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Delayed release of Li atoms from laser ablated lithium niobate

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The present vapor-phase optical (atomic) absorption measurements study the escape dynamics of Li atoms from a $LiNbO_3$ target surface upon laser ablation in vacuum. The objective is to understand the low-Li content of $LiNbO_3$ films prepared by pulsed laser deposition. A primary result is a *delayed release* of Li atoms, 2–20 μs after the laser pulse; they eject with a velocity of 6×10^5 cm s^{-1}, which is consistent with an electronic ejection mechanism. The long emission period means there are almost no intraplume Li collisions in the gas phase and no forward focusing of the delayed released atoms. This appears to explain the low-Li content usually found in films grown in the normal direction. © *2000 American Institute of Physics.* [S0003-6951(00)04605-2]

Lithium niobate crystals are well known to be of electro-optical, piezoelectric, and acousto-optic usefulness. For the development of compact waveguide devices for these applications, high-quality $LiNbO_3$films are required. Although there have been many attempts to produce such films by means of several techniques, limited success has been achieved primarily because of the low-Li content. Pulsed laser deposition (PLD), has been proven to have significant success in growing complex oxides with similar perovskite-like structure. Nevertheless, Li losses are still a problem in PLD films of $LiNbO_3$, one of the best results reported so far being obtained by using Li-enriched targets.[1,2] Furthermore, low-Li content results in films with multiphases, strains, and cracks.[2,3] Some of the mechanisms proposed to explain the loss of lithium include scattering by the ambient gas[1,4] or resputtering of the Li from the substrate.[1,5]

The aim of this work is to study the dynamics of free-Li atoms in the laser ablated $LiNbO_3$ plume to explore the processes which might lead to the low-Li content usually reported in the films grown by the PLD technique. We use optical (atomic) absorption as a measurement technique. Ablation is produced by an ArF laser beam focused onto a $LiNbO_3$ single crystal at an incident angle of 45° from the normal to the target. Two $LiNbO_3$ crystals, cut one with the *c* axis forming an angle of 14° with the normal to the surface and one with the *c* axis in the surface plane, were studied. The targets are mounted in a rotating holder and placed in a vacuum chamber. The experiments are performed in vacuum at a background pressure of 6×10^{-7} mbar. The beam deposits $I=0.06\,\mathrm{J\,cm^{-2}}$ into a 0.5×4 mm ellipse; this low-energy density has been chosen since it is very close to the plume formation threshold and thus gives significant Li absorption but little emission. A straightforward calculation[6] gives a temperature rise ΔT in excess of 2000 K for the fluence used. We have used the expression $\Delta T=(Dt/\rho)^{1/2}(1-R)2I/\kappa$, where ρ is the density, t is the ArF laser effective pulse duration, D is the thermal diffusivity, R is the reflectance, and κ is the thermal conductivity, and inserted the data reported elsewhere for $LiNbO_3$.[7] Even allowing for some overestimation due to the finite 193 nm absorption length, this result for ΔT shows that the fluence used in this experiment should be enough to melt and even vaporize $LiNbO_3$.

The experiment uses a lithium hollow-cathode lamp to measure the Li atomic absorption on the 670.8 nm unresolved resonance doublet ($2p^2P^o_{1/2,\ 3/2}\leftarrow 2s^2S_{1/2}$). The advantages of this source are: cw, economical, always at the correct wavelength, and a very narrow linewidth; the disadvantage is the low intensity of the source, sometimes being overwhelmed by the plume light. The beam from the lamp probes a cylindrical volume approximately 4 mm in diameter and centered at a distance in the 7–25 mm interval in front of the target surface and with the axis parallel to it. This minimum distance has been selected since it was the distance at which the contribution of the light emitted by the plume in our experimental conditions was smaller than the light of the Li lamp, and thus could be reliably substracted. A ~1:2 image of the beam is formed into the 150 μm entrance slit of a 3/4 m Spex 1702 monochromator tuned to the resonance wavelength to eliminate light from other lines. The probe light is finally detected by a photomultiplier (Hammamatsu R562) connected to a 100 MHz digital oscilloscope (Tektronik, TDS 320) with a 1 kΩ load resistor (to time average photon statistics). The rise time of the detection system was determined by analyzing the light emitted by the plume in the neighborhood to the target and found to be 300 ns.

For each distance, several absorption transients were averaged (256 shots) to improve the signal-to-noise ratio, specially at the longer distances, and two sets of transients were always recorded: (i) transient $I_{\mathrm{off}}(t)$ that corresponds to the plasma light collected by the photomultiplier when the laser fires but the lamp is off; and (ii) transient $I_{\mathrm{on}}(t)$ that corresponds to the light collected when the lamp is on and the laser fires. These records were then subtracted (to improve the signal-to-noise ratio and to reduce the contribution of plasma light if it were necessary) and the absorbance was finally computed by comparing $I(t)=I_{\mathrm{on}}(t)-I_{\mathrm{off}}(t)$ to the incident light I_{o} (the lamp is on but the laser has not yet fired), the optical density being $\log[I_{\mathrm{o}}/I(t)]$.

A typical result of the optical-absorption measurements

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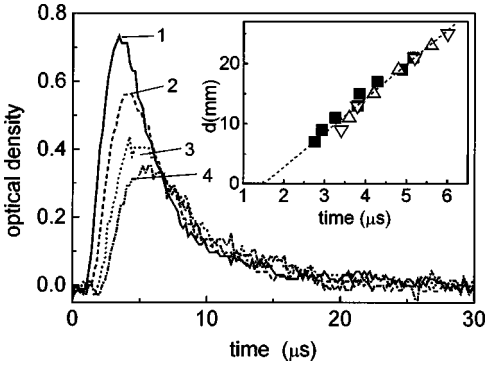

FIG. 1. Optical density of the absorption of Li atoms recorded at (1) 11 mm, (2) 15 mm, (3) 19 mm, and (4) 23 mm from the target surface. The inset shows the distance at which the measurement is done as a function of the time at which the maximum of the absorption occurs. The data were obtained sequentially by increasing the distance (■) or alternatively by decreasing the distance (△,▽). The dashed line is a linear fit of the experimental data.

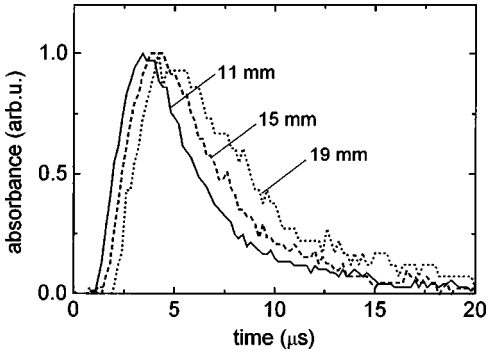

FIG. 2. Optical density of the absorption of Li atoms recorded at three distances from the target surface. Those recorded at 15 and 19 mm have been normalized to the same intensity maximum as the one recorded at 11 mm.

is shown in Fig. 1 where the absorption of Li atoms recorded at different distances d to the target is plotted. Similar results were obtained in several sets of data collected, and independently of the order followed, to record the absorption transients as a function of the distance. The results obtained using the two different targets were also similar, and thus only the results for the one having the c axis forming an angle of 14° with the normal to the surface are shown. The transients plotted in Fig. 1 evidence that the absorption of Li atoms peaks at about 2–6 μs and lasts longer than 10 μs. The intensity of absorption decreases with increasing distance, as could be expected from the angular spreading of the Li atoms. The time at which the maximum occurs has been plotted in the inset of Fig. 1 as a function of the distance to the target. It is clearly seen that the experimental results follow a linear relationship; this provides the expansion velocity of the Li atoms. This velocity turns out to be quite high, 6×10^5 cm s^{-1}, which amounts to 1.3 eV, and is similar to that reported earlier for the Li atoms generated immediately after the laser pulse (hundreds of nanoseconds) and measured through emission experiments.[8] The long period together with the high absorbance means a large flux of Li atoms. This should represent a significant or even major fraction of the free-Li atoms being generated. Evaluation of the Li time-integrated optical density versus the volume of the target removed reinforces this belief.

Both the emission and absorption transients have occasionally been interpreted as time-of-flight velocity distributions.[9,10] If the transients primarily correspond to a velocity distribution, they should broaden in time and shift their maximum to longer times due to the spreading of the Li atoms. Figure 2 shows some transients recorded in the 11–19 mm distance interval from the target and normalized to the same intensity. It is clearly seen that all of them have very similar shapes, and thus cannot be related to a velocity distribution. Furthermore, no good fit of the experimental transients could be made using the Maxwellian-type velocity distributions widely reported in the literature.[10] To prove further that the transients are not consistent with a velocity distribution, we have measured the full width at half maximum (FWHM) of the absorption transients. We have calculated the Maxwellian type of function reported elsewhere[10] that fitted the FWHM of the experimental transient recorded at the shortest distance measured (7 mm). Using the parameters of such a function, we have then determined the FWHM expected for the other distances studied if the evolution were of Maxwellian type. Both the experimental and calculated results are plotted in Fig. 3, where it is seen that the expected broadening of the FWHM with a Maxwellian type of velocity distribution is much larger than that observed experimentally. We can thus conclude that the absorption transients relate to atoms which are ejected *during a long time interval with similar velocities*, rather than to atoms released in a short time interval with significantly different velocities.

The next step is to note the direct effect of this delayed release. Gas-phase collisions are required to form a Knudsen layer with its forward-directed collimation, and under typical conditions this happens a few or tens of nanoseconds after the laser pulse.[10] The delayed and long-lasting Li desorption will mean few or no gas-phase collisions for these delayed Li atoms within the plume. A significant amount of Li atoms thus should expand at large angles and in those experiments dealing with $LiNbO_3$ film growth, will contribute very little to maintain the stoichiometry of Li along the direction perpendicular to the target.

From the point of view of velocities, direct thermal processes do not seem to explain the origin of this delayed Li

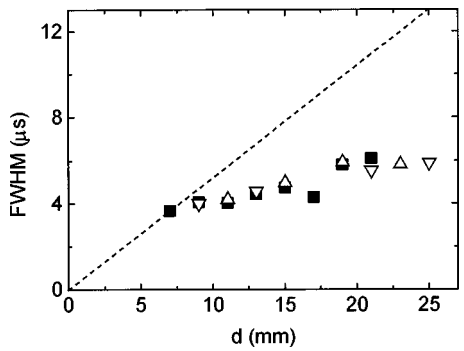

FIG. 3. FWHM of the experimentally measured optical density transients as a function of the distance from the target. The data were obtained sequentially by increasing the distance (■) or alternatively by decreasing the distance (△,▽) and they correspond to the same set of data whose time position is included in the inset of Fig. 1. The dashed line corresponds to the expected evolution for the FWHM of the velocity distribution assuming the Maxwellian type of function described in Ref. 10.

release. First, one can calculate that the $LiNbO_3$ target surface has cooled to nearly ambient temperature after 10 or 20 μs, so direct vaporization cannot be responsible. Also for thermal emission of Li a direct approach to the velocities would have given $<10^5$ cm s^{-1}, in disagreement with the velocity calculated from the data shown in Fig. 1 ($>5\times10^5$ cm s^{-1}). Thus, the Li atoms' kinetic energies are too high for a thermal process. These energies are typical for electrostatic, plasma, or color-center promoted emission.

Changes of stoichiometry in the ablated zone of $LiNbO_3$ crystals have often been reported,[11–13] which might contribute to defect-formation and thus to defect-promoted release.[14,15] It has also been reported that surface fracture can promote the ejection of neutral atoms, although through a thermal mechanism.[16] In order to analyze the validity of these mechanisms, we also performed experiments accumulating a number of pulses on the two studied targets without rotating them. The crater produced has been observed by optical microscopy, and although cracking and/or faceting during recrystallization of the target was observed, they were only observed for one of the studied target orientations. The fact that the same Li dynamics were deduced from the absorption transients, suggests that the long-lasting delayed release of Li atoms is not related to the morphological changes produced in the target surface upon ablation. This result leaves color-center/defect-promoted ablation as the remaining plausible explanation. The detailed mechanism is beyond the scope of this work and requires further investigation.

In summary, a delayed and long-lasting release of fast Li atoms upon ablation of $LiNbO_3$ crystals has been identified. The high velocities of the atoms are consistent with an electronic mechanism. The delayed release means that the majority of the Li atoms do not suffer gas-phase collisions within the plume and are thus not forward directed as the other species and only slightly contribute to $LiNbO_3$ film growth. These different dynamics for Li atoms thus can explain the low-Li content usually reported in the films deposited in the forward-directed direction.

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[1] Y. Shibata, K. Kaya, K. Akashi, M. Knai, T. Kawai, and S. Kawai, J. Appl. Phys. **77**, 1498 (1995).
[2] M. Haruna, H. Ishizuki, J. Tsutsumi, Y. Shimaoka, and H. Nishihara, Jpn. J. Appl. Phys., Part 1 **34**, 6085 (1995).
[3] S. Bauer, Thesis, Universität Köln, Mai 1995, JUEL-3056, ISSN 0944-2952.
[4] J. Gonzalo, C. N. Afonso, J. M. Ballesteros, A. Grossman, and C. Ortega, J. Appl. Phys. **82**, 3129 (1997).
[5] S.-H. Lee, T. W. Noh, and J.-H. Lee, Appl. Phys. Lett. **68**, 472 (1996).
[6] For the formula, see H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University, New York, 1948), p. 56.
[7] T. H. Lin and S. H. Lee, in *Properties of Lithium Niobate*, EMIS Data Review Ser. 5 (Inspec, London, 1989), p. 56.
[8] C. N. Afonso, F. Vega, J. Gonzalo, and C. Zaldo, Appl. Surf. Sci. **69**, 149 (1993).
[9] D. B. Geohegan, in *Pulsed Laser Deposition of Thin Films*, edited by D. B. Chrisey and G. K. Huber (Wiley, New York, 1996), Chap. 5, p. 115.
[10] R. Kelly and R. W. Dreyfus, Surf. Sci. **198**, 263 (1988).
[11] M. Affatigato, K. Tang, R. F. Haglund, Jr., and C. H. Chen, Appl. Phys. Lett. **65**, 1751 (1994).
[12] N. Omori and M. Inoue, Appl. Surf. Sci. **54**, 232 (1992).
[13] M. Sorescu, E. T. Knobbe, J. J. Martin, J. D. Barrie, and D. Barb, J. Mater. Sci. **30**, 5944 (1995).
[14] M. A. Schildbach and A. V. Hamza, Phys. Rev. B **45**, 6197 (1992).
[15] N. Seifert, D. Liu, R. G. Albridge, A. V. Barnes, N. Tolk, W. Husinsky, and G. Betz, Phys. Rev. B **46**, 83 (1992).
[16] R. L. Webb, L. C. Jensen, S. C. Langford, and J. T. Dickinson, J. Appl. Phys. **74**, 2323 (1993); J. T. Dickinson, L. C. Jensen, R. L. Webb, M. L. Dawes, and S. C. Langford, *ibid.* **74**, 3758 (1993).