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Synergistic effects of nuclear and electronic energy deposition on damage production in KTaO_3

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ABSTRACT

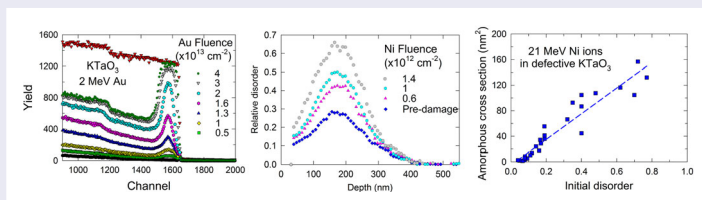
Ion irradiation of KTaO_3 has been performed to investigate the evolution of irradiation damage with and without significant electronic energy deposition. Damage accumulation under irradiation with 2 MeV Au ions follows a direct-impact/defect-stimulated model, and occurs more rapidly than in SrTiO_3 under similar conditions. Electronic energy deposition from 21 MeV Ni ions creates negligible damage in pristine KTaO_3 to depths of 1 micron; however, damage is greatly enhanced in samples containing pre-existing defects, as evidenced by rapid amorphization due to track formation. The cross-sections for amorphous tracks show a nearly linear dependence on initial disorder, comparable with SrTiO_3 .

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KTaO_3 ; ion irradiation; electronic energy loss; nuclear energy loss; ion channeling



IMPACT STATEMENT

Structural modification in KTaO_3 is sensitive to both electronic and nuclear energy deposition that can be controlled to exploit promising electronic and optical functionalities.

1. Introduction

Functional and engineering ceramics are subjected to irradiation from energetic ions in a broad range of applications, such as nuclear energy, electro-optical device fabrication, and space exploration [1–4]. Understanding ion-solid interactions and the resulting microstructure evolution is fundamental to predicting and controlling the behavior of materials, structures and devices. Incident ions deposit their energy into target materials through two fundamental mechanisms: nuclear and electronic energy loss. Nuclear energy loss through elastic scattering collisions displaces atoms from their original positions creating defects. Electronic energy loss is attributed to inelastic energy transfer to target electrons, causing excitation and ionization. The energy that electrons receive can be transferred to the atomic structure through electron-phonon coupling, causing local heating and microstructural changes [5,6]. Ionizing irradiation

has been recognized as a powerful tool for defect engineering and microstructural modification [7–9]. Nevertheless, compared with nuclear energy loss, the effects of electronic energy loss on irradiation-induced defect evolution are less understood, which might be attributed to the conflicting roles it plays. Extreme electronic energy loss may cause damage, even amorphization, along the ion track [10], or it can enhance the mobility of point defects, promoting recovery of displacement damage [11–13].

Other than the conventional focus on modifications due to swift heavy ions [14–16], recent studies have found that heavy ions in the medium energy regime (up to tens of MeV), accessible to both industrial and academic laboratories, can also affect the defect structure produced by nuclear energy deposition, and three basic types of effects have been observed [17]. First, damage produced from electronic and nuclear energy deposition can be

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simply additive, as found in ZrO_2 [18], SiO_2 [19], and ZrSiO_4 [20]. Second, as a competitive effect to displacement damage, electronic energy deposition can heal pre-existing defects, as found in SiC [13,17,21] and several complex oxides [17]. Finally, a synergistic effect has been demonstrated in SrTiO_3 , where electronic energy loss in the presence of pre-existing defects leads to amorphous track formation, while the same electronic energy loss in pristine material leads to negligible damage [10,22].

Extensive studies on ion irradiation effects have been made on perovskite-type oxides (ABO_3) because of their unique electronic and optical properties, as well as their possible role for immobilization of nuclear waste [4,23–25]. KTaO_3 is a model perovskite, an incipient ferroelectric [26] and a potential optical waveguide formed by ion implantation induced amorphization [27,28]. Ion irradiations have also been applied to modify KTaO_3 surfaces for studying low temperature quantum transport [29]. Understanding the role of energy deposition on defect evolution in KTaO_3 is important for manipulating defect structures and controlling electronic and optical properties, as well as for modifying, fabricating and designing material functionality. Furthermore, KTaO_3 and widely studied SrTiO_3 have been reported to exhibit the highest and lowest critical temperatures for amorphization under ion irradiation, respectively, representing two limits of irradiation sensitivities among seven common perovskites [24]. Therefore, investigating the combined effects of electronic and nuclear energy deposition on KTaO_3 , relative to SrTiO_3 , will provide insights on correlations between such effects and ABO_3 compositions and properties. Here, we report defect production and damage accumulation in KTaO_3 single crystals under predominate nuclear energy deposition (dE/dx_{nuc}) with and without subsequent high electronic energy deposition (dE/dx_{ele}).

2. Experimental details

Samples used in this study are epi-polished, $\langle 100 \rangle$ -oriented KTaO_3 single crystals synthesized by MTI Corp. Predominant nuclear energy deposition was achieved using 2 MeV Au ion irradiation at $\sim 5\text{--}6^\circ$ off the surface normal to avoid channeling, with $dE/dx_{\text{nuc}} = 5.2$ and $dE/dx_{\text{ele}} = 1.3$ keV/nm at 190 nm, corresponding to the displacement damage peak for 2 MeV Au ions in KTaO_3 ; while high electronic energy deposition was achieved using 21 MeV Ni ion irradiations with $dE/dx_{\text{ele}} = 9.2$ and $dE/dx_{\text{nuc}} = 0.1$ keV/nm at 190 nm. The irradiated area was defined by beam slits in front of the sample, and the broad defocused ion beam was rastered across the slits with fixed horizontal and vertical scan frequencies of 517 and 64 Hz, respectively, to provide a

continuous and uniform irradiation at 300 K using the Ion Beam Materials Laboratory at the University of Tennessee [30]. The flux for 2 MeV Au and 21 MeV Ni ions remained constant at 2.8×10^{11} and $6.0 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$, respectively. Irradiation damage was characterized using Rutherford backscattering spectrometry in channeling mode (RBS/C), with 3.5 MeV He as the probe beam and a silicon detector located at 155° from the incident beam direction. High sensitivity of KTaO_3 to electron beams resulted in rapid amorphization in scanning transmission electron microscopy, preventing microstructural characterization. The displacement and energy deposition profiles were determined using the Stopping and Range of Ions (SRIM) code [31] in full-cascade mode with a reference density of 7.015 g cm^{-3} [29]. A threshold displacement energy of 25 eV was assumed for all atoms, consistent with previous studies [24].

3. Results and discussion

Figure 1(a) shows RBS/C spectra of KTaO_3 irradiated with 2 MeV Au ions at 300 K to various fluences. The corresponding relative disorder profiles, derived using an iterative method [32,33], are shown in Figure 1(b). The damage peak occurs at ~ 190 nm, consistent with the SRIM predicted damage profile included in Figure 1(b). The relative disorder at the damage peak as a function of local irradiation dose is shown in Figure 1(c). Damage accumulation in KTaO_3 can be described by the direct-impact/defect-stimulated (DI-DS) model [25,34], where total disorder S arises from the sum of two contributions: the amorphous fraction, f_a , and the disorder, S_d , due to interstitial defects in the residual crystalline material, as described by

$$f_a = 1 - \frac{(\sigma_a - \sigma_s)}{\{\sigma_s + \sigma_a \exp[(\sigma_a + \sigma_s)/D]\}} \quad (1)$$

$$S_d = S_d^* [1 - \exp(-BD)] (1 - f_a) \quad (2)$$

where σ_a is the amorphization cross section, σ_s is the effective cross section for defect-stimulated amorphization, D is the local dose (displacements per atom or dpa), S_d^* is the saturation value for the defect-induced disorder, and B is proportional to an effective defect recombination volume. This model has been used to describe damage accumulation in SrTiO_3 [25,30], and results for 900 keV Au irradiation are included in Figure 1(c), along with the KTaO_3 results. The results indicate a higher damage rate in KTaO_3 than in SrTiO_3 that is consistent with the previously observed suppression of damage rate in SrTiO_3 relative to KTaO_3 [24] due to recovery processes at 300 K in SrTiO_3 that are not active in KTaO_3 , which also leads to

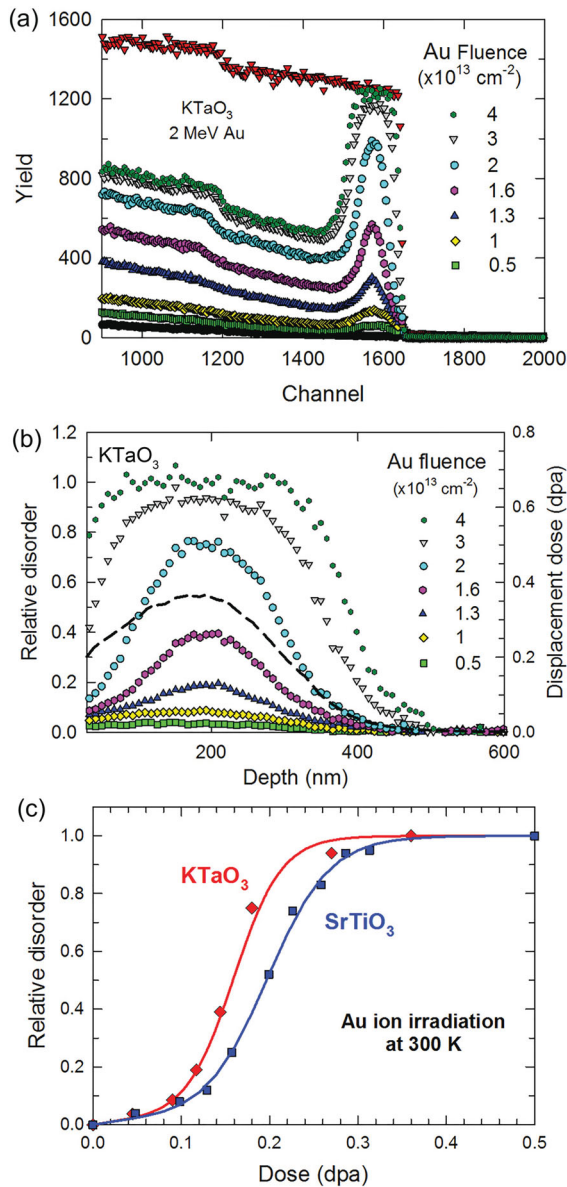


Figure 1. (a) RBS/C spectra for KTaO₃ irradiated with 2 MeV Au ions, along with unirradiated virgin (black symbols) and random (red symbols) spectra. (b) Relative disorder profiles for different Au fluences, and SRIM predicted displacement dose profile for Au fluence of $4 \times 10^{13} \text{ cm}^{-2}$ (dashed curve). (c) Damage accumulation at the damage peak for KTaO₃ under 2 MeV Au ion irradiation. Previous results for SrTiO₃ [30] irradiated with 900 keV Au ions are shown for comparison.

a critical amorphization temperature in SrTiO₃ (425 K) much lower than that for KTaO₃ (880 K).

Under 21 MeV Ni ion irradiation, electronic energy loss is predominant, and damage in pristine KTaO₃ is negligible at shallow depths ($< 1000 \text{ nm}$) at fluences up to $4 \times 10^{12} \text{ cm}^{-2}$. This is attributed to the very low displacement dose ($6.2 \times 10^{-4} \text{ dpa}$) for 21 MeV Ni ions at 190 nm, which is 50 times smaller than the corresponding value for 2 MeV Au ions, 0.045 dpa, at

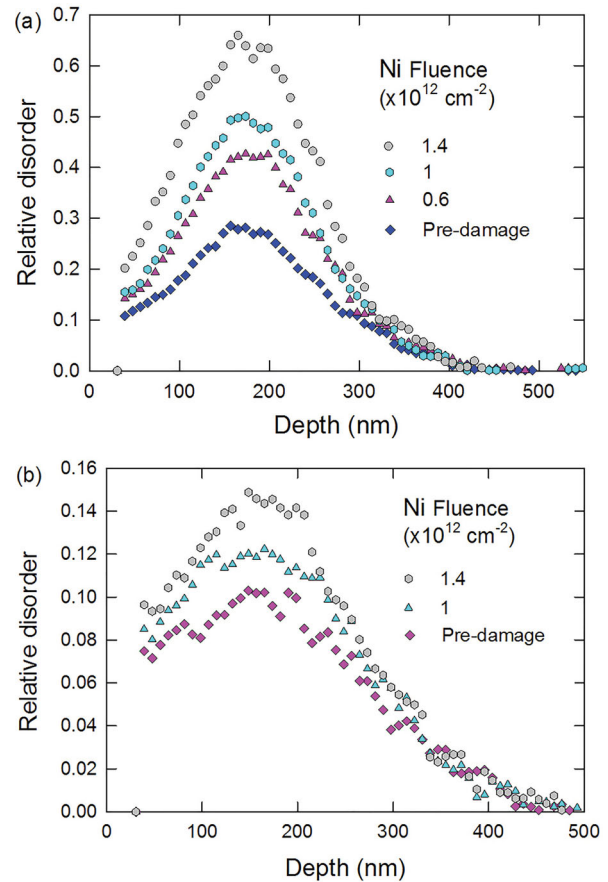


Figure 2. Relative disorder after subsequent irradiation with 21 MeV Ni ions for pre-damaged KTaO₃ at initial disorder levels of (a) 0.28 and (b) 0.1.

a fluence of $5 \times 10^{12} \text{ cm}^{-2}$, where measurable damage is first observed in Figure 1. Such negligible damage indicates that the electronic energy loss threshold for track formation in pristine KTaO₃ is higher than the 9.2 keV/nm for 21 MeV Ni ions.

In contrast, significant damage is produced at lower fluences for Ni ion irradiation of samples with pre-existing damage from Au irradiation. The disorder profiles derived from RBS/C spectra for samples with initial peak disorder of 0.28 and 0.1 are shown in Figures 2(a and b), respectively. For 0.28 initial disorder, the peak disorder increases to 0.65 with increasing fluence up to $1.4 \times 10^{12} \text{ cm}^{-2}$, while the increase in disorder is much smaller for the sample with 0.1 initial disorder under identical irradiation conditions. Such a rapid increase in disorder at low fluences suggests formation of amorphous tracks, as predicted by molecular dynamics (MD) simulations [35]. Moreover, the RBS/C spectra clearly show that the disorder returns to pristine conditions at depths beyond the pre-damage thickness, while dE/dx_{ele} decreases by only $\sim 10\%$. The rapid damage accumulation in the pre-damaged thickness suggests

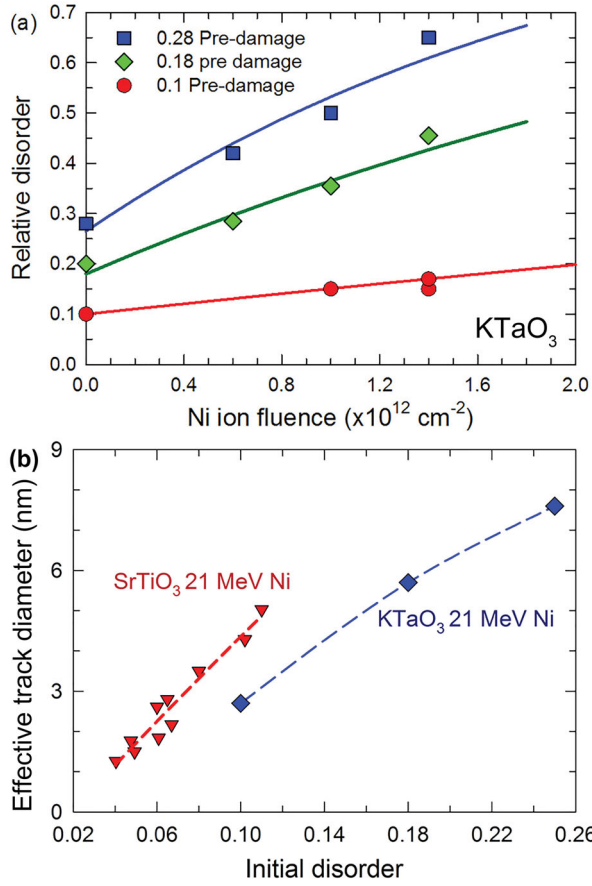


Figure 3. (a) Relative disorder as a function of 21 MeV Ni ion fluence in pre-damaged KTaO₃ and direct impact model fit. (b) Effective track diameter as a function of initial disorder for KTaO₃ [this study] and SrTiO₃ [36].

that the electronic energy loss threshold for track formation is reduced due to pre-existing disorder, similar to behavior in SrTiO₃ [22]. MD simulations using a thermal spike model have confirmed amorphous track formation under electronic energy deposition from 21 MeV Ni ions for both KTaO₃ [35] and SrTiO₃ [10,22,36], if the pre-damaged level is high enough.

A direct impact model is applied to analyze the increasing disorder due to synergistic ionization effects as a function of 21 MeV Ni ion fluence [10,22]:

$$S = S_o + f_a = 1 - (1 - S_o) \exp(-\sigma D), \quad (3)$$

where S is the total disorder, S_o is the initial disorder level, and σ is the amorphous track cross-section. Figure 3(a) shows relative disorder as a function of Ni ion fluence at different depths (from Figure 2), and the solid curves are model fits using Eq. 3. For the lowest disorder level, the fit is close to a linear relationship. Assuming a circular amorphous cross-section, an effective track diameter, d ,

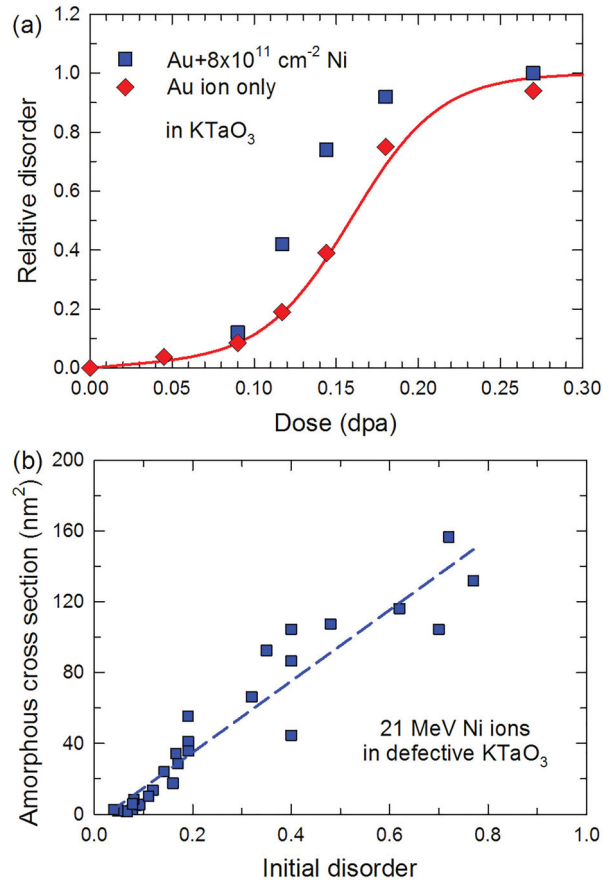


Figure 4. (a) Relative disorder in KTaO₃ as a function of dose for 2 MeV Au ions, and after subsequent irradiation with 21 MeV Ni ions to a fluence of $8 \times 10^{11} \text{ cm}^{-2}$. (b) Amorphous cross section as a function of initial disorder in KTaO₃ irradiated with 21 MeV Ni ions.

can be defined by:

$$d^2 = \frac{4\sigma}{\pi}. \quad (4)$$

The effective track diameter as a function of initial disorder is shown in Figure 3(b). The track diameter increases monotonically with increasing initial disorder. This phenomenon can be explained by the thermal spike model, where an increase in electron and phonon scattering induced by defects results in decreased thermal conductivity and increased electron-phonon coupling, which increases the melt radius with increasing defect concentration. This process may be assisted by the generalized Lindemann melting criteria [37], in which increased defect concentrations lead to decreased melting temperatures. To understand the general trend of synergistic electronic energy loss interaction with pre-existing damage in perovskites, previous results [10,36] for 21 MeV Ni irradiation of pre-damaged SrTiO₃ are included for comparison. While the higher melting temperature for

SrTiO₃ might be expected to lead to smaller track diameters for the same level of initial disorder, the higher dE/dx_{ele} (9.8 keV/nm) for 21 MeV Ni in SrTiO₃ compared to KTaO₃ (9.2 keV/nm) and a larger effect of initial disorder on melting and electronic energy dissipation in SrTiO₃ may be responsible for the larger track sizes observed. Further studies will be required to understand this behavior.

To better understand the relationship between the amorphous cross-section and initial disorder, we investigated the response of KTaO₃ at a constant 21 MeV Ni ion fluence ($8 \times 10^{11} \text{ cm}^{-2}$), but with different levels of initial disorder (0.08 to nearly 1.0). Figure 4(a) shows the increase in disorder level at the damage peak due to subsequent irradiation with 21 MeV Ni ions at each Au irradiation dose. The amorphous track cross-sections are determined, using Eq. 3, as a function of initial disorder from the disorder increase with Ni ion fluence at different depths and Au ion fluences, as summarized in Figure 4(b). A linear correlation between amorphous cross-section and initial disorder has been reported for SrTiO₃ irradiated with 20 MeV Ti ions [10] for initial disorder levels below 0.15. As shown in Figure 4(b), a linear correlation is observed to higher disorder levels, ~ 0.7 , in the present study, and extrapolation of the linear correlation to the disorder axis indicates a threshold disorder level of 0.03 for track formation in KTaO₃ from 21 MeV Ni ions.

4. Conclusions

Damage accumulation under nuclear and electronic energy depositions has been studied in single crystalline KTaO₃ and compared with SrTiO₃. For 2 MeV Au ion irradiation, damage accumulation due to nuclear energy deposition follows the DI-DS model for amorphization and occurs more rapidly than in SrTiO₃. The pristine KTaO₃ is insensitive at shallow depths ($< 1000 \text{ nm}$) to 21 MeV Ni ions up to a fluence of $4 \times 10^{12} \text{ cm}^{-2}$. However, in the case of pre-damaged KTaO₃, significant damage production occurs for relatively low fluences of 21 MeV Ni ions, indicating a strong synergistic effect, similar to the case for SrTiO₃. The increased rate of disordering is attributed to the formation of amorphous ion tracks in the pre-damaged layer. The amorphous cross-sections exhibit a linear dependence on initial disorder level. This work highlights the impact of highly ionizing particle irradiation on microstructural modification.

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Disclosure statement

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