

Structural changes in zircon under α -decay irradiation

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We study the effects of radiation damage on structural changes in zircon. By simulating high-energy recoils, we observe polymerization, shear deformation, and unit-cell expansion, seen experimentally, and point to their origins. We find that the density of the damaged region is very nonuniform, increasing from the depleted core to the densified boundary. The densified boundary is stabilized by the creation of the polymerized phase. Shear deformation and unit-cell expansion arise from the interaction of the damage with the surrounding crystalline lattice.

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Zircon, ZrSiO_4 ($I4_1/amd, Z=4$), has been proposed as a host material to encapsulate highly radioactive materials from dismantled weapons and nuclear waste from power stations, since in nature it contains radioactive ions over geologic times.^{1,2} In these applications zircon is exposed to α irradiation. Computer simulations have been employed to simulate radiation damage effects,³⁻⁶ but the origin and microscopic mechanisms of the most important structural changes in zircon—unit-cell expansion,⁷⁻⁹ large macroscopic swelling,^{8,9} strong shear deformation of the crystalline lattice,¹⁰ and polymerization of SiO_n units¹¹—remain unknown. Here, we perform-molecular dynamics (MD) simulations of highly energetic atomic recoils in zircon. We find that the density distribution in the damaged region is very nonuniform, starting from the highly depleted core to densified boundaries. The polymerized phase, consisting of connected SiO_n polyhedra, is observed in the boundary of the damaged region, stabilizing its densification and distribution of damage within the region. We find that the propagation of the damage causes shear deformation, as well as expansion of the surrounding crystalline lattice.

In an α -decay event, most of the damage inflicted on the zircon structure is produced by the heavy recoil atom that displaces about 4000 other atoms.¹¹ A common practice to simulate the event in MD is to assign one of the atoms a velocity that corresponds to a given implantation energy. Here we simulate events of 30 keV and 70 keV, with the latter being the energy of the recoil ion in the α -decay event.¹² Atomic configurations were equilibrated at 300 K and the Zr atom was given a velocity corresponding to the desired energy. The MD program DL_POLY was used in this study.¹³ We worked with constant stress ensembles, which allow the simulation cell to change its size as well as shape. This was necessary in order to account for possible effects of expansion and shear of the structure. The force field included pair and three-body potentials, which were used in our earlier study³ and found to result in very good agreement with experimental lattice constants, bond lengths and angles,³ as well as phonon-dispersion curves.¹⁴ We also included an additional short-range repulsive interaction which overcomes a well-known problem associated with the Born-Mayer potential at short distances. Configurations contained 192 000 and 375 000 atoms, and a check of finite-size effects was made.

We start by addressing the density variations within the damaged region. We observe that atoms scattered by the recoil initiate their own displacement cascades, producing the damaged region of the ellipsoidal shape, which is close to spherical (see Fig. 1). The atoms in the damaged region have essentially lost their crystalline order. We have calculated the distribution of atomic displacements before and after the radiation event, and found that for a 70-keV event the peak is around $d=1.8$ Å. Note that d lies on the characteristic scale of interatomic distances in zircon (Si-O distance is 1.6 Å, and Zr-O distance is 2.2 Å). In a simplified picture, the displacements of the majority of the atoms in the high-energy event are equivalent to the motion of atoms within shells, with atomic movements occurring outwards within the shell of width d . As atoms move outwards, they activate the atoms in the next shell. The densified boundary is formed when

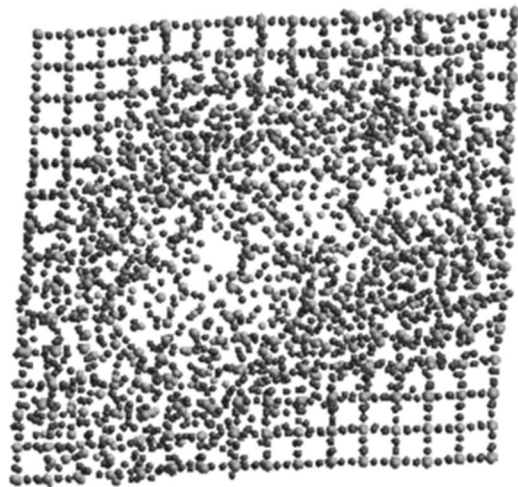


FIG. 1. (xy) projection of the structure damaged by a 30-keV radiation event. Large gray balls represent Zr and Si atoms, and small dark balls represent O atoms. The depleted region in the center and the densified boundary are seen. Strong shear deformation is observed in the crystalline lattice surrounding the damaged region. The path of the recoil atom is directed from the lower left to the upper right corner of the picture. The animation of this event is available in the electronic version of the journal (see also <http://www.esc.cam.ac.uk/movies>).

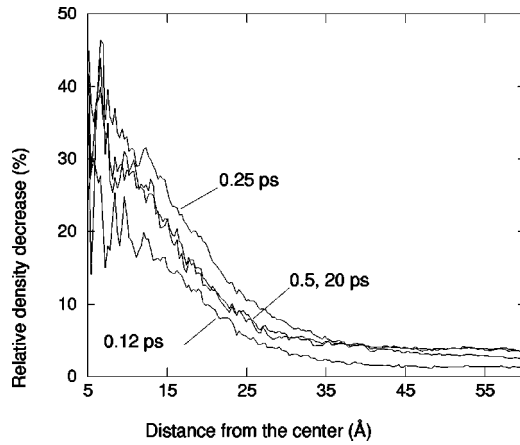


FIG. 2. Relative density decrease as a function of the distance from the core of the region damaged by the 70 keV recoil at various stages of cascade development.

atoms in the last shell possess enough energy to enter the next shell, but not displace it.

We find that the density change in the damaged region is very nonuniform. We locate the point in the damaged region that has the lowest local density and calculate the density change (relative to the ideal crystal), as a function of radial distance from this point. The relative density change is shown at various stages of cascade development in Fig. 2. At 0.25 ps, the density decrease in the damaged region reaches its maximum and then settles at its final value at 0.5 ps, remaining there for longer annealing times of 20 ps at 300 K. For a 70-keV event, the damaged region is located within the sphere of radius of about 35 Å, consistent with the estimate from TEM microscopy⁹ and diffuse x-ray scattering.¹⁰ The region of depleted matter is located within the sphere of about $R_d=25$ Å and has a highly depleted core of $R_c=10$ Å (see Fig. 2). Between R_d and $R_d+\Delta R_{\text{dens}}$, the structure is densified, with ΔR_{dens} of about 10 Å. After the annealing of 20 ps the density in the damaged region changes only slightly, with a small portion of atoms drifting to the highly depleted core of the damaged region. The depleted and densified regions can also be seen in Fig. 1 in the structure damaged by 30 keV.

The net effect of the presence of depleted and densified matter in the damaged region is nonzero, and is seen in the density decrease of about 5% at the radial distance of 35 Å (see Fig. 2), corresponding to the boundary of the damaged region. This is due to the swelling of the sample and will be related below to the unit-cell swelling seen experimentally.⁷⁻⁹

Experimentally, the polymerization of the SiO_n units is observed in recent NMR experiments of damaged zircon,¹¹ and chains of connected SiO_n polyhedra are seen in the simulation of low-energy events.^{3,4} We found that SiO_n polymers are stable on annealing at up to 300 ps and that local densification and polymerization are connected.³ Here, we also observe the connected chains of SiO_n polyhedra in the damaged structure, but find that the densified boundaries around the depleted sphere are particularly populated by SiO_n polymers (see Fig. 3). We explain this by noting that in

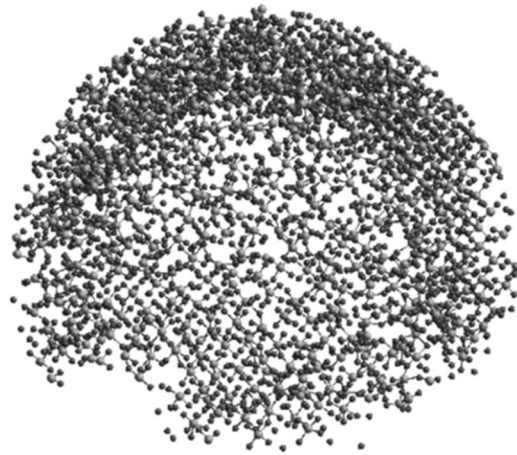


FIG. 3. Highly polymerized sphere in the densified part of the region damaged by 70 keV. Only Si and O atoms are shown.

the crystalline structure SiO_4 tetrahedra are not connected, but in the densified boundary their connection in chains is promoted. Once formed, the chains remain stable, preventing the atomic motion from the densified boundary to the depleted region in the center. The densification of the boundaries and density distribution within the damaged region are thus stabilized by the formation of the polymerized phase.

The degree of polymerization has been found to increase with radiation dose.¹¹ As the radiation dose increases, the overlap of the damaged regions deforms the polymerized boundaries, but from the simulation we conclude that the experimentally observed polymerized phase originates mostly in the densified boundaries of individual damaged regions.

Large shear deformations have been observed in diffuse x-ray scattering studies of irradiated zircon.¹⁰ Figure 1 clearly shows the shear deformation of the rectangular crystalline area around the damaged region. This is also indicated by the nondiagonality of the strain tensor of the simulation box. We observe that the damage, elongated along the direction of the recoil's momentum, causes shear of the surrounding crystalline lattice and unit cells (as is seen in Fig. 1 and in the animation). Shear deformation is preserved after annealing at 300 K for 20 ps, which is considerably longer than the spatial fluctuations in the integration algorithm. The analysis of the structure shows that shear is maximal around the damage, decreasing as one moves away from the damage to undistorted regions of the structure.

Experimentally it is found that the expansion of the unit cell matches the expansion of the sample up to around 5%; for higher radiation doses there is no further expansion of the unit cell, but there is a continued expansion of the sample.^{8,9} This expansion is associated with the presence of the damaged regions in the structure, and reaches 18% at a high radiation dose.^{8,9} In our simulation we obtain an expansion of the sample of around 5%, which is matched by an expansion of the average unit cell. It is clear that our simulations are within the low-dose limit where the expansion of the sample matches that of the unit cell. In the simulations reported here, the unit-cell expansion is associated with the shear deformation.

It is appropriate to speculate on how the correlation between unit-cell and sample expansion is broken at higher radiation doses. It is clear that the primary mechanism is the ejection of atoms out of the event region of the radioactive decay into the surrounding matrix, with the formation of a higher-density polymerized boundary. The depleted region has a low density compared to the matrix, and the polymerized boundary prevents atoms from returning into the depleted region. As a result, it will remain of low density. The polymerized boundary is likely to also remain in its polymerized state. The subsequent structural changes therefore will be controlled by the additional atoms ejected into the matrix. With only isolated damaged regions, these atoms will remain as interstitial defects in the densified boundaries. However, at higher doses damaged regions overlap, and primary recoil, as well as energetic secondary recoils produced in the next event, tend to scatter away from the densified boundary of the damaged region implanted previously. This results in the increase of the size of the damaged region formed by the overlap of radiation events. It is thus the overlap of the damaged regions that yields the local decrease of density, not the damaged region itself, as was assumed earlier.^{8,9} This idea is consistent with recent measurements of the relative portions of crystalline and damaged regions, which showed that the additional swelling kicks in at some critical dose.¹⁵ The details of the overlap process need to be better quantified, and are the subject of ongoing simulation work.

Before concluding, we note that even in the monoatomic solids the damage has been demonstrated to depend on the crystal structure. The structure of the damage is controlled by the creation of clustered interstitial defects and vacancies in metals, while in semiconductors the damage consists mostly of “amorphous” cascades.¹⁶ In both cases no or relatively small density changes associated with the damage are observed. It appears from this work that complex silicates may assume a wider range of structural changes under irradiation.

In summary, we have proposed a picture within which the origins of structural changes in irradiated zircon are explained and related. We have seen that the damaged region consists of a depleted area in the center and a densified boundary. The densification of the boundary and the density distribution within the damaged region are stabilized by the formation of the polymerized phase. We have found that the interaction of the damage with the crystalline lattice causes shear, as well as expansion of unit cells. The origins of structural changes in zircon suggested here may be useful for understanding radiation damage effects observed in other similar materials and ceramics under α irradiation.^{2,8}

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