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Citation: *J. Appl. Phys.* **103**, 093540 (2008); doi: 10.1063/1.2912494

View online: <http://dx.doi.org/10.1063/1.2912494>

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Femtosecond laser and swift-ion damage in lithium niobate: A comparative analysis

A. García-Navarro,¹ F. Agulló-López,^{1,a)} J. Olivares,^{2,b)} J. Lamela,³ and F. Jaque³

¹Centro de Microanálisis de Materiales (CMAM), UAM, 28049 Madrid, Spain

²Instituto de Óptica "Daza de Valdés," CSIC, C/Serrano 121, 28006 Madrid, Spain

³Departamento de Física de Materiales, UAM, 28049 Madrid, Spain

(Received 2 December 2007; accepted 27 February 2008; published online 14 May 2008)

Relevant damage features associated with femtosecond pulse laser and swift-ion irradiations on LiNbO₃ crystals are comparatively discussed. Experiments described in this paper include irradiations with repetitive femtosecond-laser pulses (800 nm, 130 fs) and irradiation with O, F, Si, and Cl ions at energies in the range of 0.2–1 MeV/amu where electronic stopping power is dominant. Data are semiquantitatively discussed by using a two-step phenomenological scheme. The first step corresponds to massive electronic excitation either by photons (primarily three-photon absorption) or ions (via ion-electron collisions) leading to a dense electron-hole plasma. The second step involves the relaxation of the stored excitation energy causing bond breaking and defect generation. It is described at a phenomenological level within a unified thermal spike scheme previously developed to account for damage by swift ions. A key common feature for the two irradiation sources is a well-defined *intrinsic threshold* in the deposited energy density U_{th} required to initiate observable *damage* in a pristine crystal: $U_{th} \approx 1.3 \times 10^4 - 2 \times 10^4$ J/cm³ for *amorphization* in the case of ions and $U_{th} \approx 7 \times 10^4$ J/cm³ for *ablation* in the case of laser pulses. The morphology of the heavily damaged regions (ion-induced *tracks* and laser-induced *craters*) generated above threshold and its evolution with the deposited energy are also comparatively discussed. The data show that damage in both types of experiments is *cumulative* and increases on successive irradiations. As a consequence, a certain *incubation energy density* has to be delivered either by the ions or laser photons in order to start observable damage under *subthreshold* conditions. The parallelism between the effects of laser pulses and ion impacts is well appreciated when they are described in terms of the ratio between the deposited energy density and the corresponding threshold value. © 2008 American Institute of Physics. [DOI: 10.1063/1.2912494]

I. INTRODUCTION

The modification of materials induced by different types of irradiations provides flexible and often unique methods to achieve adequate performances in a variety of technological areas, going from physics to medicine, including micro- and nanotechnologies. For example, laser irradiation is a very useful tool for surface micromachining and micropatterning.^{1,2} In the femtosecond-laser pulse regime, mechanisms related to strong electronic excitation are most relevant since the initial energy coupling to the material occurs on timescales shorter than the characteristic electron-phonon interaction time. The laser can induce^{2–5} structural changes such as melting and subsequent amorphization and ablation when the deposited energy exceeds a certain *threshold*.

On the other hand, irradiation of dielectric solids with swift ions, i.e., operating in the electronic stopping power regime, are being progressively used as an alternative to nuclear collision damage and implantation⁶ to induce struc-

tural modifications^{7–9} and produce devices, e.g., for optoelectronics and photonics.^{7,10–13} In such electronic regime, individual ions generate amorphous (latent) tracks of only a few nanometers in diameter^{14–16} when the electronic stopping power overcomes a certain *threshold* value, which depends on material and, at a lesser extent, on irradiation conditions. This technique opens new possibilities for nanostructuring of materials and may compete with femtosecond-laser pulse irradiation. Even more important, the synergy between the two different methods may result in more efficient and flexible tools to achieve novel structures and devices.¹⁷

From the fundamental point of view, one expects that in the electronic stopping regime, ion damage should present remarkable similarities with femtosecond-laser pulse damage since, in both cases, the main physical process is the massive excitation of electrons. Moreover, the interaction of femtosecond-laser pulse and swift-ion-beam irradiation occurs roughly in the same time scale. Therefore, the purpose of this work is to present experimental observations of a number of relevant phenomenological features and explore whether a correlation between laser and ion damage can be reasonably established. We will specifically focus on a relevant photonic material,¹⁸ LiNbO₃ (having a gap of around 4 eV), where some systematic information on the effect of femtosecond laser^{19–22} and swift-ion irradiation^{7–13,23–25} is al-

a) Author to whom correspondence should be addressed. Electronic mail: fal@uam.es. FAX: 00 34 91 497 3623. Also at Departamento de Física de Materiales, Universidad Autónoma de Madrid (UAM), 28049 Madrid, Spain.

b) Also at Centro de Microanálisis de Materiales (CMAM), UAM, 28049 Madrid, Spain.

ready available. To the best of our knowledge, only a few systematic comparisons have so far been reported.^{26,27} A relevant feature of this work is that both ion-beam and pulse laser experiments have been performed on plates cut from the same crystal boule. Due to the complexity of the damage morphology, our approach focuses on the main significant phenomena and parameters, thus allowing for a meaningful comparison. The overall analysis is based on thermal spike schemes that have been satisfactorily developed to understand defect formation by swift ions in LiNbO₃. We will show that within that scheme, the basic phenomenological similarities, namely,

- *existence of a well-defined threshold in the deposited energy density to achieve observable damage (thresholding),*
- *cumulative behavior of the induced damage, and*
- *incubation fluence for irradiations with energy densities below threshold,*

can be rationalized even at a qualitative (and even semiquantitative) level. The work presented here is expected to be a preliminary step to a better understanding of the processes triggered by massive electronic excitation.

II. EXPERIMENTAL DETAILS

The samples used in this study are X- and Z-cut nominally pure (integrated optics grade) LiNbO₃ plates purchased from Photox Optical Systems, UK. The ion irradiations were performed under a continuous beam in a 5 MV tandetron accelerator from High Voltage Engineering, which is installed at the Center for Microanalysis of Materials (CMAM). Experiments have used O (5 MeV), F (5 MeV), Si (5 MeV, 7.5 MeV), and Cl (11 MeV) ions in nonchanneling conditions. The corresponding electronic stopping powers S_e at the irradiated surface, which have been calculated by the SRIM 2003 code,²⁸ are below or close to the expected threshold (O, F) and slightly above (Si, 7.5 MeV). Beam current densities were kept low enough (<100 nA/cm²) to avoid excessive heating of the samples. Fluences are in the range of 10^{13} – 10^{15} cm⁻², thus assuring that individual tracks overlap and homogeneous damaged layers over the irradiated area (a few square millimeters) are formed. An analysis of the damaged regions has been performed by a dark-mode method, which measures the propagating modes and resonances through the generated refractive index profile.^{8–10} Light from a He–Ne laser (633 nm) of 5 mW power was coupled into the sample through a standard isosceles rutile prism. Also, the areal fraction of disorder has been obtained through Rutherford backscattering spectrometry^{7–10} under channeling conditions (RBS/C). Spectra were generally taken along the *c* trigonal axis using either 2–3 MeV protons or He ions.

The laser used for irradiation was a commercial chirped pulse regenerative amplification Ti:sapphire system (Spectra Physics, Spitfire), which provides linearly polarized pulses of ~ 130 fs duration at a center wavelength of 800 nm in the transparency region of the LiNbO₃ samples (which have a band gap of ~ 4 eV). A combination of a half-wave plate

and a polarizer has been used for energy attenuation of the laser beam. An electromechanical shutter synchronized with the laser system (operated at 100 Hz repetition rate) allowed a single laser pulse or multiple laser pulses to be selected from that continuous pulse train. The laser was then focused at normal incidence at the sample surface to a Gaussian spot diameter ($1/e^2$) of $2\omega_0 \sim 15$ μ m by means of a long working distance microscope objective (Mituyoto, M-PLAN-NIR, 10 $\times$, NA=0.26). All irradiations of the sample were performed in air at atmospheric pressure. The irradiation morphologies were inspected by using an optical microscope and a *scanning near-field optical microscope* (SNOM) coupled to an *atomic force microscope* (AFM). For the SNOM measurements, we have used a Nanonics Imaging Ltd. model MULTIVIEW 2000™. The continuous wave laser beam from a 532 nm frequency doubled neodymium doped yttrium aluminum garnet laser was coupled into the SNOM probe. Data were obtained by using the “reflection” mode imaging. The surface is illuminated through the probe with a 100 nm tip size and the light scattered was collected with a 10 $\times$ long work distance objective and focused into an avalanche photodiode. The shear force technique was employed in order to maintain the probe-surface distance (~ 10 nm), so that besides the reflectivity image we were also able to obtain the topographical image of the surface studied.

III. SWIFT-ION-BEAM DAMAGE IN LiNbO₃

For swift-ion irradiation on LiNbO₃, the main observable feature is *amorphization* preceded and accompanied by heavy lattice damage. No significant ablation has been detected. The main features derived from either single or multiple impact experiments are as follows.

A. Single impact experiments (low fluences): Thresholding

A number of previous experiments^{23–25} have shown that an amorphous (latent) track is generated for each single ion impact in a virgin (nonirradiated) sample whenever the electronic stopping power S_e exceeds an intrinsic threshold value S_{th} . Figure 1(a) schematically illustrates the morphology of the created track, which includes a central *amorphous core* and a surrounding defective *halo* containing point and extended defects. Evidence for this structure has been provided by *transmission electron microscopy*²⁹ (TEM) and optical methods.¹¹ The track core has a nanometer-size diameter $D_I = 2R$ at the surface and extends a certain length H_I into the crystal, which may reach several microns. Both of these magnitudes increase with stopping power S_e . The value of D_I has been measured mostly by RBS/C experiments yielding the amorphous areal fraction s at the surface as a function of the fluence in the linear (low fluence) regime. In this regime, the individual tracks are not overlapped ($s \ll 1$) and one can write $s = \phi \pi R_I^2 = \phi \pi D_I^2 / 4$. As an illustrative example, Fig. 2 shows the data obtained in our laboratory for irradiation with Cl at 11 MeV. From the histograms for the two lowest fluences [$(2$ and $4) \times 10^{12}$ cm⁻²], one can determine D_I to be around 1.7 nm. In Fig. 3, we have plotted a detailed set of data on the dependence D_I^2 vs S_e , which were taken from

FIG. 1. (a) Scheme of a single track showing *core* and *halo*. Geometrical parameters D_I and H_I are indicated. (b) Scheme of the homogeneous amorphous layer generated by overlapping random tracks.

Ref. 25, together with our own data. An extrapolation of these data to zero radius yields a threshold value of around 6 keV/nm for latent track formation in LiNbO_3 . Other works using different ions and energies locate the threshold within the 3–8 keV/nm range. The observed variations can be associated with different ion masses or velocities²⁴ (*velocity effect*), although some influence of material quality and measuring method¹¹ may also be expected. The analysis of those differences is not yet clear but is outside the scope of the present work. It can be remarked that the shape of the curve

FIG. 2. Amorphous areal fraction s as a function of depth z for LiNbO_3 irradiated with Cl at 11 MeV and different fluences (at/cm^2): 1×10^{12} (1), 2×10^{12} (2), 4×10^{12} (3), 8×10^{12} (4), 2×10^{13} (5). Data have been corrected by ion dechanneling.

FIG. 3. Experimental data from Ref. 25 for the dependence D_I^2 vs S_e in a log scale. The continuous curve stands for the theoretical dependence $D_I^2 = 4a_0^2 \ln(S_e/S_{th})$, assuming a threshold $S_{th} = 3$ keV/nm (for low velocity data, ~ 0.1 MeV/amu, full squares). The dashed line corresponds to the theoretical dependence with $S_{th} = 7$ keV/nm (for high velocity data, ~ 10 MeV/amu, open squares). Our own data for Si (7.5 MeV) and Cl (11 MeV) are also included for comparison (full triangles).

for stopping powers near the threshold is roughly logarithmic¹⁶ (see Sec. VI B 1).

The measurement of the track length H_I is more difficult, although some TEM data are available.^{30,31} One can use the RBS/C data again in the linear fluence regime as those shown in Fig. 2 and determine the depth at which the amorphous fraction s falls down to zero. One should take into account the fact that the method is not very precise since the analysis of the raw data inside the sample requires an appropriate correction for dechanneling.³² Some lengths H_I determined by that procedure (considering dechanneling correction) are given in Table I together with the stopping power at the input surface of the sample. Alternatively, it is also possible to use as a rough estimate the thickness of the initial fully amorphous layer generated at the lowest fluence causing track overlapping, e.g., $8 \times 10^{12} \text{ cm}^{-2}$ (see Sec. III B). In fact, one expects that the end point of the track corresponds to a depth such as $S_e(z) = S_{th}$ so that measuring H_I provides a method to determine the stopping power threshold.

B. Moderate fluences (10^{12} – 10^{15} cm^{-2}): Damage accumulation and incubation fluence

As commented at the end of Sec. III A, the experiments at moderate fluences ($\phi > 5 \times 10^{12} \text{ cm}^{-2}$ in Fig. 3), which induce full surface coverage, have confirmed the occurrence of an amorphization threshold and have allowed us to confirm its value. The irradiations involve a large number of ion impacts (10^{12} – 10^{15} cm^{-2}) randomly spread over the sample surface to guarantee that the individual latent tracks overlap

TABLE I. Length of ion tracks, H_I , for several ions, energies, and stopping powers.

Ion	Energy (MeV)	$S_e(z=0)$ (keV/nm)	H_I (Expt.) (μm)	H_I (Theor.) (μm)
Si	7.5	5.3	0.5 ± 0.1	0.3
Cl	11	6.1	0.6 ± 0.1	0.9
Cl	46	6.9	6.3 ± 0.3	5.8

FIG. 4. Photographs of the layered structure generated by irradiation with Si at 7.5 MeV and two different fluences.

and cover the whole surface [as schematically illustrated in Fig. 1(b)]. Indeed, it has been ascertained by optical techniques^{9,13} that a homogeneous *amorphized layer* is created *at the surface* when the stopping power is above threshold.

A new phenomenon is observed when playing with ion fluence; namely, the *thickness of the amorphous layer increases with fluence* from an initial value that corresponds to the overlapping fluence. This behavior clearly reveals the cumulative character of ion-beam damage. The evolution of the layered morphology with fluence is illustrated in the photograph of Fig. 4, which is obtained in reflection geometry on a transversal cut after irradiation with Si ions at 7.5 MeV (stopping power slightly above threshold) and two different fluences. The darker surface layer corresponds to an amorphized region, which has an isotropic refractive index $n = 2.10$ at $\lambda = 633$ nm that is lower than the two principal indices ($n_o = 2.28$ and $n_e = 2.20$) for crystalline LiNbO₃. One should note the presence of a faint dark line deeper into the crystal that corresponds to damage by nuclear collisions. The increase in thickness of the amorphous layer with fluence can be interpreted as an *increase in the track lengths due to damage accumulation*. Data for Si at 7.5 MeV (measured optically) and Cl at 11 MeV (derived from RBS/C spectra) are plotted in Fig. 5.

Another relevant consequence of the above results is that an *incubation fluence* is required to start the formation of tracks under *subthreshold* conditions. In fact, at depths that lie below one that corresponds to the threshold stopping power, amorphization is induced after sufficient fluence. This is clearly illustrated in Fig. 6, which shows the initial growth of the amorphous fraction s at the irradiated sample surface

FIG. 5. Thickness of the amorphous layer as a function of fluence for Si at 7.5 MeV (full triangles) and Cl at 11 MeV (full squares).

as a function of fluence for *subthreshold* irradiations with O at 5 MeV ($S_e = 3.1$ keV/nm) and F at 5.1 MeV ($S_e = 3.4$ keV/nm), in comparison with irradiations just around the threshold, e.g., with Si at 7.5 MeV ($S_e = 5.3$ keV/nm). The amorphous fraction has been assessed by RBS/C channeling experiments.^{7,33} One sees that in the cases of O and F, a certain prior or *incubation fluence* Φ is required to start full amorphization in comparison with Si (7.5 MeV/nm) where it starts at a much smaller fluence (in this case, $\Phi = \Phi_0$ is the overlapping fluence). The occurrence of an incubation fluence is also inferred from optical (dark-mode) data obtained for higher fluences, where a full homogeneous amorphous layer is induced.^{8,13} Figure 7 displays the data obtained for the dependence of the incubation fluence on the stopping power of the incident ion. The incubation fluence abruptly rises on decreasing S_e in accordance with its strongly non-linear effect on defect formation. On the other hand, when S_e reaches or overcomes the threshold value, the incubation fluence remains essentially constant at the value Φ_0 that corresponds to track overlapping. One may note that the product $\Phi_0 S_{th}$ represents the threshold energy density to guarantee uniform energy deposition by a random beam. Another way to describe such incubation behavior is^{8,9} that the *effective amorphization threshold is reduced by the damage induced by previous irradiation* so that after any irradiation the amorphous-crystalline boundary lies at a depth where the electronic stopping power equals such reduced effective threshold.

FIG. 6. Growth of the areal amorphous fraction s with fluence for O at 5 MeV (full squares) and F at 5.1 MeV (full circles), i.e., *under subthreshold conditions*; Si at 7.5 MeV (full triangles), i.e., *just above threshold*.

FIG. 7. Data showing the accumulated incubation fluence Φ vs stopping power S_e for irradiations with different energies and ions. The fluence Φ_0 corresponding to track overlapping (at stopping power threshold) is indicated on the plot.

IV. FEMTOSECOND-LASER DAMAGE ON LiNbO₃

For laser irradiation, the main observable effect is *ablation*, accompanied by amorphization and structural defects (lattice damage) around and below the ablated area, as revealed in a recent detailed morphological study.¹⁹ Relevant features found in our LiNbO₃ samples are as follows.

A. Single-pulse experiments: Thresholding

For a single laser pulse, a certain *incident threshold energy density (fluence)* J_{th} has to be exceeded in order to initiate an ablation crater in a nonirradiated sample. A typical crater as observed by AFM and SNOM at a fluence above threshold is shown in Fig. 8(a).

FIG. 9. Dependence of D_L^2 on single-pulse fluence J showing a well-defined threshold at 1.8 J/cm². The theoretical prediction $D_L^2 = 4\omega_0^2 \ln(J/J_{th})$ is included as a continuous curve. The dashed line is intended as an aid to the eye.

The depth profile along a diametral cut of the AFM picture is illustrated in Fig. 8(b). One should note the axial symmetry and the sharp crater boundaries that extend into a depth of around 100 nm regardless of the fluence. Inside the crater, the depth profile is less abrupt and shows a random rippled structure. The threshold fluence for our LiNbO₃ samples has been determined by measuring the ablation crater diameter D_L as a function of the laser pulse energy density J used in single-pulse irradiation (see Ref. 34 for details of the method). Results for the dependence D_L^2 vs J are illustrated in Fig. 9 for a virgin (nonirradiated) sample indicating that the dependence follows approximately a logarithmic law as found for the case of ion-induced tracks (see Fig. 3). From the extrapolation of the curve to a zero-diameter crater, a single-pulse laser damage threshold fluence of J_{th}

FIG. 8. (a) 2D and 3D SNOM and AFM pictures of the crater induced by a single laser pulse of a fluence $J = 5$ J/cm². (b) AFM depth profile of the crater. The parameters D_L and H_L are indicated on the profile.

FIG. 10. Experimental data for the crater maximum depth H_L vs single-pulse fluence J . The theoretical prediction assuming three-photon absorption with a nonlinear absorption coefficient $\alpha = 6.7 \times 10^3 \text{ cm}^3/\text{J}^2$ is included as a continuous curve.

$\sim 2.0 \text{ J cm}^{-2}$ has been obtained. It is consistent with some previous data,^{2,19,20} which range from 0.6 to 2.5 J cm^{-2} .

On the other hand, Fig. 10 shows the maximum depth at the crater axis on pulse fluence. It shows a rapid initial stage followed by a much slower rate of growth. The behavior, which is clearly indicative of the cumulative character of the damage, should be compared to that derived from the data in Fig. 5 for the case of ion irradiations. We will show (see Sec. V) that the initial stage of the curve in Fig. 10 can be described by a simple three-photon absorption mechanism, as illustrated in Fig. 10.

B. Train of pulses: Damage accumulation and incubation fluence

When the pulse energy is below the single-pulse threshold, $J < J_{\text{th}}$, ablation can still be achieved after a certain number N of pulses incident on the same spot [N is a function $N(J)$ of J]. The experiments are performed as follows: for the selected single-pulse fluence J , the number of pulses of the train is increased until an observable crater is observed. The result is that an *accumulated incubation fluence*, $\Psi = N(J)J$, is then required so that the last pulse of the train starts ablation. This phenomenon has, indeed, been previously observed.³⁵ The dependence of that incubation energy on the single-pulse fluence of the train is shown in Fig. 11, which should be compared to Fig. 7 for the case of ion irradiations.

FIG. 11. Accumulated incubation fluence $\Psi = NJ$ vs single-pulse fluence J for irradiation with a train of laser pulses. The number of pulses in the train is indicated for each point.

The value J for every single pulse of the train, which can be designated as $J_{\text{th}}(N)$, can be considered as the new threshold for amorphization when a train of N pulses is used. Obviously, $J_{\text{th}}(1) = J_{\text{th}}$. This result can be formulated in an equivalent alternative way: the *single-pulse threshold fluence for ablation decreases with the number of prior laser pulses* (accumulated fluence) applied to the same spot. In fact, it is well documented^{19,36,37} for several dielectric and semiconductor crystals that the damage threshold under femtosecond-pulsed laser irradiation decreases with the number of pulses. All those features are again indicative of the cumulative character of the damage.

V. PHYSICAL MECHANISMS

A number of proposals and strategies have been advanced to understand the damage effects of ion irradiation, namely, thermal spike models^{15,25} followed by melting and/or ablation, exciton models,^{38,39} and molecular dynamics calculations.^{40,41} For femtosecond-laser pulse irradiation, a variety of models have also been invoked. They generally involve¹⁹ multiple ionization (or tunneling ionization) followed by melting, ablation, and redeposition. Dielectric breakdown due to avalanches caused by impact ionization has also been invoked,^{42,43} as well as exciton-decay effects for wide-gap materials.⁴ Here, we will adopt a simple phenomenological scheme that may apply to the two irradiation cases. It assumes that the effects caused by irradiation should present two clearly differentiated stages. The first stage involves the generation of an *excited e-h* plasma by the interaction of the incident particle, either ion or photon, with the electron system of the material. After interaction with phonons, the excited electrons become thermalized and give rise to a *thermal spike* whose spatial profile is assumed to be correlated with that of the electronic excitation. Both the excitation and thermal profiles are the net result of the first stage and the key ingredients to trigger the generation of defects, amorphization, and ablation in the crystal.

A. First interaction stage: Electronic excitation

The description of this stage should be quite different depending on the incident particles, either ions or photons, due to the different nature of their interaction with the electron system.

- (a) *Ions.* Consider a single ion that penetrates into the crystal. The electron excitation takes place via Rutherford-type collisions between the ion and the electronic systems [valence band (VB) and core states]. The deposited energy per unit depth is characterized by the electronic stopping power S_e . At every depth z , a total concentration, $N(z) = S(z)/I$, of electrons-hole pairs are created per unit depth, with I as an average ionization energy that is around $2-3 E_G$ (gap energy). The excitation energy is divided into a fraction $Q = gS$ used for heating, i.e., the creation of the thermal spike and the remaining fraction $(1-g)S$, which accounts for the potential energy stored in the electron (hole) system. The radial distribution of the deposited energy $U(z, r)$ just

after electron thermalization ($t=0$) can be considered to be a Gaussian whose width is determined by the effective electron mean free path $\lambda=a_0$, i.e.,

$$U(z,r) = U(z,0)\exp\{-r^2/a_0^2\}, \quad (1)$$

with the condition $\int_0^\infty 2\pi r U(z,r) dr = S_e(z)$.

The peak energy density along the track axis is, obviously, given by

$$U(z,0) = \frac{S_e(z)}{\pi a_0^2}, \quad (2)$$

causing a temperature increase

$$\Delta T(z,0) = \frac{g S_e(z)}{\rho C \pi a_0^2}, \quad (3)$$

where ρ is the mass density and C is the specific heat. On the other hand, the excited electron and hole carriers turn into a correlated distribution of localized excitons. The radial distribution of exciton concentration N per unit volume is

$$N(z,r) = N(z,0)\exp\{-r^2/a_0^2\}, \quad (4)$$

with

$$N(z,0) = \frac{N(z)}{\pi a_0^2} = \frac{S_e(z)}{\pi I a_0^2}, \quad (5)$$

where $N(z)$ stands for the total number of excitons per unit depth. For experiments on LiNbO_3 , the values found for the two relevant parameters, g and a_0 , to characterize the temperature and exciton distributions are $g \approx 0.5-0.7$ and $a_0 \approx 4.5$ nm, which are essentially independent of stopping power (although some dependence on ion velocity may be expected). One should note that the value of a_0 determines the critical fluence for track overlapping, i.e., $\Phi_0 = 1/\pi a_0^2$. On the other hand, g is linked to the effective ionization energy I through the simple relation $g = 1 - E_G/I$.

- (b) *Photons.* On the other hand, for femtosecond-laser pulse irradiation at wavelengths falling in the transparency region of the dielectric material, the excitation of electrons from the VB into the conduction band (CB) mostly relies on *multiphoton absorption* that is a non-linear effect. For LiNbO_3 , at least three photons of 1.55 eV (corresponding to 800 nm wavelength) have to be absorbed simultaneously in order to create an electron-hole pair. Under intense pulse excitation, band filling effects may reduce the multiphoton absorption. On the other hand, the excited electrons can absorb additional energy from the external radiation field via *free-carrier absorption*, which can lead to the generation of additional CB electrons via *impact ionization*. Moreover, as soon as defects and disorder are created, new energy levels are introduced in the gap causing a light-enhanced absorption.

We consider a single Gaussian laser pulse with a transversal energy density profile at the sample surface

$$J(r) = J_0 \exp\{-r^2/w_0^2\}, \quad (6)$$

where $2w_0$ is the waist of the laser beam. The total energy of the pulse is $J = \pi w_0^2 J_0$. The corresponding spatial distribution of the energy deposited by the pulse is $U(z,r) = dJ(z,r)/dz$. Due to the complexity of the photon-material interaction, here, we will adopt a simple meaningful approach, i.e., three-photon absorption, and then the transversal profile for the deposited energy density per unit depth is

$$U(z,r) = \left[\frac{dJ(z,r)}{dz} \right]_{z=0} = \alpha J_0^3(z) \exp\{-r^2/\sigma^2\}, \quad (7)$$

with $\sigma = w_0/\sqrt{3}$ and α as the appropriate nonlinear coefficient. The *total deposited energy*, $U_L(z) = \pi \alpha \sigma^2 J_0^3$, is the magnitude equivalent to the *stopping power* in the case of ion irradiation and so σ plays an equivalent role to a_0 . As to the depth profile of the excitation energy density, one has to solve the equation⁴⁴

$$\frac{dJ(z,r)}{dz} = -\alpha J^3(z,r), \quad (8)$$

where the solution is

$$J(z,r) = \frac{J(z,0)}{\sqrt{1 + 2\alpha z J^2(z,0)}}. \quad (9)$$

Since the photon energy is 1.55 eV, the kinetic energy given to an electron in the three absorption process is 0.85 eV. Consequently, the fraction g of the deposited energy invested in heating is $g=0.22$. Following a calculation similar to that described in (a), one predicts a generated temperature profile

$$T(z,r,t) = T_S + \Delta T_0 \exp\{-r^2/\sigma^2\}, \quad (10)$$

with

$$\Delta T_0 = \frac{g S_L(0)}{\pi \sigma^2 \rho C}. \quad (11)$$

On the other hand, the localized excited electron-hole (exciton) cloud at the surface will have the profile

$$N_X = N_0 \exp\{-r^2/\sigma^2\}, \quad (12)$$

which is narrower than the incident light intensity profile (6).

B. Decay of the excitation: Defect formation

In our view, the two irradiation cases pose the same key questions for the irradiation damage process, i.e., which are the relevant energy transfer mechanisms from the electron system and the crystal lattice, and which are the mechanisms causing permanent damage, i.e., bond breaking and defect formation. In the case of ions, the most successful model to describe irradiation damage is the thermal spike model. Several versions have been proposed and developed. In all of them, the key point is that the damage is a function of the deposited energy or electronic stopping power. In the standard model, damage starts when the deposited energy causes lattice melting. This explains in a natural way the existence of a threshold but cannot describe damage accumulation. In later versions, the cumulative character of the damage has been introduced⁹ by means of Arrhenius laws that determine

the concentration of broken bonds (point defects) as a function of stopping power so that defects are, indeed, introduced under subthreshold conditions. The most recent version couples the thermal spike to nonradiative exciton decay to determine the generated point defect concentration.^{38,39} At this stage, we are going to use for this comparative analysis the simplest idea behind all those models; namely, the *defect concentration generated by irradiation is exclusively a function of the local deposited energy*, although the dependence is strongly superlinear (*thresholding*). It is to be remarked that the different distribution of the energy between the exciton plasma and the phonon system (i.e., the g factor) can also have significant implications on the amount of damage depending on the particular mechanism. Moreover, using this simple scheme, we will try to comparatively discuss the laser pulse and ion data in spite of the huge differences in the lateral and depth spreads of the distribution of deposited energy.

VI. COMPARATIVE ANALYSIS OF THE ION AND LASER IRRADIATION DATA

The two types of irradiation show several key common features: *thresholding*, i.e., a threshold in the deposited energy density is needed to cause observable effects, and *cumulative character*, i.e., a reduction in threshold by the damage generated by previous irradiation. Other common features related to those ones are the existence of an *incubation energy (fluence)* to start observable damage and the *increase in the size of ablated (or amorphous) regions through successive irradiations*. Let us now discuss in more detail the main experimental data in relation to the scheme proposed in Sec. V.

A. Threshold energy density

Let us now compare the thresholds in energy density deposition that have been measured for ion beam and laser damage in LiNbO_3 .

- (a) *Damage by swift ions.* For ion irradiation, the threshold for a single ion impact occurs for the electronic stopping power S_{th} in the range of 2–7 keV/nm. One may now derive from such value the *threshold energy density* U_{th} per unit volume by taking into account the area of the region where the ion energy has been deposited. In accordance with Sec. III B, that area is $\sigma = \pi a_0^2 \approx 5 \times 10^{-13} \text{ cm}^2$. Then, one readily obtains

$$U_{\text{th}}(\text{ion})\Phi_0 S_{\text{th}} = \frac{S_{\text{th}}}{\pi a_0^2} \approx 1.3 \times 10^4 - 2 \times 10^4 \text{ J/cm}^3 \quad (13)$$

as a reasonable estimate.

- (b) *Damage by a single femtosecond-laser pulse.* In a virgin sample, the *threshold incident energy density* measured by us at $\lambda = 800 \text{ nm}$ is $J_{\text{th}} \sim 2.0 \text{ J/cm}^2$, which is consistent with some previous data¹⁹ on LiNbO_3 . From the initial slope of the curve H_L vs J_L in Fig. 9, one can estimate the *deposited energy per unit depth* $(dJ/dz)_0$ at the sample surface for $J = J_{\text{th}}$. The deposited energy density becomes

$$U_{\text{th}}(\text{laser}) \approx \left(\frac{dJ}{dz} \right)_0 \approx 7 \times 10^4 \text{ J/cm}^3, \quad (14)$$

which appears comparable although *significantly higher* than that measured for the threshold under ion-beam irradiation. In other words, the efficiency for ablation is a few times lower than the efficiency for amorphization by ions. Moreover, the energies per molecule amount to $\sim 1\text{--}10 \text{ eV/atom}$, i.e., comparable to the binding energy of the crystal. In fact, more data for different exciting wavelengths and pulse durations (within the femtosecond regime) would be necessary for a better assessment of the threshold conditions. Moreover, to understand the reasons for the higher threshold found for laser pulse irradiation, one may invoke that ablation should require higher energies than amorphization. In fact, for some materials ablation thresholds by femtosecond-laser pulses⁴⁵ as well as ion beams have been found higher than those for amorphization.⁴⁶ Therefore, the laser-induced ablation may be preceded by amorphization not directly observed in our experiments. In fact, the existence of an amorphous layer at the bottom of the ablated crater suggest, indeed, that interpretation. Moreover, a more detailed comparative analysis of the two irradiation cases should possibly consider the role of the parameter g by determining the fractions of the deposited energy transferred either to phonons or excitons.

B. Morphology of the damage

The damage morphologies of the ion-beam and femtosecond-pulsed irradiated samples have been investigated by means of AFM/SNOM microscopy. For the ion irradiations, a small change in the refractive indices (both ordinary and extraordinary) is measured in the irradiated area by the sensitive dark-mode method. In accordance with previous work,^{9,10} it does not influence in a significant way the reflectivity of the surface. On the other hand, SNOM pictures of the optical response of the surface at the submicron scale do not reveal any significant change in fluences below the measured threshold. According to our scheme, the shape of the damage profile (ion track or laser crater) has to be a direct consequence of the corresponding energy density profiles. The two main morphological parameters are the diameter and the depth of the amorphous (ablated) regions to be discussed next.

1. Lateral expansion of the track (crater) diameter with the energy of the pulse (ion impact)

According to our phenomenological scheme, the size of the amorphous track or ablated crater should be given by the area exposed to a fluence equal or higher to threshold (see also Ref. 19). Let us illustrate in Fig. 12 the deposited (Gaussian) energy profiles caused by ion impact [Eq. (1)] or laser pulse [Eq. (7)] at two different stopping powers or laser pulse fluences, one at threshold (S_{th} or J_{th}) and another one at a higher value (S_e or J). In the first case, the critical energy density deposited at the track axis ($z=0$, $r=0$) is $U(0,0)$

FIG. 12. Schematic diagram illustrating the procedure to obtain the diameter either of the ion tracks or laser-pulse craters.

$= U_{th}$. Then, the intersection of the line corresponding to this concentration with the profile corresponding to S_e or J provides the radius of the generated amorphous track or ablated crater. This simple analysis predicts logarithmic dependences, $D_I^2 = 4a_0^2 \ln(S_e/S_{th})$ and $D_L^2 = 4w_0^2 \ln(J/J_{th})$, which are included in Figs. 3 and 9, together with the corresponding experimental data. The qualitative agreement is good although the quantitative accordance is only fair. For the ion irradiations at high velocities (threshold stopping power around 7 keV/nm), the agreement is quite reasonable but it becomes worse for the laser pulses. In fact, a discrepancy of a factor of ~ 1.4 between the experimental and predicted radii is observed.

To make the analogy between the two irradiation sources stand out, one may take into account the different scales for the lateral spread of the electronic excitation ($w_0 \cong 7.5 \mu\text{m}$ and $a_0 \cong 4.50 \mu\text{m}$). Then, one should plot either $(D_I/2a_0)^2$ or $(D_L/2w_0)^2$ versus the deposited energy density in either a single laser pulse or ion impact. This rescaling leads to the plot of Fig. 13, thus making the quantitative similarity between the two types of irradiation experiments stand out.

2. Length (depth) of the track (crater)

The length of the amorphous track caused by a single ion impact with incident stopping power S_e can be readily derived from the thermal spike models since the end point of the track corresponds to the depth z , where $S_e(z) = S_{th}$. Fortunately, the depth dependence of the electronic stopping power $S_e(z)$ can be determined with a reasonable accuracy by means of available SRIM codes. In fact, the last column in

FIG. 13. Rescaling of Figs. 3 and 9 to show $(D_I/2a_0)^2$ and $(D_L/2w_0)^2$ as a function of the deposited energy density U normalized to the threshold value U_{th} . Ion-beam data (full and open squares) and laser pulse data (full circles).

Table I offers the track lengths predicted from such a simple approach.

On the other hand, the situation for laser irradiation is much worse since the energy attenuation of the laser beam is not well known. Therefore, it is better to use the crater depth data to learn about the laser attenuation behavior. Assuming, as in Sec. V A, that the process is governed by three-photon absorption, the solution of Eq. (8) yields the depth h of the crater generated by a pulse of fluence $J > J_{th}$. It can be written as

$$H_L = \frac{1}{2\alpha} \left(\frac{1}{J_{th}^2} - \frac{1}{J^2} \right), \quad (15)$$

which indicates a monotonic growth up to a saturation value of $H_{LS} = 1/2\alpha J_{th}^2$. This theoretical evolution, included in Fig. 10, may account for the low-fluence experimental data if one chooses $\alpha = 6.7 \times 10^3 \text{ cm}^3/\text{J}^2$, although more data near threshold (i.e., crater depths around or below 100 nm) would be necessary for a reliable determination. Then, this mechanism predicts a top-hat shape for the crater as experimentally observed at low fluences. On the other hand, at higher fluences, the maximum depth is larger than predicted and gives rise to a rippled bottom of the crater. However, at the rim of the crater, one may still recognize the abrupt top-hat characteristic of the three-photon absorption with a depth of around 100 nm. For these high fluences, a different additional mechanism should be contributing to the attenuation. This may likely be attributed to the absorption due to the electronic levels of the defects that have been generated by prior laser pulses. This effect should be considered for a rigorous analysis of the “memory” or incubation effect experiments described in Sec. IV B. At a qualitative level, this has been also invoked in previous reports^{19,36} on LiNbO₃ and other crystals. Note that due to the rather smooth $S_e(z)$ dependence in comparison with the depth attenuation of the laser beam, the lengths of the ion tracks are, indeed, much longer than the depths of the laser craters.

VII. A STRIKING DIFFERENCE: ABLATION (LASER) VS AMORPHIZATION (IONS)

Although the above-mentioned features show relevant similarities between the two irradiation cases, there is a striking difference: the dominance of ablation over amorphization in the case of laser irradiation and the opposite situation for ion irradiation. In Sec. VI A, it has been suggested that the laser pulse irradiation experiments measure the ablation threshold that is expected to be higher than that corresponding to amorphization (i.e., the one measured in the ion-beam irradiation experiments). The reason may be associated with the abrupt energy deposition profile for the incident light and the relative proximity of the ablation and amorphization thresholds. In the case of ions, the deposited energy is a smooth function of depth and so ablation could only be observed under much higher stopping powers.⁴⁶

One may also remark a main relevant geometrical difference between the laser and ion-beam experiments. In the laser case, the ratio between the linear size of the effective illuminated and excited area ($\sim 15 \mu\text{m}$) and the penetration

depth is around 10–100. For ion-beam experiments, the ratio is typically around or smaller than 10^{-3} . This suggests that, in the latter case, bulk processes may be dominant over those related to the surface. This point will deserve more attention in future work (see also Sec. V).

VIII. SUMMARY AND CONCLUSIONS

In summary, relevant similarities have been found in the behavior of LiNbO_3 under femtosecond-laser pulse and swift-ion irradiation. The similarities include the occurrence of a well-defined threshold for observable damage and its cumulative character, as well as the existence of an incubation fluence when the energy of the laser pulse, or the ion stopping power, are below threshold. Moreover, a reasonable correlation can be established for the dependence on the deposited energy density of the main morphological features of the damage: diameter and depth of the ion track core and laser crater. It is remarkable that this occurs in spite of the very large size-scale differences between those laser and ion damage features. The observed correlations are discussed in terms of a simple two-step phenomenological scheme. The first step involves massive excitation of the electronic system and generation of a thermal plus an excitation spike. Then, the production of damage is assumed to be a function of the total energy stored in the mixed spike. Of course, this is only a basic exploratory work that needs further experiments and a deeper theoretical analysis.

ACKNOWLEDGMENTS

We are deeply indebted to J. Bonse (Berlin) for his assistance with the femtosecond-pulse laser measurements and to J. Solís and the Instituto de Optica (CSIC, Madrid) for providing experimental facilities.

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