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Laser mass spectrometric studies of high temperature superconductor ablation

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ABSTRACT

Laser ablation of bulk High Temperature Superconductor (HTS) material promises to provide a useful means of producing high quality HTS thin films. Mass spectrometric probes of the ablation plume provide a microscopic understanding of the ablation event and plume development as well as providing a process monitor for the thin film production. Detection of the nascent ions in the plume provides real time analytical information, e.g., identification of impurities, major and minor ablation species, etc. The common contaminants sodium and strontium have been easily detected by this technique in a variety of different HTS bulk materials. In contrast, detection of the ablated neutral species by Resonance Ionization Mass Spectrometry (RIMS) provides physical information about the ablation process. Time-of-flight/RIMS detection of Cu,Y, and BaO ablated from $YBa_2Cu_3O_x$ indicates the ablation involves post-desorption gas phase collisions, thereby influencing the ablation chemistry and dynamics (e.g., angular and velocity distributions). Approximately equal velocities are observed for all neutral species at constant ablation laser fluence.

1. INTRODUCTION

Soon after the recent discovery of the oxide superconductors with transition temperatures greater than 90 K, various research groups reported the successful fabrication of high temperature superconducting (HTS) thin films. In particular, laser ablation has shown great promise in producing thin films with good epitaxy, and high critical currents and transition temperatures. In this process, the bulk material is vaporized by a laser pulse, and subsequnetly condensed on an appropriate substrate to produce a thin film. Although laser evaporation and ablation have been studied for over twenty years, the tertiary and quaternary metal oxide HTS systems are by far the most complex systems to which this deposition technique has been applied. In order to gain a further understanding of the deposition process for these systems, and in part to develop process monitors for production, a variety of optical spectroscopies have been used with some success as diagnostics for the laser process.[1] In addition, mass spectrometric techniques have also been evaluated as process monitors for the thin film production and as diagnostic probes to better understand and model the ablation event.[2-9]

The results presented here are a brief introduction to the application of mass spectrometric techniques used to study the laser deposition process. In the present study, the emphasis has been placed on the detection and velocity mapping of ablated neutrals (Cu, Y, BaO) from $YBa_2Cu_3O_x$ via Resonance Ionization Mass Spectrometry (RIMS). The observations point to the basic dynamics involved in the ablation process and plume development. Studies of the detection of the primary ions produced are also documented briefly. This technique provides a convenient analytical monitor for the detection of impurities in the bulk target materials.

2. EXPERIMENTAL

The photoablation process and products were monitored by mass spectrometry, using one of two systems. A quadrupole mass spectrometer (QMS) was used to monitor nascent ions formed in the partially ionized plume, while a time-of-flight (TOF) apparatus, utilizing multiphoton photoionization, was used to detect neutrals and monitor the dynamics of the photoablation.

For analytical monitoring of bulk target material, primary ions produced by the ablation laser were detected by turning off the electron impact ionizer of the QMS (Extranuclear, model C50), and adjusting the ion optics to collect ions produced outside the normal ionization region. A base pressure of $<1 \times 10^{-8}$ Torr was maintained by a turbomolecular pump during these determinations.

The velocity distribution measurements described below took place in the TOF source region as previously described[10] and illustrated in Fig. 1. Briefly, the Q-switch synch-out from the Nd:YAG laser (QuantRay/Spectra Physics Model DCR 1A) was used to master the timing sequence. This laser was used as the ablation source and operated at either the fundamental frequency, 1.06 microns, or at the third harmonic, 355 nm. The laser was equipped with beam filling optics and produced a near-Gaussian profile.[11] The output of this laser was ~10 nsec in duration and was smooth on the time scale of the detection electronics (~2 nsec). The laser output was focused to varying spot sizes on the target material with several different lenses. The angle of incidence (as measured from the normal of the target surface) was 60 degrees. Most of the ablation studies reported here utilized a peak laser fluence of approximately 1 J/cm^2; the average fluence was ~ 1/2 of the peak fluence. The fluence was determined by measuring the energy transmitted through a 10 micron pinhole centered on the laser spot at the focal point and correcting for widow transmission and the angle of incidence. The Gaussian-like profiles were confirmed by scanning the pinhole about the central spot in orthogonal directions.

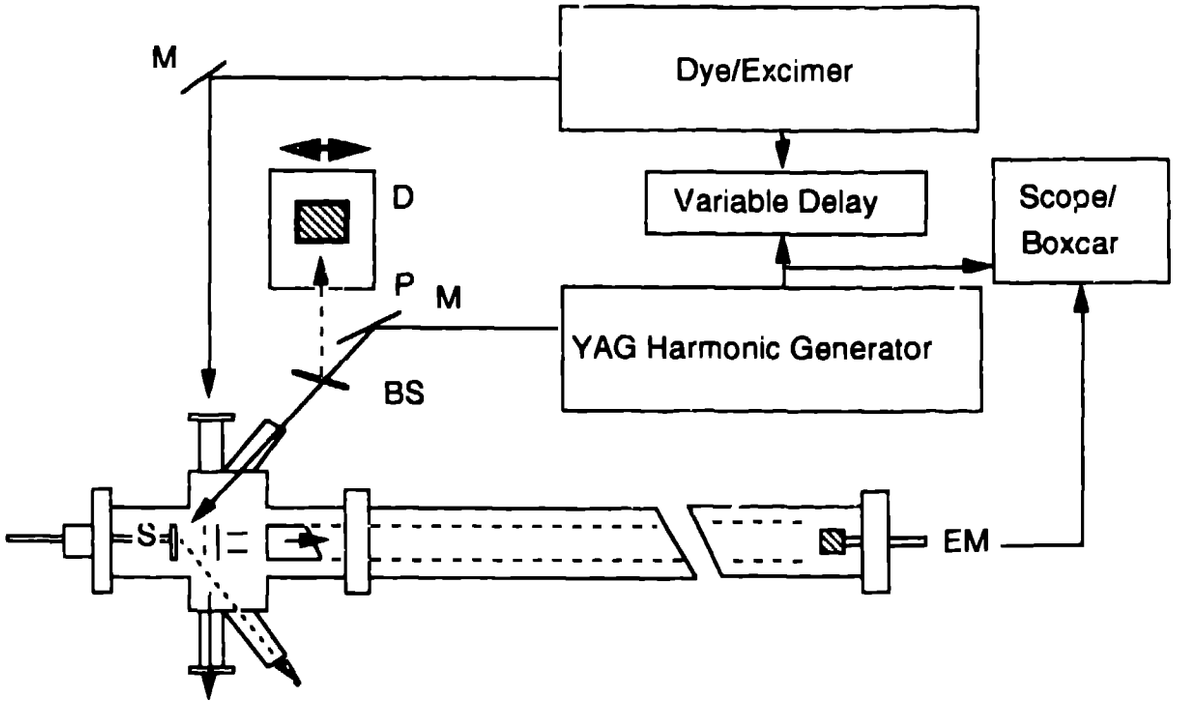

Fig. 1. Time-of-flight apparatus. Components defined as follows: BS, beam splitter; D, fast photodiode detector; M, mirror; P, pinhole; S, substrate/target holder; EM, electron multiplier.

Bulk samples of high-temperature superconductor were prepared in house using standard techniques and mounted on a vacuum feedthrough (Varian model 1371) that could be translated and rotated while in either mass spectrometer source region. The focal spot of the ablation laser was displaced from the center of rotation of the target. This displacement permitted interrogation of different sites through target rotation.

Pulses from an excimer-pumped dye laser (Lambda Physik Model 101/2002), propagating parallel to the target surface, but displaced 3.2 cm (i.e., in the center of the ionization region), were used to interrogate the ablated neutral species in the TOF studies. Ions produced directly by the ablation event were strongly discriminated against by maintaining the target holder at a negative potential (see Fig. 2). Ionization of the neutral species from ground electronic states was effected by a variety of multiphoton transition sequences described below. Dye-laser pulses (2mJ, 15 nsec) produced at a variable delay relative to the ablation laser laser were spatially filtered and loosely focused through the ionization region. The extraction field was approximately 110 V/cm, followed by by a drift tube of .4 m length at a potential of -1000V. A pair of deflection plates between the

extractor and the flight tube could be used to maximize the transmission of ions to the detector and minimize the any transmission variation that was due to ion velocity components perpendicular to the flight tube. Detection electronics consisted of a channel electron multiplier, a preamplifier, a boxcar integrator (PAR 162/164) and/or a transient recorder (Tektronix 2430).

For the purposes of spectroscopically tuning the dye laser to the appropriate transitions, a continuous source of the neutrals was available from a resistively heated tantalum ribbon filament placed within the ionization region. The filament (0.075 cm x 0.0025 cm) was either spiked with a solution of the appropriate metal salt or the appropriate metal was electrodeposited as an overlayer. Resistively heating the filament provided a stable source of the neutral specie. This source was necessarily not operated during ablation experiments.

3. TIME-OF-FLIGHT VELOCITY DISTRIBUTIONS OF ABLATED NEUTRALS

Cu Atom Detection

Detection of Cu atoms by RIMS involved a 2+1 (photons to resonance + photons to ionization) ionization process. A two-photon transition from the ground state ($3d^{10}4s^1\ ^2S_{1/2}$) to the excited state ($3d^{10}5s^1\ ^2S_{1/2}$) is followed by absorption of another photon of the same frequency (43137 cm^{-1}) to affect ionization. The ionization potential of Cu is 7.724 ev. Other studies in this laboratory indicate that the two-photon transition step is likely saturated,[12] and thus small fluctuations in the laser intensity will have little effect on the signal. Detection of Cu via this ionization scheme is illustrated in the transient mass spectra shown in Fig. 2. In this figure, time zero

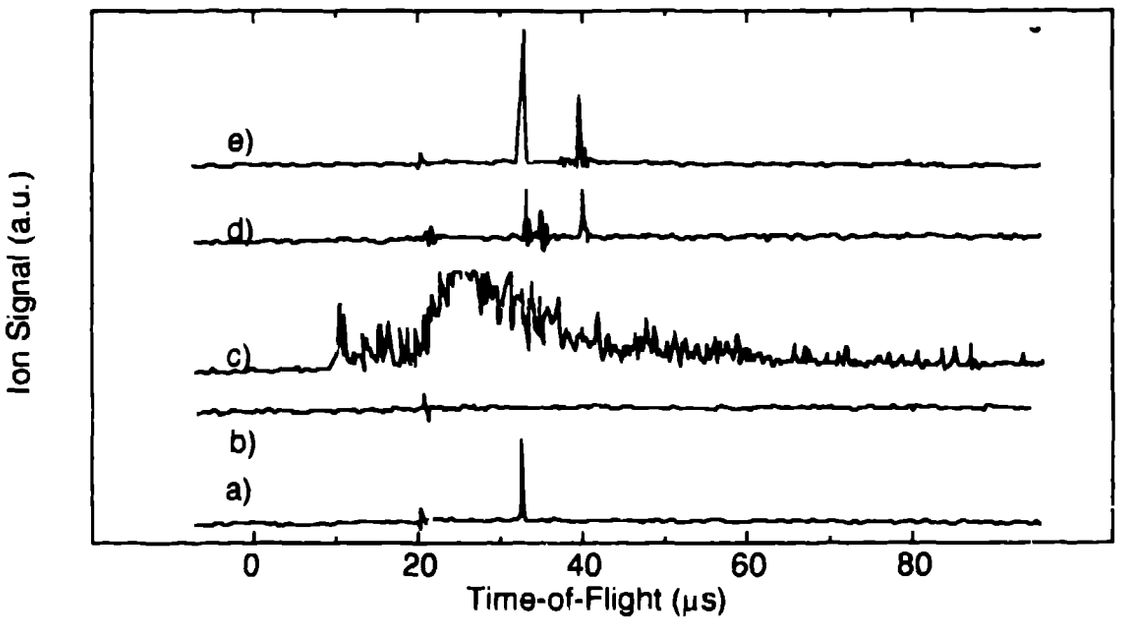

Fig. 2. Transient mass spectra recorded for a single ablation laser pulse at 355 nm and the dye laser tuned to neutral copper atom resonance: a) the copper signal from a continuous thermal copper source (used for a mass marker - subsequently turned off for all spectra that follow); b) the transient recording for dye laser only, i.e., ablation laser not directed onto the target; c) the mass signal generated with both lasers present and target holder held at ground potential; d&e) same as 2c but with a -100 V potential on the target holder. The mass peaks present in d and e have been identified as Cu, CuO, and Cu_2.

corresponds to the firing of the 355-nm ablation laser; for these spectra, the excimer laser was fired at a delay at 20 μs (corresponding to the peak time-of-flight signal intensity) . The spectra shown here have been recorded for a single pulse of the lasers. In Fig 2a, the copper signal has been recorded for the continuous thermal copper source as a mass marker (subsequently turned off for all spectra that follow); Fig 2b, the transient recording for dye

laser only, i.e., ablation laser not directed onto the target; Fig. 2c, the mass signal generated with both lasers present and target holder held at ground potential; Fig. 2d and 2e, same as 2c but with a -100 V potential on the target holder. The mass peaks present in Fig 2d and 2e have been identified as Cu, CuO, and Cu_2. Note that while the laser is tuned on resonance for the atomic copper transition, the molecules are likely ionized via accidental coincidences with vibronic transitions.

Ion trajectory simulations of the nascent ions produced in the plume and transmitted to the the detector when the target holder is held at ground potential, indicate ions of 250 au mass and 100 eV energy could be responsible for the signals observed in Fig 2c.[13] High mass and high energy particles have also recently been observed in streak camera studies at an ablation wavelength of 248 nm and low fluence (<1 J/cm^2) .[14] Although we have not determined the ion/neutral ratio in the plume in the present experiment, many previous laser ablation studies have indicated that the majority of ejected particles are uncharged. Clearly, totally ionized plasma models of this process are not correct.

Y Atom Detection

Yttrium atom detection paralleled that of copper atom detection. Either one of two ionization schemes was used to detect Y atoms. A two-photon transition from the ground state of yttrium (4d 5s^2 $^2D_{3/2,5/2}$) to either the (5s^{2}5d) $^2D_{3/2,5/2}$ excited state at ~43000 cm^{-1} or the (4d 5s 6s) $^2D_{3/2,5/2}$ excited state at ~36500 cm^{-1} preceded the absorption of an additional photon of the same frequency . The ionization potential for Y is 6.5 eV. Although easily detected transiently, the signal-to-noise ratios for Y atom detection prevented the measurement of statistically significant velocity distributions.

BaO Molecule Detection

In order to test laser ablation theory, the velocity distributions of as widely differing mass as possible should be measured. Further experimental requirements include an assignable signature absorption for the specie. For these reasons, BaO was chosen as the specie of choice for comparison to Cu data. A convenient and sensitive detection scheme for BaO exists via a multiphoton ionization pathway from the $X^1\Sigma$ ground state through the (v'=4,v"=0) $A^1\Sigma$ band system. The ionization potential of BaO (6.5 eV) is exceeded via a 1+2 multiphoton transition at this frequency (~18700 cm^{-1}). Although such transitions are usually inherently weaker than 2+1 transition, this particular ionization is extremely sensitive. We speculate that absorption of the second photon is enhanced by high-lying electronic states. This transition was particularly convenient, since it allowed Y and BaO detection using the same laser dye.

Velocity Distributions of Ablated Neutrals

The TOF signals have been recorded for several ablated neutrals from $YBa_2Cu_3O_x$ at 355 nm, similar to the excimer 308 nm wavelength used by several groups for the production of laser deposited superconducting thin films.[15] For Cu, this was compared to the TOF velocity distributions observed at an ablation wavelength of 1.06 microns. As part of the analysis, the observed TOF signals were fitted to a thermal Maxwellian velocity distribution and a shifted Maxwellian velocity distribution using a procedure previously reported.[10] In addition, the TOF data was also fit to the velocity distribution formalism used in the laser sputtering Knudsen layer model recently developed by Kelly and Dreyfus.[16] This model considers the formation of a Knudsen layer (when particles are no longer adequately described by a Maxwellian velocity distribution) via sputtered particle collisions and paralleis shifted Maxwellian distributions. Here, via collisions, ablation species acquire a common center-of-mass velocity rather than a velocity solely based upon individual specie mass and surface temperature. The observed time-of-flight data at a peak ablation laser fluence of approximately 1 J/cm^2 and model fits are shown in Fig. 3. In each, the lines indicate the best fit to three model velocity distributions: dashed lines represent Maxwellian thermal fits, solid lines represent shifted Maxwellian fits, and dotted lines represent fits to a Knudsen layer model.

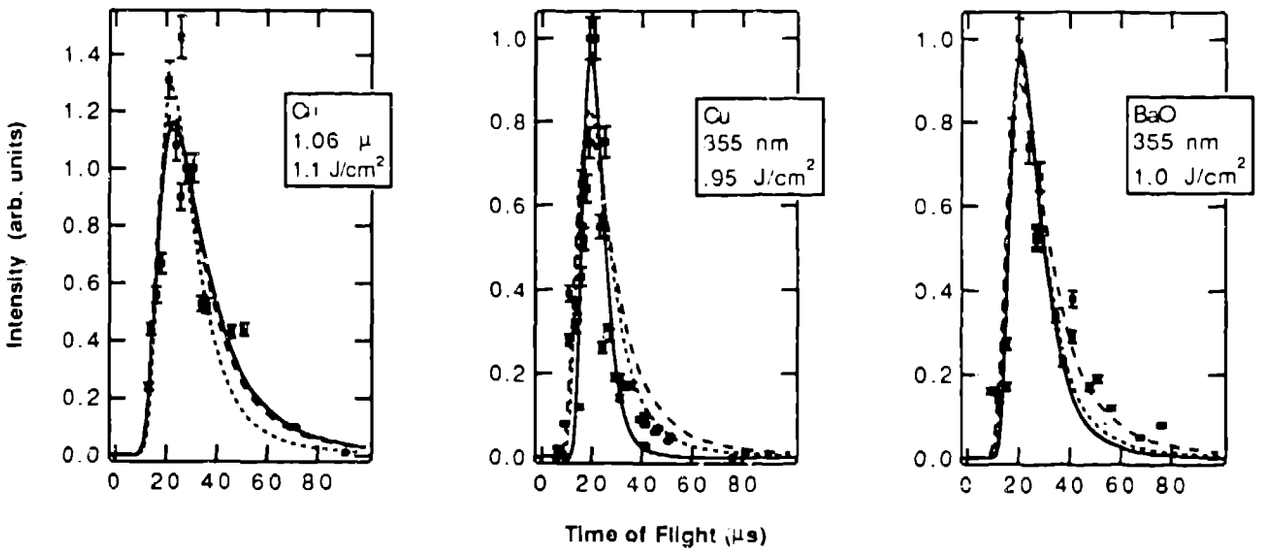

Fig. 3. TOF signals for neutrals ablated from $YBa_2Cu_3O_x$ at the wavelength and fluence indicated. In each case, the lines indicate the best fit to three model velocity distributions: dashed lines represent Maxwellian thermal fits, solid lines represent shifted Maxwellian fits, and dotted lines represent fits to a Knudsen layer model. Error bars indicate one σ variations in signal intensities.

Note that in each case, the TOF signals peak at approximately the same time-of-flight (~20-22 μs), indicating similar velocities for each specie, regardless of the mass. For Cu ablated at 1.06 microns, a thermal Maxwellian velocity distribution provides the best fit (although the differences are not great between the different fits for any of the data shown in Fig. 3), indicating a most probable velocity of 9.8×10^4 cm/s and temperature of approximately 3680 K. This temperature should be indicative of the surface temperature, since there is no evidence here of post-desorption collisions. At 355 nm, the Cu TOF signal peaks at the same time-of-flight, but possesses a substantially narrower width, although the same approximate ablation laser fluence was used. Here, a shifted-Maxwellian distribution provides the best fit to the data, indicating a center-of-mass velocity of 13×10^4 cm/s and a thermal width velocity of 4.9×10^4 cm/s. However, these velocities cannot be used directly to calculate a surface temperature, since collisions are altering the nascent distribution. Knudsen layer theory models such collisions, and a surface temperature of approximately 4000 K is calculated for this data. The presence of collisions at 355 nm indicates a greater efficiency of removing material at 355 nm compared to 1.06 μ, as has been observed for many materials. This may be due to a higher effective energy density, resulting from a shallower penetration depth at 355 nm. In addition, this may be evidence that the ablation process is in part photochemical as opposed to strictly evaporative. If these temperatures are representative of a local surface temperature, target morphology and stoichiometry changes should be anticipated since they exceed the 1288 K incongruent melting point for $YBa_2Cu_3O_x$ forming Y_2BaCuO_5 and a barium cuprate melt.[17]

For BaO at 355 nm, similar TOF signals are observed. Again here the best data fit is obtained with a shifted-Maxwellian velocity distribution, however, little statistical difference exists between the three data fits. A most probable velocity of 11×10^4 cm/s is measured from the data, while a surface temperature of 6800 K is calculated from the Knudsen layer model for BaO. If Cu and BaO shared a common surface temperature history, the ratio of their velocities ($v \propto \sqrt{T/m}$) should be 1.55:1.00 (Cu:BaO), clearly not the case here. From the present observations it is not clear whether BaO originates at the surface or by gas phase chemistry occurring in the plume

Although it was possible to collect an excitation spectra for the (4,0) $A^1\Sigma$ band of BaO from a filament source, an experimently consistent excitation spectra has not yet been successfully recorded for the ablated BaO. The problem lies in changing the target surface morphology over the time period required to record the spectrum. However, such data may provide some additional evidence as to the origin of the BaO.

The data presented here indicate the dominant role played by gas phase collisions in the UV ablation of $YBa_2Cu_3O_x$ at the minimum fluence used for thin film fabrication. The number and importance of such collisions is dramatically increased as the fluence is increased into the region of 2-5 J/cm^2 where most thin film laser deposition processes operate. Post-desorption collisions introduce some challenging scientific and technical issues that need to be addressed as the laser deposition process matures. Such issues include modifying the gas phase chemistry with additional oxidizer, minimizing target surface stoichiometry changes that occur via back-deposition and/or nonstoichiometric ablation, and compositional changes occurring by laser induced phases changes (melting). The sensitivity and selectivity of laser desorption/RIMS studies of the ablation process show promise in addressing some of these concerns.

4. ANALYTICAL MASS SPECTROMETRIC PROBES OF BULK MATERIALS

In addition to the dynamic information obtainable using RIMS detection of the ablated neutrals, laser desorption mass spectrometry of the nascent ions can provide additional insights into the chemistry of ablation event. Such studies also provide a sensitive analytical tool to detect impurities contained in the bulk materials as a result of a particular synthetic route and/or material processing step. Fig. 4 shows a narrow region of the primary ion spectrum generated from 355 nm laser radiation focused onto a $Tl_2Ca_2Ba_2Cu_3O_{10}$ (2223) pellet in the source region of a quadrupole mass spectrometer as described above. Clearly visible is a residual sodium contamination which resulted from the synthetic pathway for this pellet. Also indicated is the large dynamic range available in these measurements as illustrated by the appearance of trace isotopes of Ca. These measurements are far more sensitive than the more traditional use of Rutherford Backscattering Spectroscopy (RBS) to measure target and thin film stoichiometry.

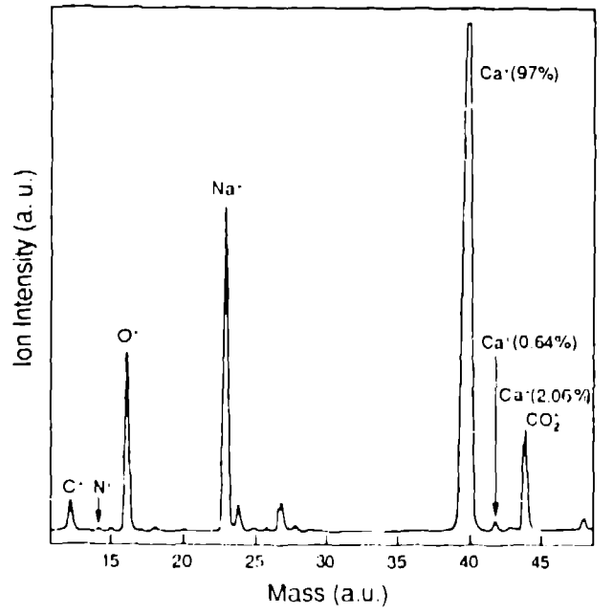

Fig 4. Quadrupole mass spectrum of the ablated plume of $Tl_2Ca_2Ba_2Cu_3O_{10}$ (2223) superconductor, showing the presence of sodium contamination as well as the dynamic range and sensitivity of the measurements. The laser wavelength was 355 nm and the fluence was ~1 J/cm^2.

For this particular sample and others of this same superconductor, no metal oxides were detected, even though their presence has been established by several groups by visible emissions. On the other hand, we were able to detect large quantities of both neutral (via electron impact ionization) and ionic oxygen atoms and molecules. These apparently inconsistent results may again suggest that the overall ablation process consists of several individual steps including desorption, Knudsen layer formation, and reactive gas phase collisions. Each step itself may be a function of target morphology and density, laser ablation wavelength, fluence, and intensity, as well as the atmosphere in which the ablation is occurring. Clearly this highly complex system merits further study.

5. ACKNOWLEDGMENTS

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