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The effect of water vapor and bulk temperature on positive ion emission from wide bandgap single crystals during exposure to 248 nm excimer laser radiation

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Abstract

We investigate the effect of low partial pressures of water vapor and bulk temperature on laser-induced positive ion emission from cleaved, single-crystal sodium nitrate and sodium chloride. Both materials yield more intense Na^+ emission in the presence of water vapor ($P_{\text{H}_2\text{O}} \sim 1 \times 10^{-5}$ Pa) than samples irradiated under UHV conditions ($P_{\text{total}} < 1 \times 10^{-7}$ Pa). Emission intensities increase rapidly with increasing temperature in a fashion consistent with activation energies on the order of 0.07–0.08 eV, both with and without water vapor. We attribute Na^+ emission to a defect-mediated photoelectronic process. Na^+ adsorbed at or near surface anion vacancies (electron traps) is ejected when the underlying or adjacent vacancy is photoionized. Vacancy formation in both materials is expected to have activation energies on the order of 0.08 eV, suggesting that Na^+ emission is rate limited by the production of surface anion vacancies. We attribute the effect of water vapor to defect-mediated sorption that increases the ion emission probability.

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1. Introduction

Sodium chloride and sodium nitrate are wide band-gap, ionic materials whose interactions with UV photons are well characterized [1–12]. The absorption of 248 nm laser radiation (5 eV photons) in these materials is dominated by lattice defects [5]. Further, both materials display significant incubation effects under 248 nm laser irradiation. Ion emission, for instance, can increase dramatically under prolonged irradiation at appropriate fluences. In many materials systems, simultaneous exposure to aggressive chemicals can accelerate laser-induced etching in a controlled fashion, but these chemicals are often extremely reactive. In this work, we show that laser-induced etching in

NaCl and NaNO_3 is strongly enhanced by low partial pressures of water vapor—a relatively inert and safe chemical, but one with significant reactivity in a number of important materials systems.

We compare Na^+ emissions from cleaved, single-crystal NaCl and NaNO_3 with and without water vapor. In previous work, we have argued that Na^+ emission in these and similar materials is due to a defect-mediated photoelectronic process. An ion adsorbed atop or very near a surface anion vacancy (electron trap) is ejected when the nearby vacancy is photoionized [9,13,14]. Thus ion emission depends strongly on the density of surface anion vacancies (e.g., surface F-centers) as well as the density of adsorbed ions. Across the range of probed water partial pressures, ion emission also displays thermally activated behavior consistent with the activation

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energy for anion vacancy defect formation. As the temperature is raised, the density of anion vacancies increases and provides more potential sites for emission. The principal effect of water is to increase the intensity of low kinetic energy ions, suggesting that defect interactions with water-related sorbed species (e.g., OH^-) increases the emission probability from specific sites. Significantly, the water vapor affects laser-induced ion emission from these two materials in very similar fashions, suggesting that water-induced effects may be common and useful in a large number of materials systems.

2. Experiment

Optical quality, single-crystal (cleavable) NaCl was obtained from Optovac, while sodium nitrate crystals were grown by slow cooling from the melt.

The general UHV system used for this experiment has been described elsewhere [15]. The samples were cleaved into 1.0 ± 0.02 mm thick plates and mounted on a sample holder normal to the long axis of a quadrupole mass spectrometer. Laser radiation at 248 nm was provided by a Lambda Physik Lextra 200 excimer laser (KrF). The laser beam was focused onto the sample to produce a 0.4×0.3 cm² laser spot with a fluence of 50 mJ/cm² (integrated over the 30 ns duration of the laser pulse). Ion counts were summed in a time-resolved fashion over 100 laser pulses. A repetition rate of 1 Hz was used to minimize cumulative sample heating by the laser. The sample temperature was controlled by resistively heating the sample holder while monitoring its temperature with a chromel–alumel thermocouple welded to the back. Experiments were conducted under ultrahigh vacuum conditions ($<10^{-7}$ Pa) except when water vapor was introduced. Water vapor was provided by leaking vapor from degassed deionized water to yield a total pressure of about 10^{-5} Pa.

3. Results

Typical Na⁺ time-of-flight (TOF) signals from NaCl and NaNO₃ due to 248 nm irradiation at 50 mJ/cm² appear in Fig. 1. Each TOF signal in Fig. 1 was acquired from a different sample. Due to

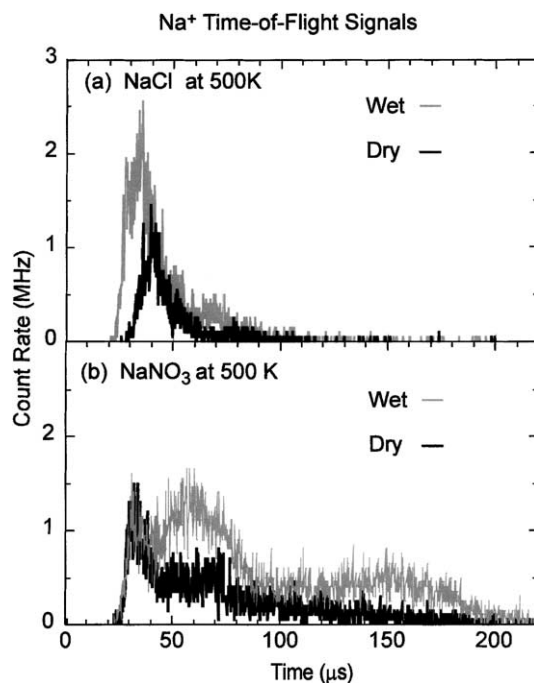


Fig. 1. Na⁺ TOF signals at water partial pressures of $<10^{-7}$ Pa (dry) and $\sim 10^{-5}$ Pa (wet) conditions from (a) NaCl and (b) NaNO₃ at a laser fluence of about 50 mJ/cm².

small variations in defect densities between samples (and from spot to spot on a single sample), detailed comparisons between the emission intensities in Fig. 1 are not possible. Nevertheless, measurements from several samples of each material show that the average intensities (total ion counts) are significantly higher under wet conditions.

TOF signals from NaCl under dry conditions at 500 K (Fig. 1(a), dark line) generally show a single prominent peak. The comparable peak in TOF signals under wet conditions (Fig. 1(a), light line) is followed by a long, low energy tail. The diffuse nature of the tail suggests that wet conditions favor the emission of ions from a wide variety of defect sites. The total number of Na⁺ counts at 500 K is typically 50% higher in the presence of 10^{-5} Pa water vapor than under UHV conditions, consistent with the stronger signal with water vapor (light line) in Fig. 1(a).

TOF signals from NaNO₃ at 500 K are shown in Fig. 1(b). Although water vapor has little effect on the fast TOF peak in Fig. 1(b), water vapor strongly increases the intensity of low energy ions (long TOF).

In previous work with MgO, we have shown that well-defined peaks in ion TOF signals can often be identified with specific surface defect configurations [13]. In the case of NaNO_3 , the emission of ions with lower kinetic energies suggests that additional defects are participating in emission processes in the presence of water vapor.

Na^+ yields (total counts over 100 laser pulses) for the two materials at water partial pressures $<1 \times 10^{-7}$ Pa (dry) and $\sim 10^{-5}$ Pa (wet) are displayed as a function of temperature in Fig. 2. Although emission from room temperature NaCl is not strongly affected by the

presence of water vapor, water vapor increases emission by at least a factor of 2 at temperatures above 600 K. Emission under both wet and dry conditions is a strong function of sample temperature. The effect of water vapor on Na^+ emission from NaNO_3 is quite similar, except that significant vapor effects are observed even at room temperature. (To avoid problems associated a phase change near 560 K, the maximum temperature in the NaNO_3 measurements was limited to 500 K.)

The effect of temperature on Na^+ emission was quantified from Arrhenius plots of the emission intensities. Typical plots are shown in Fig. 3. Significantly,

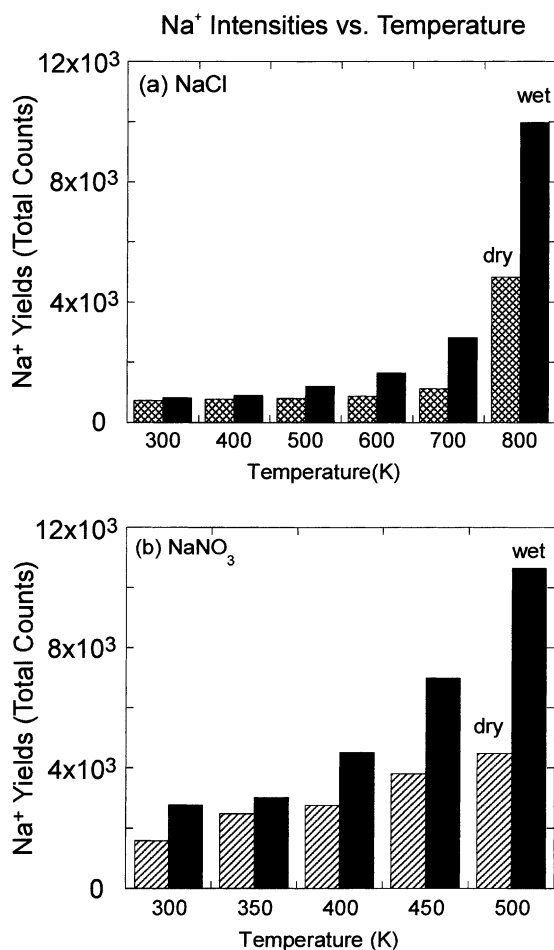


Fig. 2. Na^+ intensities under water partial pressures of $<10^{-7}$ Pa (dry) and $\sim 10^{-5}$ Pa (wet) conditions at several selected temperatures from (a) NaCl and (b) NaNO_3 at a laser fluence of about 50 mJ/cm^2 .

Arrhenius Plots of Total Na^+ Counts vs Temperature

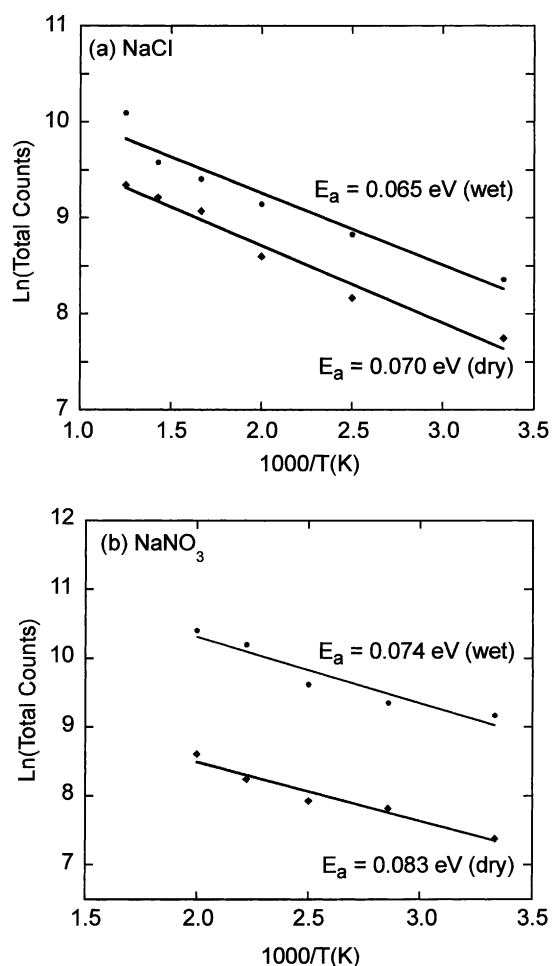


Fig. 3. Arrhenius plots of Na^+ intensities at water partial pressures of $<10^{-7}$ Pa (dry) and $\sim 10^{-5}$ Pa (wet) conditions from (a) NaCl and (b) NaNO_3 at a laser fluence of about 50 mJ/cm^2 .

Table 1
Estimated activation energies for Na⁺ emission from NaCl and NaNO₃ under 248 nm irradiation

	Activation energies (eV)	
	Dry	Wet
NaCl	0.070 ± 0.02	0.070 ± 0.02
NaNO ₃	0.080 ± 0.03	0.080 ± 0.03

the Arrhenius plots for emission under wet and dry conditions are nearly parallel, indicating that the corresponding activation energies (E_a) are not affected by the presence of water vapor. The effect of water is to increase the prefactor A in the Arrhenius expression, where the emission intensity is assumed to be proportional to $A \exp(-E_a/kT)$. From the perspective of transition state theory, the prefactor can be raised

SEM Images of Irradiated Surfaces

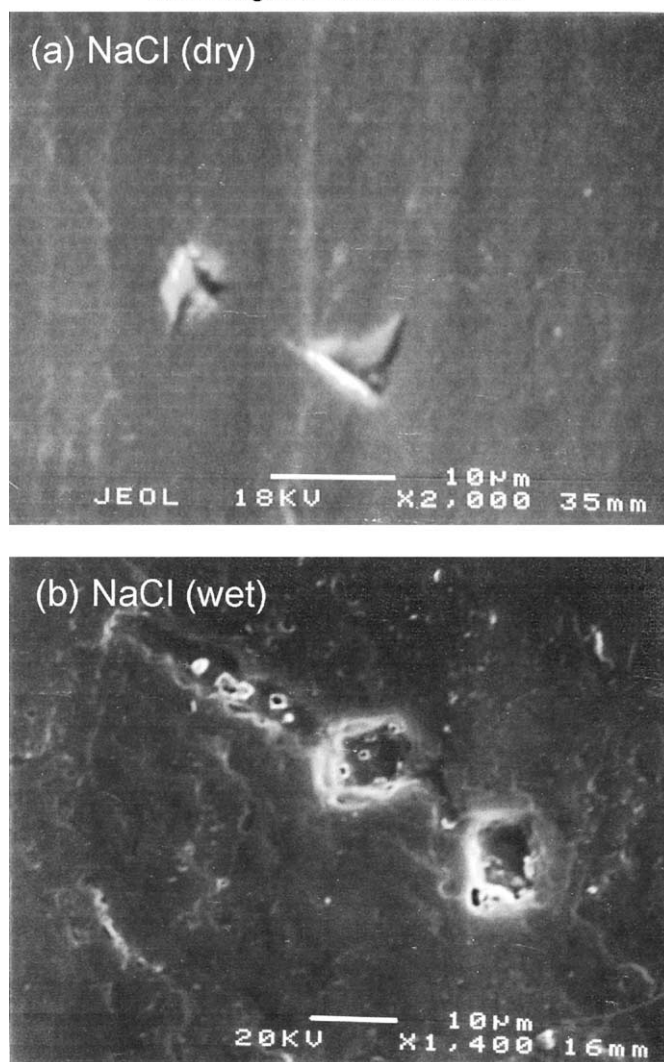


Fig. 4. SEM images of etch pits on NaCl surfaces exposed to about 5000 pulses of 248 nm radiation at 50 J/cm² under water partial pressures of (a) $<10^{-7}$ Pa (dry) and (b) $\sim 10^{-5}$ Pa (wet) conditions.

by increasing the concentration of a critical reactant, or by removing a geometric barrier to the reaction (e.g., the necessity that reacting molecules have a particular orientation in order to participate in the reaction).

Activation energy estimates made from multiple experiments under each condition were averaged and appear in Table 1. In each material, the presence of water vapor had no significant effect on the activation energy, given the experimental uncertainties. For NaCl, $E_a \approx 0.07 \pm 0.02$ eV and for NaNO₃, $E_a \approx 0.08 \pm 0.03$ eV for with and without the presence of water vapor. As discussed below, these energies are consistent with activation energies for radiation-induced vacancy formation.

Scanning electron microscope (SEM) images of irradiated NaCl surfaces show that prolonged laser exposure roughens the surface and can produce pit-like structures. SEM images of NaCl surfaces exposed to 248 nm radiation under dry and wet conditions appear in Fig. 4. Erosion is much more extensive and widespread on surfaces irradiated under wet conditions (Fig. 4(b)) with the appearance of cubic symmetry etch pits. At low doses of keV electron beam irradiation and elevated temperatures, (0 0 1) surfaces of KBr are found to form numerous cubic etch pits, much smaller than those seen by SEM [16]. It is very possible that the formation of defect-laden step edges is important for the observed cation emission. We are in the process of determining if such structures are generated by low dose exposure to excimer light of both dry and wet NaCl and NaNO₃.

4. Discussion

Na⁺ emission from NaCl and NaNO₃ under UHV conditions is attributed to the photoelectronic ejection of Na⁺ adsorbed on or near surface anion vacancies [9]. Anion vacancies in ionic lattices typically trap one or more electrons; Na⁺ emission occurs when the vacancy near an adsorbed Na⁺ ion is photoionized by the laser. Both NaCl and NaNO₃ display strong incubation effects, and so the average intensity of the observed emissions depends on the duration of laser exposure and the efficiency of defect production. Anion vacancy production in either material produces surface sites suitable for Na⁺ sorption and emission.

The production of anion vacancies by electronic excitations in the alkali halides in general and NaCl in particular has been especially well studied (see Ref. [3] and references therein). A self-trapped exciton at a Cl⁻ site can decay to form an F-center/H-center pair (anion vacancy adjacent to a Cl₂⁻ center) when the Cl⁰ at the exciton site hops to a nearest-neighbor Cl⁻ site. At room temperature, this hop is thermally activated with an activation energy of about 0.07 eV—consistent with the 0.07 ± 0.02 eV activation energies observed for Na⁺ emission in this work. Further migration of the Cl₂⁻ center produces an isolated anion vacancy, complete with trapped electron. At the surface, anion vacancies can serve as sites for Na⁺ adsorption and subsequent photoelectronic emission. Association of these defects with step edges and corners may well be involved in forming the dominant ion desorption sites.

Since the activation energy for F-center production is quite similar to the activation energy observed for Na⁺ emission from NaCl, we propose that Na⁺ emission is rate limited by the production of anion vacancies via the decay of self-trapped excitons. Although the photon energy in this work is well below the energy required to produce self-trapped excitons in intrinsic NaCl (8 eV), lower energy photons can produce similar excitons in the presence of defects. Quantum mechanical calculations on ionic materials indicate that the effective bandgap is well below bulk values at surface sites, and lower still at step and kink sites [17]. The importance of steps is strongly suggested by the localized pits found on the NaCl surfaces after laser exposure. Pits have high step densities that allow for significant erosion as steps propagate into the adjacent material. Steps also provide high densities of polarized surface defect sites that would be especially favorable for water adsorption.

Ion emission from NaNO₃ is believed to involve similar processes [8,9,18]. Although the details of anion vacancy creation by electronic excitations in NaNO₃ are theoretically less well understood than in NaCl, the radiolysis of NaNO₃ has been extensively studied [5,19,20]. In particular, the radiolytic decomposition of NaNO₃ is thermally activated, with a thermal activation energy of about 0.1 eV [21]. Several laser- and electron-induced emissions from NaNO₃ are thermally activated, with activation energies in the range 0.1–0.3 eV [7,18,22]. These activation energies

are similar to the activation energy for Na^+ emission observed in this work (0.08 ± 0.03 eV). Thus the broad features of defect formation in NaNO_3 —the role of defect creation, the need for low-energy defect sites for single photon absorption and the importance of thermal stimulation—are common to both NaCl and NaNO_3 . Furthermore, it should be emphasized that this steady-state, bulk crystal temperature can only influence slow processes—slow relative to any laser heating which normally reaches a maximum during the laser pulse and decays on time scales of several ns to a few ms.

In the presence of water vapor, both materials yield more intense emissions of relatively low kinetic energies. Although the observed enhancement is quite significant, the exposure to water vapor has little if any effect on the activation energy associated with emission. This suggests that the effect of water vapor is confined to photoelectronic processes, which are not thermally activated. In the case of NaCl , water does not adsorb in molecular form at the pressures and temperatures employed in this work [23]; physisorbed water desorbs from nearly perfect NaCl (1 0 0) above 160 K [24,25]. Significantly, dissociative adsorption at $P_{\text{H}_2\text{O}} \sim 10^{-5}$ Pa and 370 K is believed to produce a partial hydroxide layer, where some surface Cl^- is replaced by OH^- [23]. Defects are considered necessary for these reactions to occur and only limited OH^- adsorption is observed at room temperature. The elevated temperature required for the reaction of OH^- with NaCl surfaces may explain why water vapor has less effect on emission intensities at room temperature, but dramatically increases emission at higher temperatures.

The presence of adsorbed or surface OH^- would significantly affect ion emission. For instance, if an OH^- ion was to adsorb near an anion vacancy/adsorbed Na^+ defect complex, the negative charge of the OH^- ion would lower the energy required to photoionize the underlying anion vacancy as well as reduce the kinetic energy of the ejected Na^+ ion. Thus adsorbed OH^- may allow for emission from defect complexes that would not otherwise yield emission. Water interactions with NaNO_3 surfaces have not been well studied, but are likely to be generally similar to NaCl . In both cases, we are proposing that the water-derived sorbed species enhances the rate of a photoelectronic process (fast—non-thermal) which is

independent of the rate of formation of ion emitting defects (slow—thermal). The latter manifests itself through the observed $E_a = 0.07$ eV Arrhenius behavior.

Ion emission plays an important role in the formation of weak plasmas during the irradiation of ionic crystals with UV lasers [10,26]. These plasmas in turn provide energetic electrons capable of electronically exciting vaporized neutral particles—producing the visible fluorescent plume observed at the onset of rapid ablation in these materials. Increasing the ion emission intensities is expected to increase the kinetic energies of the associated electrons, and promote plume formation. Preliminary experiments show that the fluence for plasma formation are considerably lower for NaCl when water vapor is present. At much higher water vapor pressures, water can have the opposite effect [27], quenching plume formation by reducing the plasma electron density via electron attachment to water molecules. Thus vapor interactions may provide another tool for the control of laser interactions in ionic materials.

5. Conclusions

We have shown that low partial pressures of water vapor ($\sim 10^{-5}$ Pa) can have dramatic effects on Na^+ emissions from cleaved, single-crystal NaCl and NaNO_3 , especially at elevated temperatures. Ion emission appears to be thermally activated, with activation energies consistent with activation energies for anion vacancy creation in these materials. Thus the temperature dependence of Na^+ emission appears to be controlled by the rate of anion vacancy production. We propose that dissociative adsorption of water produces surface and adsorbed species (e.g., OH^-) that significantly alter the electrostatic environment of adsorbed Na^+ , allowing for emission from sites that would not normally yield emission thereby increasing the emission rate. In the case of NaCl , this hypothesis is supported by the relatively small effect of water at room temperature, where the water– NaCl interaction is weak. Although the effects of water on NaNO_3 surfaces are less well studied, the hygroscopic nature of NaNO_3 suggests that similar processes are likely.

Many geological and biological materials display strong interactions with polar water molecules and

may display similar vapor-enhanced emissions under laser radiation. Ion emission in particular is believed to play an important role in the onset of plume formation and rapid material removal in ionic crystals under UV irradiation. An understanding of these effects should provide additional tools for the control of laser interactions in this important class of materials.

Acknowledgements

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