Effect of Phase Constitution on Depth-Dependent Irradiation Damage in Ce-Doped Gadolinia by Raman Spectroscopy

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1. Introduction

Gadolinia (Gd_2O_3) is widely utilized as a solid burnable absorber due to its high neutron absorption cross-section and compatibility with ceramic fuel systems. While compositional modification through CeO_2 doping has been explored to enhance phase stability and irradiation tolerance, a quantitative understanding of phase evolution and defect accumulation remains limited. In this study, we extend our previous microstructural investigation by introducing quantitative Raman-based phase analysis for Ce-doped gadolinia systems. Pure gadolinia exhibits a monoclinic structure, whereas increasing Ce content stabilizes the cubic phase. XRD analysis confirms that 20 at% CeO_2 results in a single cubic phase, while intermediate compositions show mixed monoclinic–cubic phases. Raman spectroscopy is employed to quantitatively evaluate phase fraction evolution and irradiation-induced vibrational changes.

2. Methods and Experimental Setups

In this section, experimental techniques and procedures are described below.

2.1 Sample Preparation & Irradiation Experiment

Gd_2O_3-based ceramic pellets were fabricated via conventional powder processing and sintering. CeO_2 doping concentrations were systematically varied (0–20 at%) to control the phase constitution. The relative densities were maintained at approximately 95% of theoretical density.

Heavy-ion irradiation was conducted at the KAERI Heavy Ion Irradiation Facility (KAHIF) using 6.8 MeV Ar^{9+} ions at elevated temperature. The irradiation conditions were selected to produce displacement damage within the near-surface region (~2–3 μm), as estimated by SRIM simulations. Multiple irradiation durations were applied to compare dose-dependent structural evolution.

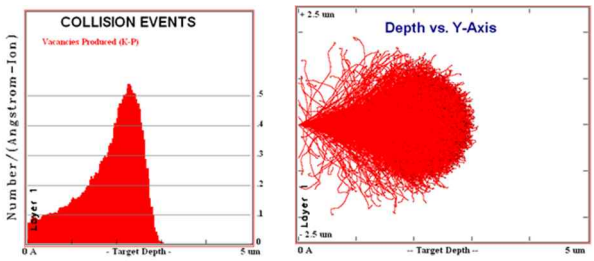


Fig 1. SRIM Simulation Result of Ar Ion Irradiated in Gadolinia. (a) Calculated depth-dpa profiles which can be seen on (b) the visualized trajectory of each simulated Ar ion

Prior to the actual ion irradiation experiment, the depth-dependent radiation damage profile was simulated using SRIM-2008. As shown in Fig. 1, the displacement per atom (dpa) as a function of depth and the possible trajectories of individual ions were calculated through a Monte Carlo-based simulation approach. This computational methodology enabled estimation of the projected ion range corresponding to the region of maximum displacement damage. According to the SRIM results assuming pure gadolinia, the projected range was approximately 2.3 μm. Beyond a depth of about 3 μm, radiation damage induced by direct ion collisions was predicted to be negligible. Based on these simulations, heavy-ion irradiation experiments were conducted on gadolinia specimens with various dopant compositions. The irradiation was performed using Ar^{9+} ions of 3.7cm^2 beam area and an average current of 15μA for durations of 30, 100, and 300 minutes, respectively.

2.2 Raman Spectroscopy

Raman spectroscopy was performed using a Renishaw inVia™ confocal Raman microscope to investigate irradiation-induced modifications in the local bonding environment. Depth-resolved measurements were carried out from the surface down to 6 μm with a step size of 0.4 μm, enabling analysis of the variation in Raman peak characteristics as a function of depth. Particular attention was given to characteristic vibrational modes near 266, 386, and 420 cm^{-1}. Changes in peak position, relative intensity, and full width at half maximum (FWHM) were systematically evaluated to assess irradiation-induced lattice distortion and defect accumulation. Both qualitative spectral features and quantitative peak parameters were compared among

specimens to identify composition-dependent differences in irradiation response.

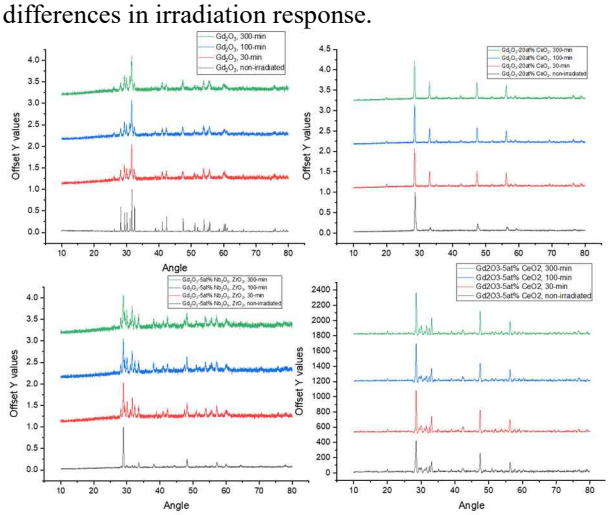


Fig 2. XRD peak patterns of four irradiated samples (a) pure gadolinia, (b) Gd_2O_3–20 at% CeO_2, (c) Gd_2O_3-5at% $Nb_2O_5ZrO_2$ and (d) Gd_2O_3–5 at% CeO_2.

Previous XRD results (Fig. 2) confirmed the monoclinic structure of pure gadolinia and cubic stabilization at 20 at% CeO_2, with mixed-phase behavior observed at intermediate compositions. Based on this structural baseline, the current study emphasizes Raman-based quantitative analysis.

3. Results

Figure 3 presents the depth-dependent variation in the full width at half maximum (FWHM) of the 266 cm^{-1} Raman mode in pure monoclinic gadolinia as a function of irradiation duration. Compared to the pristine specimen, irradiated samples exhibit a systematic increase in FWHM, particularly within the predicted displacement damage region (~2–3 μm). The broadening becomes more pronounced with increasing irradiation time (30, 100, and 300 min), indicating progressive lattice strain accumulation and enhanced defect density.

Notably, measurable FWHM changes are also observed beyond the calculated ion range, suggesting that irradiation-induced defects are not strictly confined to the primary collision region. This behavior is consistent with defect migration or strain propagation into deeper lattice regions.

While these quantitative observations were obtained for pure monoclinic gadolinia, the present study extends the analysis to Ce-doped compositions with distinct phase constitutions. XRD results previously confirmed that 5 at% CeO_2 exhibits mixed monoclinic–cubic phases, whereas 20 at% CeO_2 stabilizes a single cubic phase. It is therefore of particular interest to examine how phase constitution influences Raman peak stability, broadening behavior, and depth-dependent spectral evolution under irradiation.

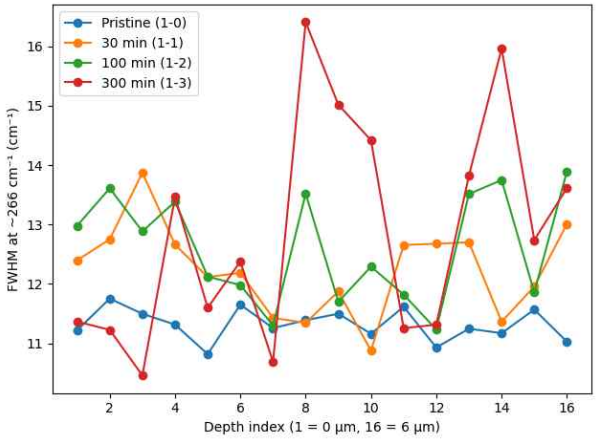


Fig 3. Depth-dependent FWHM variation of the 266 cm^{-1} Raman mode in pure gadolinia under different irradiation durations.

4. Conclusions

In this study, a quantitative Raman-based framework was developed to evaluate irradiation-induced structural modification in gadolinia ceramics. Depth-resolved analysis of the 266 cm^{-1} vibrational mode revealed systematic FWHM broadening with increasing irradiation duration, particularly within the predicted damage region, indicating progressive lattice strain accumulation and defect evolution.

Building upon previously established XRD phase information, the present work extends this quantitative approach to Ce-doped gadolinia systems exhibiting monoclinic, mixed, and cubic phase constitutions. By comparing phase-dependent spectral stability and broadening behavior under irradiation, Raman spectroscopy demonstrates strong potential as a semi-quantitative tool for assessing defect tolerance and phase stability in burnable absorber materials.

These findings provide a basis for correlating compositional phase stabilization with irradiation response in advanced nuclear fuel applications.

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