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Powder XRD methodology – main research instrument in Earth and Material sciences

Прахов рентгеноструктурен анализ – основен научен инструментариум в науките за земята и материалознанието

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Powder XRD methodology continues to be a milestone in modern Crystallography. As stated at the Opening Ceremony for the International Year of Crystallography (IYCr 2014, UNESCO Paris 20–21 January, 2014), *Crystallography becomes the Science of the future*.

At the IYCr 2014 Opening Ceremony, one of the key lectures was “Crystallography in the study of the Universe by David Bish and David Blake, demonstrating the first Powder X-ray diffraction pattern from *the planet Mars!*”. Bish et al. (2014) stated: “The Mars Science Laboratory landed in Gale crater on Mars in August 2012, and the Curiosity rover then began field studies on its drive toward Mount Sharp, a central peak made of ancient sediments. CheMin is one of ten instruments on the rover, all designed to provide detailed information on the rocks, soils and atmosphere in this region. CheMin is a miniaturized X-ray diffraction/X-ray fluorescence (XRD/XRF) instrument that uses transmission geometry with an energy-discriminating CCD detector” (Fig. 1a). This approach, coupled with data-processing software interfaced to the Crystal Structure Database (ICSD), may be the model for future remote contact diffraction analyses of the surfaces of planetary bodies.

Some of the powder XRD approaches used today intensively are: powder XRD phase analysis, Rietveld structural analyses with powder XRD data, profile fitting analysis of XRD data, quantitative analysis of polycrystalline materials, petrological samples, composites, etc.

Powder XRD phase analysis

The International Centre for Diffraction Data (ICDD) continues to be the world center for quality diffraction and related data to meet the needs of the technical community. ICDD, for about 70 years creates and develops the PDF database of all known

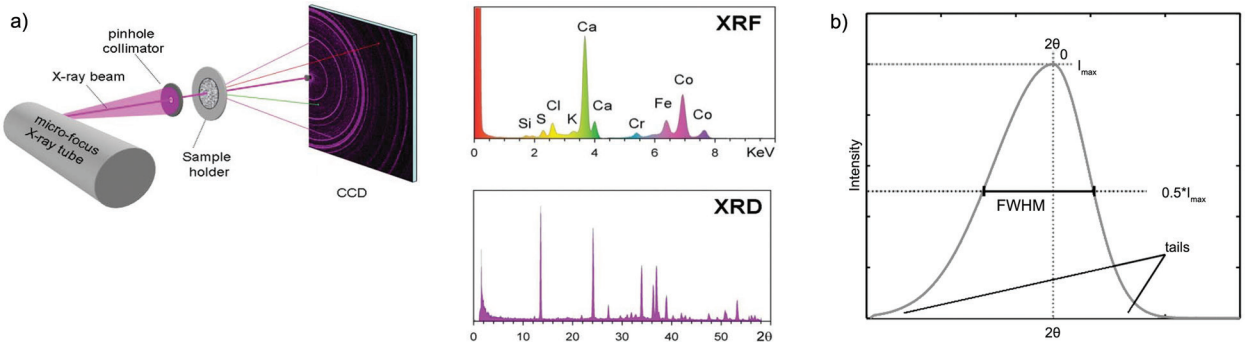

Fig. 1. *a*, scheme of the XRD/XRF technology of the CheMin instrument (after Bish et al., 2014); *b*, schematic representation of common XRD peak

crystalline phases. Main ways of collecting powder XRD data in ICDD: *Grant-in aid projects* – Each year ICDD extends financial support to qualified investigators in the form of grants-in-aid projects awarded on a competing proposal basis for the preparation of reference X-ray powder diffraction data; *Calculated powder patterns from published single crystal structural data.*

Rietveld structural analyses with powder XRD data

During the years the only way to obtain crystal structural data for new minerals and new crystalline phases is the single crystal XRD method. However, numerous scientific challenges are based on polycrystalline phases – minerals, synthetic materials, composites, ceramic and cement products, *etc*.

The continuous development and upgrade of the powder XRD instrumentation, the step-scanning technics giving numerical data, and the modern software pave the way for solving the structural problems with powder XRD (sophisticated software being GSAS, Fullprof, and others). Rietveld refinement is a technique devised by Rietveld (1967, 1969) for use in the characterization of crystalline materials including mineral structures.

Using the above structural approach Bulgarian scientists (Zidarov et al., 2009) refined the structure of Mn-rich norsethite, $Ba_{1.0}Mg_{0.8}Mn_{0.2}(CO_3)_2$, found and described for the first time in Bulgaria in Kremikovtsi ore deposit, Sofia district. In addition, for example, Dimova et al. (2011) successfully solved the crystal structure of the natural Ag-exchanged zeolite clinoptilolite (C2/m space group) and Lihareva et al. (2020) structurally controlled Cs and Sr exchange on clinoptilolite.

Profile fitting analysis of XRD data

A profile-fitting procedure is used for analyzing X-ray diffraction peak profiles broadened by microstructural factors (crystallite size and lattice disorder). In this methodology, usually a pseudo-Voigt function is suggested to obtain the shape factors (integral breadth, peak width at half maximum, Gaussian content) that contain useful information related to the microstructural properties of materials following line broadening analysis.

Each peak in the powder XRD pattern contains information together for the diffraction angle 2θ, dependent on wave length λ of the used X-ray source (Cu, Co, Fe, Ag, Mo, Cr), the line spacing d_{hkl}, peak intensity (height – h, integrated area – I), FWHM – full-with-at half-maximum 1/2 h, peak profile described by a profile function, asymmetry (Fig. 1b). Line profile analysis in powder XRD patterns allows distinguishing of phases with strong overlapping of peaks.

Crystallite size determination

In present time, importance is forwarded to nanoscience, nano-technologies and nano-materials. The determination of crystallite size of materials is crucial and the profile analysis of powder XRD patterns again comes in support with approaches based on the FWHM of peaks, the Sherrer equation and the corresponding modern software packages.

Rietveld refinement with applying various size and strain models

For example, Kostov-Kytin et al. (2017) performed a powder XRD microstructural analysis of thermally treated synthetic fluor-hydroxylapatite. The authors reported about trends and consistencies of XRD patterns in terms of domain sizes and microstrain that have emerged for the studied material upon heating. The obtained results are explained and interpreted in the light of the up-to-date views and theories on crystal growth and imperfections and modern powder XRD microstructural approaches. The authors concluded that the performed powder XRD microstructural analysis reveals distinct anisotropy in the patterns line broadening of nano-sized synthetic fluor-hydroxylapatite samples heated within the temperature range 400–910 °C. Profile broadening is caused both from the presence of nanosized crystalline domains as well as from the occurring microstructural effects.

Powder XRD quantitative analysis (using the Rietveld methodoly)

Prerequisites: 1. Advances in computer technology 2. This computing power (and the computer programmers) has enabled diffraction specialists to work with the whole XRD pattern instead of relative intensities of a few identified peaks. 3. Whole-pattern analyses is based on diffraction pattern being the sum of all effects, both instrumental and phase-related. 4. The basic approach is to obtain best data, identify all the phases present and input basic structural data for all phases, then let the computer model your data until reaching the best fit to the experimental pattern.

Examples of XRD Rietveld based quantitative determinations on geological samples obtained by Bulgarian researchers in the field of Earth Sciences:

1. *Carbonate-sulfate rock* from NE Bulgaria (Andreeva et al., 2011) – the sample is from deep drilling near Kardam town. The mineral phase

analysis gives: dolomite, anhydrite, and quartz. After the refinement, the quantities are (wt%): anhydrite – 35.9, dolomite – 58.7, quartz – 5.4. Such quantitative data is important for petrologic classification and genetic reconstruction of the geologic medium.

2. *Skarn mineralization* in Eastern Bulgaria (Tzvetanova, 2015) – the author performed accurate mineral quantification of inhomogeneous finezoned skarn rocks, containing minerals with highly variable chemical compositions. The quantification of skarns is important for classification, paragenesis and facial determinations as well as for potential useful components for industry.

Summarizing the applications of the Rietveld based powder XRD quantification we may state that this is a serious instrument for optimized and speedy quantitative determinations of minerals in various geological environments.This approach is important and express in petrological analyses and classification of rocks and minerals resources and industrial deposits. In material science the tasks are analogical – such quantification is quite needed for evaluation of synthetic products especially during controlled syntheses, ceramic preparations, composites.

Finally, the discussed modern approaches of the powder XRD methodology confirms it as a milestone in contemporary Earth and Materials sciences.

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