

In situ TEM investigation of irradiation-induced amorphization of Fe₃O₄ and γ-Fe₂O₃

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This study investigates the amorphization behavior of magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) by means of ion irradiation. For this matter, a high-purity Fe bar were oxidized in air at 600 C. At these temperatures, Fe₃O₄ and Fe₂O₃ and/or its polymorphs can both form. Although magnetite and maghemite both present the same spinel structure with some similar lattice parameters, careful measurement of the Diffraction Patterns (DP) along with simulated patterns from Crystal Diffract software made it possible to distinguish between the two phases

The Transmission Electron Microscopy (TEM) specimens prepared by Focused Ion Beam (FIB) lift-out techniques, were irradiated in-situ at the IVEM-Tandem User Facility. During irradiation the sample was oriented 15 degree with respect to the ion and the electron beams to ensure true in-situ irradiation conditions. The irradiation was conducted at 50 K using 1 MeV Kr²⁺ ions and an ion flux of 6.25×10¹⁵ ions.m⁻².s⁻¹ which corresponds to a dpa rate of 7.5×10⁻⁴ dpa/s based on SRIM simulations using displacement threshold energies of 40 eV for Fe and 28 eV for O. During the cool-down of the samples, Bright Field images (BF) and DPs were acquired. No phase transformation was recorded although d-spacing measurements reveal a slight contraction of maghemite.

For magnetite the maximum dose archived was 9.5 dpa (displacement per atoms) while for maghemite the maximum dose was 7.5 dpa. A sequence of BFs and DP acquired during the irradiation is presented in Fig. 1 for the two oxides., Loss of spot intensity and appearance of diffuse ring could be observed in the DP at less than 1 dpa for both Fe₃O₄ and γ-Fe₂O₃ suggesting a possible initialization of the amorphization. Besides, the BFs of both oxides started to display a “milky” appearance typical of amorphous samples in TEM. However, some clear diffraction spots were still present on the DPs corresponding to magnetite and maghemite even at the maximum doses attained indicating that these oxides did not amorphize completely even at the final doses reached. Indeed, a reasonable amount of magnetite grains demonstrated diffraction contrast even at the final dose (as seen in Fig. 2). There ws no apparent correlation between amorphization and size of the grains.

The similar amorphization behavior of Fe₃O₄ and γ-Fe₂O₃ is not a surprising result since both compounds as mentioned previously share similar geometric and structural factors. More precisely, both oxides present the same inverse spinel structure where oxygen anions are in a close-pack arrangement. Their anion-anion distance and lattice parameter are nearly identical. The only difference between these two crystals is that in Fe₃O₄, Fe²⁺ occupy octahedral sites while Fe³⁺ occupy both, octahedral and tetrahedral sites; whereas γ-Fe₂O₃ has arbitrarily distributed cation vacancies created at octahedral interstitials resulting in only Fe³⁺ cations.

Other spinel structures, in particular MgAl₂O₄, have been found to completely amorphize by heavy ion irradiation at under 1.5 MeV Xe ion irradiation at 30 K at a dose of 35 dpa [1-3]. This spinel is usually considered “radiation tolerant” due to the ability of the structure to accommodate irradiation-induced point defects, primarily by the inherent structural vacant sites that exist on the cation sublattice that allow for

relaxation mechanisms under irradiation. However, a continuous disordering accumulation of the cation sublattice can lead to order-to-disorder transformation [4]. It is then not surprising that Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ partially amorphized. However, the amorphization resistance of spinel structures has also a dependence on the amount of inversion of the cation sublattice. In general, the higher the amount of the inversion the lower the resistance to chemical and structural disorder [4]. Then it is highly possible that total amorphization of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ would have been observed in the present work if a higher dose was attained.

Yet, a surprising observation of these experiments is the recrystallization process of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ observed post irradiation experiments, as the samples were allowed to warm up back to Room Temperature. DPs were acquired again (Fig. 1) after the samples naturally warmed up to room temperature, which revealed the presence of Bragg spots which were not present in the DPs (Fig. 1). The formation of these Bragg spots indicates the initialization of the process of recrystallization. Interestingly, measurements of the recrystallized Bragg spots indicated they correspond to the same reflections present before irradiation. Furthermore, some recovery of the diffraction contrast in the BFs of the oxides supports the process of recrystallization (Fig. 1). The mechanism of recrystallization at play here is still unclear; since the oxides only amorphized partially, it is possible that the oxide grains may have retained some sort of memory of the grain orientation maybe through the retention of parts of the grain that retained the crystallinity and may have served as a embryos for building back the initial crystal structure.

Acknowledgements: This work was supported as part of FUTURE (Fundamental Understanding of Transport Under Reactor Extremes) and the Department of Energy. The access to the Intermediate Voltage Electron Microscopy (IVEM) facility was supported by Nuclear Science User Facilities (CINR 20-19163).

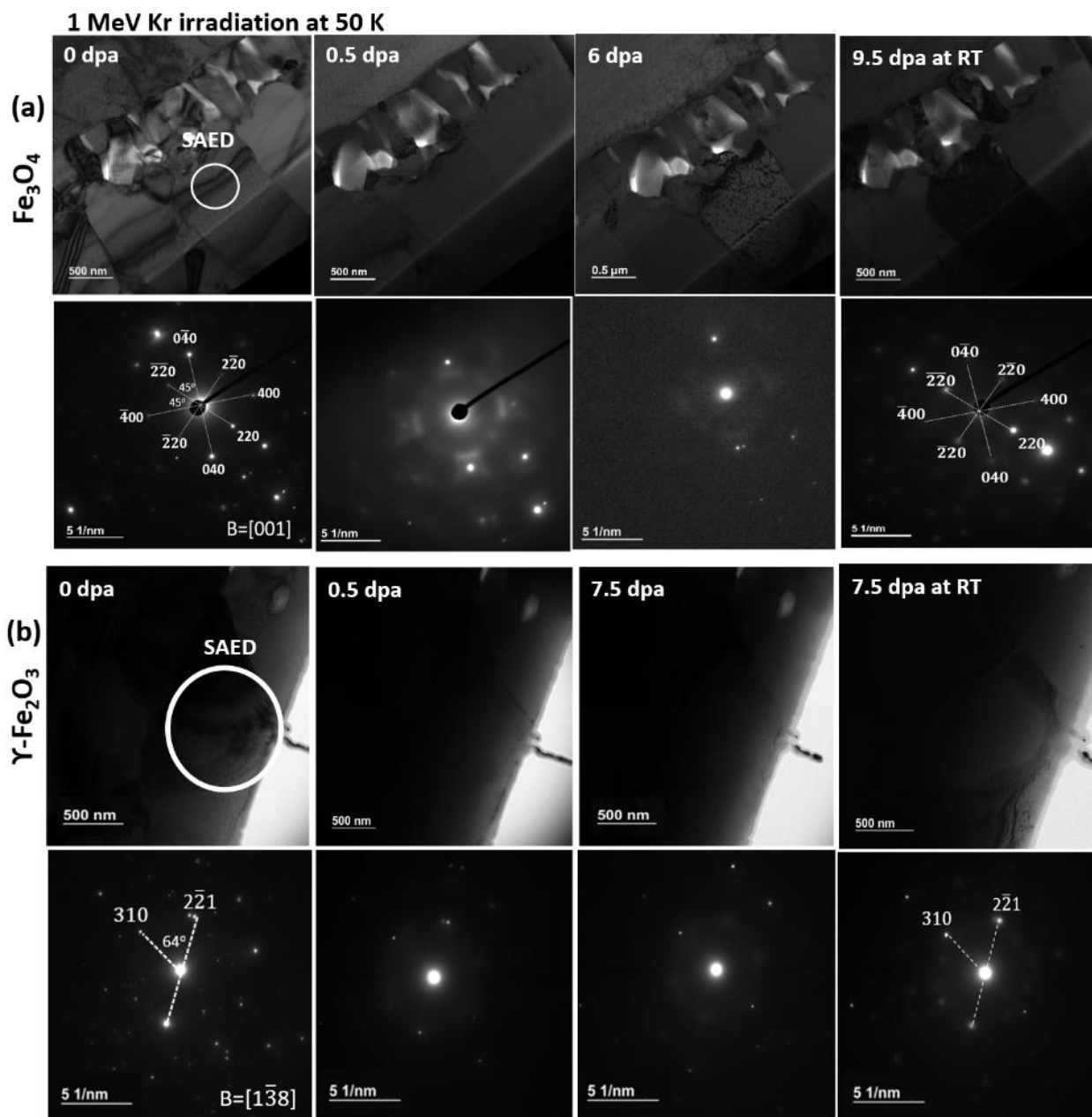


Figure 1. Fig. 1: Bright Field and diffraction pattern micrographs of (a) Fe₃O₄ and (b) γ-Fe₂O₃ irradiated at 50K using 1 MeV Kr ions. The samples were subsequently heated back to room temperature and the diffraction pattern obtained is shown in the last frame.

References

1. K. E. SICKAFUS, N. YU, and M. NASTASI, "Amorphization of MgAl₂O₄ spinel using 1.5 MeV Xe⁺ ions under cryogenic irradiation conditions," *Journal of Nuclear Materials*, **304**, 2, 237-241 (2002).
2. N. YU, R. DEVANATHAN, K. E. SICKAFUS and M. NASTASI, "Radiation-induced phase transformations in MgAl₂O₄ spinel," *Journal of Materials Research*, **12**, 7, 1766-1770 (2011).

3. M. ISHIMARU, Y. HIROTSU, I. V. FANASYEV-CHARKIN and K. E. SICKAFUS, "Atomistic structures of metastable and amorphous phases in ion-irradiated magnesium aluminate spinel," *Journal of Physics: Condensed Matter*, **14**, 6, 1237-1247 (2002).
4. B. P. UBERUGA, M. TANG, C. JIANG, J. A. VALDEZ, R. SMITH, Y. WANG and KURT E. SICKAFUS, "Opposite correlations between cation disordering and amorphization resistance in spinels versus pyrochlores," *Nature Communications*, **6**, 1, 8750 (2015).