Optical emission spectroscopy of various materials irradiated by soft x-ray free-electron laser


¹Institute of Physics ASCR, Na Slovance 2, 182 21 Prague 8, Czech Republic
²J. Heyrovský Institute of Physical Chemistry ASCR, Dolejškova 3, 182 23 Prague 8, Czech Republic
³Czech Technical University in Prague, Břehová 7, 115 19 Praha 1, Czech Republic
⁴Université Pierre et Marie Curie, LULI, UMR 7605, case 1258, 4 Place Jussieu, 75252 Paris, France
⁵Institute of Materials Research SAS, Watsonova 47, 040 01 Košice, Slovak Republic
⁶FOM-Institute for Plasma Physics Rijnhuizen, 3430 BE Nieuwegein, The Netherlands
⁷Queen’s University Belfast, University Road Belfast, BT7 1NN, Northern Ireland, UK
⁸Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA
⁹Lawrence Berkeley National Laboratory, 1 Cyclotron Road, CA 94720, USA
¹⁰Department of Physics, Clarendon Laboratory, University of Oxford, Oxford, OX1 3PU, UK
¹¹Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, D-22607 Hamburg, Germany
¹²Center for Free-Electron Laser Science, DESY, Notkestraße 85, D-22607 Hamburg, Germany
¹³SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA
¹⁴Institute of Physics PAS, Al. Lotników 32/46, PL-02-668 Warsaw, Poland
¹⁵Czech Technical University in Prague, Zikova 1905/4, 166 38 Praha 6, Czech Republic
¹⁶Instytut für Experimentelle Physik, Universität Duisburg-Essen, D-47048 Duisburg, Germany
¹⁷Optics Metrology Laboratory, STFC Daresbury Laboratory, Warrington, WA4 4AD, UK
¹⁸GKSS Research Center, Max-Planck-Strasse 1, D-21502 Geesthacht, Germany
¹⁹Laboratory of Molecular Biophysics, Uppsala University, Husargatan 3, SE-75124, Uppsala, Sweden

ABSTRACT

The beam of the Free-Electron Laser in Hamburg (FLASH) was focused by a grazing incidence elliptical mirror (32.5 nm and 13.5 nm) and an off-axis parabolic mirror coated with a Si/Mo multilayer (13.5 nm) to 20-micron and 1-micron spot, respectively. The grazing incidence and normal incidence focusing of ~25-fs pulses with an energy of 10⁻⁸ J resulted in an irradiance of 10⁻¹³ W/cm² and 10⁻¹⁶ W/cm², respectively, at the surface of various solids (Si, Al, Ti, Ta, Si₃N₄, BN, a-C/Si, Ni/Si, Cr/Si, Rh/Si, Ce:YAG, poly(methyl methacrylate) – PMMA, stainless steel, etc.). The optical emission of the plasmas produced under these conditions was registered by a grating (1200 lines/mm and/or 150 lines/mm) spectrometer MS257 (Oriel) equipped with iCCD head (iStar 720, Andor). Surprisingly, only lines belonging to the neutral atoms were observed at intensities around 10⁻¹³ W/cm². No spectral lines of ions have been identified in UV-vis spectra emitted from the plasmas formed by the FLASH beam focused in a 20-micron spot. At intensities around 10⁻¹⁶ W/cm², the OE spectra are again dominated by the atomic lines. However, a weak emission of Al⁺ and Al²⁺ was registered as well. The abundance ratio of Al/Al⁺ should be at least 100. The plasma has an excitation temperature...
equivalent to 0.8 eV found by a computer simulation of the aluminum plasma OE spectrum. A broadband emission was also registered, both from the single-element plasmas (typical is for carbon; there were no spectral lines) and the scintillating slabs (on Ce:YAG crystal, both the luminescence bands and the line plasma emission were recorded by the spectrometer).

**Keywords:** optical emission spectroscopy, free-electron laser, atomic lines, plasma plume, warm dense matter

1. **INTRODUCTION**

It has been proposed by several research groups, see for example [1-3], that focused soft X-ray laser beams should produce solid-density plasmas with unique properties due to volumetric heating of solids. Because of energy delivery in ultra-short pulses and an absence of the critical surface in irradiated solids, the material is almost perfectly isochorically heated. Very uniform energy deposition in relatively large volume leads to the formation of dense, low-temperature plasmas, often called warm dense matter - WDM [3]. The state of matter prepared in this way represents a typical example of non-ideal, strongly coupled plasma system [4].

Optical emission spectroscopy (OES) [5,6] is a very traditional, well-established technique of plasma diagnostics. The key plasma parameters, e.g., electron temperature and density, can be extracted from OE spectra in several ways. However, we should take into account that there is a serious limitation of using OES to characterize WDM. An optical opacity represents a problem in dense plasmas. We should keep in mind that at optical frequencies we may observe just a surface and a thin near-surface region of the FLASH-produced plume.

2. **EXPERIMENTAL**

2.1. **The Free Electron LASer in Hamburg – FLASH, beamlines and focusing**

The Free-Electron LASer in Hamburg (FLASH [7,8]) was used as a radiation source to generate plasmas on the surface of different materials. The laser was operated at wavelengths 32.5 nm and 13.5 nm, providing pulses with a duration of 25 fs at a repetition rate of 5 Hz. The energy of pulses was varied from 6 to 30 µJ and measured by photo-ionization GMD (gas monitor-detector). Because of an unseeded nature of SASE FEL generation, the pulse energy fluctuated during the data acquisition by several µJ around the mean value. Although we obtained GMD data for each pulse, the mean value was recorded for a particular OE measurement. We extracted the FLASH beam from two beamlines – either from BL2 or BL3 [8]. At BL2, the FLASH beam was focused by the amorphous carbon coated grazing incidence elliptical mirror (with a focal length of 2m) to a focal spot of 20 µm in diameter [9]. The BL3 end-station was equipped with an off-axis parabolic mirror coated with a Si/Mo multilayer for 13.5 nm allowing us to focus the beam on a sub-micron spot [10]. In OES experiments, the focal spot was usually 1 µm in diameter. The typical irradiance was about $10^{13}$ W/cm$^2$ and $10^{16}$ W/cm$^2$ for 20-micron and 1-micron spots, respectively. The samples were fixed to the stainless steel holder that was positioned in the chamber using accurate, remote-controlled stepper motors. The pressure of residual gases was reduced by ion and turbomolecular pumps down to $10^{-7}$ mbar in the chamber.

2.2. **UV-Vis emission spectroscopy**

An Oriel MS 257 grating spectrometer equipped with Andor iStar 720 iCCD head was used for the spectroscopy analysis of optical emission from FLASH-produced plasmas in the spectral range from 200 to 600 nm. The spectral resolution was primarily given by the grating used in a particular measurement. The grating with 150 lines/mm makes it possible to obtain a survey spectrum (i.e., the width of the whole spectrum is about 400 nm) with a resolution of ~ 1 nm (100-µm slit). The grating with 1200 lines/mm covers a spectral range of about 50 nm with much better resolution, i.e., ~ 0.1 nm (50-µm slit). The latter grating was used for a detailed study of interesting domains in the survey spectra. We have optimized the light collection from the interaction chamber in several steps. The first measurements of silicon were carried out with a lens positioned outside the chamber in front of the quartz window. The fiber with an objective was placed behind the lens. The light collecting system was first upgraded in 2006. The one lens was replaced by a system of lenses working like a beam compressor. In 2007, a spectro-microscope was developed and used at BL2 (Fig. 1). At the micro-focus (2007-2009; BL3), a commercial objective with a focal length of 35 mm purchased from Ocean Optics focused the optical emission from the plasma plume to the quartz fiber. The quartz fiber guided the OE signal by a
feedthrough from the evacuated chamber to the spectrometer equipped with a piezo-slit (piezosystem Jena, Germany). The FEL beam was focused on the surface of the chosen sample to get the intensity as high as possible. The irradiated sample was moving during the data acquisition because of crater created by laser ablation at the surface. Each FLASH pulse hits a new position on the surface. The spectrometer was synchronized by means of the 5 V TTL trigger with the FLASH pulses. The signal was registered in 2 ms window and electronically amplified in the iCCD at a gain of 200 (maximum value 255). Final OE spectrum was combined from hundreds of accumulations; typically 200 – 500. Using two calibration lamps, all the spectra were intensity calibrated with respect to the spectral changes of iCCD detector sensitivity. Atomic lines were assigned with help of the NIST database [11].

![Image](image.png)

**Fig. 1** (left) The spectro-microscope used for an efficient OE collection and guiding from the BL2 interaction chamber to the MS257 imaging spectrograph. (right) The commercial objectives (closer to the target: Ocean Optics; top-right: Oriel) in the micro-focus chamber at BL3.

### 3. RESULTS AND DISCUSSION

#### 3.1. Optical emission spectra registered in our experiments

The first emission spectrum of a plasma plume produced by the FLASH beam was spectrum of silicon measured in November 2005 (Fig. 2). This spectrum was created by accumulating 300 single-shot spectra. The measuring window was adjusted to a width of 100 ms. Such a long time interval was chosen to be sure that the emission signal would be registered over the whole history of the plume. The silicon surface was irradiated with an average value of laser beam energy of around 20 µJ. By focusing the laser beam to a 20-micron spot an irradiance of 10^{13} W/cm² was achieved. When the sample was irradiated by pulses carrying less energy, we were not able to observe any emission spectrum. It is necessary to point out that the optical setup was not efficient and only a small fraction of the optical emission was registered. Therefore we needed typically 300 accumulations of single-shot spectra to compile a well-developed OE spectrum. It can clearly be seen in Fig. 2 that three lines dominate the spectrum. The spectral line near 251.4 nm is likely composed of three atomic lines (250.7, 251.4 and 251.6 nm), which cannot be separated at our spectral resolution (the entrance slit of the spectrometer was opened wide to increase overall sensitivity of the instrument). Other lines appeared at 288.2 and 390.6 nm. All the spectral lines were assigned to silicon atoms. Silicon ions were not observed. It indicates the formation of very cold dense plasma, warm dense matter (WDM), under these irradiation conditions.
More efficient light collecting optics allowed measurement at BL2 of OE spectra at moderate and lower pulse energies. We got a spectrum composed of numerous iron lines looking at the plasma plume generated from the stainless steel. The average energy was only 6 µJ during the data acquisition, so it was necessary to collect at least 500 single-shot spectra to achieve an acceptable signal-to-noise ratio. In the high-resolution spectra (Fig. 3), many individual spectral lines may be recognized. All the lines belong to neutral atoms of iron (Fe I). We have not found any spectral line that could be assigned to charged iron species.
An irradiation of rhodium (150 nm Rh layer on the massive Si substrate) under the same conditions as iron (i.e., pulse energy fluctuated around 6 µJ) revealed a slightly different OE spectrum. The OE signal coming from the chamber was very low. Even after 500 accumulations the spectrum stays very noisy. There is a broad continuum band with the intensity increasing when going from 300 nm to 600 nm. Three lines assigned to neutral atoms of rhodium appeared at 352.8 nm, 421.1 nm, and 515.6 nm from the continuum.

Similar spectra were obtained when the nickel plume was studied. In the case of the low energy pulses (5 µJ) a noisy signal was detected. Two of three lines, near 280 and 345 nm, can be assigned to neutral nickel emission. Surprisingly, the line near 251 nm cannot be assigned to Ni I. We originally believed that it is a spectral line of singly ionized nickel (Ni II). However, we should take into account that the sample was 150 nm thick nickel layer on massive silicon substrate. The crater (a groove) created in the sample material by the focused FLASH beam was investigated by the use of atomic force microscopy (AFM). The AFM image confirms a crater depth exceeding 3 µm. So, the plasma was generated mostly from the silicon substrate. Thus the Ni/Si spectrum can be compared to the OE spectrum of silicon (Fig. 2) and the spectral line near 251 nm belongs to silicon atoms created from the substrate.

With the CCD camera of the optical microscope looking in situ at irradiated surface, we have seen a very bright spot on the 890 nm thick layer of amorphous carbon on Si substrate irradiated by the FLASH beam. However, no spectral line was resolved in the OE spectrum. The spectrum is composed of a broad band that begins to rise at 330 nm, growing up to 600 nm with the increasing wavelength. With respect to a limited spectral range of the instrument, the spectrum was not measured above 600 nm. Therefore we have not succeeded in determining the band maximum.

UV-Vis emission spectra were then measured in a new chamber at BL3. An off-axis parabolic (OAP) mirror coated with a Si/Mo multilayer for 13.5 nm was used for the beam focusing. The OAP mirror allows the FLASH beam to be focused to a sub-micron spot. We usually worked with a 1-micron spot. This beam diameter provides irradiances above $10^{16}$ W/cm$^2$ for typical pulse energies. The optical setup for emission signal collection was upgraded and the efficiency of OES registration increased. FLASH-produced plasma behavior of numerous materials, e.g., Cu, Al, Ce:YAG, a-C, PMMA, Ti, Ta, and Nb, has been studied under these irradiation conditions.
spectral lines were assigned to neutral atoms of copper (Cu I) (Fig. 4). We do not see any line belonging to charged Cu species, although the irradiance exceeded $10^{16}$ W/cm$^2$.

On the other hand, the OE spectrum of niobium, taken at the same conditions as copper, does not contain any individual spectral line. Relatively strong OE signal coming from the chamber has an origin in a broad continuum band, which appears first at 250 nm and its intensity growths with increasing wavelength, up to 600 nm. Similar behavior like Nb was exhibited under the same irradiation conditions for tantalum, deuterated niobium and amorphous carbon. Continuum emission is also typical for PMMA, although some features in its OE spectrum could be assigned to hydrogen spectral lines. Further measurements are required with improved signal-to-noise ratio.

The optical emission spectrum of the Al plume (Fig. 5) is similar to the emission of the Cu plume. The strongest lines, 308.2 nm, 394.4 nm, and 396.2 nm can be assigned to the neutral atoms of aluminum (Al I). Several weak lines indicate a presence of singly and doubly charged ions. The strongest line among these ionic lines can be found at 358.7 nm; the line belongs to Al$^{+}$. Very weak lines of Al$^{+}$ and Al$^{2+}$ have also been found in the spectral range above 450 nm. The intensity ratio of atomic and ionic lines is ~100. The very low abundance of ions in the plume indicates the low temperature plume. It should be pointed out, that this was the first instance of ionic lines being observed in an optical emission spectrum of a plume generated by focused FLASH radiation. This spectrum was used for estimation of plume temperatures; see the chapter 3.2.

![Fig. 5 The time-integrated optical emission spectrum of aluminum plume formed by 13.5-nm FLASH beam focused by the off-axis parabola to achieve irradiances exceeding $10^{16}$ W/cm$^2$.](image)

When Ce:YAG scintillating slab (cerium doped yttrium aluminum garnet – Y$_3$Al$_5$O$_{12}$:Ce [12]) was exposed to FEL pulses at BL2, two broad luminescence bands were found near 300 and 550 nm (Fig. 6). Laser pulse energy was only 2 µJ. Thus the intensity of focused radiation fluctuated around $10^{12}$ W/cm$^2$. When the irradiation occurred at BL3 to achieve intensities above $10^{16}$ W/cm$^2$, the FLASH pulses formed from Ce:YAG a plume containing ionic species. Although the spectrum is dominated by atomic lines of aluminum and yttrium (Fig.7), the yttrium spectral lines indicate relatively high abundance of singly ionized yttrium (Y II). Ce:YAG is suitable material to show an influence of the crater formation process on the OE intensity. It demonstrates how important is to move the sample during the FLASH exposure. We measured spectra of the plasma generated by 600 pulses, hitting the same place on the sample surface. The atomic lines are strong, dominating the spectra (the luminescence bands are weaker at that time) during the first 200 shots. Later on, the atomic lines are still visible in spectra but their intensities decrease during the next 200 pulses. The
same trend holds during an acquisition of the last 200 spectra, but the difference between spectral lines and bands is not as dramatic as between the first and the second portion of shots. When we are drilling a hole in the sample, the beam becomes defocused and the plume is generated in a well. This can complicate reproducibility and interpretation of the OES measurements. Therefore the target usually moved continuously during the OES acquisition.

Fig. 6 The Ce:YAG luminescence induced by low-energy FLASH beam at an irradiance around $10^{12}$ W/cm$^2$ (BL2).

Fig. 7 The optical emission spectrum of the plasma formed on the surface of the irradiated Ce:YAG slab when FLASH intensity achieved $10^{16}$ W/cm$^2$ (BL3).

It is interesting that all the spectra of plumes created with femtosecond pulses, i.e., at intensities $> 10^{12}$ W/cm$^2$, are dominated by spectral lines of atoms. Ions are formed only at highest FLASH intensities, i.e., $> 10^{16}$ W/cm$^2$, and even then in low charge states (singly charged ions prevail) with a low abundance. This is rather surprising, because similar spectra were recently collected [13] from Si, Cr and Ag irradiated by focused 46.9-nm laser radiation at intensities up to
$10^{10}$ W/cm$^2$, i. e., six orders of magnitude lower than in our case. Of course, the 46.9-nm radiation is absorbed in matter more strongly than 13.5-nm radiation. Therefore, a difference of local energy deposition rates in the near surface layer of the target is not as dramatic as the difference in intensities on the surface. Experiments dealing with the intensity dependence of absorption of FLASH radiation in various solids are in progress. Plume expansion and recombination dynamics should play a role as well. Because of low critical densities for UV-Vis wavelengths, the OE spectra in general come from a near surface layer of the plume. However, Al I, II and III are special cases that deserve more detailed investigations. Likely, all these processes might reduce the OE consequences of the intensity difference.

### 3.2. Plasma temperature calculations from OE spectra

The best OE spectrum of aluminum was used for the plasma temperature calculation. This spectrum was analyzed using the simplified version of the multilevel, multi ion stage metastable resolved collisional irradiative code MARIA [14]. The spectral distribution $I(\nu) = \sum g_j A_{ji} b_j P_{ji}(\nu_{0,\nu})$, where $g_j$ is statistical weight, $A_{ji}$ is $j \rightarrow i$ transition probability, $b_j = \exp(-E_j/kT_{ext})$ is Boltzmann factor, and $P_{ji}$ represents the line profile, is strongly sensitive to the excitation temperature $T_{ext}$ (see Fig. 8-left). The best agreement between the experimental spectra (Figs 5,8) and computer simulations (Fig. 8) was achieved for $kT_{ext} = 0.8$ eV.

![Al I spectral distribution](image)

The electron temperature $T_e$ was calculated using the equation [15]:

$$\frac{I_1}{I_2} = \frac{\omega_1 f_1}{\omega_2 f_2} \frac{e^{-h(\omega_1-\omega_2) / k_BT_e}}{e^{h\omega_2 / k_BT_e}},$$

where $f$ is the integral line intensity in a spectrum, $\omega$ is frequency corresponding to the wavelength of the atomic line, $f$ is its oscillator strength, $h$ and $k_b$ are reduced Planck and Boltzmann constants, respectively. The electron temperature was found to be $k_bT_e = 0.6$ eV according to the intensity ratio of lines 308.2 nm, 394.4 nm, and 396.2 nm. Parameters of investigated spectral lines are summarized in Tab. 1.
Table 1 Parameters of atomic lines (Al I) used for the electron temperature calculation [4].

<table>
<thead>
<tr>
<th>lines (nm)</th>
<th>oscillator strength</th>
<th>relative intens.(NIST)</th>
<th>configuration</th>
<th>spectroscopic term</th>
</tr>
</thead>
<tbody>
<tr>
<td>308.22</td>
<td>0.18</td>
<td>24</td>
<td>$3s^23p - 3s^23d$</td>
<td>$^2P_{1/2} - ^2D_{3/2}$</td>
</tr>
<tr>
<td>394.40</td>
<td>0.115</td>
<td>24</td>
<td>$3s^23p - 3s^24s$</td>
<td>$^2P_{1/2} - ^2S_{3/2}$</td>
</tr>
<tr>
<td>396.15</td>
<td>0.112</td>
<td>26</td>
<td>$3s^23p - 3s^24s$</td>
<td>$^2P_{3/2} - ^2S_{1/2}$</td>
</tr>
</tbody>
</table>

The temperatures of 0.5-1.0 eV characterizing the OE spectra are by one order of magnitude lower than those obtained from XUV emission spectra [16,17]. The XUV emission comes from the interior of the plasma plume (because of higher critical densities corresponding to the shorter wavelengths) which likely stays at higher temperatures and densities for a longer period of time than the surface of expanding plume.

**CONCLUSIONS**

In conclusion, optical emission spectra of various materials (Si, Al, Cu, Ti, Ta, a-C, Rh, Nb, NbD, Si$_3$N$_4$, BN, PMMA, etc.) irradiated by ultra-short soft x-ray laser pulses at two irradiance levels, i.e., $10^{13}$ W/cm$^2$ and $10^{16}$ W/cm$^2$, have been measured at the FLASH facility in Hamburg. Surprisingly, only lines belonging to the neutral atoms were observed at intensities around $10^{13}$ W/cm$^2$. In the micro-focused beam, i.e., at intensities exceeding $10^{16}$ W/cm$^2$, we may register singly charged ions in plumes of Al, Ti, Ce:YAG, although the spectra are still dominated by atomic spectral lines. Higher charge states (Al III) are rare in the Al spectra. An abundance of neutral Al atoms is enormous with respect to Al atomic ions. The ratio of atoms and ions in the Al plume is ~ 100. An excitation temperature of only 0.8 eV was derived from the OE Al I spectra using the computer code MARIA in a simple simulation mode to analyze atomic emission. The low electron temperature indicates that Al I emission is most probably connected with the far recombination phase. In order to extend the investigation of the recombination phase to earlier times simulations should also include the analysis of Al II and Al III optical emission lines. This work is in progress.

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