WHAT IS THE STRUCTURE OF ION TRACKS IN SPINEL?

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$MgAl_2O_3$ spinel is a very well-studied material. Despite this fact, the nanostructure of SHI induced tracks in this material is still not clear. Luminescence studies show broad emission peaks from an unknown source while TEM imaging reveals complex diffraction contrast, suggesting multiple concentric structures. Molecular dynamics simulation predicts various structures depending on chosen interatomic potential, but these structures are not directly comparable to TEM images without simulation of the electron wave propagation through the simulation cell. In this work we follow a combined experimental-theoretical approach to understand the structure of SHI induced tracks in spinel.

Keywords: SHI; spinel; TEM; molecular dynamics; image simulation.

Introduction

Radiation-induced structural modification of $MgAl_2O_4$ remains a popular subject over the last few decades. $MgAl_2O_4$ exhibits improved resistance to neutron exposure as compared to Al_2O_3 [1–2]. However, spinel is sensitive to defect formation through dense electronic excitation with a relatively low threshold energy deposition for ion track formation of about 7.5 keV/nm [3,4]. [5-8] reported on $MgAl_2O_4$ irradiated with 200 MeV Xe and 350 MeV Au. Track morphology was studied in detail using transmission electron microscopy (TEM) and high angular resolution electron channeling X-ray spectroscopy (HARECXS). It was suggested that a phase transformation into a defective rock-salt structure occurs within the track core where Al and Mg ions form antisite defects and strained regions were detected around the defective structure. No amorphization was reported inside the track core even for electronic stopping powers up to 35 keV/nm deposited by 350 MeV Au ions [5]. Detailed analysis of defect accumulation in $MgAl_2O_4$ irradiated with 152 MeV Xe and 2.24 GeV Au ions using absorption spectroscopy and EPR was published by [9]. Defect concentration was shown to increase with fluence up to 2×10^{12} cm^{-2} with no detectable saturation. The authors interpreted their results based on the creation of complexes of defects, including antisite defects and Al^{3+}, Mg^{2+} vacancies. Such point defects are generally invisible to TEM within bulk specimens. On the other hand, molecular dynamics simulation of the relaxation of a system after ion passage offers detailed insight into the production and distribution of single atomic defects provided that a suitable potential is employed. Verification of such potentials is typically done by reproducing macroscopic properties such as thermal conductivity, crystal structure, heat capacity etc. In the present work we compare experimental TEM images of 670 MeV Bi ions in spinel to simulated TEM images of MD supercells to verify the ability of the potential to reproduce similar size and shaped structures as observed through experiments.

Experimental

Single crystal (100) oriented stoichiometric $MgAl_2O_4$ with thickness of 500 μm was purchased from CRYSTAL GmbH. The specimens were irradiated with 670 MeV Bi ions to fluences ranging from 1×10^{11} cm^{-2} to 6×10^{12} cm^{-2} at room temperature at the U-400 FLNR JINR cyclotron, Dubna. Plan view TEM lamellae were produced by FIB lift out technique using an FEI Helios NanoLab 650 dual beam. TEM imaging was performed at 200 kV accelerating voltage in a double Cs corrected JEOL ARM200F. Simulated STEM images were computed from MD supercells using the abTEM python package [10].

Results

Figure 1 shows a bright field TEM image of the irradiated spinel in plan view. Ion tracks are clearly visible, and a separate track core and halo can be distinguished. Contrast reversal of the track halo in regions with varying local orientation (sue to sample bending) shows that the halo is crystalline.

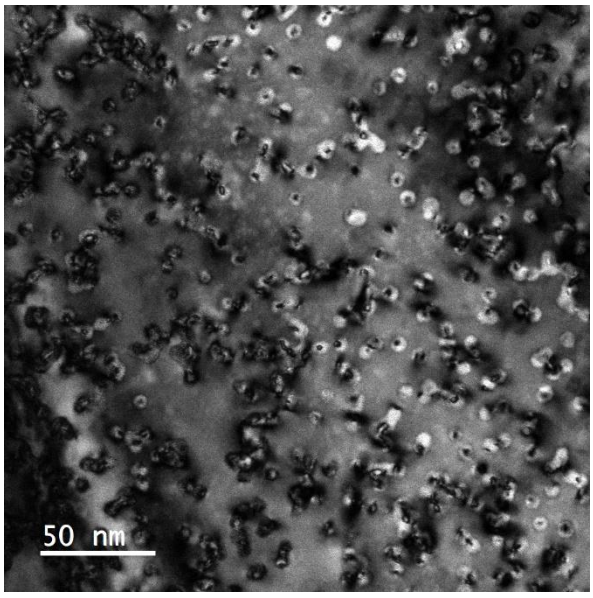

Fig. 1. BF TEM micrograph showing diffracting ion tracks in irradiated spinel.

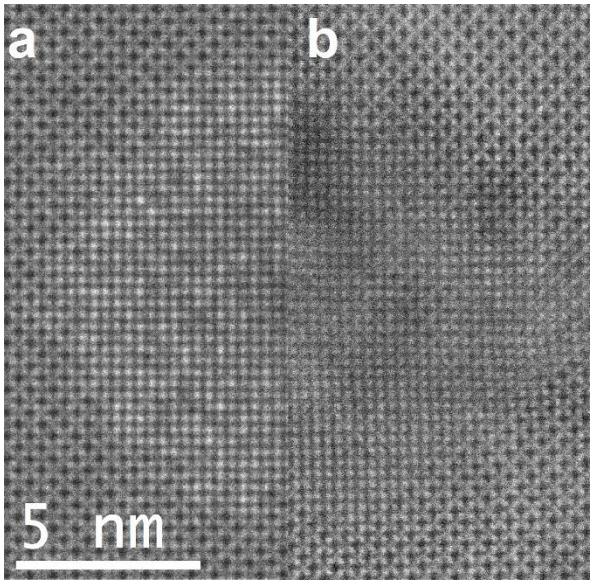

Fig. 2. Experimental (left) and simulated (right) HAADF STEM images of 670 MeV Bi ion tracks in spinel

Figure 2 shows an experimental HAADF image (b) and simulated (a) image from a 14x14x20 nm MD supercell at the same scale for comparison. The track has a diameter of about 6.5 nm in both cases and shows a different ordering than the surrounding matrix. Detailed analysis of the MD output suggests that the main defect is Mg-Al antisite defects. There is a discrepancy in the column intensity within the tracks with the simulated image showing stronger variation in intensity. The thickness of the TEM lamella at the point of imaging was approximately 3x more than that of the simulation box. It is believed that this is the main reason for the reduced contrast in the experimental image as well as several approximations made during image simulation such as infinite potential projections over 0.2 nm slices in order to decrease computation time and a reduced collection angle of 62-166 mrad as opposed to 62-248 mrad experimentally (Maximum scattering angle is limited by the potential extent of 14x14 nm. Furthermore only 2 frozen phonons were considered to further decrease computation time.

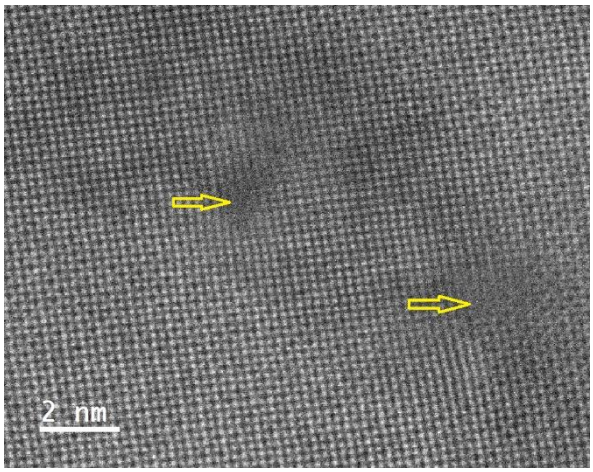

Fig. 3. Edge dislocations within track cores

Figure 3 shows an HAADF image of 2 closely spaced ion tracks. Edge dislocations of opposite burger's vectors (marked by arrows) can be identified within the tracks. Such dislocations were observed in almost all experimental tracks and are believed to be the source of contrast within the track cores in Figure 1. Currently these dislocations are not visible in the MD cells, this might suggest that several nearby impacts are required to generate sufficient shear stresses for

dislocation production although such dislocations were visible experimentally even for 1×10^{11} cm^{-2} irradiation.

Discussion

The structure of experimental and simulated 670 MeV Bi ion tracks in $MgAl_2O_4$ are similar in size and column arrangement. In both cases the (220) diffraction spots suppressed within the track, consistent with simulated XRD spectra of the modified phase obtained by MD. Column contrast is stronger and more irregular in simulated HAADF images but such irregularity is common when insufficient phonons are sampled. experimental contrast is also reduced w.r.t. simulation by means of a thicker specimen of roughly a factor of 3. However, the MD output does not reproduce edge dislocations aligned along the ion trajectory. Such dislocations were near universal in experimental images. TEM analysis of specimens irradiated to 6×10^{12} cm^{-2} shows the formation of sub grains with small angle boundaries and grain boundary amorphization. Such structural evolution is a natural consequence of dislocation production during irradiation. It would be very instructive to simulate partial track overlap in order to see if dislocation production can be observed in the supercells. More detailed TEM image simulation is also required to confirm convergence of image contrast between simulated and experimental images.

Conclusions

TEM and molecular dynamics is a powerful combination to study defects in materials. Contrast in TEM is a complex function of specimen and beam parameters, even for HAADF STEM and single point defects are typically not resolvable in bulk specimens. MD offers an opportunity to study such defects in detail provided the employed potential accurately describes the relaxation dynamics after excitation by a fast ion. By simulating TEM images from MD supercells we further validate the ability of the potential to produce realistic output

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