Irradiation Behavior of 2M, 3O and 4M Polytype Zirconolite Solid Solutions under α Particles

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Abstract

The long-term irradiation stability of high-level waste forms constitutes one of the key indicators for evaluating the safety of deep geological disposal. This study employs a 500 keV He2+ ion beam to irradiate 2M, 3O, and 4M type zirconolite ceramic waste forms, investigating the damage behavior of ceramic structures under long-term α-decay irradiation from high-level radionuclides. The three zirconolite samples were synthesized via a conventional high-temperature solid-state method (1400 °C, two sintering steps of 48 h each). Grazing-incidence X-ray diffraction (GIXRD), Raman spectroscopy, and XPS results reveal that under α-particle irradiation, the zirconolite-2M waste form underwent a structural evolution from zirconolite-2M to zirconolite-4M to pyrochlore during the irradiation-induced amorphization process; zirconolite-3O exhibited partial transformation of its crystal structure to perovskite at a fluence of 5\$×10^{15}\$ ions/cm^2, and rapidly transformed to disordered pyrochlore at fluences above 1\$×10^{16}\$ ions/cm^2; the zirconolite-4M sample still retained the zirconolite-4M main phase at a fluence of 1\$×10^{17}\$ ions/cm^2, with secondary disordered pyrochlore/defect fluorite crystalline phases. In summary, in terms of maintaining crystal structure stability, the α-particle irradiation resistance of zirconolite-2M and zirconolite-3O is similar, being slightly weaker than that of the zirconolite-4M waste form.

Full Text

Irradiation Behavior of 2M, 3O, and 4M Polytype Zirconolite Waste Forms Under α-Particle Bombardment

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Abstract

The long-term irradiation stability of high-level radioactive waste forms represents a critical safety criterion for deep geological disposal. This study investigates the structural damage behavior of 2M, 3O, and 4M polytype zirconolite ceramic waste forms under 500 keV He^{2+} ion bombardment, simulating the effects of prolonged α-decay irradiation from actinide nuclides. The three zirconolite samples were synthesized via conventional high-temperature solid-state reaction (1400 °C, 48 h, double sintering). Grazing incidence X-ray diffraction (GIXRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) revealed distinct structural evolution pathways: zirconolite-2M underwent progressive transformation from zirconolite-2M to zirconolite-4M and finally to pyrochlore during irradiation-induced amorphization; zirconolite-3O partially converted to perovskite at 5×10^{15} ions/cm^2, then rapidly transformed to disordered pyrochlore at doses above 1×10^{16} ions/cm^2; zirconolite-4M retained its primary phase even at 1×10^{17} ions/cm^2, with secondary disordered pyrochlore/defect fluorite phases. Overall, zirconolite-2M and zirconolite-3O exhibited similar α-particle irradiation resistance, both slightly inferior to zirconolite-4M in terms of structural stability.

Keywords: zirconolite; α particles; ion beam irradiation; high-level waste immobilization; irradiation effects

Deep geological disposal is internationally recognized as the ultimate solution for high-level radioactive waste, with waste immobilization serving as its core component. Since Ringwood et al. proposed synthetic rock (SYNROC) for waste immobilization in 1979, various ceramic matrices have been developed, including titanates, phosphates, and silicates, among which fluorite-derived oxide ceramics such as zirconolite and pyrochlore demonstrate particularly outstanding performance [1-3]. Fluorite-derived structures undergo internal structural evolution upon immobilizing radionuclides. For instance, when both A and B sites in zirconolite (ABC_2O_7) simultaneously incorporate actinides, a phase evolution from zirconolite-2M to zirconolite-4M to pyrochlore typically occurs. Our previous work found that when trivalent Al/Fe substitutes at the C site for charge compensation while immobilizing actinides at the A site, zirconolite-2M transforms to zirconolite-3O, with perovskite impurities coexisting in zirconolite-2M [4-8]. Zirconolite-2M and zirconolite-4M are monoclinic structures with two and four layers, respectively (space group C2/c, No. 15), while zirconolite-3O is orthorhombic (space group Acam, No. 64). Their structural schematics are shown in [Figure 2: see original paper] [9-11]. All three polytypes belong to the fluorite-derived structural family and represent potential matrices for high-level waste immobilization, with their structural stability under long-term deep geological disposal having attracted widespread attention from researchers worldwide.

[Figure 1: see original paper] shows the structural schematics of zirconolite-2M (a), zirconolite-3O (b), and zirconolite-4M (c).

Structural damage and degradation in high-level waste forms primarily arise from self-irradiation by radionuclides and groundwater corrosion. While multi-barrier systems in deep geological repositories can effectively prevent groundwater intrusion, radioactive decay continuously damages the waste form structure. Irradiation studies of zirconolite began in the 1980s. In 1983, Ewing and Headley found that natural zirconolite ($CaZrTi_2O_7$) became amorphous at a dose of 10^{26} α/m^3 or ~2 dpa (displacements per atom) from spontaneous α-decay [12]. In 1986, Lumpkin et al. reported that naturally irradiated zirconolite from Sri Lanka (~2 dpa dose) possessed a randomly arranged three-dimensional network structure that recrystallized upon annealing at 1000-1100 °C, following a transformation path from disordered fluorite to zirconolite-2M. Zirconolite subjected to 550 million years of natural irradiation showed only minor geochemical alteration [13]. In 2011, Gilbert et al. irradiated $Ca_{0\cdot 8}Nd_{0\cdot 2}ZrTi_{1\cdot 8}Al_{0\cdot 2}O_7$ zirconolite with 200 keV He^+ ions at room temperature, observing no significant structural damage even at ~2 dpa, only He^+ enrichment and atomic displacement at depths of ~0.55-0.75 m [14]. In 1984, Clinard et al. found that 5 mol% ^{238}Pu-doped zirconolite exhibited ~5.5 vol.% cell swelling approaching saturation after 800 days at room temperature, with zirconolite-2M undergoing a process from high disorder to atomic rearrangement and eventual amorphization [15]. Foltyn et al. used differential thermal analysis to correlate radiation heat release in $CaPuTi_2O_7$ with stored energy, phase transition temperature, and transition abruptness during 35-1198 days of storage, though without detailed investigation of damage mechanisms [16]. In 2006, Jorion et al. reported self-irradiation damage in 10 wt.% $^{238}PuO_2$-doped zirconolite (90% theoretical density) at room temperature, 250 °C, and 500 °C, finding macroscopic and microscopic swelling rates of ~2.2%/10^{18} α/g and ~1.3%/10^{18} α/g at room temperature, respectively, with swelling rates decreasing at higher temperatures and amorphization initiating at 2.2\$×10^{18}\$ α/g [17]. Strachan et al. observed severe amorphization in ^{238}Pu self-irradiated zirconolite at 2.6\$×10^{18}\$ α/g [18].

Investigating self-irradiation of actinide-containing waste forms involves high operational risks and technical difficulties, prompting many researchers to employ external irradiation to simulate spontaneous decay effects. Deschanels et al. compared ^{238}Pu self-irradiation with Au ion external irradiation, finding zirconolite amorphization doses of ~0.3 dpa at room temperature, macroscopic saturation swelling of ~6%, and defect recovery annealing temperatures of ~800 °C, whereas self-irradiation defects recovered at only 500 °C [19]. Ewing and Wang used 1.5 MeV Kr^+ irradiation to determine a natural zirconolite amorphization dose of ~0.3 dpa at 25 °C, nearly six times lower than self-irradiation, attributing this to Kr^+ damage rates being 2$×10^{12}$ times higher than α-decay, which prevents spontaneous recovery of point defects during the damage cascade [20]. In 1999, Wang et al. observed a structural damage sequence from zirconolite to pyrochlore to disordered fluorite and finally to amorphization under 1.5 MeV Xe^+ and 1.0 MeV Kr^+ irradiation, with critical amorphization temperatures of 710 K and 654 K, respectively [21]. In 2000, they reported similar damage processes in six zirconolite compositions irradiated with 1 MeV Kr^+ ions [22]. Dacoisne et al. irradiated $Ca_{0\cdot8}Nd_{0\cdot2}ZrTi_{1\cdot8}Al_{0\cdot2}O_7$ with 2 MeV Kr^+ at room temperature, finding complete transformation to fluorite-type superlattice before amorphization, with unchanged Ti valence but altered coordination number during amorphization [23]. Smith et al. conducted in situ irradiation studies, revealing similar critical doses for zirconolite and pyrochlore under 1.5 MeV Kr^+ irradiation (~3.5-6.1$×10^{14}$ ions/cm^2), lower than that for perovskite (~1.8$×10^{15}$ ions/cm^2) [24]. Professor Li Yuhong's group has extensively investigated irradiation damage in titanate pyrochlores, establishing that the damage process involves lattice swelling, disordered pyrochlore formation, disordered fluorite development, and final amorphization [25-29].

In summary, previous irradiation studies on zirconolite (primarily zirconolite-2M) concentrated on the late 20th century, while pyrochlore irradiation behavior has been more extensively investigated. However, many studies have shown that zirconolite-2M often transforms to other ordered zirconolite structures such as zirconolite-3O and zirconolite-4M when used as an end-member for waste immobilization. Investigating the irradiation damage behavior and radiation tolerance of these polytypes is crucial for evaluating long-term geological disposal stability [4-8, 30, 31]. Therefore, this study employs 500 keV He^{2+} ion irradiation on zirconolite-2M ($Ca_{0\cdot6}Nd_{0\cdot4}ZrTi_{1\cdot6}Fe_{0\cdot4}O_7$), zirconolite-3O ($Ca_{0\cdot2}Nd_{0\cdot8}ZrTi_{1\cdot2}Fe_{0\cdot8}O_7$), and zirconolite-4M ($Ca_{0\cdot53}Nd_{0\cdot7}Zr_{0\cdot72}Ti_2O_7$) waste forms to simulate long-term α-decay irradiation damage in geological repositories. Pre- and post-irradiation crystal structure damage, phase evolution, and amorphization were investigated using TRIM simulations, grazing incidence X-ray diffraction (GIXRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The radiation tolerance and structural damage mechanisms of the three zirconolite polytypes were evaluated through analysis of crystalline phase evolution, disordering, and amorphization degree under ion beam irradiation.

2.1 Pre-Irradiation Sample Preparation

Zirconolite samples with compositions $Ca_{0\cdot6}Nd_{0\cdot4}ZrTi_{1\cdot6}Fe_{0\cdot4}O_7$ (zirconolite-2M), $Ca_{0\cdot2}Nd_{0\cdot8}ZrTi_{1\cdot2}Fe_{0\cdot8}O_7$ (zirconolite-3O), and $Ca_{0\cdot53}Nd_{0\cdot7}Zr_{0\cdot72}Ti_2O_7$ (zirconolite-4M) were synthesized via conventional high-temperature solid-state reaction at 1400 °C with double sintering for 48 h. Non-radioactive Nd^{3+} served as a surrogate for trivalent actinides. Starting materials included $CaCO_3$, Nd_2O_3, ZrO_2, Fe_2O_3, and TiO_2 powders ($ $99.99% purity) from Shanghai Aladdin. XRD and backscattered SEM confirmed the synthesis of zirconolite-2M containing trace perovskite and single-phase zirconolite-3O and zirconolite-4M. Well-sintered ceramic blocks were sequentially polished with diamond suspension sprays of 9, 6, 3, 1, 0.5, and 0.25 m until mirror-like surfaces were obtained. Samples were then ultrasonically cleaned in water and ethanol to remove polishing residues, yielding pristine pre-irradiation specimens.

2.2 Alpha Ion Beam Irradiation Experiments

He^{2+} irradiation experiments were conducted at the 320 kV Low-Energy Heavy Ion Research Platform at the Institute of Modern Physics, Chinese Academy of Sciences, Lanzhou. The He^{2+} ion energy was 500 keV with fluences of 5\$×10$^{\{15\},1\times10}$\{16\}, 5×10$^{\{16\},and1\times10}$\{17\}\$ ions/cm^2. Experiments were performed at room temperature with beam currents of ~5.09 A (front) and ~6.8 A (back), a beam spot area of ~2.7 cm^2, and a flux rate of ~7.8\$×10^{12}\$ ions/cm^2 · s.

The SRIM-TRIM code was used to calculate α-ion irradiation damage in the three zirconolite compositions, assuming a displacement threshold energy of 50 eV and full cascade damage model. Results are presented in [Figure 2: see original paper]. At 1\$×10^{15}\$ ions/cm^2, the maximum DPA values for 2M, 3O, and 4M zirconolites were 0.0196, 0.0192, and 0.0194, respectively, with corresponding peak damage depths of ~0.71, 0.67, and 0.69 m. The maximum irradiation damage depths were 0.82, 0.80, and 0.81 m, respectively. These calculations demonstrate that the three zirconolite polytypes exhibit similar DPA values and damage depths under α-ion irradiation.

[Figure 2: see original paper] TRIM simulation of displacement damage (DPA) in 2M, 3O, and 4M zirconolites under 500 keV He^{2+} irradiation.

2.3 Characterization Methods

Grazing incidence X-ray diffraction (GIXRD) measurements were performed on a Rigaku SmartLab diffractometer at the School of Nuclear Science and Technology, Lanzhou University. The X-ray source was Cu-Kα radiation (λ 5.42 Å) operating at 40 kV and 40 mA. Data were collected in continuous scan mode from 2 = 5-80° at a scan rate of 1°/min. The penetration depth of GIXRD depends on the incidence angle and material absorption coefficient. The calculated penetration depths for Cu Kα radiation in the three zirconolite polytypes at various incidence angles are listed in [28, 33, 34].

Raman spectroscopy, with a typical probing depth of ~10 nm, efficiently identifies medium- and short-range ordering changes in crystals, making it an effective tool for irradiation damage studies. Raman data were collected using a HORIBA JY LabRAM HR Evolution high-resolution spectrometer with 2 m^2 spatial resolution. Measurements employed standard mode with 532 nm excitation wavelength and collection range of 100-4000 cm^{-1}. The instrument was calibrated using a silicon wafer (520.7 cm^{-1}) prior to analysis.

X-ray photoelectron spectroscopy (XPS) effectively probes valence state changes and crystallization behavior induced by irradiation. XPS spectra were acquired using a Thermo Fisher Scientific K-Alpha instrument with Al Kα X-ray source (h = 1486.8 eV) under vacuum of ~2$×10^{-9}$ mbar. The X-ray spot size was 400 m, operating at 12 kV and 6 mA filament current. High-resolution elemental scans used pass energies of 30/50 eV with 0.05/0.1 eV step sizes, accumulating >5 cycles per element. All spectra were calibrated to the C 1s binding energy at 284.8 eV.

3.1 Irradiation Damage in Zirconolite-2M

[Figure 3a: see original paper] presents normalized GIXRD patterns of zirconolite-2M irradiated to 1$×10^{16}$ ions/cm^2 (~0.2 dpa) at various incidence angles. At 1° incidence, all diffraction peaks except a weak feature at ~33° correspond to zirconolite-2M, though with significant peak broadening [11]. This indicates that at ~0.43 m depth, the primary phase remains zirconolite-2M with cation disordering, suggesting relatively low damage accumulation at this depth based on [Figure 2: see original paper]. At 1.5° incidence (probing depth ~0.65 m, near the peak DPA depth), zirconolite-4M diffraction peaks appear at ~31.2° (Z(008)), the ~15.8° peak intensifies, high-angle peaks (50-60°) change markedly, and perovskite characteristic peaks (~33°) exhibit clear splitting [6, 10, 35]. This demonstrates phase transformation at this damage depth, comprising at least three crystalline phases (zirconolite-2M, zirconolite-4M, and perovskite) with some disordered/amorphous components. At 2° incidence (probing near maximum damage depth), diffraction peaks broaden further with evident diffuse scattering. The zirconolite-2M characteristic peak near 32° shows a new Z(008) feature, the ~15.8° peak weakens, peaks at ~39° (Z(-406)/P(331)) and 52° (Z(-4010)/P(440)) broaden and intensify, and sharp peaks emerge near 59° and 62°, indicating coexistence of 2M, 4M, and pyrochlore phases with significant perovskite and amorphous/highly disordered components [6, 10, 21, 24, 28, 36]. At 3° and 4° incidence, probing depths exceed the irradiated layer, revealing sharper, narrower zirconolite-2M peaks. Thus, GIXRD at 1.5° and 2° provides complete irradiation damage information. Zirconolite-2M transforms to zirconolite-4M, disordered pyrochlore, and amorphous phases at 1$×10^{16}$ ions/cm^2, consistent with Wang et al.' s reports [21, 22].

[Figure 3: see original paper] Normalized GIXRD patterns of zirconolite-2M before and after irradiation. P(hkl): pyrochlore; Z(hkl): zirconolite-4M.

[Figure 3b: see original paper] shows normalized GIXRD patterns at 1.5° incidence for zirconolite-2M irradiated from 5$×10^{15}$ to 5$×10^{16}$ ions/cm^2. At 5$×10^{15}$ ions/cm^2, diffraction peaks match zirconolite-2M Bragg positions, indicating only swelling and mild disordering [11]. At 1$×10^{16}$ ions/cm^2, the 2M-to-4M phase transformation initiates. At 5$×10^{16}$ ions/cm^2, peaks continue broadening and shifting to lower angles, matching zirconolite-4M and pyrochlore patterns, indicating the primary phase transforms to zirconolite-4M or pyrochlore with continued lattice swelling and increased disorder/amorphization. [Figure 3c: see original paper] displays GIXRD patterns at 2° incidence. At 5$×10^{15}$ ions/cm^2, peaks correspond to zirconolite-2M with structural swelling, distortion, and disordering. At 1$×10^{16}$ ions/cm^2, two sharp peaks appear near 60°, most peaks broaden and shift to lower angles, indicating enhanced lattice swelling and disorder/amorphization with irradiation-induced zirconolite-4M formation [6, 10]. At 5$×10^{16}$ ions/cm^2, major peaks broaden significantly, P(400)/Z(406) and P(800) intensify, matching zirconolite-4M and pyrochlore patterns, while the ~32° zirconolite-2M peak persists. This indicates a primary zirconolite-4M phase with secondary pyrochlore and zirconolite-2M, plus substantial atomic disorder/amorphous components. Combined analysis of [Figure 3b: see original paper] and [Figure 3c: see original paper] reveals gradual lattice swelling and phase evolution with increasing dose, with transformation to highly disordered zirconolite-4M and pyrochlore at 5$×10^{16}$ ions/cm^2 rather than sequential amorphization. This is explained by DPA analysis showing minimal increase in DPA within ~0.4 m from the surface, sharp DPA increase at 0.6-0.7 m depth, and detection of unirradiated substrate at 2° incidence, resulting in multiple coexisting phases rather than direct amorphization.

[Figure 4a: see original paper] presents normalized Raman spectra of zirconolite-2M before and after 1$×10^{17}$ ions/cm^2 irradiation, probing chemical coordination changes. The pre-irradiated zirconolite-2M spectrum shows a TiO$_6$ octahedral stretching vibration at ~760 cm^{-1} and M-O bond vibrations below 700 cm^{-1} [30, 37, 38]. Peaks at 179 and 398 cm^{-1} correspond to internal vibrations of ZrO$_7$ and TiO$_6$ polyhedra, 317 cm^{-1} to CaO$_8$ polyhedra, and 457 cm^{-1} primarily to Ti-O bending [38]. Post-irradiation, the 317 and 398 cm^{-1} peaks remain essentially unchanged. The 317 cm^{-1} peak represents typical Eg+F$_2$g bending vibrations characteristic of fluorite-type oxides, while 398 cm^{-1} arises from TiO$_6$ internal vibrations [7, 8, 30, 39-41]. Pyrochlore characteristic Raman peaks at 236 (F$_2$g), 317 (Eg+F$_2$g), 510 (A$_1$g), and 578 (F$_2$g) cm^{-1} confirm pyrochlore phase presence [39, 40]. Post-irradiation TiO$_6$ stretching splits into a sharp peak at ~740 cm^{-1} and a shoulder at 796 cm^{-1}, indicating structural transformation with multiple TiO$_6$ coordination environments. The ~1550 cm^{-1} peak likely originates from Fe-O vibrations and Nd 4f electron fluorescence/free Nd-O vibrations, suggesting Fe and Nd migration from the zirconolite-2M lattice to form free ions or highly disordered structures upon irradiation [42-45]. Additional peaks at ~166, 367, and 479 cm^{-1} belong to monoclinic zirconolite (2M/4M) [38, 40]. Combined GIXRD and Raman analysis indicates that

1×10^{17} ions/cm^2 irradiation transforms the sample to pyrochlore with residual 4M/2M zirconolite and substantial disorder/amorphization.

[Figure 4: see original paper] Normalized Raman spectra of three zirconolite (ABC_2O_7) samples before and after 1×10^{17} ions/cm^2 irradiation: (a) zirconolite-2M, (b) zirconolite-3O, (c) zirconolite-4M.

[FIGURE:5a-f] display high-resolution XPS spectra of Ti 2p, Zr 3d, Nd 3d, Ca 2p, Fe 2p, and O 1s for zirconolite-2M before and after 1×10^{17} ions/cm^2 irradiation. Post-irradiation Ti 2p, Zr 3d, and Nd 3d peaks shift to lower binding energies, indicating increased electron density (effective negative charge) around these cations and enhanced covalency of Ti-O, Zr-O, and Nd-O bonds, possibly due to glassy or amorphous phase formation [46, 47]. Ca 2p and Fe 2p peaks show dramatically reduced intensity while shifting to higher binding energies, suggesting decreased local electron density and increased coordination number for Fe and Ca ions. This may result from easier displacement and migration of Ca and Fe under α-particle irradiation, forming disordered/free ions that rearrange into short-range ordered structures (nano-pyrochlore/fluorite, weberite, etc.) [27, 41, 46], consistent with Raman results. The significantly reduced intensity of metal cation XPS peaks indicates lattice destruction, cation antisite disordering, and migration, with substantial amorphization. O 1s XPS peaks show subtle differences depending on oxygen coordination with various cations: the ~531.5 eV shoulder primarily originates from O^{2-} in Nd-O [48, 49], while the strong ~529.5 eV peak arises from lattice O^{2-} in M-O bonds (M = metal cations) such as Ca-O and Ti-O [31, 49-51]. Post-irradiation O 1s changes from a doublet to a singlet shifted to ~532.4 eV, confirming lattice M-O bond distortion and destruction. The formation of numerous non-lattice oxygen species or vacancies, including metastable oxygen, free oxygen, and complexes between incident He^{2+} and O^{2-}, combined with Raman evidence, indicates highly disordered structures with extensive amorphous components [48, 49, 51].

[Figure 5: see original paper] Normalized XPS spectra of zirconolite-2M before and after 1×10^{17} ions/cm^2 irradiation.

3.2 Irradiation Damage in Zirconolite-3O

[Figure 6a: see original paper] shows normalized GIXRD patterns of zirconolite-3O irradiated to 5×10^{16} ions/cm^2 at various incidence angles. At 1° incidence, diffraction peaks (except ~32.5°) match zirconolite-3O, with the ~32.5° peak belonging to perovskite. Peak broadening and splitting near 30° indicate either zirconolite-3O with varying lattice swelling or another disordered fluorite-derived phase (disordered pyrochlore/defect fluorite) [4, 9, 35]. At 1.5° incidence, increased peak width and preferred orientation with diffuse scattering suggest enhanced structural disorder/amorphization, though the main phase remains zirconolite-3O. At 2° incidence, further peak broadening indicates higher disorder/amorphization. Multiple peaks near 30° at 1.5° and 2° suggest new phase formation, with some peaks intensifying at 2° while weak zirconolite-3O features nearly disappear, indicating possible transformation to disordered pyrochlore or defect fluorite [6, 28, 52]. At 2.5° incidence, derivative peaks show clear preferred orientation, with pyrochlore diffraction peaks (~30°, 35°, 37°, 51°) becoming more prominent. Since this probing depth approaches the maximum irradiation damage depth (and [Figure 2: see original paper]), the sample undergoes zirconolite-3O to pyrochlore transformation at 5$×10^{16}$ ions/cm^2, accompanied by structural disorder and amorphous components.

[Figure 6b: see original paper] presents normalized GIXRD patterns at 2° incidence for irradiated zirconolite-3O. With increasing fluence, diffraction peaks shift to lower 2 angles, indicating progressive lattice swelling. At 5$×10^{15}$ ions/cm^2, peaks (except 31.7° and 48.3°) match zirconolite-3O, while 31.7° and 48.3° correspond to perovskite. Significant peak broadening compared to unirradiated material indicates partial lattice swelling and cation disordering. The absence of perovskite peaks in unirradiated zirconolite-3O XRD confirms irradiation-induced transformation to orthorhombic perovskite [9, 35]. At 1$×10^{16}$ ions/cm^2, perovskite peaks nearly merge into the background, peak intensity ratios change markedly, zirconolite-3O characteristic peaks (50-60°) weaken dramatically, while P(331) and P(440) pyrochlore peaks intensify, suggesting pyrochlore formation [7, 8, 28]. Peak shifting to lower angles without further broadening indicates continued lattice swelling without increased disorder/amorphization, likely because perovskite transforms to pyrochlore at higher doses, slowing amorphization. At 5$×10^{16}$ ions/cm^2, pyrochlore and zirconolite-3O show increased disorder/amorphization (peak broadening), with the phase composition primarily containing zirconolite-3O and pyrochlore structures with continued lattice swelling and disorder. Based on and [Figure 2: see original paper], GIXRD at 2° and 2.5° incidence best reflects irradiated layer damage, with 2.5° probing nearly the entire damage profile. [Figure 6c: see original paper] shows the 2.5° GIXRD pattern: at 5$×10^{15}$ ions/cm^2, clear preferred orientation distinguishes perovskite and zirconolite-3O peaks, confirming the transformation. Zirconolite-3O peaks broaden and slightly shift to higher angles, indicating that cation disordering and rearrangement into perovskite cause zirconolite-3O lattice contraction. At 1$×10^{16}$ ions/cm^2, peak positions match the unirradiated sample without significant broadening, perovskite peaks vanish, and pyrochlore P(331), P(511), and P(440) peaks appear. This demonstrates that orthorhombic perovskite transforms to pyrochlore with increasing dose, while disordered cations rearrange into relatively less disordered zirconolite-3O or pyrochlore. At 5$×10^{16}$ ions/cm^2, preferred orientation reappears, pyrochlore peaks are fully developed, zirconolite-3O peaks persist, and no further broadening occurs, indicating the main structure transforms to pyrochlore, which may suppress disorder/amorphization. In summary, GIXRD reveals that zirconolite-3O undergoes lattice swelling and progressive disorder/amorphization with dose, following a transformation sequence from zirconolite-3O to perovskite to pyrochlore and finally to amorphous phases. Phase transformations partially inhibit atomic disordering and amorphization evolution.

[Figure 6: see original paper] Normalized GIXRD patterns of zirconolite-3O before and after irradiation. P(hkl): pyrochlore.

[Figure 4b: see original paper] shows normalized Raman spectra of zirconolite-3O before and after 1$×10^{17}$ ions/cm^2 irradiation. Pre-irradiation strong peaks appear at ~1319 and 1570 cm^{-1}, with clear peaks at ~2692 cm^{-1} and a weak peak at 2446 cm^{-1}. The high intensity of the ~1500 cm^{-1} peaks obscures sub-1000 cm^{-1} vibrations, though inset magnification reveals zirconolite-3O M-O bond vibrations. The strong ~1319 and 1570 cm^{-1} peaks likely originate from Fe-O vibrations (with possible Nd^{3+} 4f fluorescence contribution), while 2446 and 2692 cm^{-1} peaks belong to Nd-O characteristic vibrations [42, 44, 45, 53-55]. Post-irradiation, sub-1000 cm^{-1} peaks emerge with increased relative intensity at 764, 658, 588, 517, 398, 310, 240, and 166 cm^{-1}, primarily from M-O stretching and bending vibrations in pyrochlore and zirconolite-3O [7, 8, 30, 37, 52]. The lattice Nd-O peaks at ~2446 and 2692 cm^{-1} disappear, indicating severe disruption of Nd-O coordination. Combined with GIXRD analysis, this suggests Nd has low solubility in perovskite and precipitates during zirconolite-3O to perovskite transformation, failing to reincorporate into the pyrochlore lattice during subsequent transformation [4, 5, 53]. The ~1500 cm^{-1} peaks broaden dramatically, indicating Fe-O bond distortion and weakened binding/reduced content, possibly with contributions from amorphous/Nd^{3+} 4f fluorescence and free Nd-O vibrations [42-45]. This confirms that 1$×10^{17}$ ions/cm^2 irradiation produces a predominantly disordered pyrochlore structure with possible zirconolite phases and significant lattice disorder/amorphization. Combined GIXRD, Raman, and XPS analysis suggests Nd and Fe may be partially expelled during the disorder-order-disorder process, explaining the broadened, weakened Nd and Fe-O vibrational modes in irradiated zirconolite-3O.

[Figure 7: see original paper] shows normalized XPS spectra of zirconolite-3O before and after 1$×10^{17}$ ions/cm^2 irradiation. [Figure 7a: see original paper] and [Figure 7e: see original paper] reveal dramatically reduced Ti 2p and Fe 2p intensities nearly submerged in background noise, indicating severe lattice distortion and destruction of Fe-O and Ti-O bonds, consistent with Raman analysis. Combined with GIXRD, this suggests Fe and Ti atoms in zirconolite-3O undergo disordering, rearrangement, and redistortion, leading to elemental segregation and bond destruction. [Figure 7b: see original paper] shows weakened Zr 3d intensity, indicating Zr-O bond damage. [Figure 7c: see original paper] displays narrowed, sharpened Ca 2p peaks after irradiation, possibly because Ca exists primarily as lattice atoms in zirconolite-3O, perovskite, and pyrochlore structures. Post-irradiation Zr 3d and Ca 2p peaks shift to higher binding energies, suggesting local atomic rearrangement with decreased electron density and increased coordination number for Ca and Zr [46, 47]. This supports the transformation from zirconolite-3O to cubic defect fluorite-derived structures (pyrochlore/fluorite) where Ca and Zr have higher coordination numbers than in zirconolite. [Figure 7d: see original paper] shows Nd 3d peaks shifting to lower binding energy, weakening and broadening, indicating weakened Nd-O bonds. The shift suggests increased electron density around Nd and enhanced Nd-O covalency, with significant Nd expulsion from the lattice during the disorder-order-disorder process, forming disordered/free Nd-O bonds and possible glassy phases [46, 47]. [Figure 7f: see original paper] reveals O 1s becomes a single peak at ~532 eV after irradiation, attributed to severe lattice disordering and partial amorphization reducing lattice oxygen stability, while disordered/free oxygen and vacancies may combine with atmospheric H_2O/CO_2 to form surface-contaminating C-O/H-O bonds, ultimately producing the ~532 eV single broad peak [50]. Combined GIXRD, Raman, and XPS analysis demonstrates that 1×10^{17} ions/cm^2 irradiation transforms zirconolite-3O to predominantly cubic pyrochlore/fluorite structures with high lattice disorder and amorphization.

[Figure 7: see original paper] Normalized XPS spectra of zirconolite-3O before and after 1×10^{17} ions/cm^2 irradiation.

3.3 Irradiation Damage in Zirconolite-4M

[Figure 8a: see original paper] displays normalized GIXRD patterns of zirconolite-4M irradiated to 1×10^{16} ions/cm^2 at various incidence angles. At 1° incidence, peaks match zirconolite-4M Bragg positions with broadened full width at half maximum (FWHM), indicating the phase remains zirconolite-4M with lattice swelling and atomic disordering, possibly containing amorphous components [10]. At 1.5° incidence, peaks still match zirconolite-4M but with narrower FWHM, suggesting lower disorder/amorphous content at this depth. According to [Figure 2: see original paper] and , 1° and 1.5° incidence probe depths of 0.36 and 0.54 m, respectively, where DPA increases with depth. Thus, highly disordered zirconolite-4M partially transforms to defect fluorite/pyrochlore structures (both fluorite-derived with overlapping peaks) as DPA increases. At 2° incidence, preferred orientation appears with peak splitting at ~31°, 35°, and 38°, indicating formation of disordered pyrochlore or defect fluorite phases [25, 27, 29]. At 2.5° incidence, the pattern resembles zirconolite-4M but with further broadened FWHM, indicating the phase remains zirconolite-4M with high amorphization. The 2.5° probing depth of ~0.1 m encompasses the high-DPA region at 0.72-0.80 m, thus detecting more amorphous components.

[Figure 8: see original paper] Normalized GIXRD patterns of zirconolite-4M before and after irradiation. P(hkl): pyrochlore.

[Figure 8b: see original paper] shows GIXRD patterns at 1.5° incidence for irradiated zirconolite-4M. From 5×10^{15} to 5×10^{16} ions/cm^2, diffraction peaks match zirconolite-4M Bragg positions, indicating the primary phase remains zirconolite-4M even at 5×10^{16} ions/cm^2 [10]. At 5×10^{15} ions/cm^2, zirconolite-4M characteristic peaks at ~7.6° and 31° split with preferred orientation, likely due to overlapping diffraction from partially swollen/disordered and unirradiated/slightly damaged regions, causing broadened FWHM. At 1×10^{16} ions/cm^2, no obvious splitting occurs, but near-equal doublets appear at ~35°, with increased relative intensity of fluorite-type peaks at ~38° and 51°, suggesting transformation of highly disordered zirconolite-4M to other fluorite-derived structures (defect fluorite or pyrochlore) [7, 8, 10, 29]. At 5$×10^{16}$ ions/cm^2, peak positions remain essentially unchanged, indicating near-saturation swelling, but FWHM increases significantly, indicating enhanced atomic disorder/amorphization and increased defect fluorite/pyrochlore content. [Figure 8c: see original paper] shows similar 2° incidence patterns, but without obvious splitting at 5$×10^{15}$ ions/cm^2. The 2° incidence probes maximum DPA damage, where high fractions of swollen/disordered zirconolite-4M may mask unirradiated phase diffraction. At 1$×10^{16}$ ions/cm^2, zirconolite-4M peak splitting and defect fluorite/disordered pyrochlore peaks confirm irradiation-induced transformation of highly disordered zirconolite-4M. At 5$×10^{16}$ ions/cm^2, broadened peaks with observable zirconolite-4M features indicate a predominantly highly swollen/disordered zirconolite-4M phase containing disordered pyrochlore/defect fluorite and amorphous components.

[Figure 4c: see original paper] presents normalized Raman spectra of zirconolite-4M before and after 1$×10^{17}$ ions/cm^2 irradiation. No significant changes occur in sub-1000 cm^{-1} peak positions, indicating the primary phase remains zirconolite-4M. However, characteristic pyrochlore Raman peaks are observed, particularly the A_1g peak confirming pyrochlore presence. Several peaks near 2000 and 2500 cm^{-1} likely originate from Nd-O vibrations, with increased relative intensity after irradiation due to lattice swelling, distortion, and atomic disordering/rearrangement forming disordered pyrochlore/defect fluorite structures [53]. A post-irradiation peak near 1500 cm^{-1} arises from highly disordered/amorphous Nd-O coordination and Nd^{3+} 4f electron fluorescence [42, 55]. Combined with GIXRD results, this indicates coexistence of zirconolite-4M and disordered/amorphous phases, possibly containing defect fluorite/disordered pyrochlore.

[Figure 9: see original paper] displays normalized XPS spectra of zirconolite-4M before and after 1$×10^{17}$ ions/cm^2 irradiation. [Figure 9a: see original paper] and [Figure 9b: see original paper] show Ti 2p and Zr 3d peaks nearly obscured by background noise, indicating severe lattice swelling and disordering that severely distorts Ti-O and Zr-O bonds, possibly leading to Ti/Zr segregation. [Figure 9c: see original paper] reveals Ca 2p peaks shifting to higher binding energy with sharpened $2p_1/_2$ features, indicating decreased Ca electron density and increased coordination number. Ca-O bonds are less susceptible to distortion during lattice swelling and disordering, possibly because Ca exists primarily as CaO_8 (with minor CaO_7) in 4M zirconolite but exclusively as CaO_8 in cubic defect fluorite-derived structures [46, 47]. [Figure 9d: see original paper] shows weakened, broadened Nd 3d peaks shifting to lower binding energy, with a possible satellite peak at ~992 eV, suggesting different Nd coordination and binding energies in 4M zirconolite versus defect fluorite, enhanced Nd-O covalency, and possible Nd segregation forming amorphous components [46, 47]. [Figure 9e: see original paper] shows the O 1s peak shifting to ~532 eV as a single peak, which combined with GIXRD and Raman analysis indicates severe lattice swelling, disordering, and amorphization causing metal-oxygen disorder and oxygen vacancies, possibly combined with surface contamination from atmospheric H_2O/CO_2, ultimately forming the ~532 eV single broad peak [50]. [Figure 9f: see original paper] shows survey spectra confirming structural distortion and damage after irradiation.

[Figure 9: see original paper] Normalized XPS spectra of zirconolite-4M before and after 1$×10ˆ{17}$ ions/cm^2 irradiation.

This study employed 500 keV He^{2+} ion irradiation to simulate long-term α-decay damage in zirconolite-2M, zirconolite-3O, and zirconolite-4M waste forms during geological disposal. Zirconolite-2M undergoes phase evolution from zirconolite-2M to zirconolite-4M to pyrochlore/defect fluorite with increasing He^{2+} fluence, accompanied by lattice swelling, atomic disordering, and amorphization. Above 5$×10ˆ{16}$ ions/cm^2, the phase transforms to highly disordered zirconolite-4M and pyrochlore. Zirconolite-3O transforms from zirconolite-3O to pyrochlore/defect fluorite, transiently forming perovskite intermediate phases, accompanied by lattice swelling and disorder/amorphization. The rearrangement of highly disordered atoms into new relatively ordered phases consumes substantial irradiation energy, thereby slowing amorphization. This phenomenon provides valuable guidance for waste form material selection and performance evaluation. Zirconolite-4M transforms from zirconolite-4M to disordered pyrochlore/defect fluorite with lattice swelling and moderate disorder/amorphization, yet retains zirconolite-4M as the primary phase even at 1$×10ˆ{17}$ ions/cm^2 with increased disorder/amorphization.

In conclusion, all three zirconolite polytypes undergo phase transformation to pyrochlore or defect fluorite during He^{2+} irradiation-induced amorphization, with phase transformations slowing disorder/amorphization evolution. Radiation tolerance follows the approximate trend: 4M > 2M 3O. However, quantitative analysis of amorphization resistance differences and compositional effects require further investigation. These results provide positive guidance for formulation design and irradiation stability evaluation of zirconolite waste forms.

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