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Damage in yttria-stabilized zirconia by Xe irradiation measured by X-ray diffraction

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Abstract

The evolution of microstructure in yttria-stabilized zirconia under irradiation is examined. YSZ was irradiated with Xe ions at 320 and 450 keV. Transmission electron microscopy confirms the resulting dislocation network with no amorphization as previously reported in literature. Hi-resolution X-ray diffraction was used to further study the ion damage characteristics. θ–2θ scans measure an increasing out of plane lattice constant with dose. Reciprocal lattice maps indicate a strained surface layer, lattice matched to the unirradiated material.

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1. Introduction

Yttria-stabilized zirconia (YSZ) is an oxygen ion conducting material that is widely used for solid oxide fuel cell (SOFC) electrolytes. The yttria doping produces a high oxygen vacancy concentration resulting in substantial transport of oxygen via a vacancy diffusion mechanism. For SOFC applications, high temperatures are required for sufficient ionic conductivity. Devices with YSZ electrolytes typically run at temperatures greater than 800 °C. It is desirable to lower this operating temperature due to thermal expansion and sealing issues as well as to reduce the cell's startup energy.

Ionic conductivity can be modified by microstructural features such as grain boundaries and dislocations. For grain boundaries, different studies have demonstrated an increase [1–3] as well as a decrease [4–8] in ionic conductivity. Around a grain boundary there is a non-equilibrium space charge distribution that affects the vacancy concentration in the vicinity of the grain boundary [9]. This enhancement is particularly pronounced in nanocrystalline materials as the size of this

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space charge region approaches the grain size [3]. At the same time, this effect can be masked by blocking impurities, primarily silica, which will segregate to the grain boundaries [6,10].

Similarly, dislocations may have a strong effect on ion conductivity. In the vicinity of an edge dislocation core there is a local dilatation [11] of the crystal lattice that may increase ion mobility. Furthermore, in ionic crystals, the dislocation core has an associated charge [11] which may alter the oxygen concentration in its vicinity. As dislocations and grains boundaries may have similar effects on the material, one can isolate the dislocation effect by starting with YSZ single crystals, then introducing dislocations into the material.

The microstructure can be modified with ion irradiation. YSZ has a unique resistance to radiation damage and has been widely studied as a fuel matrix material for nuclear applications [12–15]. Under irradiation with heavy ions at high energies, the ceramic will remain crystalline to doses well beyond those at which most ceramics become amorphous. Good radiation damage resistance has also been observed with neutrons, I^+ [16], O^+ [17], Pt^+ [18], Sr^+ [19], Fe^+, Ti^+, Ag^+ [20] and Cs^+ [21] with little amorphization observed except when the implanted ion forms precipitates. A summary of neutron and Xe experiments was given by Sickafus et al. [12].

In particular, YSZ has been shown to remain single crystal under Xe irradiation, even to high doses at high energies [22]. Damage accumulates in 3 stages with increasing dose, measured in a damage parameter, χ, by Rutherford backscattering/channelling (RBS/C) [23]. Ion dose is measured in units of displacements per atom (DPA) where 1 DPA corresponds to each atom in the lattice being displaced one time on average, at the peak damage depth of the material. $\chi = 0$ indicates a perfectly crystalline material. $\chi = 1$ indicates a completely amorphous material.

In stage I damage, below 3 DPA, χ is stable around 0.2. Defects consist of point defects and isolated dislocation loops, as identified by RBS/C [23]. From 3–10 DPA, stage II, the damage increases rapidly to a saturation point. Saturation, stage III, occurs above 10 DPA and the material has χ around 0.7. Damage appears as a dense dislocation network with other long range, interacting defects but the overall crystal structure is maintained. Under Xe irradiation, the material never becomes completely amorphous [22]. A similar microstructural evolution has been observed with Ar irradiation and identified using positron annihilation measurements [24].

In this study, we further examine the irradiated microstructure using triple axis X-ray diffraction (XRD). X-ray θ–2θ scans can provide information about the evolving lattice constants in the irradiated region. Furthermore, reciprocal lattice maps can provide information about the stress state in the irradiated layer of the single crystal [25].

2. Experiment

Single crystal $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ substrates with a (1 0 0) orientation were obtained from MTI Crystal. They were irradiated with Xe ions in a Varian 3500-DF ion implanter at the Ion Beam Materials Laboratory at Los Alamos National Labs. The first set of samples was irradiated with Xe^{3+} to a dose of 5×10^{15} ions/cm^2 at 450 keV, or 23 DPA, under liquid N_2 to maximize the damage in the crystal. These were then heat treated in air at 800 °C for 3 h. The second set of samples was irradiated with Xe^{2+} at 320 keV at room temperature over a range of doses from 1×10^{13} to 1×10^{16} ions/cm^2, or 0.049 to 49 DPA. The implant energies and doses are summarized in Table 1.

Table 1
Sample irradiation summary, apparent out of plane lattice distortion

Sample	Ion	Energy (keV)	Dose	DPA	Distortion (%)
02-1	Xe^{3+}	450	5.0×10^{15}	22.6	
03-1	Xe^{2+}	320	1.0×10^{13}	0.049	0.25
03-2	Xe^{2+}	320	3.2×10^{13}	0.155	0.35
03-3	Xe^{2+}	320	1.0×10^{14}	0.490	0.47
03-4	Xe^{2+}	320	3.2×10^{14}	1.55	0.57
03-5	Xe^{2+}	320	1.0×10^{15}	4.90	0.70
03-6	Xe^{2+}	320	3.2×10^{15}	15.5	0.51
03-7	Xe^{2+}	320	1.0×10^{16}	49.0	0.60
04-1	Xe^{2+}	300	5.0×10^{15}	24.5	