

Application for beam time at ESRF – Experimental Method

Proposal Summary (should state the aims and scientific basis of the proposal) :

The aim of this proposal is to investigate the application of highly-curved HAPG analyzer crystals in WD-XRF spectroscopy for the simultaneous analysis of lanthanides in unique extraterrestrial materials and explore its 3D voxel scanning capabilities at low excitation energies. For this a novel analysis technique is proposed to obtain non-destructive, selective volume information of rare earth elements (REEs) in μm -sized analogues of coarse grain asteroid samples in preparation for the initial analysis of materials from asteroid sample return missions, such as the Hayabusa 2 (JAXA) and Osiris-REx (NASA). The combination of cylindrical HAPG optics with ultra-high curvature having a mm-sized working distance is expected to provide higher throughput and collimation as compared to high energy resolution fluorescence detection (HERFD) spectroscopy. **In addition to establishing a novel method for determining REE abundances in complex extraterrestrial materials, these measurements will contribute to the so-called Sample Analysis Readiness Test (SART) in the framework of the Osiris REx initial analysis programme.**

Scientific background :

Highly annealed pyrolytic graphite (HAPG) is a relatively new kind of graphite based crystal optic which can serve as a monochromator and a focusing device for primary X-ray beams or as an analyser crystal and confocal optic between sample and detector. With its reduced mosaicity and better energy resolution, it gained popularity over the earlier HOPG (highly oriented pyrolytic graphite) optics which are in use for more than 20 years in energy-dispersive X-ray fluorescence (ED-XRF) spectroscopy. The proposed study investigates selective volume scanning of the REE L-lines at relatively low excitation energies, combining the advantages of confocal XRF detection with high spectral resolution, which is sufficient to resolve REE L-lines in complex geological matrices in the presence of interfering, e.g. transition metal, K-lines.

The direct comparison of HAPG optics at von Hamos geometry with ideal crystals such as Si, Ge and with mosaic crystals such as LiF demonstrates in all cases a significant integrated reflectivity gain at comparable resolving power. The thickness of a single HAPG film with mosaicity 0.1° is limited by $120\ \mu\text{m}$ [1]. The smallest radius of curvature (ROC) for HAPG films published is $51.7\ \text{mm}$ and provides a mosaicity of $0.11^\circ/0.15^\circ$ at respective thickness values of $40\ \mu\text{m}/100\ \mu\text{m}$ [2]. In general, a smaller ROC needs a thinner crystal layer if the same energy resolution should be obtained. Our designed HAPG optic, manufactured by Optigraph GmbH, has a ROC of $3.9\ \text{mm}$ and a mosaicity of $0.10^\circ \pm 0.01^\circ$. Its cylindrical shape and small ROC allow for a larger solid angle detection when compared to other curved HAPG optics. The proposed study has the potential to supply fundamental insights on the effect of ultra-low ROC on the resolving power and pave the way towards low-energy, high-throughput wavelength-dispersive X-ray fluorescence (WD-XRF) spectroscopy.

Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity...etc) :

A Si-drift fluorescent detector, equipped with our own polycapillary confocal optic and placed under 90° with respect to the incident X-ray beam, will aid sample positioning and will allow us to identify mineral grains of interest based on their (ED-XRF) K-lines of their main elements, such as S, Ca, Mn, Fe and Ni. A second detector, combining the above mentioned HAPG analyser/confocal optics with an energy-dispersive pnCCD detector (SLcam) will be used for WD-XRF to analyse the energy range spanned by the fluorescent REE L-lines. Standard ED-XRF detection is not sufficient for this application as the achievable energy resolution cannot resolve individual REE L-lines in the presence of interfering K-lines of lower atomic number elements. Our full-field ED pnCCD detector will be placed opposite to the confocal setup and will be used to detect the REE signals, as the analyser crystal's dimensions and focal distance is specifically designed for this instrument. Its 264×264 pixel array is used to obtain spatially and energy resolved data, with the dispersed fluorescent lines detected as diffraction rings. Higher order diffraction lines and low-energy background can be filtered out via the SLcam's ED capability.

Several thin metal foils, e.g. Ti, Fe and Cu, will be used as reference materials to investigate the crystal's energy range and the resulting resolving power. Secondly, the reference NIST SRM 613 with thickness of 100 μm and REE concentration values around 40 ppm, will be analysed as its REE concentration range matches that of typical unknown geo-materials. Lastly, our optic will be used for the selective volume scanning of mineral inclusions in asteroid Ryugu thin sections ($<10\ \mu\text{m}$ in depth) to investigate their REE abundance and for the exploration of 3D voxel scanning at low excitation energies. The theoretical positions of detected REE L_{α} -lines are presented in Fig. 1A. Earlier experiments using a flat Ge(111) analyser crystal in conjunction with the SLcam could clearly resolve REE L-lines (see Fig. 1B and C), albeit without the confocal capability and with a comparatively low integrated reflectivity, resulting in relatively high REE detection limits.

For the proposed WD-XRF experiment a fixed, monochromatic μ -beam of 11 keV is optimal to maximize the XRF production cross-section of the REE L-lines. The spot size of the X-ray beam on sample should not be larger than 20 (H) x 20 (V) μm^2 , to minimize the source size error which contributes to the total energy resolution while keeping the flux of the incident X-ray beam as high as possible.

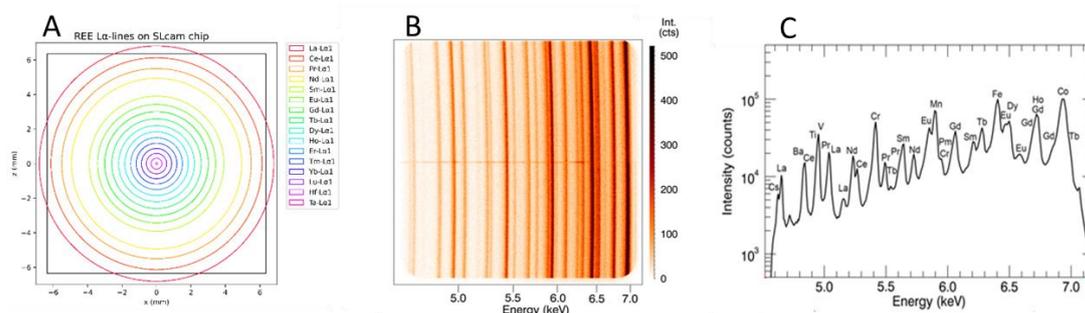


Fig. 1: Theoretical radial positions of the REE L_{α} -lines on the SLcam chip using the proposed cylindrical HAPG optic (A) and WD-XRF spectroscopic analysis of a NIST SRM 611 calibration standard using a flat Ge(111) crystal (B) [3].

The use of the SLcam utilizing a flat Ge(111) analyser crystal was successfully demonstrated for the trace-element analysis of REEs in Ti-rich inclusions found in a deep-Earth diamond [3]. However, an acquisition time of 1 hour was needed for each single point measurement using a beam flux of 10^{11} ph/s. In the proposed experiment we expect that the new HAPG analyser crystal, as a result of its higher overall efficiency, will decrease the total measurement time by 1-2 orders of magnitude, making 2D/3D imaging possible in a reasonable amount of time.

Beamline(s) and beam time requested with justification :

The described experiment requires a 11 keV micrometer sized ($< 20\ \mu\text{m}$) X-ray beam. As such, we request 12 shifts to perform our experiment at the DUBBLE BM14 beamline using polycapillary focusing. One shift is needed for the installation of the detector system and three shifts for the alignment scans using the fluo-detector. Four shifts will be used for analysing the NIST reference material and the asteroid Ryugu mineral grains or OSIRIS-Rex SART samples, and in a second step another four shifts will be dedicated to explore the curved HAPG 3D voxel scanning capabilities.

Results expected and their significance in the respective field of research :

The utilization of WD-XRF/XAS using curved HAPG optics has received much attention in the last 10 years [2,4-9]. However, detection approaches making use of these devices typically only allow for single/few elements to be detected at a given time. Our proposed experiment, therefore, will investigate the possibility of simultaneous analysis of REEs combined with a 3D voxel scanning approach. These exploratory studies will provide a non-destructive approach to determine up to now inaccessible REE trace composition in pristine asteroid materials (originating from asteroids Ryugu and Bennu), expected to provide crucial insights into the early evolution of the Solar System.

References :

- [1] Grigorieva, A., et al., *Condens. Matter*, 2019. **4(18)**. [2] Zastrau, U., et al., *J. Instrum.*, 2013. **8**: P10006. [3] De Pauw, E., et al., *Anal. Chem.*, 2020. **92**: 1106-1113. [4] Anklamm, L., et al., *Rev. Sci. Instrum.*, 2014. **85**: 053110. [5] Schlesiger, C., et al., *J. Anal. At. Spectrom.*, 2015. **30**: 1080-1085. [6] Malzer, W., et al., *Rev. Sci. Instrum.*, 2018. **89**: 113111. [7] Scordo, A., et al., *Condens. Matter*, 2019. **4(38)**. [8] Schlesiger, C., et al., *J. Anal. At. Spectrom.*, 2020. **35**: 2298-2304. [9] Scordo, A., et al., *J. Anal. At. Spectrom.*, 2020. **35**: 155-168.