Study of the potassium bromide surface after laser effects using x-ray photoelectron spectroscopy

A P Savintsev, Yu O Gavasheli, Z Kh Kalazhokov and Kh Kh Kalazhokov
Kabardino-Balkarian State University, Chernyshevskogo Street 173, Nalchik, Kabardino-Balkaria 360004, Russia
E-mail: savinal@mail.ru

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

1. Introduction
The creation of lasers emitting femtosecond pulses opened up a different perspective in addressing many aspects of laser–matter interaction. Ultra-short laser pulses allow us to reach not only the electron shells of atoms and molecules, but also the terawatt power range and study physics of high and ultrahigh radiation fields and effects of laser exposure.

Within the framework of the further research of ionic crystals in the field of ultra-short laser pulses [1,2], another piece of work has been done, the aim of which was to study the impact (at the molecular level) of high-intensity laser pulses on the surface of potassium bromide. Similar studies have not been performed before.

2. Experimental procedure
Experiments were carried out using the unique facility “Terawatt Femtosecond laser Complex” in the Center for Collective Usage “Femtosecond Laser Complex” JIHT RAS [3,4]. The laser pulses generated by a titanium-sapphire system at a wavelength of 800 nm, 40 fs duration, were focused on the crystal surface at an angle of 60° and created of processing power density up to 90 TW/cm² [5] in the spot.

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

The spatial resolution of the examination procedure reached 30 µm. Diagnostics was done at the depth of 2–3 atomic layers of potassium bromide (0.5–0.8 nm) [1]. Studying the elemental composition of the surface, the content of the sample components was determined with the accuracy to ±0.3 %.

The samples were placed into the spectrometer chamber evacuated to about 10⁻⁹ mbar. To compensate for the binding energy shifts caused by the effect of the surface charge, we used a
Figure 1. The spectrum of the sample surface (a) outside and (b) inside the crater.

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

| Name | $E_m$ (eV) | FWHM (eV) | Atomic (%) | $E_m$ (eV) | FWHM (eV) | Atomic (%) |
|------|------------|-----------|------------|------------|-----------|------------|
|      | outside the crater | inside the crater | outside the crater | inside the crater | outside the crater | inside the crater |
| Br3d | 70.01      | 3.005     | 48.89      | 70.23      | 3.690     | 21.27      |
| K2p  | 294.32     | 2.955     | 46.35      | 294.95     | 4.615     | 20.41      |
| C1s  | —          | —         | —          | 294.45     | 3.705     | 48.28      |
| O1s  | 532.25     | 5.657     | 4.77       | 532.37     | 3.197     | 10.04      |

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 lines of the main components were calibrated with respect to the line of carbon C1s (284.8 eV [6]), corresponding to C–C-bonds in carbon impurities which allowed to consider a possible shift of the binding energies of the components due to the residual charge of the surface layer.

The results of preliminary measurements revealed a layer of the adsorbed carbon and oxygen atoms on the surface, which attenuated the signal of main components forming the surface of the sample [7]. To mitigate this effect, the surface was cleaned by the 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(a). One can see that the spectrum mostly contains the lines of potassium (K2s, K3s, K2p, K3p, and Auger line of K LMM) and bromide (Br3s, Br3p, Br3d, and Auger line of Br LMM). All of these lines precisely coincide with the binding energies given in the known x-ray photoelectron spectrometer (XPS) handbooks [8, 9].

The quantitative results of the sample (inside and outside the crater) are shown in table 1. There, the names of the component line are indicated; $E_m$ is the maximum value of the binding energy line; FWHM is the full width at half maximum (a half-width of the line); atomic is the
content of the components. As we can see from the table, the composition of the cleaned surface outside the crater is determined by the atoms of potassium and bromide, as well as by oxygen. For the analysis of the chemical states of the components present on the surface of the sample, high-resolution spectra of K2p, Br3d [figures 2(a) and 3(a)], were recorded, the Auger peaks of bromine and potassium were also studied.

To get the best signal-to-noise ratio, we varied the transmission energies of the spectrometer energy analyzer, the number of passes for spectrum measurement, and the energy scanning step. Also, the XPS spectra were recorded on the surface of KBr crystal in the crater after laser irradiation shown in figure 1(b).

The results of the quantitative analysis in a point inside the crater are also given in table 1. Higher-resolution spectra of K2p and Br3d lines taken in the crater are shown in figures 2(b)

---

**Figure 2.** Spectrum of high-resolution of K2p doublet recorded (a) outside and (b) inside the crater.

**Figure 3.** The high-resolution spectrum of Br3d doublet recorded (a) outside and (b) inside the crater.
Table 2. The value of the binding energy of the sample components outside and inside the crater.

| Name | \(E_r\) (eV) | \(E_m\) (eV) | \(\eta\) (%) | \(E_m\) (eV) | \(\eta\) (%) |
|------|-------------|-------------|-------------|-------------|-------------|
|      | outside the crater | inside the crater |
| Br3d | 69.00 | 70.01 | 1.4 | 70.23 | 1.7 |
| K2p  | 294.35 | 294.32 | 0.0001 | 294.95 | 0.002 |
| C1s  | 284.40 | — | — | 294.45 | 3.4 |
| O1s  | 531.60 | 532.25 | 0.12 | 532.37 | 0.15 |

and 3(b). An important parameter that can be found by the XPS method is the binding energy of electrons in atoms. The value of the maximum line, given in table 1, determines the measured binding energy \(E_m\). Comparison of \(E_m\) (outside and inside the crater) with a reference value of the binding energy \(E_r\) is given in table 2. The relative shift of the lines calculated by the formula \(\eta = [(E_m - E_r)/E_m] \times 100\%\) is also shown here.

4. Discussion of results

Analysis of K2p doublet line, which is taken outside the crater (figure 2), shows that potassium exists in the one state only. Auger peak of K was studied for accurate identification of this state. The value of the Auger parameter that equals 543.92 eV (calculated as the sum of the binding energy of K2p\(3/2\) line and the peak of the Auger line of K LMM) together with the information on the elements present on the surface definitely indicates that we deal with potassium in KBr compound [10].

Analysis of the high resolution spectrum of the bromine showed the presence of Br3d doublet [figure 3(a)]. Here, all the doublet parameters indicate that bromine atoms predominantly exist in one state, and the value of the Auger parameter (taking into account the data for Br LMM line) that equals 1457.94 eV indicates that bromine outside the crater is also present entirely in KBr compound [11]. The comparison of figures 2(a) and 2(b), as well as figures 3(a) and 3(b), shows that the spectrum of K2p and Br3d lines after irradiation exhibits some asymmetry. In this case (according to table 1), broadening of K2p, Br3d lines and narrowing (almost 2 times) of O1s line is observed. Such measurements are not available in a similar paper [1].

Decomposition of the peak in figure 2(b) to Gaussian components shows that atoms of K are present in two chemical states: the peak with the binding energy of 292.95 eV corresponds to sodium in KBr compound (46.2%), and the peak at 294.45 eV—to potassium combined with carbon (53.8%). According to [12], the compound is KC8. Decomposition of the peak in figure 3(b) to Gaussian components shows that atoms of bromine are also present in two chemical states: the peak with the binding energy of 68.78 eV corresponds to bromine in KBr compound (48.88%), and the peak at 70.4 eV, to bromine combined with carbon (51.12%). According to [12], the compound is CH3Br.

The common mechanism of surface damage in transparent solids for femtosecond laser pulses is ablation. In case the ablation threshold is exceeded, a molten zone forms on the surface, and then a portion of the melt is removed leaving a crater on the surface of the sample [5, 13]. The research that was carried out 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.

The comparison of results of this work and from paper [1] indicates that if ultra-short exposure to femtosecond high-intensity laser pulses and thermo mechanical ablation of NaCl results in the
enrichment of the surface of this ionic crystal, mainly oxygen, then a similar effect for KBr leads to surface enrichment, mainly by carbon and its compounds. The model of emerging of some of new compounds in the subsurface volume of an ionic crystal can be represented as follows.

Potassium and bromine vapors near the sample surface actively interact with molecules of carbon dioxide and water vapor to form KC₈ and CH₃Br, which then pass into the subsurface region. In addition, the analysis of table 1 showed that in the crater of KBr, in comparison with the area outside the crater, an increased oxygen content was observed (10.04 against 4.77%). This indicates the interaction of potassium and bromine vapors with air oxygen, which has been previously stated in [1].

Table 2 shows that the binding energies measured in the experiment exceed the reference energies. The measured and reference values coincide for K only. This indicates that the atoms and molecules (except K) under studies are in the state of tangible interaction with the other components on the surface of the crystal.

It is seen that the parameter \( \eta \) increases after irradiation. Thus, the relative shift of the spectral lines Br and O increased by 22–25%. For potassium, the measured value became greater than the reference value. This indicates that ultra-short high-intensity laser irradiation increases the interaction of the studied atoms and molecules with the other components of the upper layers of the investigated ionic compound. The obtained data are also important for consideration of similar phenomena in other environments [14–16].

Thus, in the series of studies on the ultra-short laser pulses effects on ionic crystals [2, 5, 13, 17–20], a new actual section appeared. The irradiation effect on the alkali-halide crystals surface composition (at the molecular level) has been studied.

5. Conclusions
We can note the following:

- Exposure of potassium bromide crystal to high-intensity femtosecond laser pulses causes changes in the molecular composition of the subsurface layer.
- The high-resolution spectrum of K₂p and Br₃d lines after irradiation exhibits asymmetry. In this case, the broadening of K₂p, Br₃d lines and the narrowing (almost 2 times) of O₁s line is observed. The laser action on potassium bromide leads to the enrichment of the surface of the crystal, mainly by carbon and its compounds. On the irradiated surface one can detect KC₈ and CH₃Br. In the crater of KBr, in comparison with the area outside the crater, an increased oxygen content is observed (10.04 against 4.77%), this indicates the interaction of potassium and bromine vapors with air oxygen.
- Ultra-short high-intensity laser irradiation increases the interaction of the atoms and molecules under study with the other components of the upper layers of the test compound. For this reason, the relative shift of the spectral lines Br and O increased by 22–25%.

Acknowledgments
This work was supported in the framework of the base part of the Russian Ministry of Education and Science task KBSU for years 2017–2019 (project No. 3.8382.2017).

References
[1] Savintsev A P, Gavasheli Yu O, Kalazhokov Z Kh and Kalazhokov Kh Kh 2016 J. Phys.: Conf. Ser. 774 012118
[2] Savintsev A P and Gavasheli Yu O 2015 J. Phys.: Conf. Ser. 653 012011
[3] Agranat M B, Anisimov S I, Ashitkov S I, Ovchinnikov A V, Kondratenko P S, Sitnikov D S and Fortov V E 2006 JETP Lett. 83 501–4
[4] Ashitkov S I, Komarov P S, Ovchinnikov A V, Struleva E V, Zhakhovskii V V, Inogamov N A and Agranat M B 2014 Quantum Electron. 44 535–9
[5] Gavasheli Yu O, Komarov P S, Ashitkov S I and Savintsev A P 2016 *Tech. Phys. Lett.* **42** 565–7
[6] Khamdokhov A Z, Teshev R S, Khamdokhov Z M, Khamdokhov E Z, Kalazhokov Z Kh and Kalazhokov Kh Kh 2015 *J. Surf. Invest.: X-Ray, Synchrotron Neutron Tech.* **9** 710–4
[7] Kalazhokov Z Kh, Karamurzov B S, Kochur A G, Misakova I B, Kardanova Z V and Kalazhokov Kh Kh 2015 *J. Struct. Chem.* **56** 576–81
[8] Crist B V 1999 *Handbooks of Monochromatic XPS Spectra* vol 1 (Mountain View, CA: XPS International Inc.)
[9] Wagner C D, Riggs W M, Davis L E, Moulder J F and Muilenber G E 1979 *Handbook of X-Ray Photoelectron Spectroscopy* (Eden Prairie, MN: Perkin-Elmer Corp., Physical Electronics Division)
[10] Seyama H and Soma M 1985 *J. Chem. Soc., Faraday Trans. 1* **81** 485–95
[11] Hammond J S, Holubka J W, Devries J E and Duckie R A 1981 *Corros. Sci.* **21** 239–53
[12] Barrie A and Street F J 1977 *J. Electron Spectrosc. Relat. Phenom.* **7** 1–4
[13] Gavasheli Yu O, Komarov P S, Ashitkov S I and Savintsev A P 2016 *Dokl. Phys.* **61** 577–8
[14] Geras’kin A A, Khishchenko K V, Krasyuk I K, Pashinin P P, Semenov A Yu and Vovchenko V I 2009 * Contrib. Plasma Phys.* **49** 451–4
[15] Povarnitsyn V E, Itina T E, Khishchenko K V and Levashov P R 2013 *Phys. Chem. Chem. Phys.* **15** 3108
[16] Krasyuk I K, Pashinin P P, Semenov A Yu, Khishchenko K V and Fortov V E 2016 *Laser Phys.* **26** 094001
[17] Savintsev A P 2008 *Tech. Phys. Lett.* **34** 122–3
[18] Karpenko S V, Savintsev A P and Temrokov A I 2008 *Dokl. Phys.* **53** 128–32
[19] Savintsev A P and Gavasheli Yu O 2017 *Dokl. Phys.* **62** 454–6
[20] Savintsev A P and Gavasheli Yu O 2018 *J. Phys.: Conf. Ser.* **946** 012006