Contract No:

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

Title of Project
Characterization of Properties for a Gamma-Irradiated 'Revised' International Simple Glass

Project Start and End Dates
Project Start Date: 10/1/2020
Project End Date: 9/30/2021

Project Highlight

Simulated high-level waste borosilicate glasses were irradiated with gamma dose to simulate in-situ radiation exposure and damage in the glass. After irradiation, several measurements of optical, physical and corrosion properties were determined to compare with the unirradiated glass.

Unirradiated 500-gram glass bar vs. irradiated bar: top view of bars (left) and unpolished cross sections (middle left & right); Revised ISG-1 plate glass (right). Ionizing radiation discolors the original dull lime-green hue of the ISG glass and the clear ISG-1 glass to a darkened color.

Project Team
Principal Investigator: Charles L. Crawford
Team Members: Robert J. Lascola, Katie A. Hill
External Collaborators: Professor Jose Lugo Jimenez (Augusta University via Visiting Faculty Appointment)

Abstract
Simplified surrogate high-level waste glasses from recent national and international testing were irradiated to gamma doses of 100 Mrad and 200 Mrad. Properties of the irradiated glass were measured for comparison to the pristine unirradiated glass. Glass transition temperatures as well as infrared and Raman spectroscopy measurements show no change in the irradiated glass. Short-term aqueous corrosion tests on the glass powders also indicate no measurable differences comparing the irradiated to pristine samples. Some corrosion differences were observed in the pristine glasses due to slight compositional changes. As expected from the observed radiation darkening of the glass, absorbance spectra of the irradiated glass with the pristine glass used as

reference indicates a broad absorbance over the range of 400 to 700 nm that is centered around 550-600 nm.

Objectives

- Irradiate International Simple Glass (ISG) with SRNL Gamma Irradiator to nominal dose of 200 Mrad
- Irradiate 'revised' ISG glasses (ISG-1 and ISG-2) to nominal dose of 100 Mrad
- Compare measured properties of the unirradiated and irradiated glasses
- Measure optical properties with Raman spectroscopy and Photoluminescence (PL)
- Apply the American Society for Testing and Materials (ASTM) static powder glass leach test to measure corrosion properties of all glasses

REVIEWS AND APPROVALS

1. Authors:

____

____

____

Name and Signature Date

2. Technical Review:

____

Name and Signature Date

3. PI's Manager Signature:

____

Name and Signature Date

4. Intellectual Property Review:

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

____

Name and Signature

Introduction

Borosilicate glass has been adopted internationally for the treatment of nuclear waste with the object of long-term stabilization of the waste through vitrification [1,2]. Still, the effects of self-radiation through radioactive element decay over hundreds or even thousands of years on glass composition can only be modeled or simulated [3]. Accelerated tests considering worst-case scenarios are therefore useful for understanding glass behavior on the longer time scales in the interest of future generations. Accordingly, the object of the proposed research is to gain understanding of the effects of gamma radiation resulting from radioactive element decay on the physical properties of borosilicate glass for use in the vitrification process. To this aim, the well characterized glass system referred to as International Simple Glass (ISG) [4] agreed upon by the international community as representative glass will be employed. The ISG, a 6-component (Si, B, Na, Al, Ca, Zr) glass available at the Savannah River National Lab (SRNL), was originally subjected to a 100 Mrad dose via a Co-60 gamma irradiation and an additional 100 Mrad dose to attain a cumulative 200 Mrad dose. Revised ISG glasses were obtained that introduce minor chemical additives of La and Mg, and these glasses were also irradiated to a 100 Mrad dose. The effects of gamma rays on the ISG glasses were then studied by spectroscopic analysis methods, dilatometry/calorimetry and corrosion, in comparison with the unirradiated reference. The primary methods included optical absorption, Raman spectroscopy, glass transition temperature and short-term corrosion performance. The research is expected to provide insights into the long-term effects of gamma radiation emitted during radioactive waste decay.

Approach

This study examined a 100 Mrad and 200 Mrad dose to the original ISG glass, as well as 100 Mrad doses to revised ISG glasses (ISG-1 and ISG-2). A 500-gram bar of the ISG was irradiated in the SRNL Co-60 gamma irradiator for a duration of 1,096 hr at a dose rate of ~ 9E+04 rad/hr to obtain a cumulative gamma dose of ~ 100 Mrad. A portion of the original ISG dosed glass was further irradiated to attain cumulative 200 Mrad dose. **Figure 1** shows the modeled dose rate from the Co-60 source to the central bar of glass. The colors shown in the central rectangle indicate expected dose rates of ~9.15E+04 rad/hr (yellow), 9.45E+04 rad/hr (blue) and 9.75E+04 rad/hr (purple). After irradiation exposure several 'slices' of the glass were cut/polished by the SRNL Glass Shop using a wet diamond cut blade and manual polishing aids including Silicon Carbide (SiC), Cerium impregnated discs and 3-9 micron Al_2O_3 grinding sheets. Photographs of the ~ 800 grit and ~ 8,000 grit (clear) cross section slides from the unirradiated glass are shown in **Figure 2**. A comprehensive physico-chemical evaluation was carried out comparing the three pristine ISG specimens. The different characterizations performed were the following: XRD and vibrational spectroscopy (structural properties); static dissolution PCT (chemical durability); dilatometry and calorimetry measurements (thermal behavior); photoluminescence spectroscopy with decay kinetics assessment (optical properties). **Table 1** shows the chemical composition of the revised ISG-1 and ISG-2 glasses vs. the original ISG glass. Trace La was added into ISG-1 and Mg was substituted for some of the Ca in the ISG-2 glass.

Accomplishments

- The original ISG glass that had been dosed to 100 Mrad in FY20 was further irradiated to achieve a cumulative 200 Mrad dose. Samples of the newer ISG-1 and ISG-2 glass plates were both dosed to 100 Mrad.
- Corrosion testing (**Table 2**) indicates that the three pristine glasses (ISG, ISG-1 and ISG-2) display measurable differences in normalized release of B and Na. Similar comparisons amongst pristine vs. irradiated samples indicate no measurable differences in corrosion behavior.
- Raman spectroscopy **(Figures 3 – 5**) shows similarity in the three pristine glasses (ISG, ISG-1, ISG-2) as well as very similar spectra comparing the ISG to the 100 Mrad (ISG 1x) and 200 Mrad (ISG 2x). The 100 Mrad irradiated ISG-1 and ISG-2 also show similar Raman spectra to their pristine samples.
- Photoluminescence (PL) emission spectra (**Figures 6 – 9**) were collected for all glasses to enable comparison of the pristine glasses and the irradiated samples. PL spectra for the ISG and irradiated samples do not show new PL peaks. New PL peaks and peak shift were noted for the irradiated ISG-1 and ISG-2 glasses vs. the pristine samples.

Future Directions

Data obtained from this LDRD is planned to be presented at a 2021 American Ceramic Society Conference in December of 2021. "Investigation of physical, optical and corrosion properties of nuclear waste glass simulants and the effects of gamma-ray irradiation" http://ceramics.org/pacrim14

FY 2021 Peer-reviewed/Non-peer reviewed Publications

A draft manuscript describing comparisons of the pristine ISG, ISG-1 and ISG-2 glasses has been completed and submitted to a peer-reviewed journal (*J. Amer. Ceramic Soc.*) for publication:

Physicochemical properties of the International Simple Glass (ISG) and the ISG-1 and ISG-2 variants: Luminescence baseline study, José A. Jiménez [a,*], Charles L. Crawford[b], Robert J. Lascola[b]

[a] *Department of Chemistry & Physics, Augusta University, Augusta, GA 30904, USA*

[b] *Savannah River National Laboratory (SRNL), Aiken, SC 29808, USA; *Corresponding Author*

A follow-on peer review journal manuscript is also anticipated that will detail all the irradiated glass properties vs. the pristine samples.

Intellectual Property - NA

Total Number of Post-Doctoral Researchers - NA

Total Number of Student Researchers - NA

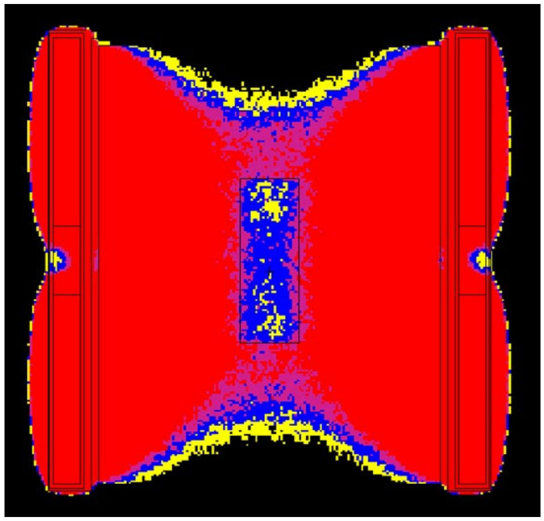

Figure 1. Modeled dose rate to the central/vertical glass bar.

Figure 2. Low (left) and high polish (right) unirradiated glass corrosion section specimens

Table 1. Compositions (mass%) of the various ISG Specimens

Oxide	ISG[a]		ISG-1[b]		ISG-2[b]	
	Target	Actual	Target	Actual	Target	Actual
SiO_2	56.2	56.30	56.2	56.38	56.54	56.87
B_2O_3	17.3	17.65	17.3	17.31	17.40	17.38
Al_2O_3	6.1	5.90	6.1	5.94	6.14	5.96
Na_2O	12.2	12.40	12.2	12.06	12.27	12.10
MgO	—	0.03	—	0.04	1.8	1.76
CaO	5.0	4.57	5.0	4.88	2.52	2.51
ZrO_2	3.3	3.20	3.3	3.29	3.32	3.31
La_2O_3	—	—	0.1	0.15	0.10	0.12
Density (g/cm^3)	2.516 ± 0.013		2.508 ± 0.001		2.475 ± 0.001	

[a] Impurity of note: Fe (equivalent to 0.065-0.068 mass% oxide)

[b] Impurities of note: Sn, Hf (0.05-0.09 mass% oxides)

Table 2. Corrosion test normalized concentration (g/L) results on pristine and irradiated glasses

Glass ID	NL B	NL Na	NL Si
ISG	2.4	2.3	0.5
St. Dev.	0.04	0.03	0.004
%RSD	1.7	1.3	0.8
ISG-1	2.2	1.9	0.5
St. Dev.	0.1	0.1	0.02
%RSD	4.4	3.9	4.8
ISG-2	4.3	3.2	0.4
St. Dev.	0.29	0.13	0.003
%RSD	7.3	4.3	0.7
ISG 100 Mrad	2.3	2.3	0.5
St. Dev.	0.06	0.08	0.007
%RSD	2.5	3.7	1.6
ISG 200 Mrad	2.5	2.1	0.5
St. Dev.	0.05	0.04	0.009
%RSD	2.3	2.1	1.9
ISG-1 100 Mrad	2.2	1.9	0.5
St. Dev.	0.02	0.01	0.003
%RSD	1.2	0.6	0.7
ISG-2 100 Mrad	4.2	3.2	0.4
St. Dev.	0.38	0.25	0.01
%RSD	9.9	8.5	2.7

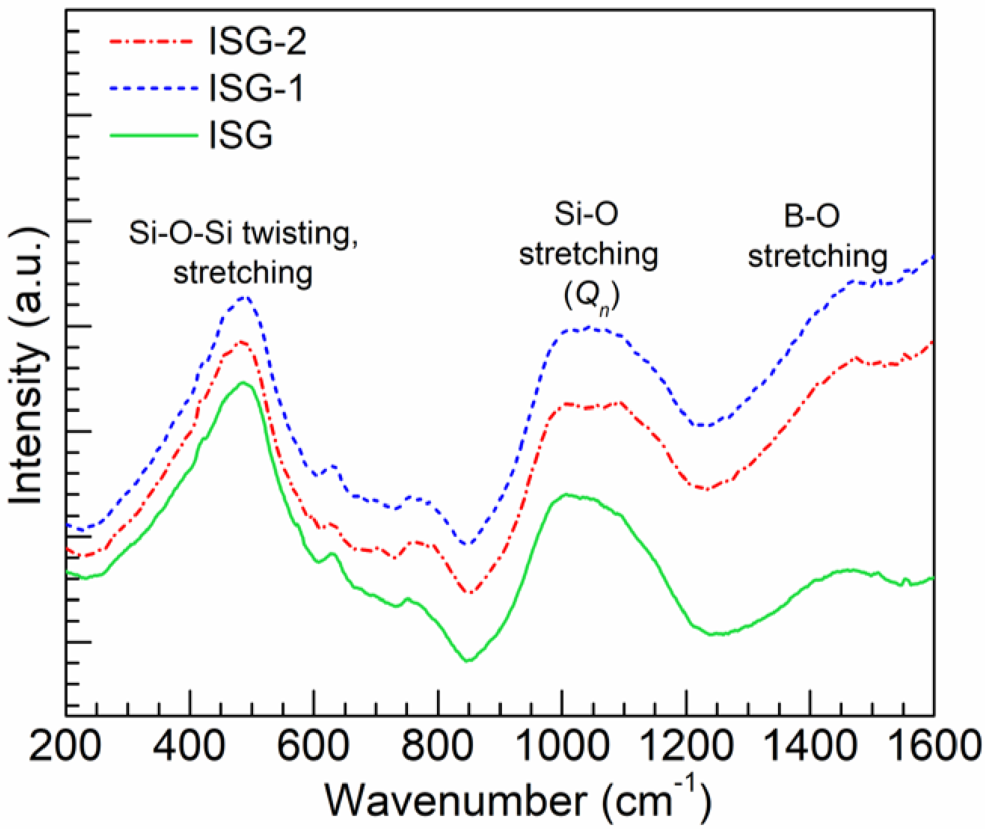

Figure 3. Raman Spectra obtained with 532 nm excitation for the various ISG samples.

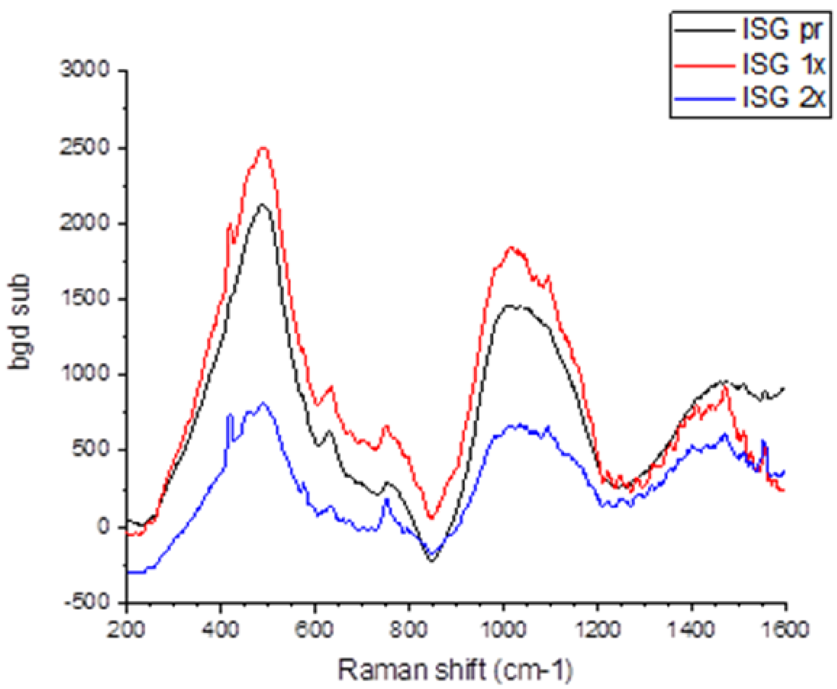

Figure 4. Raman Spectra of the original ISG and the 100 Mrad and 200 Mrad samples.

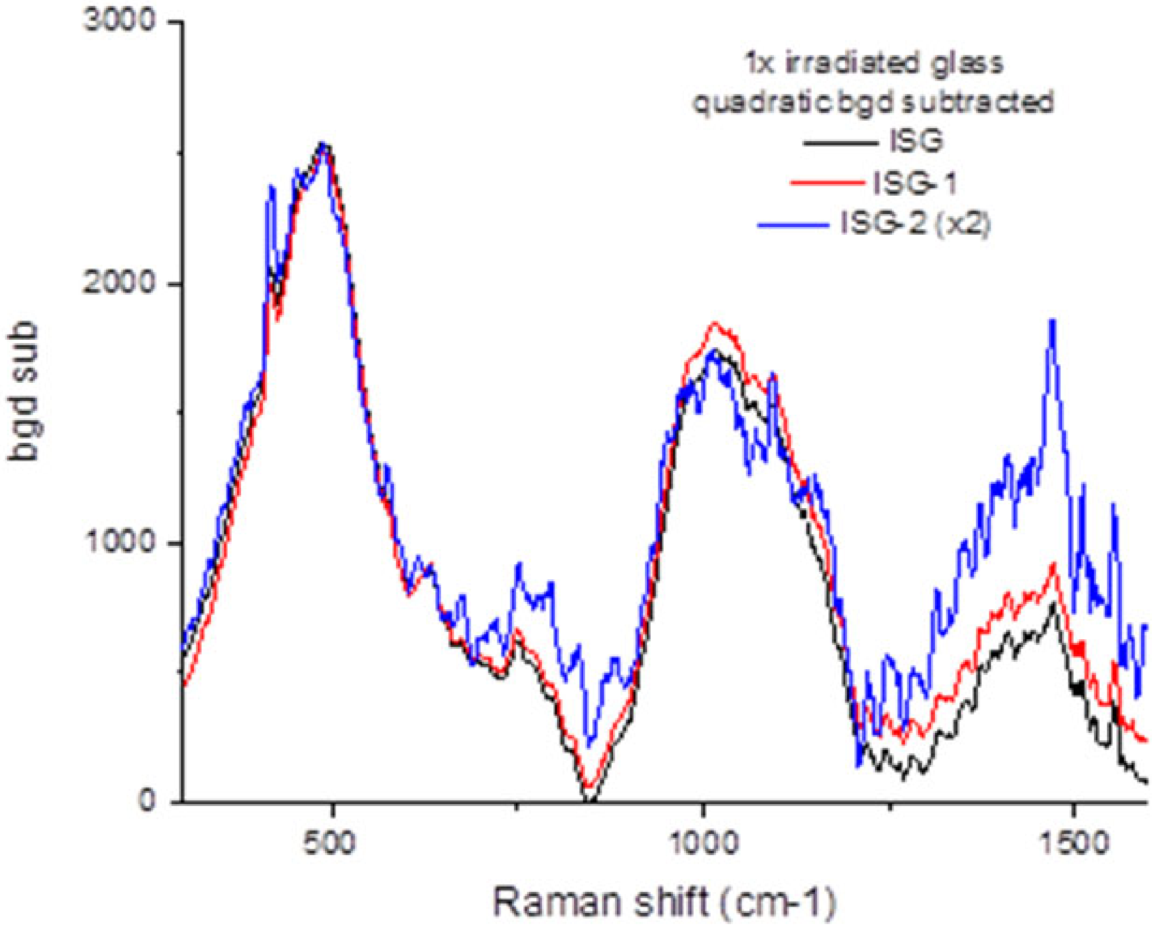

Figure 5. Raman Spectra of the pristine and irradiated ISG-1 and ISG-2 samples.

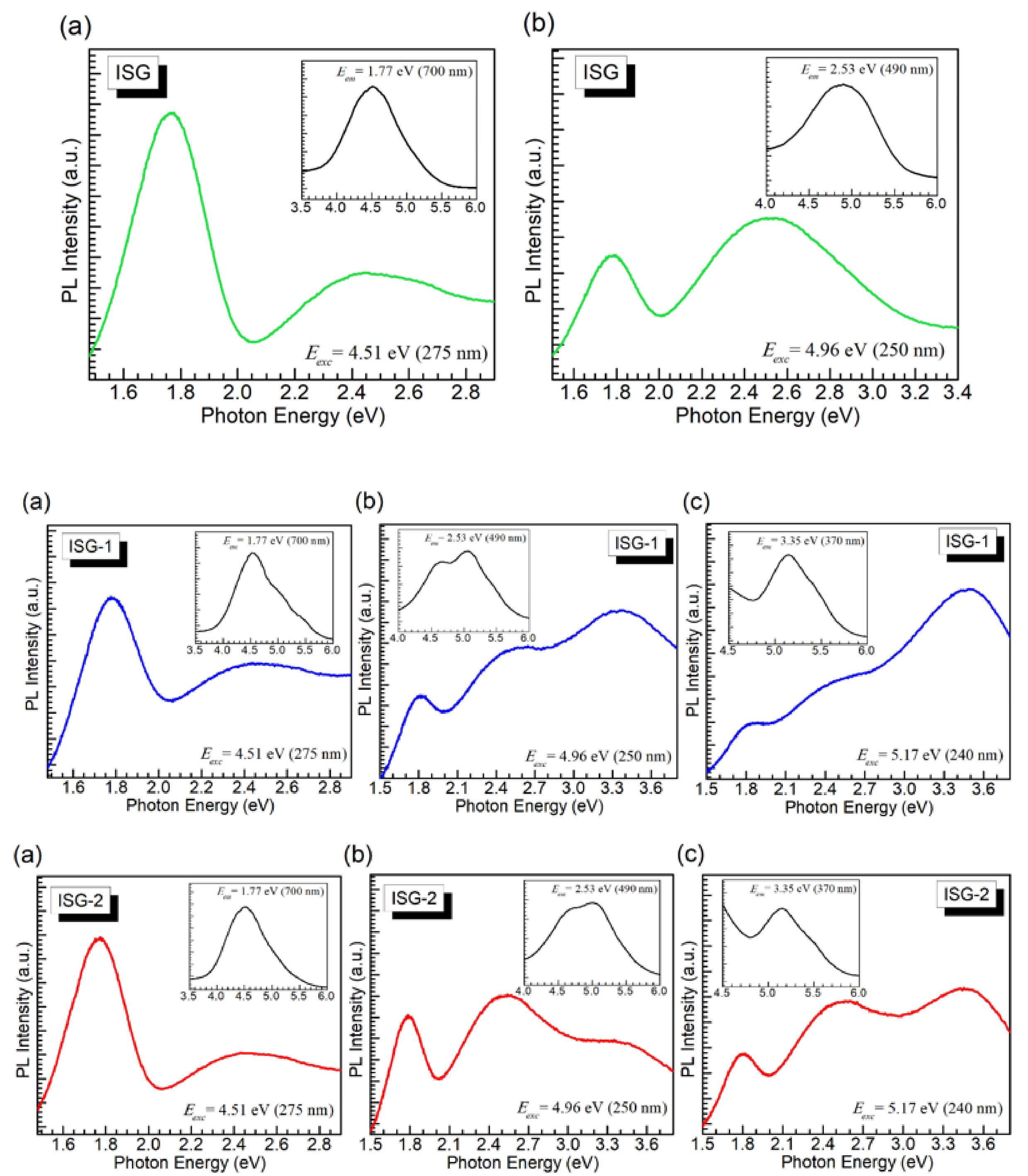

Figure 6. PL emission spectra obtained for the ISG (top), ISG-1 (middle) and ISG-2 (bottom)

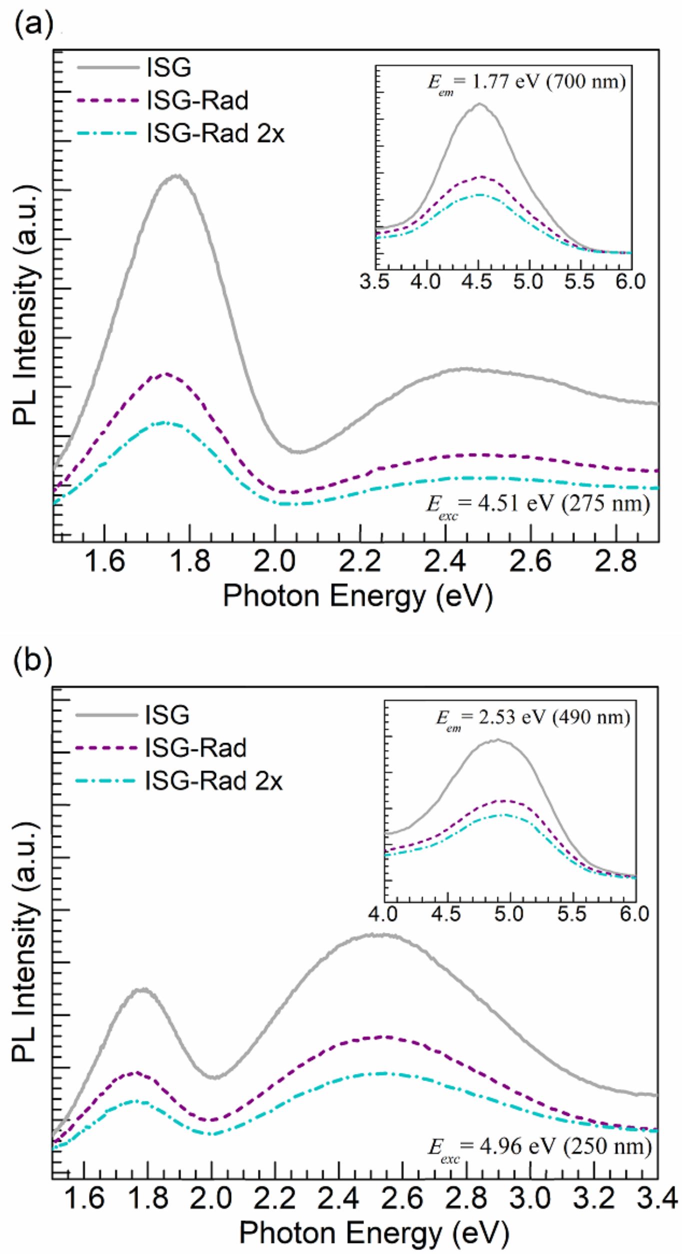

Figure 7. PL emission spectra obtained for ISG and irradiated (100 Mrad and 200 Mrad) samples. The irradiated ISG samples did not show any new luminescence.

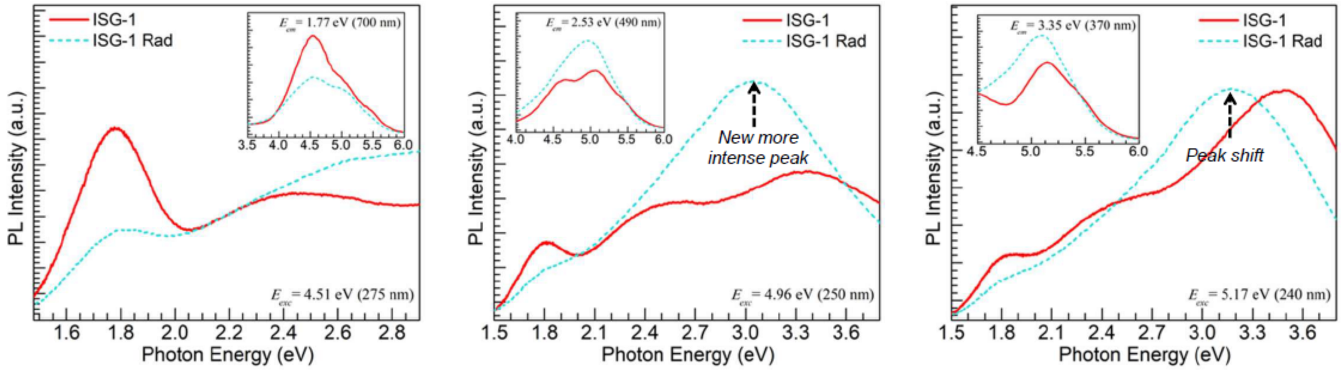

Figure 8. PL emission spectra obtained for ISG-1 and irradiated samples. A PL increase (middle spectra) and shift (right spectra) occurs for irradiated ISG-1.

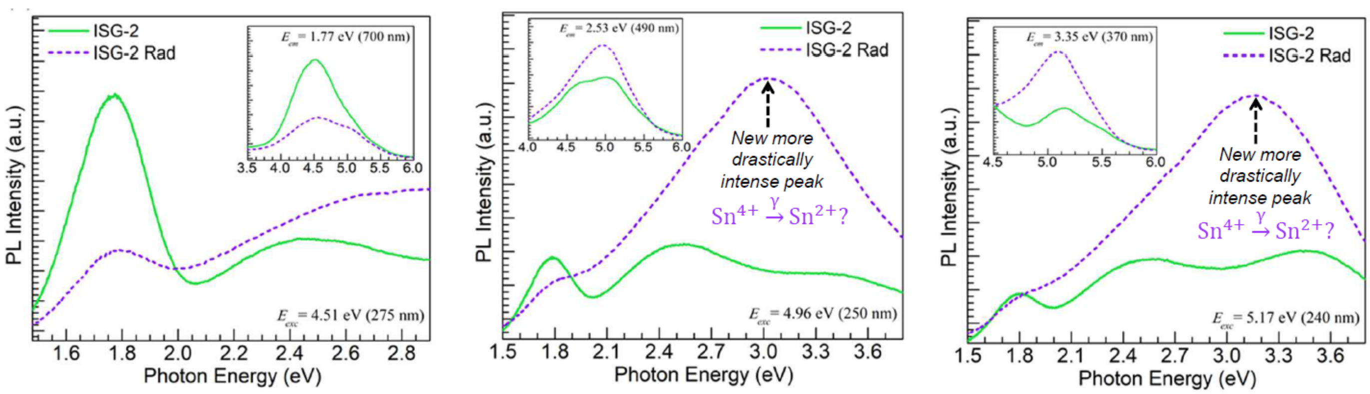

Figure 9. PL emission spectra obtained for ISG-2 and irradiated samples. New more intense PL observed for irradiated ISG-2 (middle & right spectra).