Malvern PANalytical

Benefits of hard X-radiation

White paper

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Introduction

This white paper outlines the main benefits of using hard radiation for material analysis studies. X-ray powder diffractometers are generally equipped with X-ray sources using Cu anodes. For specific applications, however, switching to shorter wavelength, 'harder' radiation, like obtained from X-ray tubes with Mo or Ag anodes, gives significant improvements over Cu, or even allows experiments that are impossible with Cu radiation, like experiments where a large Q range needs to be probed.

Often, people make use of synchrotron radiation, but new developments on source, optics and detector technologies allow a variety of hard radiation experiments in the home lab. In this white paper we present six key advantages of hard radiation studies.

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Edition notice
First edition, July 2017

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Larger penetration depth

For inorganic materials, the penetration depth of Cu K-alpha is often only a few micrometers (see Table 1). In order to extract information from a larger sample volume, hard radiation is an advantage in transmission experiments. Thanks to the larger penetration depth, it is possible to observe crystallographic changes in working devices, such as Li-ion batteries, and perform high-pressure experiments with diamond anvil cells. Hard radiation allows using transmission geometry for inorganic samples.

	Cr (2.29 Å)	Co (1.79 Å)	Cu (1.54 Å)	Mo (0.71 Å)	Ag (0.56 Å)
Al	19	39	60	572	1131
Cu	6	11	17	18	35
Steel	9	9	4	28	54
W	1	2	2	4	8
Inconel	6	7	7	26	37
Ni-35Al	7	14	22	29	55
Fe_2O_3	16	32	7	58	112
Co_3O_4	13	25	5	43	84
NdFeB	7	6	3	26	50
Si	18	36	54	527	1040
$LiFePO_4$	23	46	18	155	298

Table 1. Example of penetration depth in µm for different materials and different X-ray wavelengths

Better crystallographic information

Crystallographers prefer to measure their samples in the Debye-Scherrer capillary geometry – preparing samples in glass capillaries is the best way to minimize preferred orientation effects of powdered samples.
Working with Mo radiation in combination with optics focusing on the detector allows the usage of large-diameter capillaries without a loss in angular resolution or excessive absorption problems.
Furthermore, it allows a better determination of the atomic thermal parameters like B_{iso}.

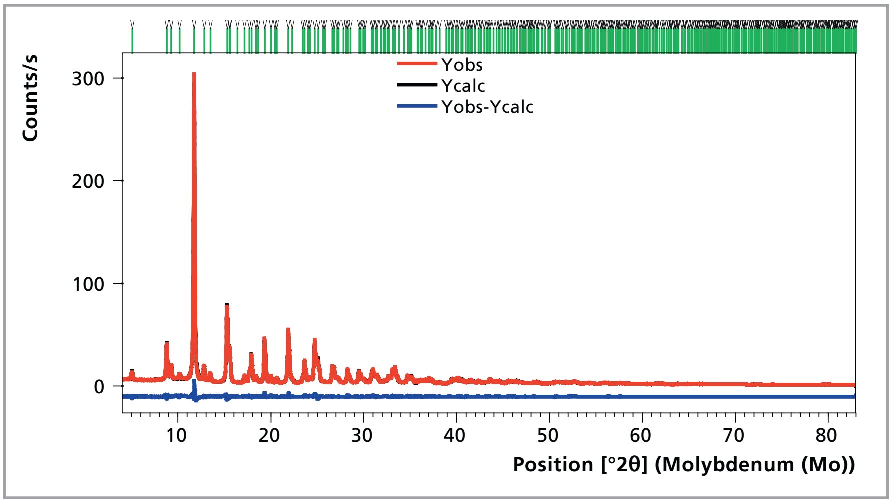

Figure 1. Rietveld refinement of $Fe(IO_3)_3$ carried out with the HighScore suite [1]
Space group $P6_3$ with cell parameters a = b = 9.2361(1) Å, c = 5.23882(7) Å; Rwp = 2.4, GoF =3.4

Reliable information on the local structure of materials (PDF analysis)

Pair distribution function (PDF) analysis, previously the domain of synchrotron sources, has become possible on laboratory multipurpose diffractometer, like PANalytical's Empyrean, by a carefully optimized optical path with a low and featureless background. With Mo, a maximum Q range of 17 $Å^{-1}$ can be reached and with Ag even 21 $Å^{-1}$

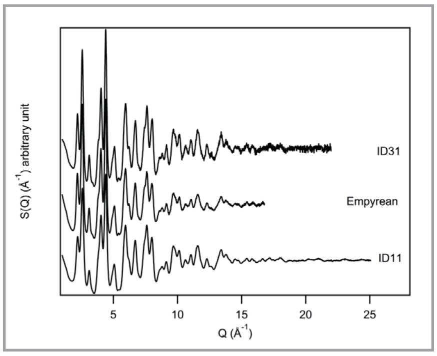

Figure 2. Structure function S(Q) comparison between two synchrotron beamlines and the Empyrean with GaliPIX^{3D}, from [2].

Allowing X-ray imaging and computed tomography for a large class of materials

Hard radiation allows X-ray imaging and computed tomography for a larger class of materials. The more penetrating Mo or Ag radiation allows thicker and/or denser samples to be successfully evaluated.

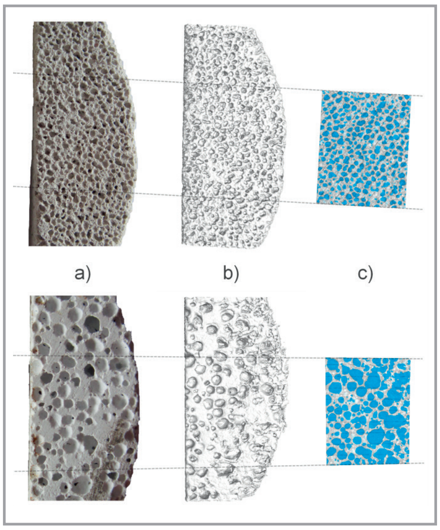

Figure 3. Porous concrete. Top row with small pores, bottom row with large pores. a) picture of the concrete slab, b) 3D view using Isosurface render, c) cross section of the sample showing in more detail the pores (blue) and the concrete framework related to the selected area where the pores are determined in.

Hyper-speed data collection

When using hard radiation instead of Cu radiation, the 2theta range required for collecting the same number of reflections decreases. A range of 100° 2theta with Cu radiation corresponds to ~30° 2theta with Ag radiation. A full-pattern one-second time resolution becomes possible.

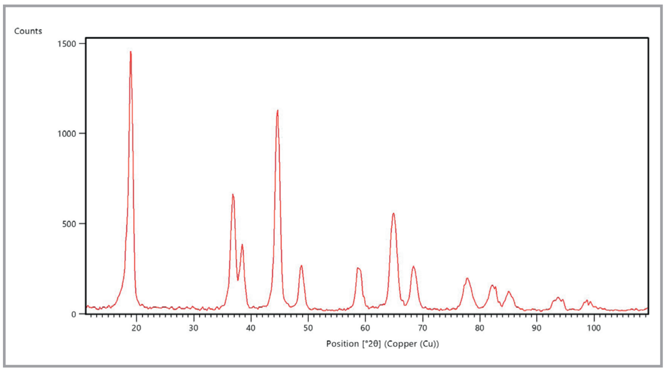

Figure 4. Hyper-speed full pattern snapshot (33 deg with Ag radiation, equivalent to ~100 deg with Cu radiation) recorded in just 2 seconds

Better preparation for synchrotron beam time

Although lab systems inherently have a much lower X-ray flux, their main advantage is the direct availability. Samples can be tested prior to submissions for beam time so the chances for project approval increase.

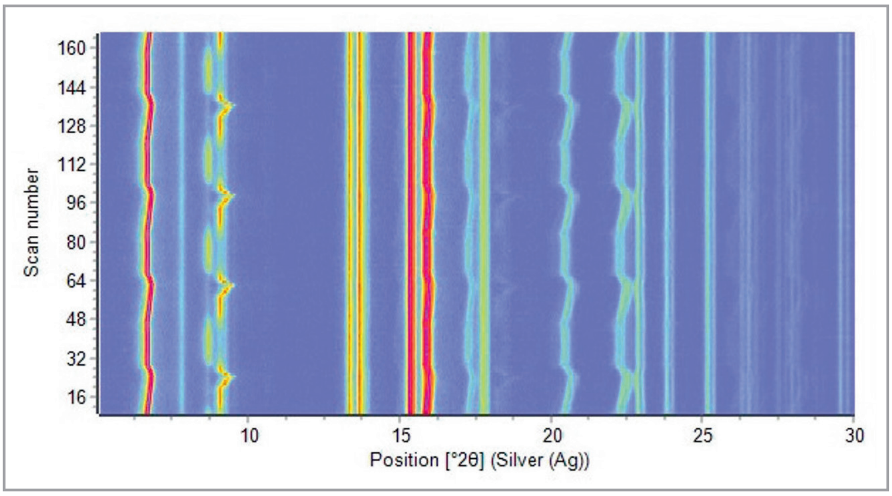

Figure 5. Four complete charge-discharge cycles of a commercial prismatic battery cell, measured with Ag radiation (5 minutes per scan, 14 hours total measuring time)

Who should be interested in hard radiation studies?

- Researchers who investigate chemical reactions. The increased penetration of Mo and Ag radiation allows the observation of chemical reactions in sealed containers without the need to open them. *In operando* Li-ion battery studies are a good example. With the latest 2D X-ray detectors, even spatially resolved information can be obtained.
- Researchers interested in the amorphous state. X-ray pair distribution function (PDF) analysis, although a technique available for a long time, has now become accessible to a larger group of researchers thanks to improvements in hardware and software. PDF gives valuable information about the interatomic distances in amorphous and nano-crystalline materials.
- Crystallographers. Novel focusing optics for Mo and Ag radiation, as well as optimized detectors, help to find details in crystal structures that could previously be only found in synchrotron data.
- Directors of central research facilities in universities, governmental research institutes and companies. Hard radiation diffraction is attractive for a variety of applications. Thanks to Empyrean's unrivalled PreFIX concept, users can switch between different configurations to get the most information from samples ranging from biomaterials to electrochemical cells to pharmaceuticals to metals.

Malvern Panalytical, your partner of choice for hard radiation applications

The Empyrean system has been designed for state-of-the-art data quality, including the much more demanding hard radiation applications. All following aspects of the system contribute to a superior data quality:

- An **instrument enclosure** designed for continuous operation at 60 kV excitation voltage, for maximal flux of Mo and Ag K-alpha radiation. The instrument recognizes the X-ray tube in use, and stores that information automatically in the .xrdml data files, thus avoiding interpretation errors and preventing users to apply settings to the tube that it cannot handle.
- An **X-ray generator** designed for 4 kW operation – so a continued operation at the maximum 3 kW for the Mo tube is well within limits.

- **X-ray tubes** specially optimized for anode stability. All diffraction angles in a hard radiation system are per definition smaller than in a Cu system, so the stability of the optical path (e.g. X-ray-tube to X-ray mirror) is of prime importance. With our in-house X-ray tube development team, we have made several enhancements to the traditional tube design in order to facilitate stable, long lifetime operation.
- High-quality **X-ray mirrors** for transmission geometry. With focusing mirrors, data with high angular resolution becomes possible for samples in glass capillaries and in working devices like batteries.
- **An optical path** designed for a low and featureless background. Hard radiation X-rays will penetrate also slits and masks that are perfectly opaque for Cu radiation, and cause increased scatter at edges and in the air itself. Especially sensitive applications like PDF require a background that is absolutely free of features – key to successful analysis. Only in Empyrean this has been fully evaluated, and it is proving its value in several installations around the world.
- **Ample experience** in using hard radiation for non-ambient experiments. Our applications team has run hard radiation experiments with virtually every commercially available non-ambient chamber, and requested improvements to the suppliers of these wherever required. We work closely together with leading manufacturers of non-ambient environments and can integrate your custom non-ambient environment as a special project.
- Optimized **X-ray detectors** for collection of hard radiation data. Hard radiation requires strongly absorbing sensor materials. Conventional X-ray detectors are equipped with gas or silicon sensors. These sensors only partially absorb hard radiation. In some designs, the transmitted radiation ends up in the read-out circuitry, potentially causing radiation damage in the sensitive underlying readout circuitry.
- **Our proprietary Pixirad technology** uses cooled, high-quality CdTe sensors, which are opaque up to 90 keV and give superior image resolution with pixels of only 60 microns in size. Thanks to a point spread function of just one pixel, blooming of images is not occurring, yielding very sharp images. Thanks to a background noise only limited by cosmic radiation, the dynamical range of this detector technology is so high, that even X-ray imaging, radiography and computed tomography are possible. Occasional irradiation of the detector by the direct beam will not cause damage.

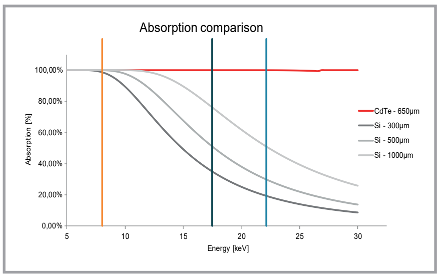

Figure 6. Detection efficiency as a function of photon energy for Si and CdTe with different thicknesses (h).

- **Analysis software** set up for hard radiation. Our .xrdml data format includes the used wavelength. Our HighScore software can readily be used for analyzing hard radiation powder diffraction data and offers unique routines developed at the Rutherford Appleton Laboratories for the calculation of the PDF out of experimental data. Our computed tomography solution interfaces directly with the well-known VG StudioMax software from Volume Graphics.
- **Flexibility**. Our instruments are designed with the future in mind. We understand that your research interests will change over the years. Thanks to its unique PreFIX philosophy, allowing each user to change the configurations without laborious re-alignment procedures, any user can, for instance:
  - Change the X-ray tube from hard radiation to Cu, and back,
  - Switch between different optical components and (non-ambient) sample stages
  - Switch between reflection and transmission geometry (keeping the sample horizontal) and capillary geometry
- **Longevity**. We hold the track record in industry for making the latest technological advances available to the installed base, in some cases even to systems that were installed more than 10 years ago.
- **Safety**. Our instruments meet the most stringent safety regulations. Each instrument is tested with a hard radiation tube prior to shipment. We actively involve renowned third-party radiation safety officers to verify our designs and processes.

Bibliography

[1] T. Degen, M. Sadki, E. Bron, U. König, G. Nénert, Powder Diffraction 29 (S2), S13-S18 (2014).
[2] G. Confalonieri, M. Dapiaggi, M. Sommariva, M. Gateshki, A.N. Fitch, A. Bernasconi, Powder Diffraction 30(2), S65 (2015).

Acknowledgments

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