{-sec}$. The sample was cooled using a forced air system and maintained below 100°C. Further GYGAG(Ce) scintillator samples were irradiated using a calibrated 3.0 MeV Dynamitron accelerator in air operated by IBA Industrial. The electron energies which were used ranged from 0.5 MeV to 2 MeV, with a Full Width Half Max (FWHM) energy distribution at the target estimated by MCNPX Monte Carlo simulations to be approximately 5.5% at 0.5 MeV, decreasing to 2% at 2 MeV. This energy distribution was broader than the distribution of solely the accelerator and energy loss in air due to the inclusion of a secondary 40-micron thick titanium shield which was included to protect the accelerator window from possible debris if the sample fractured during irradiation. Monte Carlo simulations included this secondary shield and were verified against dosimeter measurements. The samples irradiated at IBA Industrial were irradiated in air on a water-cooled aluminum square tube platform maintained below 55°C under maximum beam power. Samples were held in thermal contact with the aluminum platform using a silicone oil and zinc oxide-based thermal joint compound. A COMSOL thermal model was used to estimate the approximate maximum temperature of the samples under the flux and energies used. Upper bounds on temperatures were determined using Tempdaq thermal paint on calibration samples prior to irradiating the test samples. Three paints were used which indicated when the samples exceeded 83°C, 95°C, and 371°C respectively by darkening. A calibration sample used to

determine the maximum temperature at each flux used is shown in Fig. 2.



Fig. 2. A GYGAG(Ce) scintillator with three temperature sensitive paints was used to determine the maximum temperature at each of the fluxes used in the electron irradiations.

Irradiations were performed at 0.5 MeV, 0.75 MeV, 1 MeV, and 2 MeV with a flux of 2.5×10^{13} $\text{e}/\text{cm}^2\text{-sec}$ to a fluence of 10^{17} e/cm^2 over approximately 1 hour or until the estimated fluence was reached as indicated by integrated beam current monitoring of the accelerator. These samples were held below 100°C throughout the irradiation as indicated by irradiated thermal paint indicators. A further irradiation was performed at a flux of $1.66 \times 10^{14}/\text{cm}^2\text{-sec}$ on a sample at 0.75 MeV to 10^{19} e/cm^2 over approximately 16.5 hours. This sample was maintained below 400°C throughout the irradiation. For all irradiations, the flux was ramped up to the stated flux over the course of 10-15 minutes to minimize thermal shock to the parts.

C. Light Yield and Optical Absorption Characterization

The light yields for the samples were measured before and after irradiation using first a beta emitting $^{90}\text{Sr}/^{90}\text{Y}$ source followed by a ^{210}Po alpha source as ionizing radiation sources to excite their radioluminescence, which was measured with a Princeton Instruments/Acton Spec 10 spectrograph coupled to a thermoelectrically cooled CCD camera. The range of the endpoint energy beta particles from the $^{90}\text{Sr}/^{90}\text{Y}$ source used for beta radioluminescence measurements in the GYGAG(Ce) material was approximately 2 mm, which excited the irradiated volume of the electron-irradiated samples. The range of the ^{210}Po alpha particles in the samples was only approximately 10 μm , as previously described, thus only excited the surface region of the electron-irradiated samples.

Scintillation pulse height spectra were acquired with a ^{137}Cs source using a 2" Hamamatsu R6231-100 PMT. The signals from the photodetector anode were shaped with a Tennelec TC 244 spectroscopy amplifier and recorded with an Amptek MCA8000-A multi-channel analyzer. The photopeak full width at half maximum (FWHM) of the ^{137}Cs gamma spectrum was measured and compared to an unirradiated sample as reported by Cherepy using an equivalent spectroscopy system [12]. The half-value layer thickness of the ^{137}Cs gamma rays in GYGAG(Ce) is approximately 15.5 mm and thus excited the full volume in both the 3 mm and thinned samples [13]. The experimental error for the light yield measurements was determined through previous calibrations to be approximately

5% [12]. The optical absorption spectra of the scintillators, reported as the wavelength dependent absorption coefficient, $\alpha(\lambda)$, versus wavelength was measured at room temperature before and after irradiation using a Thermo Evolution 220 UV-Vis spectrometer. To reduce the effects of self-absorption on the measurements and provide a more clearly resolved spectrum, 500-micron thick discs were cut from the top and bottom of the irradiated samples. The samples were optically polished on the cut faces. The irradiated face of the samples was not polished to avoid altering the surface structure.

III. RESULTS AND DISCUSSION

A. Post-Irradiation Beta Radioluminescence

An example of the beta radioluminescence spectra of the electron-irradiated scintillators are shown in Fig. 3.

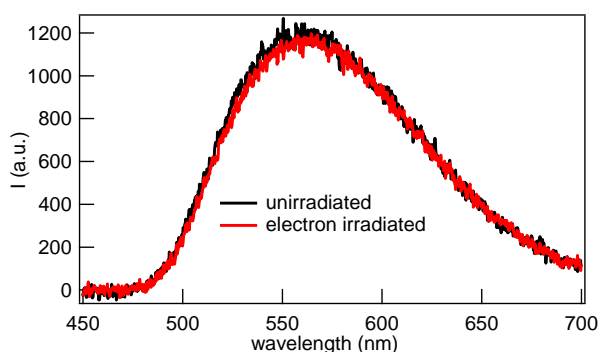


Fig. 3. The quantitative $^{90}\text{Sr}/^{90}\text{Y}$ -excited radioluminescence spectra from a GYGAG(Ce) sample before and after irradiation with 750 keV electrons to a fluence of $10^{19} \text{ e}^-/\text{cm}^2$.

The results of the electron irradiations at various energies (in MeV) and fluences Φ in e^-/cm^2 on beta-excited light yield ΔLY , are given in Table 1. The change in light yield ΔLY is the percent reduction in light yield as a function of electron fluence and is reported in percent change per $10^{17} \text{ e}^-/\text{cm}^2$. The change in light yield is expressed as a function of fluence to allow for direct comparison between measurements when the sample fluence varies as in the case of the sample irradiated to a fluence of $10^{19} \text{ e}^-/\text{cm}^2$.

B. Alpha Radioluminescence of Irradiated Samples

Following the beta-excited emission measurement, the electron-irradiated samples were characterized for alpha light yield with the ^{210}Po source. This probing method separates surface effects from bulk effects. Both sides of the GYGAG(Ce) samples were excited with the alpha source and the light yield measured separately for each side.

For the electron-irradiated samples, degradation in excess of the measurement error of $\sim 10\%$ was observed for the two lowest energies when alpha radioluminescence was measured. The results of the electron irradiations at various energies and fluences on alpha-excited light yield are given in Table 2. For the two lowest electron energies the apparent degradation is slightly beyond the estimated error of the measurement.

The depth which is probed by alpha-excited

TABLE I
BETA-EXCITED LIGHT YIELD AS A FUNCTION OF IRRADIATION ENERGY AND FLUENCE

Energy (MeV)	Range (cm)	Fluence (cm^{-2})	Dose (gigarad)	Δ Light Yield (% / 10^{17} cm^{-2})
0.5	0.06	10^{17}	3.6	-8.0 ± 8
0.75	0.1	10^{17}	3.1	-5.0 ± 7
0.75	0.1	10^{19}	310	$(-3.5 \times 10^{-2}) \pm 0.07$
1	0.14	10^{16}	0.58	0 ± 5
1	0.14	10^{17}	2.9	-6.9 ± 6
2	0.30	10^{17}	2.6	-0.4 ± 5

radioluminescence is limited to the first few microns beneath the surface and is sensitive to the surface cleanliness and composition of the scintillators. These results, when taken in combination with those of the beta-excited light yield measurements indicate that the irradiation process altered the scintillator composition near the surface. This is likely due to surface contamination or reaction of the near-surface material with air during irradiation but is unlikely to be from direct radiation damage based on the results of beta-excited light yield measurements.

TABLE II
ALPHA -EXCITED LIGHT YIELD DEGRADATION AS A FUNCTION OF ELECTRON ENERGY AND FLUENCE

Energy (MeV)	Range (cm)	Fluence (e^-/cm^2)	Dose (gigarad)	Δ Light Yield (% / $10^{17} \text{ e}^-/\text{cm}^2$)
0.5	0.06	10^{17}	3.6	-15 ± 12
0.75	0.1	10^{17}	3.1	-11 ± 11
1	0.14	10^{17}	2.9	-9 ± 10
2	0.30	10^{17}	2.6	-9 ± 10

C. Gamma Light Yield and Spectroscopy

The light yield and gamma spectroscopy performance of a GYGAG(Ce) sample irradiated to a fluence of $10^{19} \text{ e}^-/\text{cm}^2$ with 750 keV electrons and a dose of 310 gigarad in the irradiated region was measured using a several microcurie ^{137}Cs source as shown in Fig. 4.

No degradation to the light yield, within the approximate 5% error of the measurement, was detected with the ^{137}Cs gamma-excited light yield measurement, although the gamma spectroscopy is mildly degraded from a typical resolution, R , of $R(662 \text{ keV}) = 5\%$ to about 6% FWHM. This measurement probed the full depth of the sample, including the unirradiated region beyond the $\sim 1 \text{ mm}$ range of the 750 keV electrons in the sample.

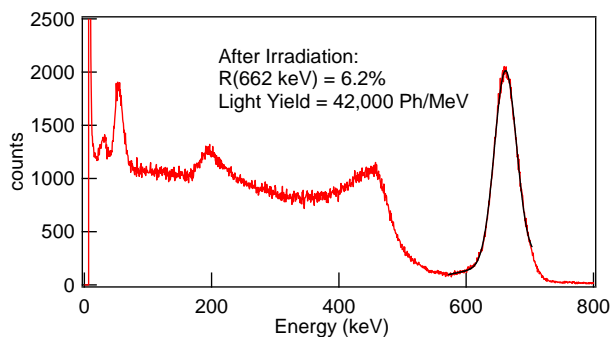


Fig. 4. The ^{137}Cs gamma spectrum measured using a GYGAG(Ce) sample irradiated to $10^{19} \text{ e}^-/\text{cm}^2$ at 750 keV. The photoelectric peak has a resolution of $\sim 6\%$ and is consistent with a Gaussian distribution.

D. Effects of Irradiation on Optical Absorption Spectrum

The optical absorption spectrum of a sample irradiated to $10^{19} \text{ e}^-/\text{cm}^2$ at an energy of 0.75 MeV is shown in Figure 5. Both irradiated and unirradiated regions of the same sample were measured for comparison. An increase in parasitic absorption in the emission wavelength range following irradiation was measured to be 0.20 cm^{-1} . The induced parasitic absorption results in a transmission of approximately 99% of the unirradiated value for the 500-micron thick samples which were measured. For a 1 cm pathlength the transmission would be reduced to $\sim 63\%$ of the unirradiated transmission.

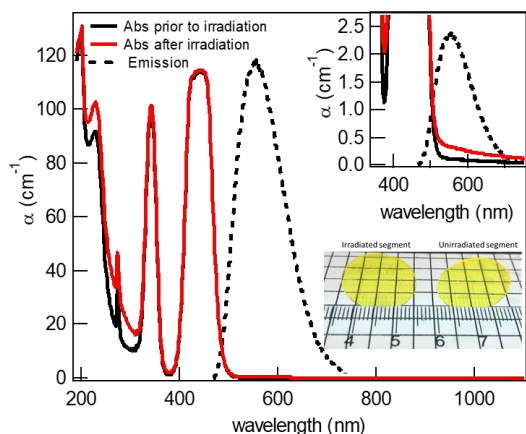


Figure 5. The optical absorption spectrum in terms of $\alpha(\lambda)$ of irradiated and unirradiated regions of an electron irradiated GYGAG(Ce) sample. A small increase in the absorption coefficient in the emission wavelength range was measured for the sample irradiated to $10^{19} \text{ e}^-/\text{cm}^2$ at an energy of 0.75 MeV.

E. Discussion of Irradiation Effects

The GYGAG(Ce) transparent ceramics irradiated with high energy electrons showed no measurable decrease in the light yield irrespective of fluence, energy, or dose when excited by beta or gamma sources when measured with a system capable of approximately 5% error. This result indicates that the scintillating centers in the samples are unaffected by electron irradiation at the tested fluences and energies. Future work will investigate the effects of electron irradiation on after-glow and decay time for spectroscopic applications. Further future work will seek to identify the fluence where the light yield of the GYGAG(Ce) scintillators noticeably degrade. A possible cause

of the observed resilience to point defects, especially in the case of the $10^{19}/\text{cm}^2$ irradiated sample, may be the migration of point defects to the grain boundaries in the ceramic scintillator during irradiation, since the irradiation results in elevated temperatures. Alternatively, the defect complexes which form may have minimal cross-section for absorption at the scintillation emission energy and do not therefore significantly degrade the light yield.

For the highest dose sample, which was irradiated using 750 keV electrons, the gamma spectroscopy resolution, R , of the sample when measuring a ^{137}Cs source was slightly degraded from $R(662 \text{ keV}) = 5\%$ for unirradiated samples, indicating that some material inhomogeneity in light yield was introduced into the sample by irradiation.

The transmission of the irradiated samples was reduced due to induced parasitic absorption on the order of 0.20 cm^{-1} in the emission wavelength range. The reduction in transmission could be significant over long pathlengths, on the order of 1 cm or more. However, for applications where the expected pathlength is significantly less than 1 cm such as in compact nuclear battery design this absorption becomes negligible.

IV. CONCLUSIONS

The results of high-energy electron irradiation indicate that the light yield of GYGAG(Ce) polycrystalline ceramic scintillators is unaltered up to a dose of 310 Gigrad and at energies up to 2 MeV. Furthermore, the radiation induced parasitic absorption is minimal over pathlengths less than 1 cm. These promising results indicate that a beta particle-fueled GYGAG(Ce)-based nuclear battery should be capable of withstanding a cumulative radiation dose to the scintillator of at least 310 Gigrad, allowing for the use of high energy beta emitters such as Sr-90 at high power densities without degrading the scintillator light yield or significant absorption losses.

ACKNOWLEDGMENT

The authors thank Rick Galloway of IBA Industries for his assistance in configuring and executing the electron irradiation of the garnet samples.

REFERENCES

- [1] S. Xue, C. Tan, P. Kandlakunta, I. Oksuz, V. Hlinka, and L. R. Cao, "Methods for improving the power conversion efficiency of nuclear-voltaic batteries," *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, vol. 927, no. September 2018, pp. 133–139, 2019, doi: 10.1016/j.nima.2019.01.097.
- [2] P. Lecoq, A. Gektin, and M. P. Korzhik, *Particle Acceleration and Detection Inorganic Scintillators for Detector Systems Physical Principles and Crystal Engineering*, Second. Springer, 2017.
- [3] W. A. Hollerman, J. H. Fisher, L. R. Holland, and J. B. Czirr, "Spectroscopic analysis of proton induced fluorescence from yttrium orthosilicate," *IEEE Nucl. Sci. Symp. Med. Imaging Conf.*, vol. 11, no. pt 1, pp. 637–640, 1994, doi: 10.1109/nssmic.1993.701731.
- [4] T. Hirouchi *et al.*, "Effect of ion beam and neutron irradiations on the luminescence of polycrystalline Ce-doped Y3Al5O12 ceramics," *J. Nucl. Mater.*, vol. 386–388, no. C, pp. 1049–1051, 2009, doi: 10.1016/j.jnucmat.2008.12.253.

- [5] P. W. O. C. Scintillators *et al.*, “Proton-Induced Radiation Damage in BaF₂, LYSO,” vol. 65, no. 4, pp. 1018–1024, 2018.
- [6] M. T. Lucchini, K. Pauwels, K. Blazek, S. Ochesanu, and E. Auffray, “Radiation Tolerance of LuAG:Ce and YAG:Ce Crystals under High Levels of Gamma-and Proton-Irradiation,” *IEEE Trans. Nucl. Sci.*, vol. 63, no. 2, pp. 586–590, 2016, doi: 10.1109/TNS.2015.2493347.
- [7] C. Hu *et al.*, “Neutron-Induced Radiation Damage in LYSO, BaF₂ and PWO Crystals,” *IEEE Trans. Nucl. Sci.*, vol. 9499, no. c, pp. 1–1, 2020, doi: 10.1109/tns.2020.2989116.
- [8] S. G. Bailey, D. M. Wilt, S. L. Castro, C. D. Cress, and R. P. Raffaele, “Photovoltaic development for alpha voltaic batteries,” *Conf. Rec. IEEE Photovolt. Spec. Conf.*, pp. 106–109, 2005, doi: 10.1109/pvsc.2005.1488080.
- [9] H. V. Watts, M. D. Oestrich, and R. J. Robinson, “A Nuclear-Photon Energy Conversion Study,” 1963.
- [10] B. Han, X. Feng, G. Hu, Y. Zhang, and Z. Yin, “Annealing effects and radiation damage mechanisms of PbWO₄ single crystals,” *J. Appl. Phys.*, vol. 86, no. 7, pp. 3571–3575, 1999, doi: 10.1063/1.371260.
- [11] C. Greskovich and S. Duclos, “Ceramic scintillators,” *Annu. Rev. Mater. Sci.*, vol. 27, no. 1, pp. 69–88, 1997, doi: 10.1146/annurev.matsci.27.1.69.
- [12] N. J. Cherepy *et al.*, “Development of transparent ceramic Ce-doped gadolinium garnet gamma spectrometers,” *IEEE Trans. Nucl. Sci.*, vol. 60, no. 3, pp. 2330–2335, 2013, doi: 10.1109/TNS.2013.2261826.
- [13] J. H. Hubbell and S. M. Seltzer, “Tables of X-Ray mass attenuation coefficients and mass energy-absorption coefficients (version 1.4),” *Http://Physics.Nist.Gov/Xaamdi*, 2004.
<http://physics.nist.gov/xaamdi>.