Damage processes in MgO irradiated with medium-energy heavy ions

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Abstract

The micro-structural modifications produced in MgO single crystals exposed to medium-energy heavy ions (1.2-MeV Au) were investigated using Rutherford backscattering spectrometry in channeling geometry coupled to Monte-Carlo analyses, secondary ion mass spectrometry, X-ray diffraction and transmission electron microscopy. The damage accumulation and the elastic strain variation were interpreted in the framework of the multi-step damage accumulation (MSDA) model. Both build-ups follow a multi-step process similar to that recently observed for ion-irradiated yttria-stabilized zirconia (YSZ) single crystals. However, in MgO, an unexpectedly high disorder level occurs far beyond the theoretical damage distribution. These results strongly suggest that the migration of defects created in the near-surface layer is most likely at the origin of the broadening of the damage depth distribution in MgO.

Keywords: radiation defect; defect diffusion; ceramic; transmission electron microscopy; nuclear reaction analysis; x-ray diffraction.

1 - Introduction

Understanding the formation of radiation defects is a resurgent topic of reflection in the ion-solid interaction research field. In particular, investigations are performed to go further in the comprehension of the materials response to radiation environments in terms of microstructural rearrangements (i.e. defect creation, phase transition, atomic diffusion, etc.). Hence, probing these nanoscopic-scale phenomena allows uncovering the underlying physical reasons of the macroscopic-scale behavior of crystals upon irradiation (e.g. swelling, amorphization etc.). For this purpose, the evolution of residual defects created by cascade events is investigated in the present study in magnesia (MgO). Research on the behavior of ceramics exposed to different irradiation environments has made steady progress in recent years and has been particularly stimulated by the growing interest of ceramics for applications in the nuclear industry. The motivations are particularly driven by specific demands from, on one hand, the detailed design of proposed advanced fission reactors (e.g. Generation IV) and, on the other hand, the urgent situation regarding nuclear waste management for which long-term storage of transuranium elements or actinide transmutation targets are envisioned solutions. In this context, ceramics have been identified as potential candidates for highly durable waste forms due to the stability of their chemical and physical properties under harsh radiation environment [1-2].

Among promising ceramics for transmutation targets, MgO meets the demanding requirements for use in a nuclear context [3], i.e. a low neutron capture cross section, a high thermal conductivity, and a good radiation resistance. MgO is also a likely candidate for neutron reflector in future sodium fast reactors. The simple electronic and atomic structure of MgO in comparison with other complex ceramics (e.g. pyrochlores, spinels) allows considering this material as a model system for a more global investigation of radiation effects in ceramic oxides,

such as the radiation resistance of crystals with the cubic structure [1-3] or the mobility of defects in ceramic oxides highlighted by numerical studies [4-6].

Irradiations with medium-energy heavy ions (namely 1.2 MeV Au ions) were performed to induce radiation damage mainly by nuclear (ballistic) interactions. Microstructural modifications occurring through collision cascades were investigated by the combination of complementary techniques: (a) the irradiation-induced damage accumulation was monitored by Rutherford backscattering spectrometry in channeling mode (RBS/C), (b) the Au-ion depth distribution was measured by secondary ion mass spectrometry (SIMS), (c) the microstructural modifications and elastic strains were studied by high-resolution X-ray diffraction (HRXRD), and (d) the nature of the radiation damage was characterized by transmission electron microscopy (TEM). This coupling of several techniques offers a more comprehensive view of the MgO response to irradiation by scanning the radiation behavior at different length scales. Processes of radiation-induced disordering and the interaction of the defects with the structure are discussed in the aim of better understanding the radiation response of magnesia.

2 – Experimental methods

In this study, <100>-oriented magnesia (MgO) single crystals were used. MgO presents a NaCl-type cubic structure and belongs to the $Fm\bar{3}m$ space group; the lattice parameter is $a_0 = 0.4212$ nm and the density is 3.58 g/cm³. Samples were irradiated at room temperature (RT) with 1.2 MeV Au⁺ ions delivered by the Ion Beam Materials Analysis Laboratory facility

(IBMAL) of the Pacific Northwest National Laboratory (PNNL) at Richland (USA). Ion fluences ranged from a few 0.01 to 100 nm^{-2} . To avoid the channeling of Au ions, samples were tilted by an angle of 7° relatively to the $\langle 100 \rangle$ main axis. The ion flux was limited to a few $0.001 \text{ nm}^{-2}\text{s}^{-1}$ in order to avoid excessive heating of the samples during irradiation. According to calculations with the SRIM2008 program [7], the maximum contributions of the nuclear (S_n) and electronic (S_e) stopping powers to the Au-ion slowing down are $\sim 5 \text{ keV/nm}$ and $\sim 2.4 \text{ keV/nm}$, respectively, and the mean projected range of the Au ions is $\sim 180 \text{ nm}$ (with a range straggling of $\sim 20 \text{ nm}$) (Fig. 1). According to previous molecular dynamic simulations, the threshold displacement energies were taken as $E_{d(\text{Mg})} = E_{d(\text{O})} = 55 \text{ eV}$ [4,8-9].

Irradiated crystals were analyzed by RBS/C with the IBMAL facilities at PNNL and Joint Accelerators for Nano-science and Nuclear Simulation (JANNuS) of the Centre de Sciences Nucléaires et de Sciences de la Matière (CSNSM) at Orsay, France. A $3 \text{ MeV } ^4\text{He}^{2+}$ ion beam was used to entirely probe the irradiated layer of the MgO specimens. The Si detector was placed at a scattering angle of 150° and 165° at the IBMAL and JANNuS facilities, respectively. The detector resolution was on the order of 15 keV , which corresponds to a depth resolution of $\sim 10 \text{ nm}$. Prior to RBS/C analyses, a thin carbon layer was deposited on the sample surface to avoid charging effects. Channeling data were analyzed with the McChasy Monte-Carlo code developed at the National Center for Nuclear Research (NCNR) in Warsaw (Poland) [10].

The depth profiles of implanted Au atoms in MgO crystals were determined by time-of-flight SIMS at the Environmental and Material Science Laboratory (EMSL) facilities of PNNL, by using a IONTOF V spectrometer (IONTOF GmbH, Münster, Germany). A dual-beam depth profile strategy was employed: (i) the sputtering beam was 2 keV Cs^+ with a scan area of $300 \times 300 \text{ }\mu\text{m}^2$, (ii) the analysis beam was 25 keV Bi^+ ions which was rastered at the center of the

sputtering crater with a scan area of $100 \times 100 \mu\text{m}^2$ during data acquisition. The implanted Au profiles were measured assuming a constant sputtering rate that was determined by profilometry measurements. The depth of each square crater resulting from the SIMS measurements was determined by using a Dektak 6 M profilometer with a $12.5 \mu\text{m}$ diamond-tipped stylus that is in physical contact with the sample surface.

XRD measurements were carried out on a Philips X'Pert PRO MRD diffractometer equipped with a standard Cu tube. An intense and monochromatic ($\text{Cu}_{K_{\alpha 1}}$ radiation) beam was obtained by using a multilayer mirror behind the tube followed by a four-crystal monochromator (4xGe220) in asymmetric configuration; the resulting primary-beam divergence was ~ 0.18 arc sec. A $1/8^\circ$ slit was placed in front of the detector to enhance resolution along the 2θ axis. For some measurements, instead of the slit, a three-bounce crystal analyzer (3xGe220) was used to further limit the detector acceptance (this configuration is usually referred to as 'triple-axis configuration'). θ - 2θ scans and reciprocal space maps (RSMs) were recorded in the vicinity of the (400) MgO Bragg reflection ($2\theta \sim 94^\circ$). The formalism used in this work was extensively presented in [11].

Ex situ TEM observations were carried out with a JEOL 2010 microscope operated at 200 kV on selected irradiated MgO samples. Cross-sectional specimens were prepared and thinned down initially by mechanical polishing with diamond discs using the tripod technique down $\sim 20 \mu\text{m}$, and then finally thinning was performed by Ar-ion milling using a Gatan 691 ion polishing system (PIPS) with a low-energy beam of 3 keV (and then of 1 keV to reduce any radiation-induced artefact created by the preparation) at an angle of 5° for both Ar guns down to the electron transparency. Finally, the cross-sectional TEM specimens were coated with a carbon layer with a thickness on the order of 7 nm to avoid charging effects.

3 – Results

3.1. Damage accumulation

Figure 2 displays random and $\langle 100 \rangle$ -aligned RBS/C spectra recorded with a 3 MeV He^{2+} beam on MgO single crystals irradiated with 1.2 MeV Au^+ ions at increasing ion fluences. The random spectrum presents two plateaus (below 1600 and 1150 keV) which are due to the backscattering of analyzing particles from Mg and O atoms, respectively. It is worth noting that the normalized yield from the oxygen sublattice is more intense in the surface region (between 1050 and 1150 keV) owing to the energy of He particles, which is close to 3.04 MeV, the $^{16}\text{O}(^4\text{He}, ^4\text{He})^{16}\text{O}$ resonant scattering energy. The aligned RBS/C spectrum recorded on a virgin single crystal presents a low value of the normalized yield ($\chi_{\min} \sim 0.03$), which attests to the good quality of the MgO single crystals. The $\langle 100 \rangle$ -aligned spectra recorded on irradiated crystals exhibit a dechanneling bump around 1450 keV that increases with increasing ion fluence and saturates at an ion fluence of 2.1 nm^{-2} (not shown on the graph for clarity purpose, but the corresponding damage depth profile is presented in Fig. 3). At higher fluences, the dechanneling bump moves toward lower energies with a nearly constant value of the normalized yield.

Channeling data were analyzed with the McChasy Monte Carlo simulation code [10]. This code allows obtaining a quantitative assessment of the depth distribution of the atomic disorder inside the crystal assuming that, at a given depth, a fraction of lattice atoms (called displaced-atom fraction - f_D) are randomly displaced from their initial crystalline lattice site. Fits (represented in solid lines in Fig. 2) with the McChasy code of the RBS/C experimental data provide f_D for both Mg and O sublattices. Figure 3 displays the damage depth distributions in the Mg cationic sublattice; the O anionic sublattice follows a similar evolution. Upon irradiation, the

shape of the damage profiles exhibits important modifications. Below 2.1 nm^{-2} , the maximum of f_D (f_D^{max}) stays located around 120 nm, and it increases with increasing ion fluence (up to ~ 0.6). Above 2.1 nm^{-2} , f_D^{max} shifts in depth (up to $\sim 500 \text{ nm}$ at a fluence of 100 nm^{-2}), and its level first increases with increasing fluence (up to ~ 0.75 at 5 nm^{-2}) and then slowly decreases. It is worth mentioning that MgO crystals do not amorphize but remain crystalline over the whole fluence range.

Figure 4 shows the damage accumulation build-ups extracted from RBS/C data at two different depths in the crystals, i.e. 120 and 400 nm. In this figure, f_D is plotted as a function of the Au fluence (Fig. 4(1)) or of the number of displacements per atom (dpa) calculated with the SRIM program (Fig. 4(2)). At 120 nm, the damage build-up occurs in three well-defined steps. The first step (below 0.4 nm^{-2} or 0.07 dpa) exhibits a very low disorder level (f_D is lower than 0.05); then the damage sharply increases during step 2 to reach $f_D \sim 0.6$; the third step takes place above 3 nm^{-2} or 0.4 dpa where a decrease of f_D is observed. At 400 nm, the damage (step 2) also starts to increase above $\sim 0.4 \text{ nm}^{-2}$, but two main differences may be noticed as compared to the behavior observed at 120 nm: 1) the increase is less abrupt, and 2) the onset of step 2 occurs at a two orders of magnitude lower in dose on the dpa scale. The damage build-ups shown in Figure 4 were interpreted in the framework of the multi-step damage accumulation model [12], and the results are discussed in the next session.

Figure 5 presents the results of SIMS measurements for the determination of the depth distribution of Au atoms in MgO samples irradiated at fluences of 2.1 and 50 nm^{-2} . We observe that the maximum of the Au atom distribution is located at a depth of about 160 nm for both samples. It is interesting to note that the distribution of the damage recorded by RBS/C extends

deeper (up to 400 nm) in the samples whereas the maximum of the ion Au distribution is relatively stable close to the surface.

3.2. Microstructural modifications

Figure 6 shows θ - 2θ scans recorded in the vicinity of the (400) Bragg reflection for virgin and ion-irradiated MgO single crystals. The intensity (in logarithmic scale) is plotted as function of the 2θ diffraction angle (bottom axis) and the elastic strain in the direction normal to the sample surface, ϵ_N (top axis). All spectra exhibit a narrow and intense peak at a diffraction angle around 94.05° arising from the virgin part of crystals. Indeed, the X-ray penetration depth extends over a few microns, so that both irradiated and virgin parts of the crystals are probed. This signal is used as a reference to calculate the radiation-induced elastic strain. The spectra recorded on irradiated crystals display an additional signal, located on the left side of the peak corresponding to a virgin sample, that spreads toward lower diffraction angles. It can be noted that this signal exhibits a particular shape (it is not a single Bragg peak) that indicates that the out-of-plane lattice parameter in the damaged layer is not constant over the whole irradiated thickness. In the present study, the focus is primarily on the maximum strain level that can be obtained from the position of the last peak position in the irradiated-layer signal [11]. It is hence observed that the irradiated layers exhibit a larger out-of-plane lattice parameter than the virgin MgO one. The corresponding positive maximum elastic-strain level increases with increasing fluence up to 0.4 nm^{-2} where it reaches $\sim 0.65\%$. Above this fluence, a broad diffuse signal is recorded, revealing a partial relaxation of the elastic strain. This statement is corroborated by reciprocal space maps recorded at 0.4 nm^{-2} (Fig.7a) and at 3 nm^{-2} (Fig.7b): while the scattered intensity is confined along the normal component of the scattering vector (i.e. along K_N) in the

former case, a pronounced diffuse scattering signal is observed in the latter, suggesting the formation of extended defects that may have induced a strain relaxation, as already observed in other materials [13].

3.3 Nature of radiation defects

Figures 8 display TEM images of MgO specimens irradiated at 2 nm^{-2} (Fig. 8 a,b) and 20 nm^{-2} (Fig. 8 c,d) in different regions of samples. At the irradiation fluence of 2 nm^{-2} , the image in Fig. 8-a was recorded at a depth close to the surface (around 120 nm) corresponding to the highest level of damage measured in the RBS/C experiments (Figs. 3 and 4) and shows a clear network of dislocations. At a larger depth (around 400 nm), isolated and smaller dislocation loops are observed (Fig. 8-b). At a higher ion fluence of 20 nm^{-2} , the TEM image recorded at a depth of 120 nm (Fig. 8-c) exhibits a network of large dislocations linked to each other surrounding quite large zones with no detectable defects. This particular microstructure explains the reduction of the disorder level measured by RBS/C (see Figs. 3 and 4). In contrast, at 400 nm a highly damaged region is observed (Fig. 8-d) consisting of a network of dislocation loops that induces the large increase of f_D exhibited on Figs. 3 and 4. Kinoshita *et al.* have demonstrated the formation of interstitial dislocation loops under electron irradiation with an energy of 1MeV [14]. Moreover, Sonoda *et al.* have confirmed the formation of dislocation loops with similar interstitial nature upon irradiation with different types of ions [15]. These results led us to assume the formation of similar interstitial dislocation loops in our samples.

4 – Discussion

4.1. Phenomenological description of the damage accumulation process

The damage build-up obtained in MgO over the whole depth range may be interpreted in the framework of the phenomenological Multi-Step Damage Accumulation (MSDA) model (see solid lines in Fig. 4) [12], which relies on the assumption that the damage accumulation results from a series of atomic rearrangements (steps) triggered by microscopic and/or macroscopic events. Each new defect configuration corresponds to a new step of the damage build-up that occurs when the current configuration is destabilized by the damage accumulation. For the interpretation of the irradiation processes, the MSDA model uses a direct-impact description which assumes that each ion impact, leading to the formation of collision cascades, modifies the atomic configuration of a given volume of the irradiated solid. It is worth mentioning that the MSDA is particularly relevant to describe the damage formation that is driven by discontinuous processes where different configurations of defects are observed (e.g. irradiation of cubic zirconia), while other phenomenological models (Direct-Impact/Defect Simulated - DI/DS, Direct Amorphization - DA) are well suited for the description of phase transitions (e.g. amorphization) or damage build-ups occurring continuously in a single-step process (e.g. irradiation with swift heavy ions [16-17]). The multi-step transformation process assumed in the MSDA model is described by the following equation:

$$f_D = \sum_{i=1}^{n-1} \left\{ f_{D,i}^{sat} G [1 - \exp(-\sigma_i(\Phi - \Phi_i))] \prod_{k=1}^n [\exp(-\sigma_{k+1}(\Phi - \Phi_{k+1}))] \right\} + f_{D,n}^{sat} G [1 - \exp(-\sigma_n(\Phi - \Phi_n))] \quad (1)$$

where $f_{D,i}^{sat}$ is the level of damage at saturation, n is the number of steps required for the achievement of the total disordering process, Φ_i is the threshold ion fluence of the i^{th} step, and σ_i

the disordering cross-section at the i^{th} step. G corresponds to the Heaviside function H multiplied by its argument. The values of the parameters calculated from the fits to the damage build-ups at 120 and 400 nm using the MSDA model are summarized in Table I. It has to be noted that the use of the MSDA model is well adapted to interpret the data recorded at 120 nm where defects are directly generated by the irradiation process. Nevertheless, the model was also used for describing and comparing the damage created at 400 nm where diffusion phenomena seem to play an important role in the damage build-up (see further discussion section 4.2).

The interpretation of the various steps of damage accumulation presented in Figure 4 relies on the XRD and TEM results shown in Figures 6 to 8 and also on previous data obtained on cubic yttria-stabilized zirconia (YSZ) [16]. Point defects and small defect clusters, which induce a low disorder level in RBS/C but a significant strain level, are likely formed during the first step (at fluences below 0.4 nm^{-2}). The sharp increase of the damage yield occurring during step 2 (above 0.4 nm^{-2}) corresponds to the formation of dislocation loops (Fig. 8-b), which progressively merge into a dense network of dislocations (Figs. 8-a and 8-d); this process induces a plastic relaxation of the elastic strain. The surprising decrease of the disorder level exhibited at 120 nm during step 3 (above 3 nm^{-2}) may be attributed to the reorganization of the tangled and disordered dislocations into a network of long dislocations acting as defect sinks where small migrating defects are trapped, and therefore inducing the formation of slightly damaged regions (see Figure 8c).

Partitioning of the damage accumulation build-up into several stages corresponding to specific defect configurations is a characteristic feature of ion-irradiated oxides that do not undergo amorphization [13, 18]. In that respect, Figure 9 compares (in dpa scale) the damage and strain build-ups obtained in MgO (present work) and in YSZ [13] which is typical of fluorite-

type oxides (like the nuclear fuel UO_2 [19]). It should be noted that the damage kinetics of MgO displayed in Figure 9 corresponds to the defect build-up at 120 nm. At this depth, the irradiation process is similar in MgO and YSZ, which permits a comparison between the two materials. In both cases, the damage build-ups (f_D versus dose expressed in dpa) obey a three-step process and the strain build-ups (ϵ_N versus number of dpa) obey a two-step process (the third step being undetectable in XRD experiments), with rather similar magnitudes (the maximum of both f_D and ϵ_N is a bit higher for MgO than for YSZ). Regarding the strain build-up (ϵ_N vs. dpa), it must be noted that in order to compare the strain level in both MgO and YSZ, the mechanical behavior of the crystals upon ion irradiation has been modeled using linear elasticity to account for the effect of the elastic properties of the materials, as extensively described in [20]. TEM experiments show that rather similar defects are created in both materials at the various damage steps: small defect clusters during step 1, dislocation network during step 2 and long dislocations during step 3. However, the dose in dpa at which the onset of step 2 occurs is shifted by two orders of magnitude (Φ_2 values in Table 1: 7-8 dpa for YSZ and 0.07-0.08 dpa for MgO) for both f_D and ϵ_N . The same difference is observed concerning step 3 for f_D (it occurs at ~ 30 dpa for YSZ and ~ 0.4 dpa for MgO).

Another important difference between the damage production in MgO and YSZ is the rather large shift of the damaged layer towards greater depths observed in MgO at high ion fluence (or number of dpa) that does not occur in YSZ. Figure 10 illustrates this result by representing the relative variation with the fluence of the depth at which the damage is maximum (R_D) for both YSZ [13] and MgO (this work). The data clearly show that no shift of the damage distribution occurs in YSZ (up to 50 nm^{-2}), whereas a significant increase of the thickness of the damaged layer occurs in MgO above $\sim 1 \text{ nm}^{-2}$ (see Fig. 3). It is interesting to note that this

phenomenon may be more or less pronounced depending on the crystallographic orientation of the samples relatively to the incident ion beam [21].

4.2 Damage depth distribution

As it was already mentioned in section 4.1, the main discrepancy between the damage accumulation processes occurring in MgO and YSZ relies on the fact that, in MgO, the kinetics of damage accumulation significantly varies with the depth. For instance, according to Figure 4 and to the parameters extracted from the fits of RBS/C data (Table I), the second step of damage accumulation develops faster in fluence at 120 nm than at 400 nm. Actually the saturation values of f_D at the end of the second step are almost identical in the two regions, but the fluence at which this saturation occurs is about one order of magnitude lower (in fluence scale) at 120 nm than at 400 nm ($f_{D2}^{120}=0.63$ at $\phi=3 \text{ nm}^2$ and $f_{D2}^{400}=0.66$ at $\phi=30 \text{ nm}^2$). In addition, the value of σ_2 strongly decreases with depth ($\sigma_2^{120}=1.6\pm0.6 \text{ nm}^2$, $\sigma_2^{400}=0.1\pm0.04 \text{ nm}^2$), indicating that different damage accumulation mechanisms operate in the region close to the surface and at larger depth. It has to be noted that the equivalent amount of disordered material observed close to the surface and deeper in the sample corresponds to a similar nature of defects that consist in a dense network of dislocations (Fig. 7-a and 7-d).

The results are consistent with the fact that, in the near-surface layer (up to 200 nm), incident Au ions highly interact with target atoms and induce important damage directly through collision cascades (Fig. 1). Conversely, at 400 nm, i.e. beyond the implantation peak ($R_p \sim 200 \text{ nm}$), according to simulations carried out with the SRIM code [7], the probability of collisions between Au ions and target nuclei, leading to sufficient energy transfer to displace target atoms to such large depths, is rather low. It should be noted that the dpa scale was

calculated with the SRIM program (assuming same threshold displacement energies of 55 eV for both Mg and O elements) and allows an estimation of the defect concentration induced by nuclear energy loss (Fig. 1). The dpa level at 400 nm, calculated from knock-on Mg and O atoms (KA), is roughly two orders of magnitude lower than that observed in the layer implanted with Au ions (Fig. 5), although an increase of the damage is experimentally measured up to 700 nm (Figs. 2, 3 and 8). In addition, at 120 nm, the damage build-up starts at about 0.1 dpa as compared with the 0.001 dpa observed at 400 nm. These results point out the clear discrepancies between the two considered damage build-ups, labeled "near-surface" and "deep". This huge difference evidences the fact that the radiation process alone, materialized by the dpa scale, is the main cause of the "near-surface" damage formation, whereas defect migration is likely at the origin of the "deep" damage build-up.

This assumption is supported by previous experimental and theoretical studies that have highlighted the diffusion of defects in MgO [22-24]. In particular, some computational works have been performed for determining the defect energetics in MgO, using classical methods with selected empirical potentials [4- 6, 25] but also ab initio techniques such as the density functional theory [26, 27, 28]. All studies point out that (Mg and O) vacancies are immobile in MgO at RT, in term of thermodynamic considerations, with migration energies of a few electronvolts. On the contrary, the migration barriers for both Mg and O interstitial defects were found to be low, allowing defect migration at RT. This is particularly true for point defects, which have been demonstrated to be predominantly formed during collision cascades [4, 5, 25]. For instance, migration barrier values of 0.32 eV and 0.40 eV for O and Mg single-interstitials [4, 5, 25] and between 0.06, 0.33 and 1.04 eV for O^- , O^{2-} and O^0 single-interstitials [28] were computed. In [4, 5, 25], di-interstitials and tri-interstitials were also found to be mobile at RT, but the migration

barrier increases with the cluster size making them immobile at RT, except for the peculiar hexa-interstitial cluster with a diffusion barrier of 0.24eV. Therefore, during irradiation of MgO at RT, point interstitial defects and very small defect clusters (di- and tri interstitials) as well as larger defect clusters (hexa-interstitials) may migrate, and their annihilation with vacancies or aggregation with other interstitials depends on the complex electric field created by the defects present in their vicinity [25, 4, 5]. The binding energy per atom in a cluster increases with increasing the cluster size (up to ~5 eV per atom for a 10-atom cluster), explaining why large defects are stable. These high values of binding energies and the clustering of the pre-cited defects eventually lead to formation of interstitials dislocation loops [14, 15] which are primarily formed at the damage peak where the defect density is the highest. With increasing fluence, the migration of isolated small defects continues in particular towards those deep regions, so that the probability to (experimentally) observe defects well beyond the SRIM-predicted dpa distribution tail increases.

This phenomenon may be also favorized by the incoming highly-energetic Mg and O atoms occuring beyond the damage peak and leading to creation of small amount of deep damaged regions, where numerous point defects are gathered. The probability of such energetic atoms is rather low [7] but statistically enough to induce small amounts of disordered local zones. These regions may consist in highly reactive centers, since the local charge neutrality is disrupted by the presence of a sufficient quantity of vacancies and interstitials created which may react with the (pre-cited above) radiation-induced interstitial clusters and promote their diffusion toward the depth. These features would provide an explanation of the progressive and continuous extension of the damage deep towards the bulk of the material.

As a final remark, it should be noticed that, in MgO, two distinct damage accumulation mechanisms are observed depending on the depth and leading to a similar level of damage: (i) direct damage creation close to the surface of crystals arising from ballistic processes and (ii) migration of defects deeper in the crystal. These features may account for the main discrepancy between the behavior of MgO and YSZ upon irradiation. In particular, a huge energy barrier for defect migration in YSZ has been predicted by MD calculations [29], which may explain why no displacement of the disorder profile is observed in zirconia.

5 - Conclusion

The damage processes occurring in MgO single crystals exposed to medium-energy heavy ions (1.2-MeV Au) were investigated by coupling the RBS/C, XRD, SIMS and TEM techniques. The damage accumulation and the elastic strain evolve following a multi-step process that was interpreted in the framework of a phenomenological model (MSDA) describing the overall behavior of materials upon irradiation. According to this model, each step corresponds to the formation of a specific defect configuration. A similar relationship between the damage and the elastic-strain build-ups was already observed in YSZ, indicating that a damage evolution occurring in several steps is typical for many non-amorphizable oxides.

In ion-irradiated MgO crystals, an unexpectedly thick damaged layer, extending far beyond the theoretical damage distribution, was also highlighted, contrarily to the results obtained for YSZ. This effect was interpreted as being due to the large mobility of interstitial defects in MgO. Hence, in this material the damage mechanisms depend on the depth: the "near-surface" damage is mainly induced by direct displacements of target atoms through collision events, whereas the "deep" damage is essentially due to a migration phenomenon.

Finally, the results obtained in this work have to be considered for the selection of materials dedicated to advanced fission reactors and for the long-term storage of transuranium elements.

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Table captions

Table I: Values of the parameters extracted from the fits to RBS/C data of Figure 4 by using the MSDA model (equation 1) [12].

Figure captions

Figure 1: Color on line. Variation with depth of S_e , S_n , f_D , number of dpa and implanted Au ions at a fluence of 1 nm^{-2} for MgO irradiated with 1.2-MeV Au ions.

Figure 2: Color on line. RBS spectra recorded in random (crosses) and $\langle 100 \rangle$ -axial (other symbols) directions on MgO single crystals irradiated with 1.2-MeV Au ions at increasing fluences. The energy of He ions is 3 MeV. Solid lines are fits to experimental data using the McChasy MC code [10].

Figure 3: Color on line. Depth distributions of the fraction of randomly displaced atoms in the Mg sublattice of MgO single crystals irradiated with 1.2-MeV Au ions at increasing ion fluences.

Figure 4: Color on line. Variation of $f_D^{\max}$ at two different depths: (1) 120 nm (blue circles) and (2) 400 nm (red triangles) versus the Au ion fluence (top) and the number of dpa (bottom) at corresponding depth. Solid lines are fits to experimental data using the MSDA model [12]. The letters on the graphs refer to the TEM micrographs shown in Fig. 6.

Figure 5: Depth profiles (measured by SIMS) of Au ions implanted into MgO at 1.2-MeV at fluences of 2.1 nm^{-2} (crosses) and 50 nm^{-2} (circles).

Figure 6: Color on line. $(\theta-2\theta)$ scans around the (400) plane of MgO single crystals irradiated with 1.2-MeV Au ions at increasing fluences. The 2θ scale was transformed in an elastic strain scale (ϵ_N).

Figure 7: Color on line. XRD reciprocal space maps recorded in the vicinity of the (400) Bragg reflection for MgO crystals irradiated with 1.2 MeV Au ions at (a) 0.4 nm^{-2} and at (b) 3 nm^{-2} .

Figure 8: TEM micrographs on MgO specimens irradiated at a fluence of 2 nm^{-2} (a-b) and 20 nm^{-2} (c-d). Micrographs a and c were recorded close to surface (around 120 nm); micrographs b and d were recorded at large depth (around 400 nm). Arrows show isolated dislocation loops.

Figure 9: Color on line. Variation with the number of dpa of $f_D^{\max}$ (circles and squares) and $\epsilon_N^{\max}$ (triangles and diamonds) for MgO (black symbols) and YSZ (blue symbols). The values of $f_D^{\max}$ are obtained from RBS/C data recorded at 3 MeV for MgO (this work) and 3.07 MeV for YSZ [13]. The values of $\epsilon_N^{\max}$ are extracted from the XRD data recorded on MgO (this work) and on YSZ [13]. Lines are fits to experimental data using the MSDA model [12].

Figure 10: Color on line. Variation with the irradiation fluence of the relative shift of the depth at which the damage is maximum for MgO (black circles) and YSZ (blue squares). These results are obtained from RBS/C data recorded at 3 MeV for MgO (this work) and 3.07 MeV for YSZ [13]. Lines are fits to experimental data using the MSDA model [12].

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

	n	f_{D1}	σ_1 (nm ²) σ_1 (dpa ⁻¹)	Φ_2 (nm ⁻²) Φ_2 (dpa)	f_{D2}	σ_2 (nm ²) σ_2 (dpa ⁻¹)	Φ_3 (nm ⁻²) Φ_3 (dpa)	f_{d3}	σ_3 (nm ²) σ_3 (dpa ⁻¹)
120 nm	3	0.03±0.09	18±80 100±400	0.34±0.14 0.061±0.025	0.63±0.06	1.6±0.6 9.7±3.7	3.0±2.0 0.5±0.4	0.43±0.06	0.11±0.13 0.57±0.66
400 nm	2	0.23±0.08	1.1±0.7 570±300	0.34±0.14 7x10 ⁻⁴ ±2x10 ⁻⁴	0.66±0.03	0.11±0.04 57±24	-	-	-

Table 1