

Radiation damage in Fe and Cr Oxides multilayers through in-situ Irradiation

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Outline

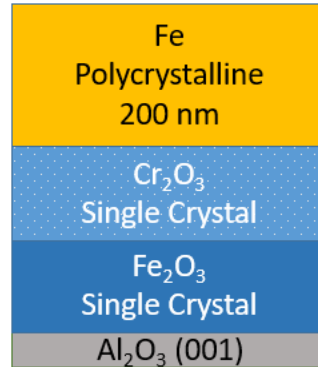
- **Material and Methods**
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- **Results**
 - **Irradiation induced damage in terms of loop formation in the oxide layers**
 - **Phase stability through DP analysis**
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- **Discussion**
- **Conclusions**

Samples: Al_2O_3 - Fe_2O_3 - Cr_2O_3 - Fe Multilayers

Material and sample preparation

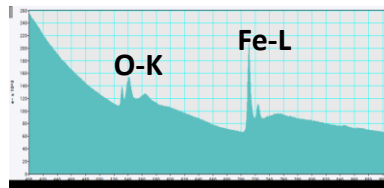
- The multilayer samples were grown by pulse laser deposition at Pacific Northwest National Laboratory (PNNL) for the oxides and by sputter deposition for the Fe layer by LANL
- TEM- sample was prepared by FIB lift-out at Analytical Instrumentation Facility (AIF), NCSU such that they contain regions of different thicknesses.
- EELS spectrum were taken from these samples before irradiation.

Schematic of the sample



Pre-irradiation characterization

EELS spectra of Fe_2O_3



Materials and Methods

Pre-irradiation characterization



- The interfaces $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$ in the multilayer samples were in general coherent and with minor defects.
 - The epitaxial growth between the layers was evidenced in the Fast Fourier.
 - Small expected mismatch in the FFT was observed for $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$.
- For the interface $\text{Cr}_2\text{O}_3/\text{Fe}$, however; the orientation of both crystals is different as indicated by the high-magnified images and the FFT.

Materials and Methods

☐ **α -Fe₂O₃, Cr₂O₃ and Al₂O₃,**

- ☐ These oxides are hcp
- ☐ The oxygen anions are stacked in an ABAB sequence
- ☐ The metal cations (Fe and Cr respectively) occupy two-thirds (2/3) of the octahedral interstitial position for a M/O ratio of 2/3.
- ☐ Each metal cation is coordinated by 6 oxygen anions



In-situ TEM irradiation

➤ Samples were irradiated in-situ at the IVEM-Tandem User Facility at Argonne National Laboratory.

SRIM Profile

- 1 MeV Kr²⁺ ions
- Flux = 6.25×10^{11} ions.cm⁻².s⁻¹.
- Temperature of 300 C and 25 C

SRIM Kinchin-Pease calculation mode assuming an energy of displacement of 40 eV for Fe and Cr, 24eV for Al and 28 eV for oxygen ref

IVEM-User Facility

The maximum dose reached in the sample was about 10 dpa (as calculated in the hematite)

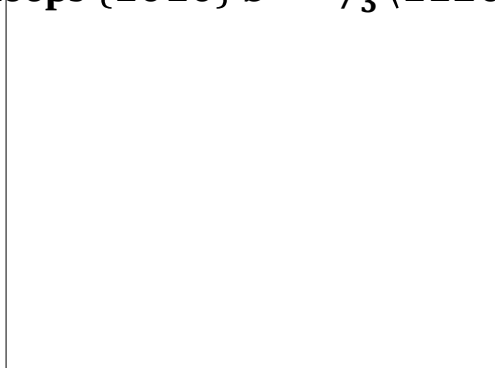
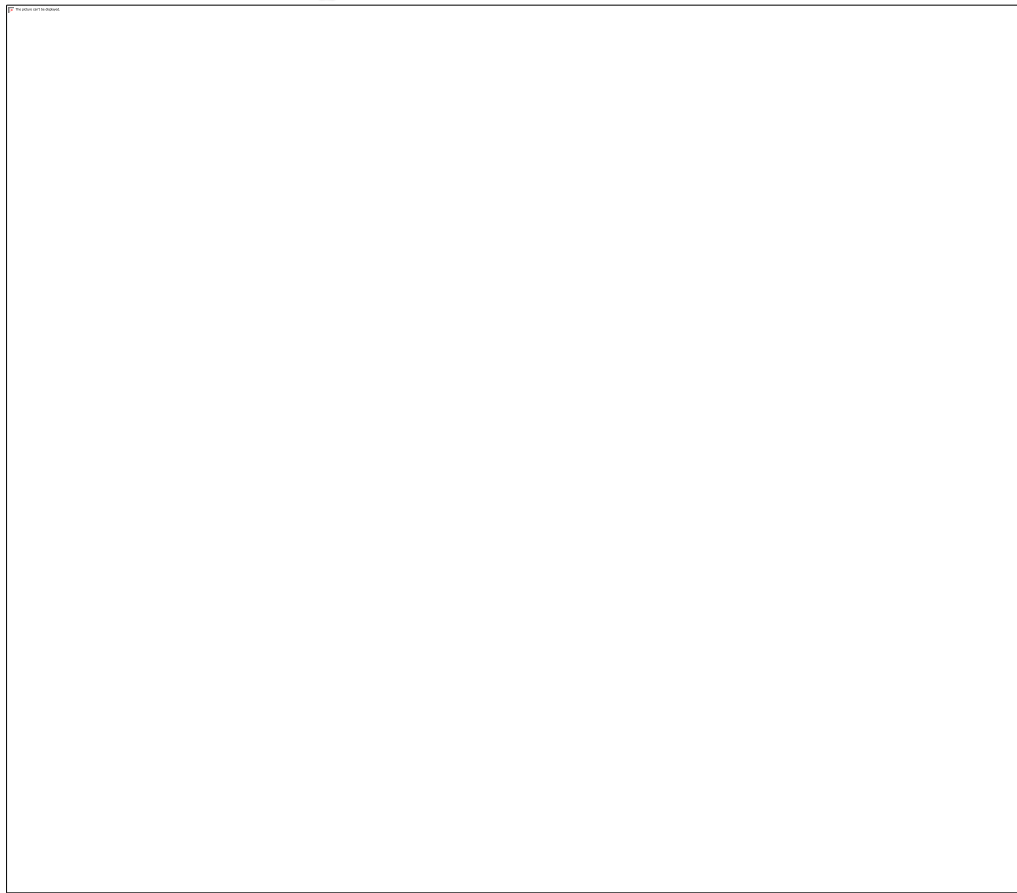
Irradiation induced damage in terms of loop formation

Multilayer irradiated at RT

- Large loops observed in the Cr_2O_3 already at 1 dpa, no resolvable loops was found in Fe_2O_3
- DP present the orientation of the sample
- The average size of the loops that forms in Cr_2O_3 increase in size with dose

$\langle c \rangle$ -loops $\{0001\}$ $b = 1/2 \langle 0001 \rangle$

$\langle a \rangle$ -loops $\{10\bar{1}0\}$ $b = 1/3 \langle 11\bar{2}0 \rangle$



Irradiation induced damage in terms of loop formation

Multilayer irradiated at 300 °C

- Loops readily form in Fe_2O_3 and Cr_2O_3 at 1 dpa
- Loops growth in both oxides with dose
- Loops growth faster in Fe_2O_3 (slope)
- Lower density of loops in Fe_2O_3
- Moire fringes at Fe_2O_3 layer

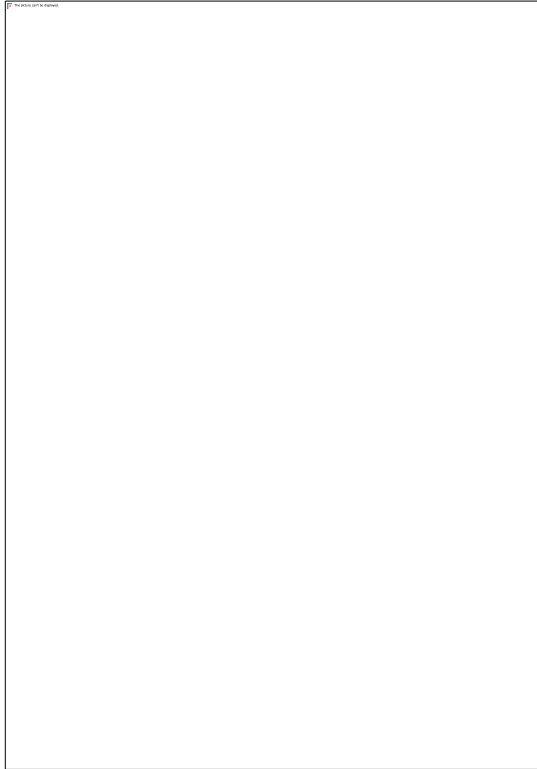
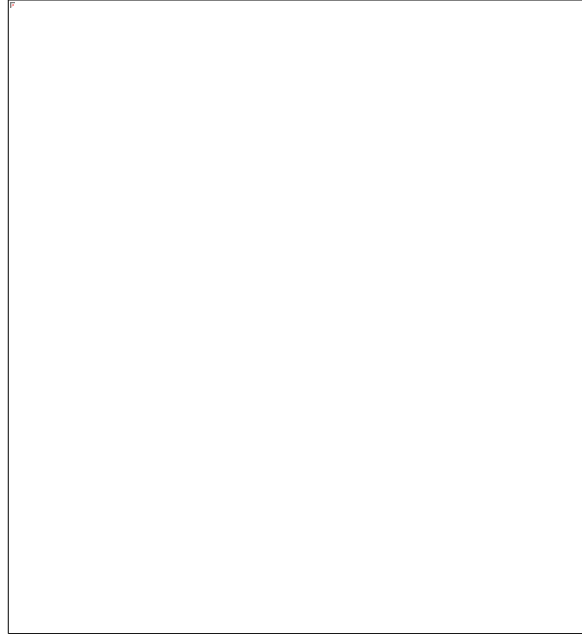
Phase stability through Nano Beam DP analysis

Multilayer irradiated at RT

- The DP corresponding to Fe_2O_3 evolve with irradiation while the DP corresponding to Cr_2O_3 and Al_2O_3 does not present any notable change with an increase in dose.

Phase stability through DP analysis

Multilayer irradiated at 300 °C

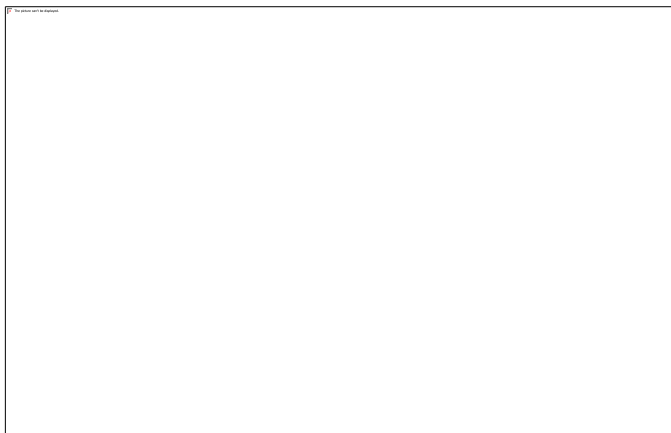


- Change in the DP of Fe_2O_3 with dose
- This observation is indicative of a phase transformation in the hematite layer

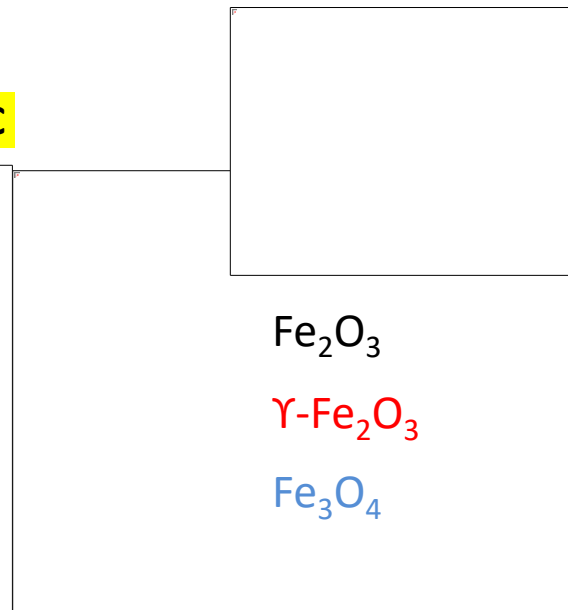


Transformation of Fe_2O_3 under ion irradiation

Multilayer irradiated at **RT**



Multilayer irradiated at **300 °C**



- $\text{Fe}_2\text{O}_3 \rightarrow \gamma\text{-Fe}_2\text{O}_3$ transformation for the sample irradiated at 300 °C and 10 dpa

EELS spectra acquired from reference iron oxide samples. EELS analysis of the Fe 2p L2,3 edge experimentally acquired from pure samples of Fe_3O_4 (blue), $\gamma\text{-Fe}_2\text{O}_3$ (red) and $\alpha\text{-Fe}_2\text{O}_3$ (black). [1]

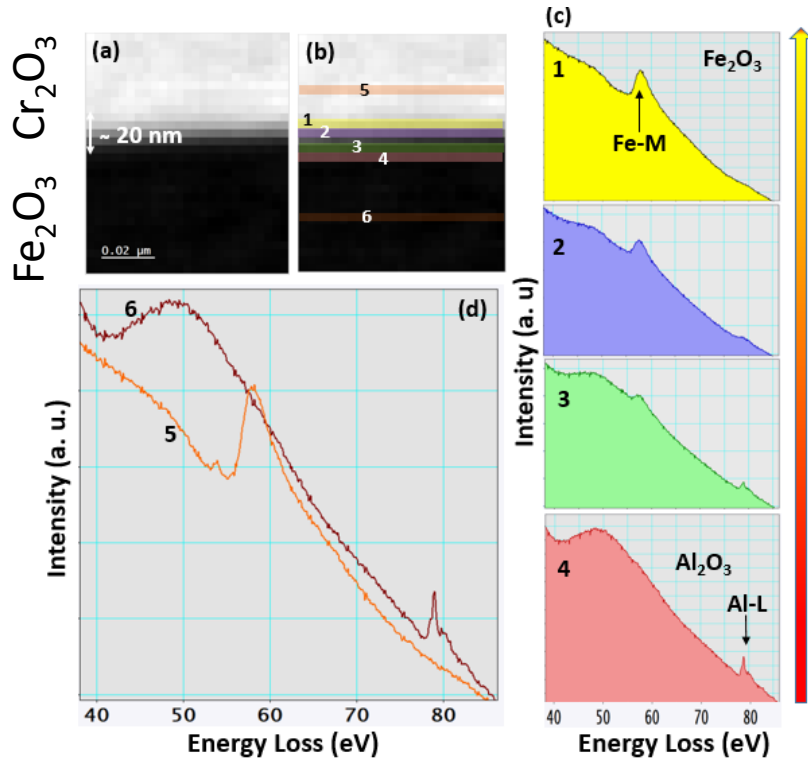
Discussion on the phase change of hematite

- ⇒ A phase change (reduction) of hematite under ion irradiation had been related to the formation of some local nano-porosity along with the formation of voids [2].
 - Neither of these two factors were observed to be present in this study.
- ⇒ The reduction of hematite under ion irradiation in vacuum conditions might happen by a preferentially sputtering of the oxygen atoms which are light atoms
 - $O/Fe \downarrow \equiv$ reduction of Fe_2O_3

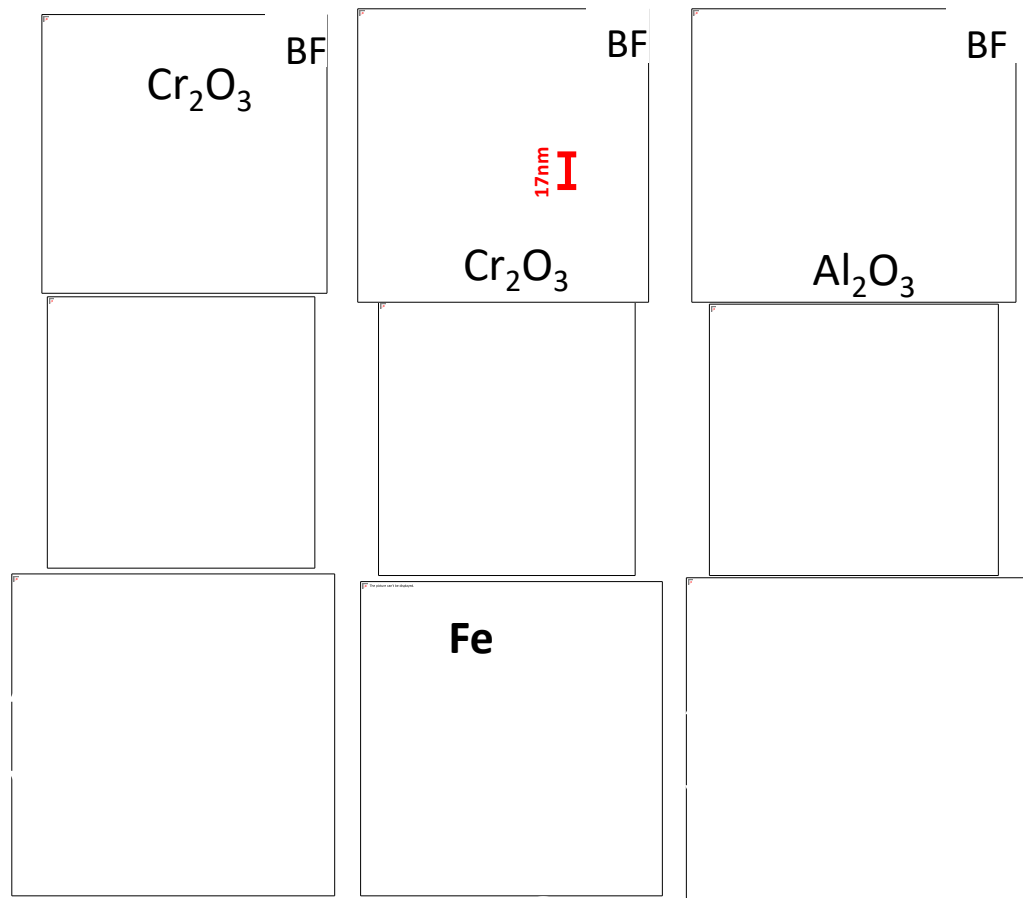
Why the phase transformation of hematite only happened in the sample irradiated at 300 °C while no/limited reduction in the hematite layer was observed for the sample irradiated at RT?

Atomic mixing at interfaces

Multilayer irradiated at RT



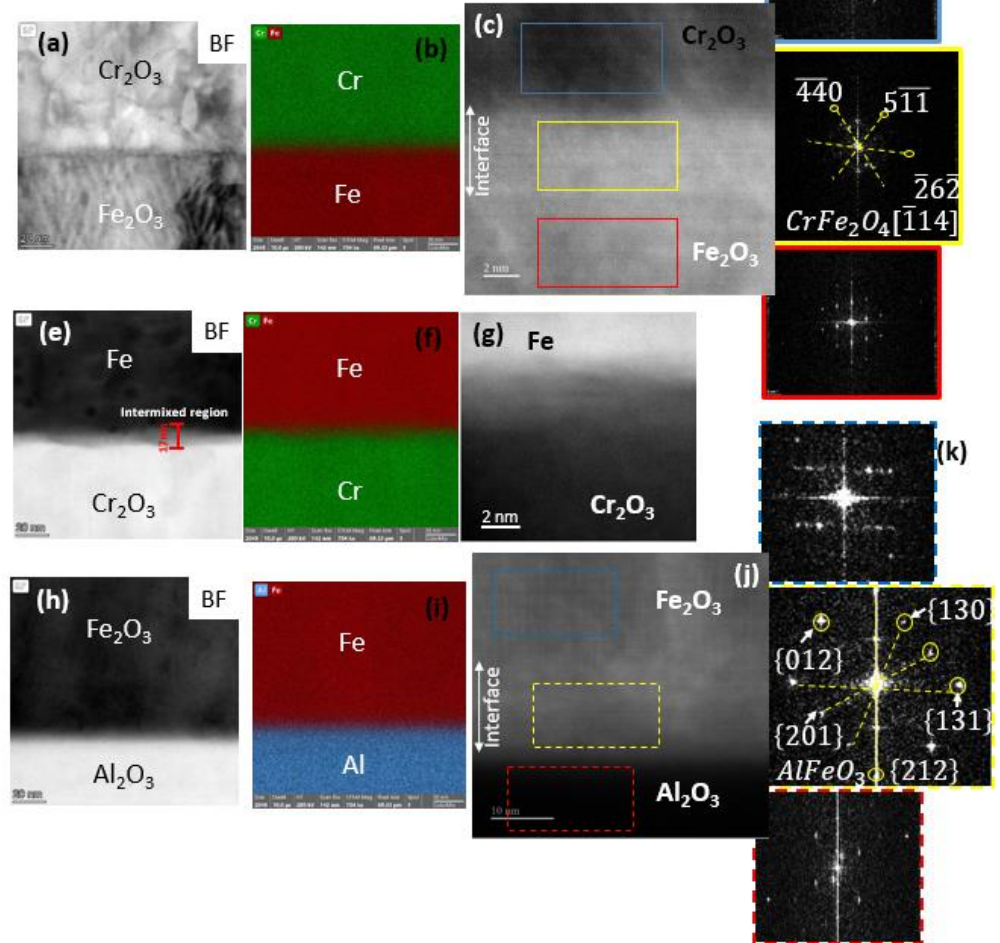
- Atomic intermixing of the layers at the interfaces



Atomic mixing at interfaces

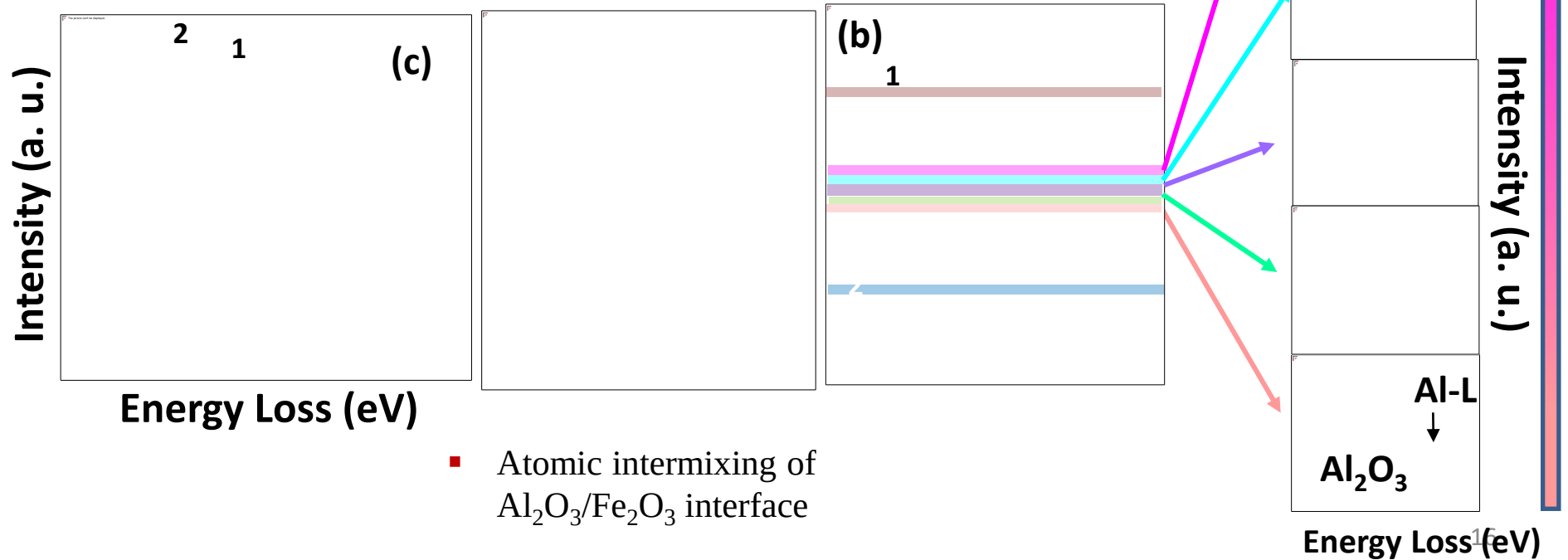
Multilayer irradiated at RT

- Atomic intermixing of the layers at the interfaces
- Formation of stacking fault and nano-twin boundary in the the Fe_2O_3 layer



Atomic mixing

Multilayer irradiated at 300 °C



Discussion

- Atomic mixing (ballistic mixing) happens at the interfaces
 - enthalpy of mixing
 - kinetic energy deposited by the incident particles into nuclear collisions,
 - energy of displacement (E_d)
- Al ions may have a larger probability to be displaced and relocated at the Fe_2O_3 adjoining phase since
 - Al^{3+} is the smallest of the ions at play (0.053 nm)[3]
 - presents the lowest energy of displacement (18-40 eV) [4]

- ⇒ *If more Al^{3+} ions are relocated in the Fe_2O_3 layer compared to the number of Fe^{+3} ions relocated at Al_2O_3 layer, this can propitiate an oxygen diffusion towards the $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ interface to maintain the charge neutrality at this region, leaving more Fe toward the top layer (may consider Fe diffusion towards the top layer)*
- ⇒ The diffusion is more favorable in the sample irradiated at 300° C explaining why the transformation Fe_2O_3 to $\gamma\text{-Fe}_2\text{O}_3$ and CrFe_2O_4 at the Cr oxide/ Fe oxide interface only observed for the sample irradiated at higher temperatures

[3] Weber, W.J., et al., Journal of Materials Research, 2011. 13(6): p. 1434-1484.

[4] Yano, K.H., et al., Chemistry of Materials, 2021. 33(7): p. 2307-2318.

Conclusions

Multilayer Fe/Cr₂O₃/Fe₂O₃/Al₂O₃ samples were irradiated with 1 MeV Kr ions at room temperature and at 300 °C.

- At room temperature and 300 °C dislocation loops form in the Cr₂O₃ layer. These loops increase in size with dose and temperature.
- In the hematite Fe₂O₃ layer, loops were not easily observed at RT unlike at 300 °C where the loops formed readily and grew even larger than in the Cr₂O₃ layer.
- A transformation of hematite Fe₂O₃ into a spinel structure typical of maghemite γ -Fe₂O₃ was observed in the proximity of the interface for the sample irradiated at 300 °C. This reduction could be driven and helped by the atomic mixing happening at the interfaces.

The results indicate that the response of Fe₂O₃ to ion damage is influenced by whether or not the hematite is standing alone or if other oxides of different chemistry are presented at nearby interfaces. When it shares interfaces with oxides of different compositions and properties, atomic mixing (and possible radiation enhanced interdiffusion at higher temperatures) can take place likely driving redistribution of the anions and cations leading to the formation of new phases or reduction of the layer and affecting the loop formation and growth behavior.

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