Two-stage synergy of electronic energy loss with defects in LiTaO$_3$ under ion irradiation

Neila Sellami $^{a}$, Miguel L. Crespiillo $^{b}$, Yanwen Zhang $^{a,b}$ and William J. Weber $^{a,b}$

$^a$Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA; $^b$Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, USA

ABSTRACT

Understanding energy dissipation in electronic and atomic subsystems and subsequent defect evolution is a scientific challenge. Separate and combined effects of electronic and nuclear energy deposition in z-cut LiTaO$_3$ have been investigated. Irradiation of pristine LiTaO$_3$ samples with 2 MeV Ta ions leads to amorphization due to atomic displacement damage, described by a disorder accumulation model. While 21 MeV Si ions do not produce significant damage in pristine LiTaO$_3$, introduction of pre-existing defects sensitizes LiTaO$_3$ to the formation of ion tracks from the electronic energy loss by 21 MeV Si ions that induce a synergistic two-stage phase transition process.

IMPACT STATEMENT

Experimental study shows that the introduction of pre-existing defects prior to high energy irradiation sensitizes LiTaO$_3$ to ion track formation leading to a synergistic two-stage phase transition process.

1. Introduction

Understanding the mechanisms involved in energy dissipation to the electronic and atomic subsystems and their effects on defect evolution is a long-standing challenge in materials science. Lithium tantalate (LiTaO$_3$) has outstanding nonlinear optical [1], pyroelectric, piezoelectric, acousto-optic and electro-optical properties that make it a promising ferroelectric material in many fields, including surface acoustic wave devices, laser and photonic devices [2]. The attractive properties of LiTaO$_3$ make it a superior alternative to LiNbO$_3$ for device applications [3], since it has smaller birefringence and higher resistance to optical damage compared to LiNbO$_3$ [4]. Moreover, optical waveguides can be successfully fabricated by light-ion irradiation [4].

Knowledge about material response to ion irradiation is critical for a wide range of research and applications, since ion beam techniques can modify and tune material properties [5,6]. Fundamental understanding is essential to utilize ions to functionalize and analyze materials, create nanostructures and emulate radiation environments [7]. Damage creation under inelastic ionization processes and elastic nuclear collisions is well established [5–7]. Inelastic and elastic processes are generally assumed to be independent and noncorrelated. This concept has been disproved by several studies performed in different ceramics, such as LiNbO$_3$ [8,9], SiC [6,10,11] and SrTiO$_3$ [7,12]. Ionization effects and the combination of elastic and inelastic processes in Li-based oxide ceramics, specifically LiTaO$_3$, have not been established in the MeV energy regime, and little is understood about the coupled electronic and atomic processes.

In this Letter, we report the separate and coupled effects of electronic and atomic processes induced by
irradiation with 2 MeV Ta ions and 21 MeV Si ions in z-cut LiTaO₃ single crystal. The 2 MeV Ta ions are also used to introduce initial disorder that sensitizes LiTaO₃ to ionization damage by 21 MeV Si ions. A two-stage synergy occurs between the initial disorder and the electronic energy deposition from the highly ionizing beam. The investigation of the combined effects of elastic and inelastic energy losses contributes to the atomic-level foundation for the design and control of new functionalities in oxide electro-ceramics.

2. Experimental methods

Surface acoustic wave (SAW) grade stoichiometric LiTaO₃ (+z-cut) one-side-polished samples, provided by MTI Corporation (Richmond, CA), were used in this study. A thin layer of carbon, tens of nanometers thick, was used to coat sample surfaces to avoid surface charging [13] during ion irradiation and analysis by Rutherford Backscattering Spectrometry in channeling configuration (RBS/C). Irradiations and RBS/C analyses were performed using the 3 MV tandem accelerator within the University of Tennessee Ion Beam Materials Laboratory [14]. Irradiations were conducted at room temperature (RT) at 7° off the surface normal to avoid channeling effects: 2 MeV Ta²⁺ ion irradiations (low energy) of pristine samples, with fluences ranging from 0.02 to 0.05 ions/nm², to create a damage peak at a depth of about 165 nm, deep enough to minimize surface effects; and highly ionizing 21 MeV Si⁷⁺ ion irradiations (high energy) of virgin and pre-damaged samples to fluences ranging from 0.001 to 0.3 ions/nm². For sequential irradiations, a virgin area was initially pre-damaged with 2 MeV Ta²⁺ to 0.17 ions/nm² to create low-level fractional disorder ($f_0 \sim 0.20$); this was subsequently irradiated with 21 MeV Si⁷⁺ to different ion fluences. The change in disorder profile of each damage area was characterized by RBS/C [14]. A 3.5 MeV He⁺ beam was used only for the case of Ta²⁺ irradiations of virgin LiTaO₃ samples; 2 MeV He⁺ was used for the rest of the experiments to gain better depth resolution and statistics. The He⁺ backscattered yield was collected using a silicon detector located at a scattering angle of 155° with respect to the incident beam [8].

The nuclear ($S_n$) and electronic ($S_e$) energy loss profiles predicted by the Stopping and Range of Ions in Matter code (SRIM-2013) [15] are shown in Figure 1 for 2 MeV Ta and 21 MeV Si ions, assuming a density of 7.46 g cm⁻³. For the 2 MeV Ta²⁺ irradiation (Table 1), $S_n \sim 4S_e$ at the damage peak (DP ~ 165 nm); thus, damage evolution is primarily due to energy lost by ions via elastic nuclear collisions. In contrast, under 21 MeV Si⁷⁺ irradiation, $S_e$ is about 6.23 keV/nm near the surface region, and the ratio $S_e/S_n$ is about 567 at the surface and 478 at ~ 165 nm. These high ratios indicate that electronic processes are predominant for 21 MeV Si ions, while nuclear energy deposition is negligible.

3. Results and discussion

3.1. 2 MeV Ta Ion Irradiation

The RBS/C spectra were collected from pristine and 2 MeV Ta²⁺ irradiated regions. The relative disorder on the Ta-sublattice was extracted from the RBS/C spectra using an iterative procedure [16], and channel number was converted to depth, as shown in Figure 2(a). For visual clarity, data for some fluences are omitted. The Ta disorder increases with ion fluence, and the damage peak reaches the random level at 0.4 ions/nm² (~0.3 displacements per atom), which indicates that an amorphous state has formed. With further irradiation to 0.5 ions/nm², a homogeneous amorphous layer is formed that extends from the surface to a depth of ~300 nm. The disorder accumulation on the Ta-sublattice at the DP is shown in Figure 2(b) as a function of Ta²⁺ fluence. Due to the rather high $S_n$ and low $S_e$ at the DP (see Table 1), the damage accumulation is mainly attributed to elastic collisions created by $S_n$ along the ion path and is in good

![Image 317x577 to 546x741](http://example.com/image.png)
damage induced by nuclear collisions is very low and negligible; thus the increase in the backscattering yield is mainly attributed to \( S_E \). The relative disorder was determined near the surface region as a function of Si-fluence using the Kamarou et al. method [19]. The small increase in disorder may be attributed to an ionization effect that leads to bond breakage or formation of space-charge regions around the charged domain walls, which is frequently observed in ferroelectric semiconductors, such as in LiNbO\(_3\) [20].

### 3.3. 21 MeV Si ion irradiation in pre-damaged crystal

The effect of pre-damage on the response of LiTaO\(_3\) to 21 MeV Si ions is studied using RBS/C (data not shown here). The derived disorder profiles, shown in Figure 4, exhibit a continuous increase of the disorder as a function of fluence, with a more pronounced effect around the pre-existing DP. The results show a clear synergy between the \( S_E \) and pre-existing defects. A fully amorphous state is reached at the DP for a \( Si^{7+} \) fluence of 0.3 ions/nm\(^2\).

The relative disorder on the Ta-sublattice after subsequent 21 MeV \( Si^{7+} \) irradiation of pre-damaged LiTaO\(_3\) samples is determined at different depths as a function of ion fluence, using the Kamarou et al. method [19]. The results are shown in Figure 5. For virgin LiTaO\(_3\) irradiated with 21 MeV \( Si^{7+} \), the disorder accumulation at the same depth as the DP is determined from the data in Figure 3 and included in Figure 5 for comparison.

The results in Figure 5 indicate two distinct stages for accumulation of disorder as a function of ion fluence, \( \phi \), for both pristine and pre-damaged LiTaO\(_3\). Each stage has been fit to a direct impact disorder accumulation model [21]. For the initial accumulation stage (Stage 1), the disorder, \( S \), has been fit to the expression:

\[
S = S_1 + A_1[1 - \exp(-\sigma_1 \phi)],
\]
Figure 4. Disorder profiles on Ta-sublattice after 21 MeV Si\textsuperscript{2\textsuperscript{+}} irradiation of pre-damaged Li\text{Ta}O\textsubscript{3}.

Figure 5. Relative disorder as a function of 21 MeV Si ion fluence for pre-damaged Li\text{Ta}O\textsubscript{3} near the surface (from analysis of data in Figure 3). Solid lines are the best fits obtained with a direct impact disorder accumulation model at each step for the pre-damaged case.

where \( S_1 \) is the initial pre-damage disorder at a given depth, \( A_1 \) is the change in disorder at the saturation level for Stage 1, and \( \sigma_1 \) is the damage cross-section for Stage 1. In the case of the second disorder accumulation stage (Stage 2), the disorder has been fit to the expression:

\[
S = S_2 + A_2 [1 - \exp(-\sigma_2 (\phi - \phi_o))],
\]

where \( S_2 \) is the sum \( S_1 + A_1 \), \( A_2 \) is the difference \( 1.0 - S_2 \), \( \sigma_2 \) is the damage cross-section for Stage 2, and \( \phi_o \) is the ion fluence for the onset of Stage 2. The fit parameters for pre-damaged Li\text{Ta}O\textsubscript{3} are summarized in Table 3.

For pristine Li\text{Ta}O\textsubscript{3}, the linear increase in disorder with ion fluence above 0.10 ions/nm\textsuperscript{2} indicates a damage cross section of \( \sim 1.0 \) nm\textsuperscript{2}, which is one to two orders of magnitude lower than the synergistic cross sections for Stage 1 and 2.

The Stage 1 cross-section is large due to the rapid increase in disorder that saturates. While due to \( S_e \), this increase in disorder may be associated with excitation of pre-existing defects, but it is more likely due to a local ferroelectric phase transition at \( \sim 610^\circ\text{C} \) [22] that is induced and quenched within an ion track by the thermal spike associated with \( S_e \). The radius of these phase transition tracks is very large, \( \sim 8.8 \) nm, and the overlap of these tracks leads to the phase transition of the pre-damaged layer, which is described as a displacive or order–disorder transition [22].

The Stage 2 cross-section is an order of magnitude smaller than Stage 1, and since the damage evolution in Stage 2 follows a direct impact model to a fully amorphous state, it is consistent with direct impact amorphization along the ion path, similar to that observed in Sr\text{Ti}O\textsubscript{3} [7] and K\text{Ta}O\textsubscript{3} [23]. This process starts at about the same ion fluence for each depth. Both pre-existing defects and the step change in disorder, or phase transition, may be required for initiating the Stage 2 process. Comparing pre-damaged to pristine Li\text{Ta}O\textsubscript{3} in Figure 5, we note the large increase in disorder in the case of pre-damaged Li\text{Ta}O\textsubscript{3}. Unambiguously, this highlights the strong interaction between initial disorder and \( S_e \), similar to behavior observed in Li\text{Nb}O\textsubscript{3} [8,9], but with less sensitivity to amorphization. Although possessing many similar structural properties, Li\text{Nb}O\textsubscript{3} and Li\text{Ta}O\textsubscript{3} exhibit significant difference in melting temperatures (\( T_m \)), curie temperatures (\( T_c \)) and band gaps, which may explain the differences in track formation. The \( T_c \) for Li\text{Ta}O\textsubscript{3} is low (\( 610^\circ\text{C} \)) and the \( T_m \) is high (\( 1650^\circ\text{C} \)); thus a thermal spike may be sufficient to cause phase transition above \( T_c \) but insufficient to cause melting (amorphous track formation). In contrast, \( T_c \) (\( 1160^\circ\text{C} \)) and \( T_m \) (\( 1250^\circ\text{C} \)) for Li\text{Nb}O\textsubscript{3} are similar, and much below \( T_m \) for Li\text{Ta}O\textsubscript{3}. Thus, a thermal spike that is sufficient to cause melting in Li\text{Nb}O\textsubscript{3} may be insufficient to cause melting in Li\text{Ta}O\textsubscript{3} but sufficient to cause a phase transition in Li\text{Ta}O\textsubscript{3}. As noted, the first stage in Li\text{Ta}O\textsubscript{3} may be due to a ferroelectric phase transition above \( 610^\circ\text{C} \), and this transition may sufficiently change the electronic structure.

| Depth (nm) | \( S_1 \) | \( A_1 \) | \( \sigma_1 \) (nm\textsuperscript{2}) | \( S_2 \) | \( A_2 \) | \( \sigma_2 \) (nm\textsuperscript{2}) | \( \phi_o \) (ions/nm\textsuperscript{2}) |
|-----------|----------|----------|----------------|----------|----------|----------------|----------------|
| 30        | 0.10     | 0.09     | 207            | 0.19     | 0.81     | 10.3           | 0.040          |
| 80        | 0.17     | 0.13     | 245            | 0.31     | 0.69     | 16.9           | 0.044          |
| 120       | 0.21     | 0.16     | 249            | 0.37     | 0.63     | 23.0           | 0.047          |
| 160       | 0.23     | 0.18     | 242            | 0.41     | 0.59     | 29.6           | 0.049          |
(e.g. bandgap and electron–phonon coupling), similar to adding defects, such that the thermal spike is now sufficient to cause local melting and quenching of LiTaO$_3$ as the 21 MeV Si$^+$ ions overlap with the phase transition layer. Although the damage in LiTaO$_3$ is consistent with a thermal spike model, it should be pointed out that other relevant models for insulators, such as exciton [24] and thermo-elastic [25] models, may also be consistent with the observed behavior. In the exciton model, structural modification is initiated in the lattice relaxation stage ($<0.5$ ps) due to exciton concentrations close to the molecular concentration, and the observed sensitization due to pre-existing defects may be partly due to increased energy localization in excited states. Both models address track formation and morphology, but the exciton model is more reliable for determining the threshold stopping power for track formation. The thermo-elastic model uses the thermal spike model and concomitant elastic deformation; however, track diameter can only be correctly described in the elastic limit [25].

The introduction of defects in materials is well known to introduce scattering centers for electrons and phonons, which lead to decreases in the electronic and lattice thermal conductivity and increases in the electron–phonon coupling, which within the inelastic thermal spike model lead to increases in intensity and radial confinement of the thermal spike. Another explanation is based on the generalized Lindemann melting criteria [26], in which point defects, defect clusters and disorder introduced into a crystal will decrease its melting temperature. These are possible mechanisms by which the pre-existing defects sensitize LiTaO$_3$ to track formation and eventual amorphization. Thus, the local disorder produced by 2 MeV Ta$^{2+}$ ions intensifies and localizes the thermal spike from 21 MeV Si$^+$ ions, leading first to a phase transition and then to amorphization.

As an important material for photonic applications, the synergistic interaction between the initial damage and $S_c$ in LiTaO$_3$ could be used as a powerful tool to pattern and tune the optical properties of the material, i.e. change the refractive index and optimize waveguide performance. Through a wise choice of initial damage level, ion mass and energy of subsequent ionizing ion irradiation, one can tailor the track size and structure within the material.

4. Conclusions

Separate and coupled effects of low and high energy irradiations have been investigated. Irradiation of LiTaO$_3$ with 2 MeV Ta$^{2+}$ results in amorphization through damage accumulation processes, driven by nuclear collision cascades between Ta ions and target nuclei. The highly ionizing irradiations, using 21 MeV Si ions, do not produce significant damage in pristine LiTaO$_3$. However, a small amount of pre-existing damage sensitizes LiTaO$_3$ to the formation of ion tracks, via the thermal spike associated with electronic energy loss, that induce a synergistic two-stage phase transition process that leads to amorphization. This synergistic effect could be a promising tool to functionalize materials for optical devices applications.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. One of the authors (M.L.C.) was supported by the University of Tennessee Governor’s Chair program.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. One of the authors (M.L.C.) was supported by the University of Tennessee Governor’s Chair program.

ORCID

Neila Sellami http://orcid.org/0000-0001-8048-3329
Miguel L. Crespillo http://orcid.org/0000-0001-5941-8426
Yanwen Zhang http://orcid.org/0000-0003-1833-3885
William J. Weber http://orcid.org/0000-0002-9017-7365

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