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MS-5-O-1585 Direct imaging of surface non-stoichiometry in nanoscale magnesium aluminum oxide spinel

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Spinels form a class of mixed-metal oxides with a general composition XY_2O_4, where X and Y are divalent and trivalent cations respectively. The spinel structure is robust against irradiation via fast neutron or ion beams, with minimal formation of defects or dislocations. Such radiation tolerance in spinel structures has yielded applications in the nuclear industry, including use as an inert matrix for fuel containment. Cation mobility and an ability to easily invert antisite defects in the cation sublattice are thought to contribute to the radiation tolerance of spinel and associated retention of an ordered anion sublattice. Direct imaging of the constituent ionic sublattices under neutron or ion-beam irradiation is crucial in understanding the nanoscale response of spinel to irradiation. Here we report on in-situ electron irradiation of spinel crystals and direct visualisation of the atomic structure via aberration-corrected high-resolution electron microscopy. Specimens of spinel prepared by ultramicrotomy were imaged using a JEOL R005 aberration-corrected transmission electron microscope, operating at a beam energy of 300keV and with Cs compensated to -4mm. The surfaces of spinel crystals were studied as a function of dose, with figure 1(a) showing the initial surface structure and figure 1(b) the same following a beam exposure of approximately ten minutes. Initially the crystal surface profile is stepped, with small terrace lengths and short {111} facets showing enhanced surface contrast. Following exposure to the electron beam elongated {111} facets are formed. Figure 2 shows a more detailed view of the structure of the {111} facets in a crystal that has been exposed to the electron beam. The terminating atomic layer deviates from the bulk atomic arrangement and shows enhanced contrast on the {111} facets. The indicated region in figure 2(a and b) has been compared to simulated exit-wavefunctions calculated for a range of crystal thicknesses. Figure 2 (c) shows a simulated exit-wavefunction for crystal thicknesses of 4.6nm and yields a qualitative match of atomic column positions with the experimental data. The location of the more intense of the two surface features is consistent with the positions expected for Mg sites in a {111} surface terminated with Mg. The second less intense column is consistent with either an aluminium or oxygen site. MgO layers have been reported to form when spinel is subject to electric fields under high temperature. Here we confirm via direct imaging, that a non-stoichiometric surface layer exists in nanoscale spinel, with electron irradiation enhancing the formation of elongated {111} surfaces and the Mg ion diffusion that contributes to the surface MgO layer.

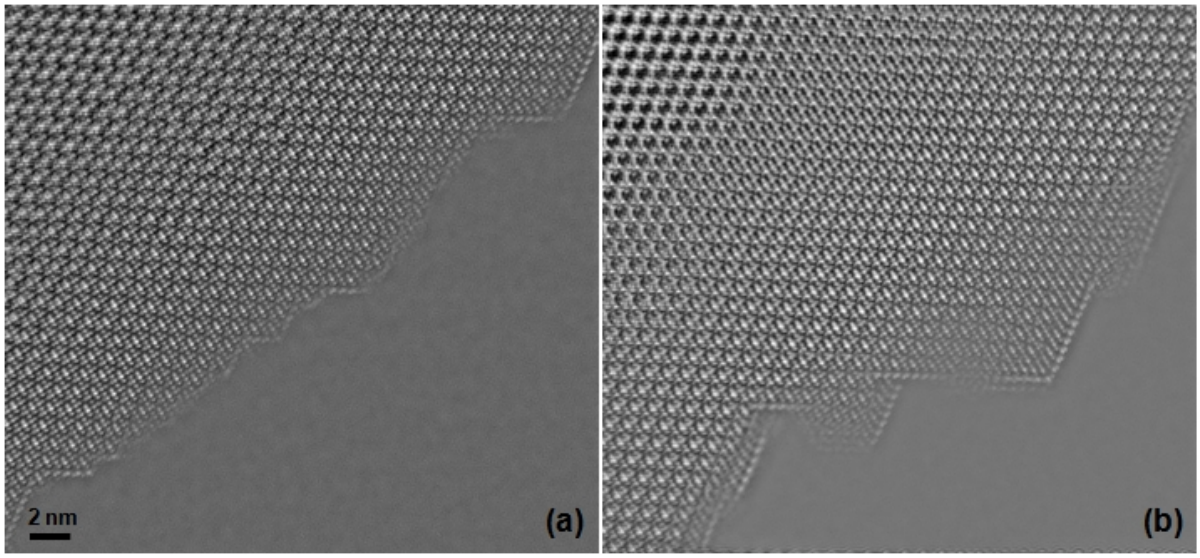

Fig. 1: Phase of the reconstructed exit-wavefunction of spinel specimens. (a) Initial specimen. (b) The same area following approximately 10 minutes of exposure to a 300kV electron beam.

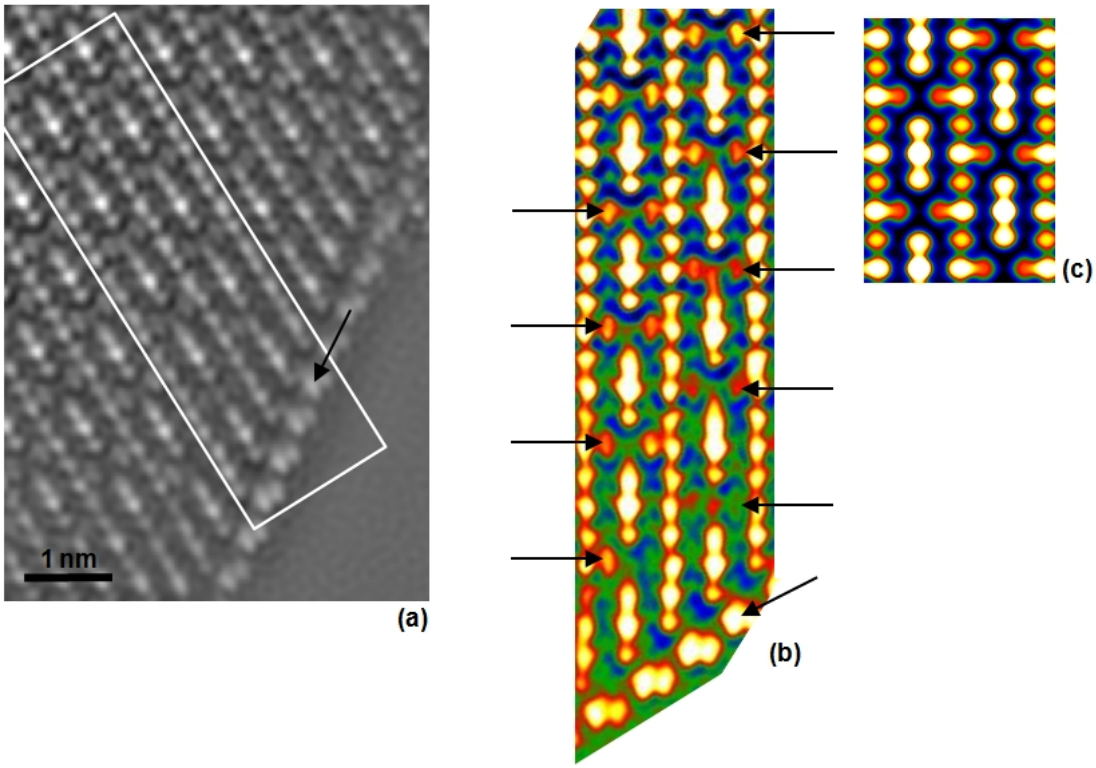

Fig. 2: (a) Enlarged area of figure 1(b). Strong surface contrast is evident as marked with an arrow. (b) False-colour image of the highlighted region in 2(a) with locations of the Mg sites indicated with arrows. (c) Simulated exit-wavefunction phase for a 4.6nm thick section of spinel crystal.