

# X-ray photoelectron spectroscopy studies of the sodium chloride surface after laser exposure

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**Abstract.** The surface of NaCl crystals outside and in the crater was examined using an x-ray photoelectron spectrometer. The comparative analysis of the XPS spectra showed that high-intensity laser irradiation has a significant impact on the state and composition of the surface of the ionic crystal.

## 1. Introduction

Creation of lasers emitting femtosecond pulses opened up a different perspective in addressing many aspects of laser-matter interaction. Ultrashort laser pulses allow us to reach the terawatt power range and to study physics of high and ultrahigh radiation fields and effects of laser exposure not only on the electron shells of atoms and molecules.

As part of our continued study of ionic crystals in the field of ultrashort laser pulses [1, 2], we executed another piece of work, the aim of which was to study the impact (at the molecular level) of high-intensity laser pulses on the surface of sodium chloride. Such studies have not been performed before.

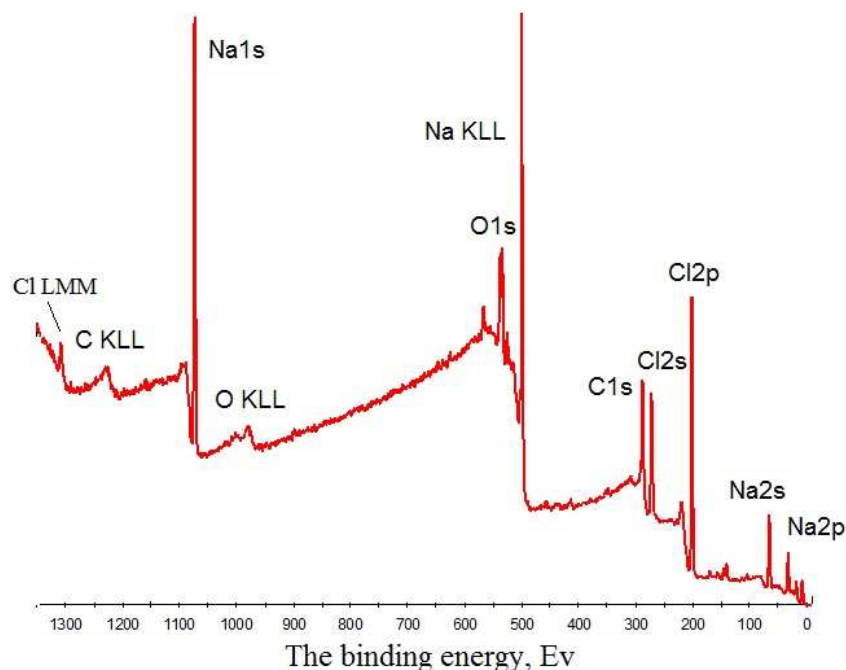
## 2. Experimental procedure

Experiments were carried out on a unique femtosecond laser facility (“Laser femtosecond complex”) at the Joint Institute for High Temperatures RAS [3, 4]. Laser pulses generated by the titanium-sapphire system at a wavelength of 800 nm having a duration of 40 fs were focused on the crystal surface at an angle of 60° and produced a power density of more than 50 TW/cm<sup>2</sup> [5] in the treatment spot.

The laser exposure produced optical damage (a crater) on the sample surface. The changes in the elemental composition of the medium were studied using an x-ray photoelectron spectrometer “Thermo Scientific K-Alpha”, which was used to examine the surface of NaCl crystals outside and in the crater.

The spatial resolution of the examination procedure was as high as 30 m. Diagnostics was done to a depth of 2–3 atomic layers of sodium chloride (0.5–0.8 nm [5]). In the analysis of the elemental composition of the surface, the content of the sample components was determined to within ±0.3%. The samples were placed into the spectrometer chamber evacuated to about 10<sup>−9</sup> mbar.





**Figure 1.** The spectrum of the sample surface outside the crater.

To compensate for the binding energy shifts caused by the effect of the surface charge, we used a low-energy electron gun, which allowed us to minimize the impact of this effect on the results of the energy measurement. The binding energies of the lines of the main components were calibrated with respect to the line of carbon C1s (284.8 eV [6]), corresponding to the C–C-bonds in carbon impurities to allow for a possible shift of the binding energies of the components due to the residual charge of the surface layer.

The results of the preliminary measurements revealed a layer of adsorbed carbon and oxygen atoms on the surface, which attenuated the signal of the main components forming the surface of the sample [7]. To mitigate this effect, the surface was cleaned by bombardment with 1000 eV argon ions for 60 s.

### 3. Experimental results

The panoramic spectrum of the sample taken at the point on the surface outside the crater is shown in figure 1.

One can see that the spectrum mostly contains the lines of sodium (Na1s, Na2s, Na2p and Auger line of Na KLL) and chlorine (Cl2p doublet, Cl2s line and Auger line of Cl LMM). All of these lines precisely coincide with the binding energies given in the known XPS handbooks [8,9].

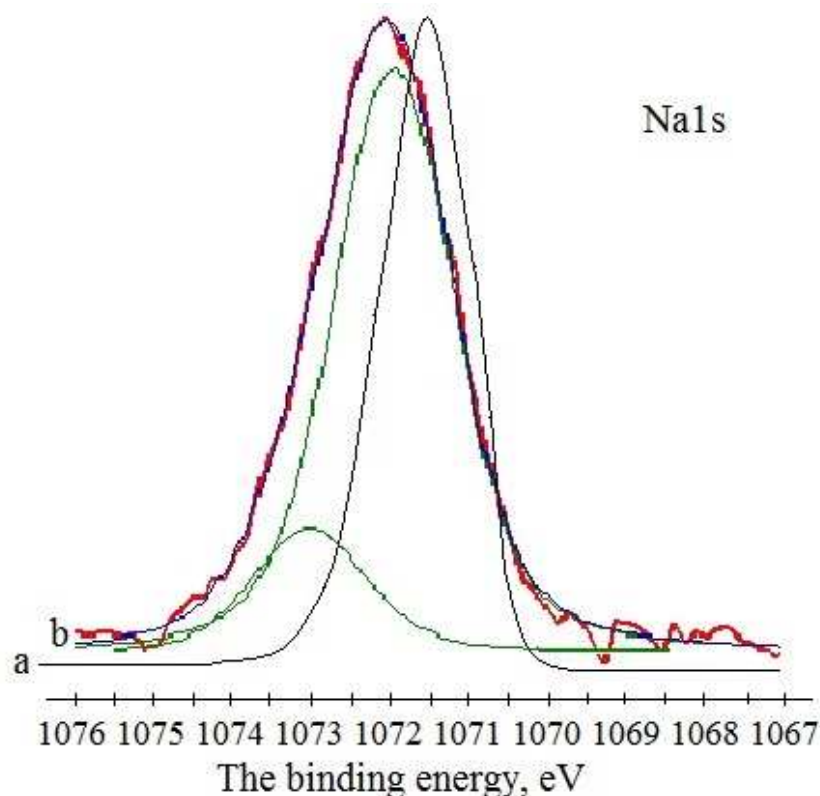
The quantitative results are shown in table 1.

As we can see from the table, the composition of the cleaned surface is determined by the atoms of sodium and chlorine, and oxygen and carbon. For the analysis of the chemical states of the components present on the surface of the sample, high-resolution spectra of the Na1s, Cl2p, C1s and O1s lines were taken. To get the best signal-to-noise ratio, we varied the transmission energies of the spectrometer energy analyzer, the number of spectrum measurement passes and the energy scanning step.

Analysis of the Na1s doublet line taken at a point outside the crater (line symmetry and the peak half-width) shows that sodium exists entirely in one state.

**Table 1.** The results of the quantitative analysis of the sample outside the crater.

Name	Peak BE	Height CPS	FWHM, eV	Area (P) CPS, eV	Atomic %	SF
Na1s	1073.93	396920.46	3.487	1532057.64	34.63	10.588
Cl2p	201.75	177587.56	3.780	748082.00	28.45	2.741
O1s	538.76	67444.24	4.432	412140.37	18.82	2.881
C1s	286.73	25774.29	5.088	164712.81	18.10	1.000

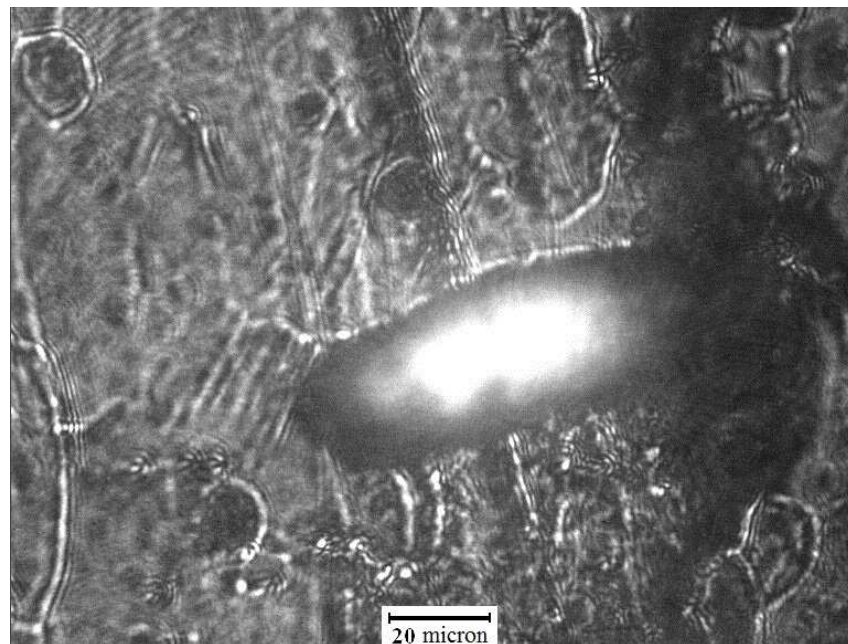
**Figure 2.** High-resolution spectra of the Na1s line taken outside (a) and in the crater (b).

For accurate identification of this condition we studied the Auger—peak of Na. The value of the Auger parameter that equals 2061.52 eV (calculated as the sum of the binding energy of the Na1s line and the peak of the Auger line of Na KLL) together with the information on the elements present on the surface definitely indicates that we deal with sodium in the NaCl compound [10].

Analysis of the high resolution spectrum of the chlorine doublet also showed a symmetrical, without significant broadening, Cl2p doublet.

Here, all the doublet parameters indicate that chlorine atoms predominantly exist in one state, and the binding energy of Cl2p<sub>3/2</sub> that equals 199.1 eV indicates that chlorine outside the crater is also present entirely in the NaCl compound [11].

Following this, we compared the high-resolution spectra of the Na1s line taken on the surface of the NaCl crystal outside and in the crater (figure 2).



**Figure 3.** The surface of sodium chloride 0.5 ns after laser irradiation.

#### 4. Discussion of results

The comparison of figures 2a and 2b shows that the spectrum of the NaIs line after irradiation exhibits some asymmetry.

Decomposition of the peak in figure 2b to Gaussian components showed that atoms of sodium are present in two chemical states: the peak with the binding energy of 1071.92 eV corresponds to sodium in the NaCl compound (87%), and the peak at 1073.01 eV, to sodium combined with oxygen (13%). According to [12], the compound is  $\text{Na}_2\text{O}$ .

The common mechanism of surface damage in transparent solids for femtosecond laser pulses is ablation. If the ablation threshold is exceeded, a molten zone forms on the surface (figure 3), and then a portion of the melt is removed leaving a crater on the surface of the sample [5].

New studies using the method of photoelectron spectroscopy showed that the exposure of the surface of ionic crystals to high-intensity femtosecond laser pulses in addition to phase changes [2] causes atomic changes in the subsurface matter.

One of the reasons for this for sodium chloride can be high pressure, which, according to [13], may lead to the formation of new compounds of sodium and chlorine.

Although in [13] this is considered to be possible for pressures as high as 200 kbar and calculations suggest that the values of ablation pressures in the experiments conducted [5] can be not less than 3 mbar [14], the method of photoelectron spectroscopy does not provide any clear evidence of the existence of new sodium and chlorine compounds in the surface layer after irradiation.

Due to the impact of short (including femtosecond) high-intensity laser pulses (including ionic crystals), new phenomena and transformation regimes can be achieved in dielectrics. Detailed information about this (including fundamental differences with respect to simple heating, melting, *etc*) is given, for example, in [15,16] and other references.

In [14], in this regard, the following is noted.

In contrast to the evaporation process typical of materials exposure to millisecond, microsecond and nanosecond pulses, in the femtosecond case, the basic mechanism of surface damage is thermo-mechanical ablation that removes the surface layer as a result of severe tensile

stresses in the substance. The surface layer of a transparent dielectric heated by multiphoton absorption during the femtosecond exposure starts to deform and suffer damage [17, 18].

To consider the model of formation of a molecule of  $\text{Na}_2\text{O}$ , let us turn to our other experiments on the effects of short laser pulses on ionic crystals (and at the same time compare the cases of crystal exposure to laser pulses of varying intensity and duration). Previously we have studied breakdown thresholds on the surface and in the bulk of an ionic crystal being a mixture of sodium and potassium chlorides (as well as quartz and glass). In that series of experiments, pulses produced by a neodymium laser at a wavelength of 1.06 microns with FWHM of 10 ns reached the intensity of 6 GW/cm<sup>2</sup>. The observation showed the following [19, 20]. The surface breakdown of the ionic crystal was accompanied by yellow luminescence.

We found that by varying the power density we can obtain a non-sustained air breakdown at the focus of the laser beam. As the focal plane of the objective lens moved closer to the dielectric surface, the nature of the laser spark changed: there was a stable discharge running from the focus area to the surface of the material. It turned out that the stabilization of the laser spark occurs when the focus area is located very close to the surface of quartz (0.1 mm) and glass (0.3 mm) and at a much greater distance from the surface of potassium chloride (2.1 mm).

The reason for the observed laser spark stabilization is its transition to the stage of a steady arc. The originally non-sustained breakdown is accompanied by UV emission, gas heating in the focal area, a shock wave and streamers. With the appearance of the hot spot on the surface of the ionic crystal, metal atoms start to migrate towards the subsurface region. Following this, the UV radiation and thermal ionization (that runs much easier in vapors of alkali metals than in the air) raise the ion concentration in the subsurface region, which facilitates further propagation of streamers to the surface of the ionic crystal, transition of the unstable laser spark into an arc discharge, heating of the discharge channel and development of thermal ionization of the air.

In the case of a laser air breakdown at the surface of silicate glass and quartz, the supply of easy-to-ionize vapors of alkali metals to the subsurface region of the substance and streamers ceases. As a result, the stationary arc discharge can exist for quartz and glass only when the laser beam focus is in immediate proximity to the dielectric surface.

Thus, we can conclude that the high-intensity laser radiation near the surface contributes to the appearance of sodium atoms, which allows us to observe the well-known yellow doublet of sodium (589 nm) [5]. Thus, the model of formation of molecules of  $\text{Na}_2\text{O}$  in the subsurface region of an ionic crystal can be represented as follows.

At high temperatures, vapors of sodium near the sample surface actively interact with oxygen to form sodium oxide, which then falls into the liquid-phase range and actively passes into the subsurface region, which is recorded by the x-ray photoelectron spectrometer.

## 5. Conclusion

Thus, in a series of studies on the effects of ultrashort laser pulses on sodium chloride [1, 2], it became possible not only to analyze fast phase transitions on the high-temperature phase diagram of sodium chloride [2, 21–23], but also to study the effect of radiation on the surface composition (at the molecular level).

The results of the work allow us to draw the following conclusions.

- (i) Exposure of the surface of sodium chloride to high-intensity femtosecond laser pulses causes changes in the molecular composition of the subsurface layer.
- (ii) The high-resolution spectrum of the NaIs line after irradiation exhibits some asymmetry. On the irradiated surface one can detect sodium which is present in combination with oxygen:  $\text{Na}_2\text{O}$ . The changes in the molecular composition will need to be taken into account when considering these phenomena in other media [24–26].

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