Elemental Characterization and Speciation
CEEFI

Miguel A. Reis

The Elemental Characterization and Speciation work line of ITN Ion Beam Laboratory (CEEFI/LFI), carries out R&D work on ion beam based nuclear analytical techniques aiming at elemental composition characterization and instrumental speciation methods. Focusing being on applications to small mass samples (self-supported thin films, micro and nanoparticles) and/or small mass structures (deposited and deep laying thin films, embedded micro and nanostructures).
The main issue being originally, particle induced x-ray emission (PIXE) applied to the characterization of airborne material and its impacts, lead to the installation of an aerosol characterization set-up, which includes a DOAS system (operational since June 2007), a meteorological station (operational since January 2008), on-line in the Portuguese Meteorological Institute Urban Stations Network, and a PM10 and PM2.5 sampling station.

The installation, in 2008, of the High Resolution High Energy PIXE (HRHE-PIXE) set-up at ITN, the world first cryogenic microcalorimeter high resolution EDS X-ray detector based PIXE system, lead to very important results showing the advantages of these detectors use for both fundamental research as well as applications.

As a consequence of this a revision of the objectives of the CEEFI main work line was carried out, and the emphasis was shifted towards fundamental, technical and software development for PIXE, as well as frontier applications of the technique.

Within the organics of the Ion Beam Laboratory (LFI), CEEFI is the responsible for the maintenance and improvement of PIXE facilities.

In respect to 2010 developments, it was possible to show that the details put in evidence in the PIXE spectra by using the microcalorimeter detector do contain information related to the electronic environment of the x-ray emitting ion, which results were presented and discussed at the International Conference on PIXE and its Analytical Applications held in Guildford U.K.

Regarding frontier applications, nanoparticles, thin films, and chemical or electronics environment mapping are presently the main scope of CEEFI work line.

Within this context, during 2010, important results on thin film analysis, spot scans of a polished agate stone and analysis of Gd nanoparticles were published and accepted for publication.

In respect to airborne particulate matter, an one month training program for an IAEA fellow was carried out, and PIXE services were provided to the scientific community

Research Team

Researchers

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Students

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Fundamental Developments and Solid State Effects in PIXE

M.A. Reis, P.C. Chaves, A. Taborda, N. Barradas, A. Carvalho[1], L. Carvalho[2], A. Ferraz[3]

Objectives

Elemental and speciation characterization methodologies for small mass samples, like airborne particles are nowadays a more and more important issue, needed for both a better monitoring of airborne particulate matter and its impacts, including nano particulate matter hazards, as well as for technical and industrial developments niches associated to particulate matter engineering. During 2010 most of the line activities were focused on the single subject of "Fundamentals Developments and Solid State Effects in PIXE", mainly as consequence of two ongoing PhD thesis on the subject, but also due to the overlap between this subject and that of Key task 15 of the 7th FP project "Support of Public and Industrial Research Using Ion Beam Technology (SPIRIT)", Grant agreement No 227012-CP-CSA-Intra (starting date of 2009/03/01), in which the team is involved.

Results

In respect to results during 2010, and as a consequence of a significant amount of effort put in the exploitation of the spectra from the energy dispersive high resolution microcalorimeter x-ray detector POLARIS, installed in 2008, a few major outcomes were reached, two of which (presently in press) are illustrated in fig. 1.

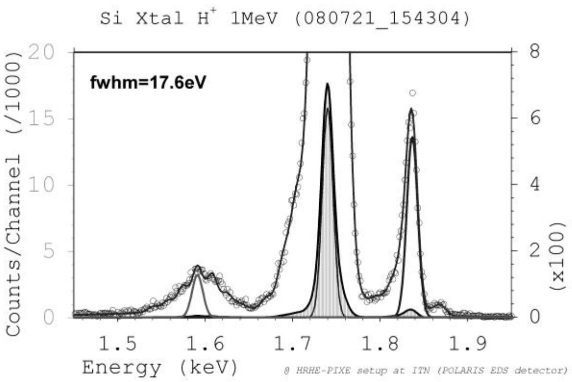
Two supporting by products necessary to achieve these results were also established during 2010, namely: (1) the robustness of the Python code P2HA.py, specially developed by the team for the conversion of POLARIS detector pulses data onto histogram spectral data, and (2) a set of important developments carried out in the PIXE spectra fitting Fortran 2003 code DT2fit.for, presently under development by the team.

The major final outcomes reached in 2010 all share, a common base result that was only possible due to the high resolution, large energy window, low background and purity characteristics of the spectra from the POLARIS microcalorimeter.

Making use of this properties it was possible within the ongoing PhD thesis of P.C. Chaves, to infer the importance of X-rays low energy satellites upon the experimentally measured values of main lines intensity when determine using standard Si(Li) detectors.

In parallel to this, the studies of silicon oxide material (of a polished agate sample) and those of the corresponding reference, a pure Si single crystal slab, showed an highly probable presence of plasmon satellites accompanying both the main line as well as Radiative Auger Emission (RAE) satellites (the KL23L1 RAE line is shown in grey in fig.1 (left)).

These results also lead to a better interpretation of data determined on the analysis of Gd2O3 nanoparticles, which when irradiated by 750 keV show a spectrum too much different from that of a Gd2O3 powder pellet irradiated in the same conditions (fig.1 (right)). These differences are interpreted as due to differences in the plasmon and RAE satellites structure.



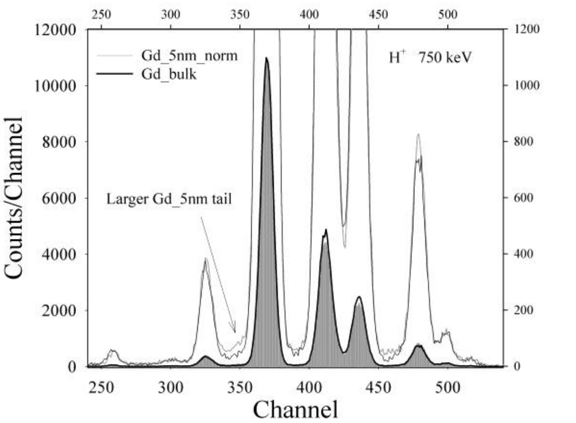


Fig.1 (Left) High Resolution PIXE spectrum of a pure Si single crystal sample irradiated with a 1.0 MeV proton beam provided by the ITN 3.0 MV Tandetron and collected using the POLARIS microcalorimeter X-ray detector. Open dots being a vertical zoom of the full spectra shown in grey, allow the clear identification of Radiative Auger Emission (RAE) KL23L1 satellite as well as plasmon satellites of both the main KL23 (Lα1) and of the RAE transition (in: M.A. Reis et al. *X-ray Spectrometry* (2011), in press). (Right) Gadolinium Lα low energy tail structure, being higher for a spectrum of Gd2O3 5nm particles than for a pellet of pressed Gd2O3, irradiated in the same experimental conditions, clearly reflects a solid state effects signatures originated in satellite contributions such as those shown in the Si spectrum in the left. (in: A. Taborda et al., Physics Research International, (2011) in press).

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Radiative Auger Satellites Influence Upon Relative Line Ratios in PIXE

P.C. Chaves, M.A. Reis, A. Taborda, N. Barradas, M. Kavcic

The study of relative line intensities for transitions to the same sub-shell,was initiated in 2003 after a strange results was found, which pointed to a significant and unexplainable result showing that when measured using Si(Li) detectors these ratios were apparently changing with the change of the energy of the irradiation beam. A result not compatible to the established knowledge in the field. Results were then presented to the international community in 2004 and a PhD program, which included studies within this context was initiated in 2005. In 2010, after 5 years of data gathering, discussions within the international community about possible origins for the observations, the use of the very high resolution wave length dispersion systems from the Institute Josef Stefan, the development of specific fitting software and finally the analysis of high resolution spectra from the POLARIS detector, a very important conclusion was reached. Radiative Auger Emission satellites, first proposed by Bloch on 1935 to be associated to magnetic quadrupolar transitions, and first observed by Aberg and Utriamen in 1969 associated to electric dipolar transitions, were recognised as a major contribution for low energy tails of main lines. Since the detector response functions are fixed structures, variations in main lines yield will affect the intensity measured for close by transitions due to the lack of accountability of associated RAE transitions, when Si(Li) detectors are used.

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Eu L3 sub-shell alignment by proton impact and Lα2/Lα1 relative yield ion energy dependence

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Polish pure graphite targets were implanted with ~5 x 10^{16} at/cm^2 of ^{152}Eu isotopes accelerated to 150 keV on the ITN Danphysic Ion Beam Implanter. A thin Eu target was then irradiated by proton beams of 1.25, 1.5, 1.75 and 2.0 MeV at the Ruder Boskovic Institute (RBI) in Zagreb, Crotia, in order that high resolution PIXE spectra could be obtained using the RBI wave length dispersive (WDS) detector, under the scope of the Joint Research Activities of the Key Task 15 of the project “Support of Public and Industrial Research Using Ion Beam Technology (SPIRIT)”, Grant agreement No 227012-CP-CSA-Intra (starting date 2009/03/01). Spectra covering two different energy regions were obtained at different irradiation times, and simultaneous Si(Li) spectra were used to normalize WDS spectra relative to different collection times. The experiment complexity makes that so far only the Lα2/Lα1 spectra and ratio could be dealt with. Still the comparison of experimental line ratios and theoretical line ratios determined after correction to L3 sub-shell alignment, show that even in the case of the Lα2/Lα1 , oscillations are observed, which are not explained by theory. Spectral data for the determination of Lβ2/Lα1 ratios and its variation with proton beam energy is also being processed, but collected data requires a more complex calculation because corrections are necessary to compensate for small variations on the WDS unit observed during the long run irradiations needed to obtain good spectral data.

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