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HEAVY ION PLASMAS AND HIGHLY CHARGED BEAMS

J. Pálinkás[1], E. Takács[1], S. Kökényesi[1], S. Biri[2], G. Szitási[1], I. Iván[2], É. Fekete[2], L.T. Hundson[3]

[1] University of Debrecen, Experimental Physics Department, Bem tr 18/A, Debrecen, Hungary
[2] Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Bem tér 18/C, Debrecen, Hungary
[3] National Institute of Standards and Technology (NIST), Gaithersburg, MD, 20899

Abstract

We use an x-ray CCD device to study the images and spectra of highly charged ions created at the electron cyclotron resonance ion source facility of ATOMKI. Injecting C60 molecules into the plasma chamber we produced exotic heavy ions, such as endohedral and hetero fullerenes that have a potential for medical applications. We also studied the interaction of the ions with surfaces. Our studies included materials for optoelectrics and for functionalized surfaces to be used as bio-implants.

I. Scientific background

I.1 Physics with highly charged heavy ions

The creation and existence of highly charged heavy ions in nature is usually connected to the presence of high-temperature plasmas. This state of the matter occurs in astrophysical plasmas like in supernova explosions, in the solar corona, in the solar wind, and in coronas of stars. On Earth these special atomic systems exist in arc discharges or during lightning and

thunderbolts. In laboratories very highly charged ion states are created in special ion sources like Electron Cyclotron Resonance Ion Sources (ECRIS) [1, 9], Electron Beam Ion Sources and Traps (EBIS, EBIT) [1] and in fusion experimental facilities [2]. Nowadays the research and application of slow heavy ions (in most cases: *highly charged* ions, HCI) intensively spreads in laboratories involved in physical, chemical, and even in bio-physical or medical research. Heavy ions are used in many fields, from nanotechnology to space research [3].

Heavy ion plasmas are used for direct applications (e.g. plasma etching) and to study certain plasma-wall interactions. These investigations are continuously required and are basically important for laboratories involved in fusion research. The diagnostic research of HCI plasmas themselves is a relatively new and undiscovered field.

Depending on the accepted terminology heavy ions cover almost all elements from helium to uranium. Special facilities can generate plasmas from molecules like water or metallocenes. Even giant molecules (e.g. fullerenes) can be transformed into plasma state out of which singly-charged and multiply-charged fullerene ion beams can be extracted. Mixture plasmas (plasmas consisting of two or more ion components) can be formed for materials research and to create new materials.

Another example is the so called "capillary guiding", which allows ions to travel along nanochannels that are typically 100 nanometer in diameter. Even for a deliberate large misalignment of the channel axis slow HCIs pass through, and leave the nanochannels in the direction of their axis [4]. It is needless to emphasize that such a phenomenon might get a wide range of applications where low energy ions should be directed, focused, deposited and implanted on a nanoscopic scale.

The interaction of HCI with solid surfaces and thin layers are not conventional, because such ions can modify the surfaces on the nanoscale level. Due to their charge, the highly charged ions show attractive force to all charged systems (or polarize them). The recombination of ions during collisions damages the material, while the recombination process is still not understood well. This process usually results in the local explosion of crystal structures, breakings of chemical bonds, generally causing changes on

the nanometer scale. This gives opportunity for nanotechnological applications that can be extended even to biomedical directions.

Heavy ion facilities offer to companies in space or aeronautics the possibility to simulate cosmic ray bombardments in the upper atmosphere by accelerated heavy ion beams, and to validate the radiation hardness of the critical electronic devices to be used on-board. The Heavy Ion Irradiation Facility in Belgium, created in collaboration with the European Space Agency, is an important example of this type of research [5]. There are also ideas to design ion propelled rockets with Xe or C_{60} ion fuels [6].

I.2 Techniques to make highly charged heavy ions

Both in nature and in laboratories the production of highly charged ions (i.e. the removal of the electron cloud) is usually performed by energetic electrons or by intensive electromagnetic fields. In laboratories high energy electrons are created by microwaves (ECRIS), by electrostatic acceleration (EBIS, EBIT) or with lasers [1].

Ten years ago an electron cyclotron resonance (ECR) ion source (ECRIS) was built and set in operation at the Institute of Nuclear Research (ATOMKI) of the Hungarian Academy of Sciences, Debrecen [7], called ATOMKI-ECRIS. An ECRIS is a magnetic trap that confines a plasma consisting of hot (energetic) electrons and cold (slow) ions. Plasma electrons are heated by the interaction with high frequency electromagnetic waves (usually 2–18 GHz) and these fast electrons confine the slow ions. The atoms and ions are ionized step-by-step up to the required charge states. The electrons and ions form a plasma in an ECR discharge where the lifetime of the particles is large and the number of collisions between the particles is high (electron-atom, electron-ion, ion-ion, ion-atom collisions). The highly charged ions can be extracted electrostatically from the plasma chamber to form a beam of such species. The abbreviations ECR and ECRIS thus simultaneously mean plasma source, ion source and particle accelerator.

At the ATOMKI-ECRIS various plasmas and beams have been produced: H, He, C, N, O, Ne, Ar, Kr, Xe (from gases), and F, Fe, Ni, Zn, Pb, C, I, C^{60} (from solids). The energy of the beams are E=Q*U (in keV), where

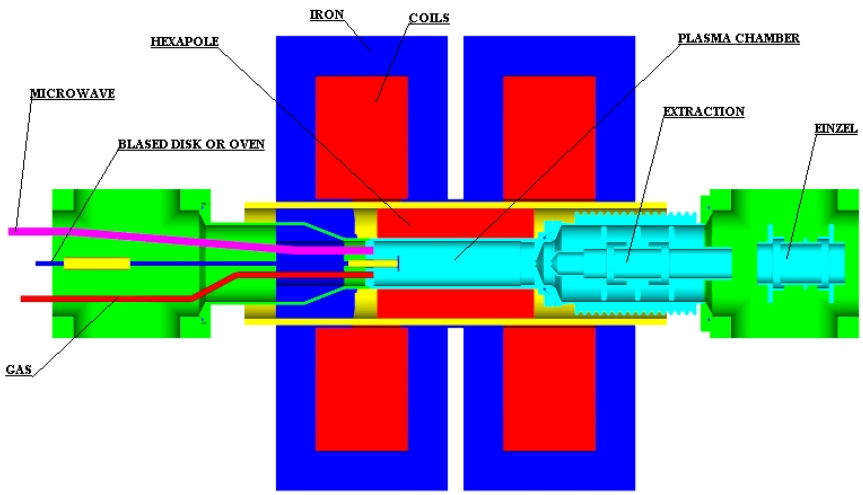

Figure 1: The ATOMKI-ECRIS. Diameter of the coils with iron yoke is 60 cm.

Q is the ion charge and U is the extraction voltage (in kV). The charge can be varied from 1 to 25 (depending on the element, 25 was obtained for xenon). The extraction voltage covers the range of 0.2–30 kV. The ATOMKI-ECRIS and several other ECR ion sources can make plasmas and beams from special materials, like solids (including hard metals) or powders (e.g. metallocenes, fullerenes). More information can be found on the homepage of the ECRIS Laboratory: http://www.atomki.hu/atomki/ECR.

In this paper we show the status and results of some selected research which are all based on the plasmas (Section 2) or ion beams (Section 3) delivered by the Debrecen ECR ion source.

II. Investigation of heavy ion plasmas

II.1 X-ray spectroscopy and imaging of laboratory plasmas

With the advent of high spatial resolution x-ray CCD cameras mainly developed for space applications new possibilities have opened for laboratory research of HCI plasmas. Using these devices plasmas can be imaged to fine details and dispersive spectrometers equipped with CCD cameras can provide high energy resolution spectra of heavy ions. In Debrecen we have started a series of investigations to both image and study the spectrum of the ECRIS plasma of the source at ATOMKI. In collaboration with the scientists at the National Institute of Standards and Technology in Gaithersburg, MD we have developed a technique where low x-ray signal levels can be detected taking advantage of the intrinsic properties of x-ray CCD cameras. In imaging this allows us to investigate the fine spatial changes of the ion cloud distribution and in spectroscopy the removal of the background noise that usually hinders the observation of weak features in atomic x-ray spectra.

Our imaging studies focus on the determination of the spatial distribution of the different plasma components within the ECRIS [20]. The intrinsic energy resolution of the CCD devices allows the filtering of the images determining of the positions of sources of the different spectral components within the plasma chamber. Fig. 2. shows such an example where the different spectral components and their location within the ECRIS can be seen. In our ongoing effort we are investigating the variation of such features with the plasma parameters to further our understanding of the plasma dynamics within the ECRIS.

Apart from the spatial variation of the x-ray signal within the source, the detailed spectral features of the ECRIS also carry information about the plasma properties. We have started an effort to install a high energy resolution x-ray crystal spectrometer onto the ECRIS. The Johann-type spectrometer has the same design that have been used in several studies at the NIST electron beam ion trap [21]. The CCD camera that has been used for the imaging studies is attached to the detector arm of the instrument allowing high spatial resolution detection of the dispersed spectra. The

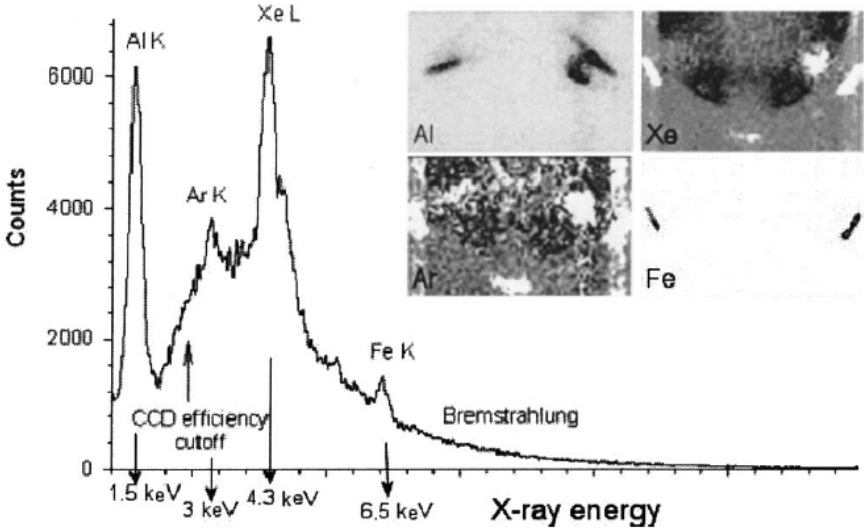

Figure 2: Spectral features of the ATOMKI ECRIS and their location within the source [20].

low signal level detection mode and feature removal developed for imaging allows us the detection of small spectral features in the spectra. Our goal is to develop a diagnostic tool that is based on the the detection of energy and density sensitive spectral lines and spectral line rations. The observation of such spectra could have direct consequence for fusion and astrophysical plasma diagnostics.

II.2 Fullerenes and fullerene modifications

Heavy ion plasmas and beams can be formed not only from elements of the periodical system, but from natural and artificial molecules, as well. One of the heaviest and most famous molecules of our days is the buckminsterfullerene which consist of 60 carbon atom. The fullerenes have actively been studied up to now because of their unique electric/magnetic/optical properties. The fullerenes typified C_{60} can produce compounds by trapping other atoms and/or molecules inside its cage or by replacing carbon atoms

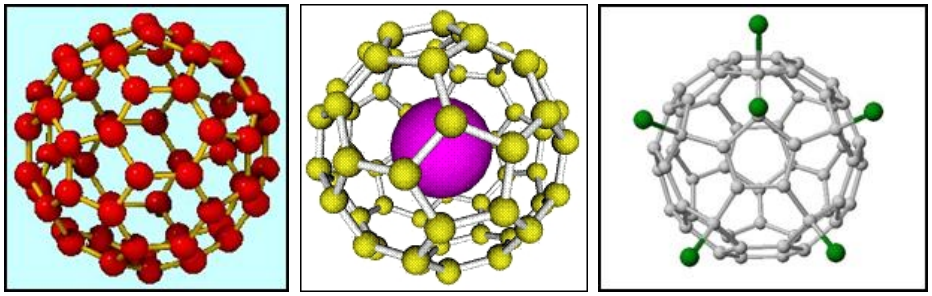

Figure 3: Fullerene (left, endohedral fullerene (middle) and heterofullerene (right) molecules.

of the cage with atoms which are called endohedral or hetero-fullerenes, respectively. Recently, organic semiconductors and quantum computing devices have been investigated as alternative devices to silicon semiconductors. C_{60} and related materials have attracted considerable interest as candidates for such devices. In particular, N-C_{60} compounds such as nitrogen-atom-encapsulated fullerene (N@C_{60}) and azafullerene (C_{59}N) have been investigated [10, 11]. In case N@C_{60} the curiosity is the magnetic nitrogen atom encapsulated by C_{60} shows characteristic fine and hyperfine structure in the electron-spin-resonance (ESR) spectrum. Another promising combination is the Fe-C_{60} case [12]. In particular, as endohedral iron and iron-oxide are very sensitive to the magnetic fields and to the electromagnetic waves, it might be possible to use them one day for diagnosis and treatment of cancer, as MRI contrast agents, drug delivery, information recording media, blocks for nano-parts [13].

The ATOMKI-ECRIS became a suitable tool to make and study fullerene and related plasmas. In ECR discharges there exist methods not only to ionize but also to excite and/or damage the atoms/molecules/ions to produce x-ray photons, to form metastable molecule states or non-ball-shape carbon cages. In recent years we have successfully produced various fullerene plasmas and world record intensity beams, and synthesized N@C_{60} in a mixture plasma [14-16]. An important conclusion was that in the future more attention should be given to fullerenes consisting of less than 60

carbon atoms: C_{60-n} (n=2, 4, 6,...). They are less stable than the C_{60}, therefore $C_{60-n}X$ or $X@C_{60-n}$ (X=N, Ar, Fe, ...) molecules can be formed more easily.

In the near future we plan to carry out series of experiments to explore and improve the production methods of plasmas and beams of fullerenes and their modifications, and to study the properties of fullerene plasmas mixed with other component(s). Our second goal is to understand the mechanism of putting different atoms inside and outside of fullerene molecules. One of the planned methods is the off-line analysis of the deposited films on the plasma chamber wall or on any cooled surfaces placed nearby. These films are always created and are a mixture of carbon, fullerene, fullerene fractures, $C_{60-n}X$ and $X@C_{60-n}$ (X=N, Ar, Fe, etc., n=0, 2, 4, ...), etc. Similarly, a few monolayers of the extracted beam particles can also be gathered on substrates (e.g. Si, PET, Ti or on TEM sample holders). Afterwards, these films or the ion-treated surfaces can be investigated by different analytic and material research techniques and examined in order to create functionalized surfaces of bio-implants.

III. Interaction of ions with solid surfaces

Interaction of ions with amorphous chalcogenide layers was further investigated in order to establish possibilities of enhanced surface relief formation in these functional materials for optoelectronics. Investigations were also extended to the interaction of fullerene ions with titanium in order to create functionalized surface of bio-implants.

The high, (at the molecular level), spatial resolution of the localized structural transformations induced by different irradiations in amorphous chalcogenides promotes applications of this inorganic resist for optical recording, data storage and is attractive for nanolithography as well. Last year we focused our investigations on the comparison of surface reliefs recorded at nano- micrometer length scales in a direct, one-step process of recording by light or proton, Xe^{+24} , Ne^{+8} ion beam on Se, As_2S_3 layers or Se/As_2S_3 nanolayered films.

0.5 - 1.0 μm thick chalcogenide films were fabricated by vacuum evaporation of crushed high purity bulk materials onto Si wafer or Corning 7059 glass. To study the surface modification induced by light or ion beams, samples were irradiated with He-Ne laser (output power 25 mW), green diode

laser (max output power 20 mW), 180 keV D^+ or Xe^{24+} (with 60-240 keV kinetic energy) as well as with 240 keV Ne^{8+} ions. The laser irradiation of the samples was done in normal atmosphere. The irradiations with D^+ were done at the 200 keV linear accelerator of the Department of Experimental Physics of the University of Debrecen, while the Xe^{+24} and Ne^{+8} ions were delivered by the 14.5 GHz electron cyclotron resonance ion source of the Institute of Nuclear Research of the Hungarian Academy of Sciences. Detailed information about the experimental setups used in these experiments may be found in [17,18]. Irradiation usually was performed via a metal microgrid with mesh size 40x40 μm^2 which was placed in front of the sample. Surface relief was investigated by NT-MDT type atomic force microscope (AFM) or Carl Zeiss optical microscope.

AFM measurements directly confirmed the known effects of photoinduced expansion with $\Delta d/d \leq 1\%$ in separate As_2S_3 film due to the green laser irradiation with total exposure up to 600 J/cm^2 and the contraction of a-Se layer with $\Delta d/d \approx 1\%$ in the regime of diffraction pattern recording with red laser light and total exposures up to 10^3 J/cm^2. It was established, that such large exposures do not cause any crystallization or etching in As_2S_3, while in a-Se the mentioned illumination with low intensity, non-heating He-Ne laser beam resulted in sporadic crystallite growth on the surface. Almost the same values of thickness change were obtained with deuteron irradiation. At the same time the irradiation of As_2S_3 layers with 240 keV Ne^{+8} ions in the 5.10^{12} - $3\text{-}10^{13}$ ion/cm^2 range caused optical transmission change but do not caused measurable thickness change, which appeared only at $1.8.10^{14}$ ion/cm^2 exposition in a form of etched holes, as it is shown in Fig. 4. The AFM picture and corresponding depth-profile of the etching are presented in Fig. 5.

Using highly charged ions we must also calculate with action of separate ions, which can produce few nanometer high surface bumps at the end of the exposition, as it was established earlier for Se [19] and is visible in Fig. 5. Replacing the diffraction-limited visible laser illumination by accelerated ion irradiation may lead to the improvement of the quality of the surface relief either in expansion regime (Se/As_2S_3 nanomultilayers, see Fig. 6.) or in etching regime (As_2S_3, see Fig. 5).

It appears possible to perform smooth, regulated etching or local expan-

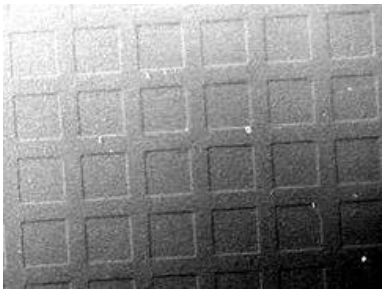

Figure 4: Optical microscope image of As_2S_3 surface etched by Ne^{+8} ions via metal grid mask.

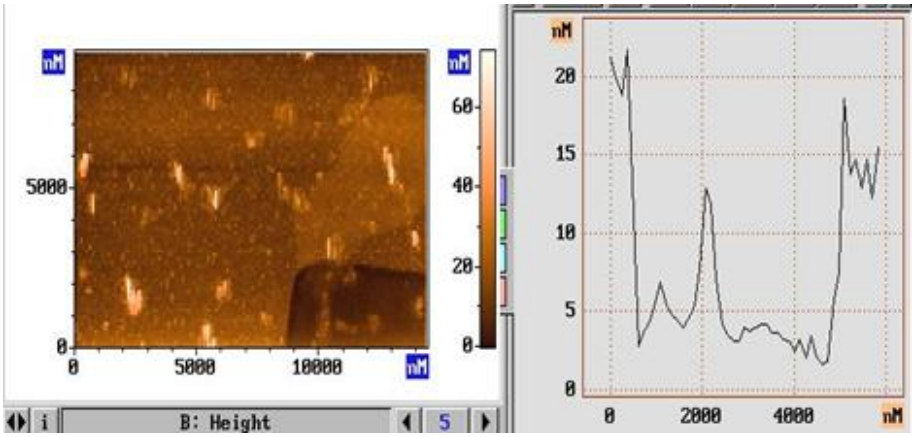

Figure 5: AFM picture of the As_2S_3 surface etched with Ne^{+8} ions (left, the hole in the right corner) and the profile of the etched hole at the selected cross-section (right).

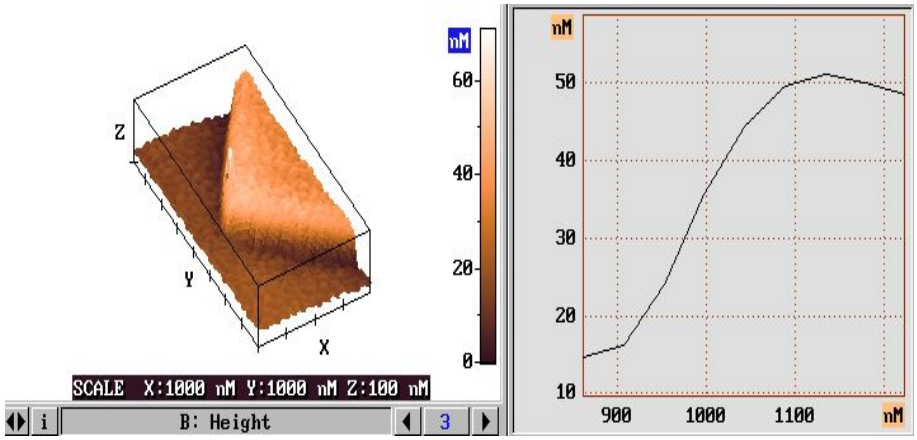

Figure 6: 3D AFM picture (left) and a cross-section (right) of the pattern recorded on Se/As_2S_3 nanolayered film with total thickness d=900nm, irradiated through a microgrid with 180 keV D^+ ions.

sion in a number of selected chalcogenide compositions and layer structures by accelerated ions with order to fabricate geometrical surface reliefs as well as amplitude-phase modulated optical elements. It is desirable to establish the role of ion charge and total energy in the prevailing process of etching or expansion, as well as compare amorphous chalcogenide with some polymer material with similar disordered structure.

References

[1] Wolf B., *Handbook of Ion Sources* (CRC Press, 1995).

[2] See e.g http://hif.lbl.gov/.

[3] Beyer H. F., Shevelko V. P., *Introduction to the Physics of Highly Charged Ions* (IOP, 2003).

[4] Mátéfi-Tempfli S. et al., *Guided transmission of slow Ne^{6+} ions through the nanochannels of highly ordered anodic alumina.* Nanotechnology **17**, 3915 (2006).

[5] http://www.cyc.ucl.ac.be/ (Electronic device irradiation facilities).

[6] Scharlemann C. A., *Theoretical and experimental investigation of C_{60}-propellant for ion propulsion*, Acta Astronautica **51(7)**, 865 (2002).

[7] Biri S., Vámosi J., Valek A., Kormány Z., Takács E., Pálinkás J., *The new ECR ion source of the ATOMKI: a tool to generate highly charged heavy ion plasma and beam*, Nucl. Instr. Methods B **124**, 427 (1997). See also the photos in: www.atomki.hu/atomki/ECR.

[8] S. Biri, E. Fekete I. Ivan I. Gal, *Transformation of the ATOMKI-ECRIS into a Plasma Device*, High energy Physics and Nuclear Physics, Vol. 31, Supp.I, 207, pp. 156-158.

[9] R. Geller, *Electron Cyclotron Resonance Ion Sources and ECR Plasmas* (IOP Publishing Ltd. 1996).

[10] Pietzak B. et al., *Buckminsterfullerene C_{60}: a chemical Faraday cage for atomic nitrogen*, Chem. Phys. Letters **279**, 259 (1997).

[11] Abe S. et al., *Effects of Ion Energy Control on Production of Nitrogen-C_{60} Compounds by Ion Implantation*, Japanese Journal of Applied Physics **vol.45, No. 10B**, 8340 (2006).

[12] Reinke P., Eyhusen S., Büttner M., Oelhafen P.,*Interaction of Fe^+ with C_{60} surface: A study about the feasibility of endohedral doping*, Applied Physics Letters **84**, 4373 (2004).

[13] Gorman J., Science News Online **162(2)**, 26 (2002), http://www.sciencenews.org/articles/20020713/bob10.asp.

[14] Biri S., Valek A., Kenéz L., Jánossy A., Kitagawa A., *Production of multiply charged fullerene and carbon cluster beams by a 14.5 GHz ECR ion source*, Rev. Sci. Instr. **73**, 881 (2002).

[15] Biri S., Fekete É., Kitagawa A., Muramatsu M., Jánossy A., Pálinkás J. *Fullerenes in ECR ion sources.*, Rev. Sci. Instrum. **77**, 03A314 (2006).

[16] Fekete É., Biri S. Iván I., *Investigation of Iron-Fullerene Mixture Plasmas in ECR Discharge, Fullerenes*, Nanotubes and Carbon Nanostructures, 15:4, 249 - 256.

[17] Ivan I., Beke D., Kokenyesi S., Szabo I.A., Csik A., Journal of Optoelectronics and Advanced Materials. **7**, 1831 (2005).

[18] Kökényesi S., Iván I., Takács E., Pálinkás J., Biri S., Valek A., Nuclear Instruments and Methods in Physics Research SectionB: beam interactions with materials and atoms **233**, 222 (2005).

[19] Kokenyesi S., Ivan I., Takats V., Pálinkas J., Biri S., Szabo I., Journal of Non-Crystalline Solids **353**, 1470 (2007).

[20] Biri S, A. Valek, T. Suta, E. Takacs, Cs. Szabo, L.T. Hudson, B. Radics, J. Imrek, B. Juhasz, J. Palinkas, Review of Scientific Instruments **75**, 1420 (2004).

[21] Takács E., Meyer, E.S., Gillaspy, J.D., Roberts, J.R., Chantler, C.T., Hudson, L.T., Deslattes, R.D., Brown, C.M., Laming, I.M., Dubau, J., Inal, M.K., *Polarization measurements on a magnetic quadrupole line in Ne-like barium*, Physical Review A **54**, 1342 (1996).