Introduction to neutron scattering experiments at large scale facilities

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1. **Introduction**

1.1. Neutrons

Neutron is a subatomic particle with mass equal 1.67×10^{-27}kg, with no charge and with magnetic moment of $-1.93\mu_N$ where μ_N is nuclear magneton. It is a fermion with intrinsic angular momentum equal to $1/2\hbar$ where $\hbar$ is reduced Planck constant and it was discovered in 1932 by James Chadwick. Together with protons it constitutes nuclei of an atom. Atoms of a chemical elements that differ only in neutron number are called isotopes. Protons and neutrons are attracted to each other via strong force. On the other hand protons repel each other via the electrostatic force. Therefore neutrons within the nucleus act like nuclear glue. They attract each other and protons which helps offset the electrical repulsion between protons. Because of the strength of the nuclear force at short distances, nuclear binding energy of nucleons is more than seven orders of magnitude larger than the energy binding electrons in atom. The mean lifetime of free neutron is 882 seconds. Free neutrons are unstable and decay via beta decay. The decay of neutron involves the weak interaction and is associated with a quark transformation (a down quark is converted to an up quark). When nuclear fission was discovered, it became clear that if fission reaction produced free neutrons, each of these neutrons might cause further fission reaction in a cascade known as a chain reaction. Neutrons are neutral particles and therefore travel in straight line which are deviating only when they collide with nucleus and then they are scattered into a new direction or they are being absorbed. The extent to which neutrons interact with nuclei is described in terms of quantities known as cross sections.

Free neutrons can be classified according to their kinetic energy:
- Cold neutron (0-0.025 eV) are in thermal equilibrium with very cold surroundings such as liquid D.
- Thermal neutrons are in thermal equilibrium with a surrounding medium with most probable energy from Maxwellian distribution of 0.025 eV at 20℃.
- Epithermal neutrons (0.025 - 0.4 eV)
- Cadmium neutrons (0.4 – 0.5 eV) are neutrons with energy below the cadmium cut-off energy
- Epicadmium neutrons (0.5 – 1 eV) are neutrons that are not absorbed by cadmium
- Slow neutrons (1 – 10 eV)
- Resonance neutrons (10 – 300 eV) which show special behavior. At resonance energies, the cross-sections can reach peaks more than 100 times higher than the expected value and it is very important for thermal reactor to quickly overcome this range of energy because probability for fission significantly increases.
- Intermediate neutrons (300 eV – 1 MeV)
- Fast neutrons (1 MeV – 20 MeV) are slowed down in reactors to thermal energies via neutron moderation.
- Relativistic neutrons (>20 MeV)

Thermal or cold neutrons have wavelengths similar to atomic spacings so they can be used in neutron diffraction experiments.

A neutron source is any device that emits neutrons. Several factors describes a neutron source: significance of the source, intensity, energy distribution, angular distribution, mode of emission (continuous or pulsed). There are different classifications of sources. One of them is on large, medium and small nuclear sources.

Large neutron sources are:

- *Nuclear reactors* where certain nuclei are undergoing nuclear fission and as a product yield neutrons
- *Fusion systems* where two or more nuclei collide at very high energy and fuse together and a byproducts are free neutrons
- *Spallation sources* that represent high flux neutron source in which protons that have been accelerated to high energies hit a heavy target material causing the emission of neutrons.

Medium neutron sources are:

- *Bremsstrahlung from electron accelerators* where high energy electrons emit gamma rays after being slowed down in a heavy target and that gamma radiation later produces neutrons when interacting with the target.
- *Dense plasma focus (DPF)* mechanism is based on nuclear fusion of short-lived plasma of D and/or T.
- *Light ion accelerators* where neutrons can be produced by particle accelerators using targets such as D, T, Li, Be and other low-Z elements. The target is bombarded with H, D or T nuclei.

Small neutron sources are:

- *Neutron generators* where neutrons are produced in the fusion of D and T in the following exothermic reaction: $^2D + ^3T \rightarrow ^4He + n + 17.6$ MeV.
- *Radioisotope source (α, n)* where in certain light isotopes the "last" neutron in nucleus is weakly bound and is released after bombardment by alpha particles.
- *Radioisotope source (γ, n)* which mechanism is the same as in previous one but with usage of gamma rays as compared to alpha particles. This source is producing monoenergetic neutrons unlike *(α, n)*.
- *Radioisotope source – spontaneous fission* where the most commonly used source is the radioactive isotope Californium-252.

1.2. X-ray scattering

X-ray and neutron scattering can be used to investigate a wide range of substances, such as poly and single crystals, metals and alloys, semiconductors, amorphous solids and liquids, synthetic polymers etc. These two methods are complementary. X rays interacts predominantly with electrons and gives information about surface of material. On the other hand, neutron are less reactive with surroundings and penetrate deeply into the material and can give information about bulk of material.

The scattering of X rays by matter is determined almost entirely by the interaction of incident radiation with electrons. A part of nuclear scattering is negligible in that the mass of the nuclei is

more than 10^3 times greater than the electron mass and the nuclear scattering energy is accordingly 10^6 times less than the electron scattering energy. For a plane monochromatic incident wave:

$$E = E_0 \exp[i(k_0 r - \omega t)]$$

where E represents the electric field intensity. Amplitude of the scattered wave can be expressed as:

$$E_s = - E_0 \frac{e^2}{mc^2} \frac{1}{r} \sin\psi$$

Where e and m are the charge and mass of the electron, c is the velocity of light, r is the distance frothe electron to the point of observation and ψ is the angle between the scattering beam and the direction of acceleration of the electron. The phase of scattered radiation relative to the phase of the incident beam changes by 180^0.
X-ray scattering length of a single electron is:

$$b_x = \frac{e^2}{mc^2} \sin\psi = r_0 \sin\psi$$

where r_0 is Thomson electron radius. Scattering intensity is equal:

$$i_x = b_x^2 = (r_0 \sin\psi)^2$$

For small-angle scattering, where $\psi=90^0$:

$$i_x = r_0^2 = 7.95 \times 10^{-25} \text{ cm}^2$$

Integral cross section, which represents total scattering energy scattered by a single electron gives the following value:

$$\sigma_x = \frac{8\pi}{3} r_0^2 = 6.66 \times 10^{-25} \text{ cm}^2$$

In the case of an atom containing Z electrons, electron density is introduced, $\rho_a(r)$, and represents the time averaged probability of the electron distribution in an atom and may be accepted as a spherically symmetric function for free atoms. The scattering length in this case equals:

$$f_a(s) = r_0 L(\theta) \int_0^\infty \rho_a(r) \frac{\sin(sr)}{sr} 4\pi r^2 dr$$

Where $L(\theta)$ is the polarization factor. For small-angle scattering studies, the scattering length of an atom is just $f_a = r_0 Z$ because polarization factor is equal to 1 and integral value is equal to the

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number of electrons. These relationships are valid when the frequency of incident radiation is much greater than frequency corresponding to the energy excitation of K, L and other shells of the atom. Than, dispersion corrections for scattering length are necessary to include.

1.3. Neutron scattering

Contrary to X rays, neutrons are not scattered appreciably by electrons. They interact mainly with the nucleus. Wavelength of neutrons is determined by equation $\lambda = h/mv$ where m and v are mass and velocity of neutron and h is the Planck constant. When the neutron beam passes through the moderator at temperature T, the mean-square velocity of the neutrons $<v^2>$ satisfies the relationship

$$m<v^2>/2 = 3k_BT/2$$

where k_B is the Boltzmann constant. The maximum intensity of the thermal neutron spectrum is at wavelength:

$$\lambda_{max} = (h^2/3mk_BT)^{1/2}$$

Dimensions of the nucleus are much smaller than the neutron wavelength so the scattering length for thermal neutrons will be isotropic, independent of the scattering angle and given by a constant real value over wide energy range, b_n, which consist of two parts: potential scattering and resonance scattering. Contrary to the X-ray scattering length it can be either positive or negative sign, depending on the contribution of the two terms in expression.

The integral cross section of neutron scattering is expressed by a simpler formula than in X-ray scattering:

$$\sigma_n = 4\pi \; b_n^2$$

This equation is derived for non-moving zerospin nucleus, and can be used for solid state, but for gasses has to be modified and becomes smaller than the tightly bound one. This decrease depends on the mass of neutron and is the biggest for hydrogen atom.

If material is magnetic it is necessary to include magnetic scattering but it is usualy weaker than nuclear scattering and is used to determine the spin density in paramagnetic, ferro, ferri and antiferromagnetic materials.

2. Neutron/X-ray data manipulation

2.1. FullProf

The program has been mainly developed for Rietveld analysis of neutron (nuclear and magnetic scattering) or X-ray powder diffraction data collected at constant or variable step in

scattering angle 2θ. Two versions of the source code exist at present. The first corresponds to a source written in standard FORTRAN 77 (F77) language, and is organised as to be easily adapted to different computers. The second version of the source code has been developed from the previous one, and it has been totally re-written in a subset (ELF90) of the new standard Fortran 95 (F95).

Some of the most important features of FullProf are: X-ray diffraction data: laboratory and synchrotron sources; Neutron diffraction data: Constant Wavelength (CW) and Time of Flight (TOF); One or two wavelengths (eventually with different profile parameters); The scattering variable may be 2θ in degrees, TOF in microseconds and Energy in KeV; Background: fixed, refinable, adaptable, or with Fourier filtering; Choice of peak shape for each phase: Gaussian, Lorentzian, modified Lorentzians, pseudo-Voigt, Pearson-VII, Thompson-Cox-Hastings (TCH) pseudo-Voigt, numerical, split pseudo-Voigt, convolution of a double exponential with a TCH pseudo-Voigt for TOF; Multi-phase (up to 16 phases); Preferred orientation: two functions available; Absorption correction for a different geometries. Micro-absorption correction for Bragg-Brentano set-up; Choice between three weighting schemes: standard least squares, maximum likelihood and unit weights; Choice between automatic generation of hkl and/or symmetry operators and file given by user; Magnetic structure refinement (crystallographic and spherical representation of the magnetic moments). Two methods: describing the magnetic structure in the magnetic unit cell of making use of the propagation vectors using the crystallographic cell. This second method is necessary for incommensurate magnetic structures; Automatic generation of reflections for an incommensurate structure with up to 24 propagation vectors. Refinement of propagation vectors in reciprocal lattice units; hkl-dependence of FWHM for strain and size effects; hkl-dependence of the position shifts of Bragg reflections for special kind of defects; Profile Matching. The full profile can be adjusted without prior knowledge of the structure (needs only good starting cell and profile parameters); Quantitative analysis without need of structure factor calculations; Chemical (distances and angles) and magnetic (magnetic moments) slack constraints. They can be generated automatically by the program; The instrumental resolution function (Voigt function) may be supplied in a file. A microstructural analysis is then performed; Form factor refinement of complex objects (plastic crystals); Structural or magnetic model could be supplied by an external subroutine for special purposes (rigid body TLS is the default, polymers, small angle scattering of amphifilic crystals, description of incommensurate structures in real direct space, etc); Single crystal data or integrated intensities can be used as observations (alone or in combination with a powder profile); Neutron (or X-rays) powder patterns can be mixed with integrated intensities of X-rays (or neutron) from single crystal or powder data; Full Multi-pattern capabilities. The user may mix several powder diffraction patterns (eventually heterogeneous: X-rays, TOF neutrons, etc.) with total control of the weighting scheme; Montecarlo/Simulated Annealing algorithms have been introduced to search the starting parameters of a structural problem using integrated intensity data.

Input files have different extensions like:

- FILE.pcr – input control file
- FILE.dat – input data files
- FILE.bac – background file
- FILE.hkl – reflection file

- FILE.irf – instrument resolution file
- FILE.shp – numerical profile file
- FLE.cor – intensity correction file
- FILE.int – reflection file

As a result of calculations connected to these files one can get results summarized in different output files:

- CODFIL.out - main output file that contains all control variables and refined parameters.
- CODFIL.prf – contains observed and calculated profile that can be fed into visualization programs. It can be automatically used by WinPLOTR.
- CODFIL.rpa – contains summary of refined parameters and it is useful when running FullProf in cyclic modes.
- CODFIL.sum – contains list of symmetry operators
- CODFIL.sum – contains parameter list after last cycle
- CODFIL.fou – contains different information about structural factors and can be used for (G)FOURIER and FOURTK programs
- CODFIL.ins – template of the input control file for the program SHELXS
- CODFIL.inp – template for (G)FOURIER input file
- CODFIL.hkl – list of reflections and can be input or output file
- CODFIL.sav – contains list of reflections between two selected angles and can be output file if an interval in the scattering variable is given
- CODFIL.dis – contains list of distances and angles for specific phase
- DCONSTR.hlp – list of strings containing eventual distance and angle constraints for specific phase
- CODFIL.mic – contains microstructural information
- CODFIL.sim – contains a simulated diffraction pattern. Can be renamed as a DAT file and used for refinement in simulation work.
- CODFIL.sub – contains calculated profile corresponding to the phase n
- CODFIL.atm – depending on a parameter *Jdi* it contains information about presence of magnetic phase, magnetic atom positions and can be used as input file for MOMENT program that calculates everything concerned with magnetic structures
- CODFIL.sch - files suitable as input files for programs SCHAKAL and STRUPLO
- CODFIL.int – files suitable as input files for integrated intensity refinements and contains a list of overlapped reflections obtained by adding integrated intensities from profile matching refinement when they belong to a cluster.

As it was mentioned in the short explanation of output files, there is connection between FullProf and many other programs. So information obtained from FullProf calculation can be used as input file for programs like (G)Fourier, WinPLOTR, DicVol, MOMENT, SCHAKAL, STRUPLO,

VESTA etc. and vice versa. In the following text you can see some of the features that can be found in WinPLOTR and it's connection to FullProf.
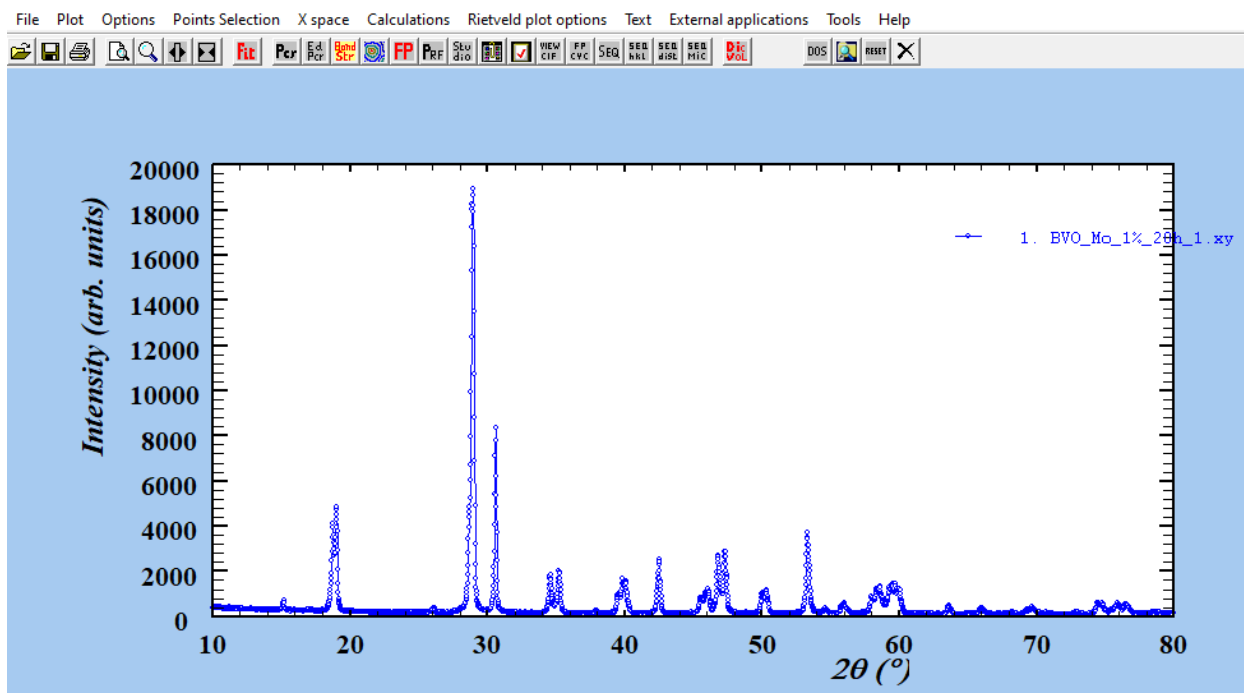
2.1.1. WinPLOTR

WinPLOTR is a software used for visualization and analysis of powder diffraction patterns. It can be used to plot raw or normalized data files coming from neutron and X-ray diffractometers as well as Rietveld files created by Rietveld type refinement programs such as FullProf. WinPLOTR has been developed to be a preferential graphic interface for Rietveld type FullProf program and can also be used as GUI for programs that are frequently used in powder diffraction data analysis such as DicVOL, TREOR, ITO. There are many other features that can be found in WinPLOTR, such as: automatic peak search; automatic background points search; one can choose different X space and do different calculations like summation, difference, smoothing, derivation, background substraction, profile fitting, FWHM calculations, microstructural analysis etc.
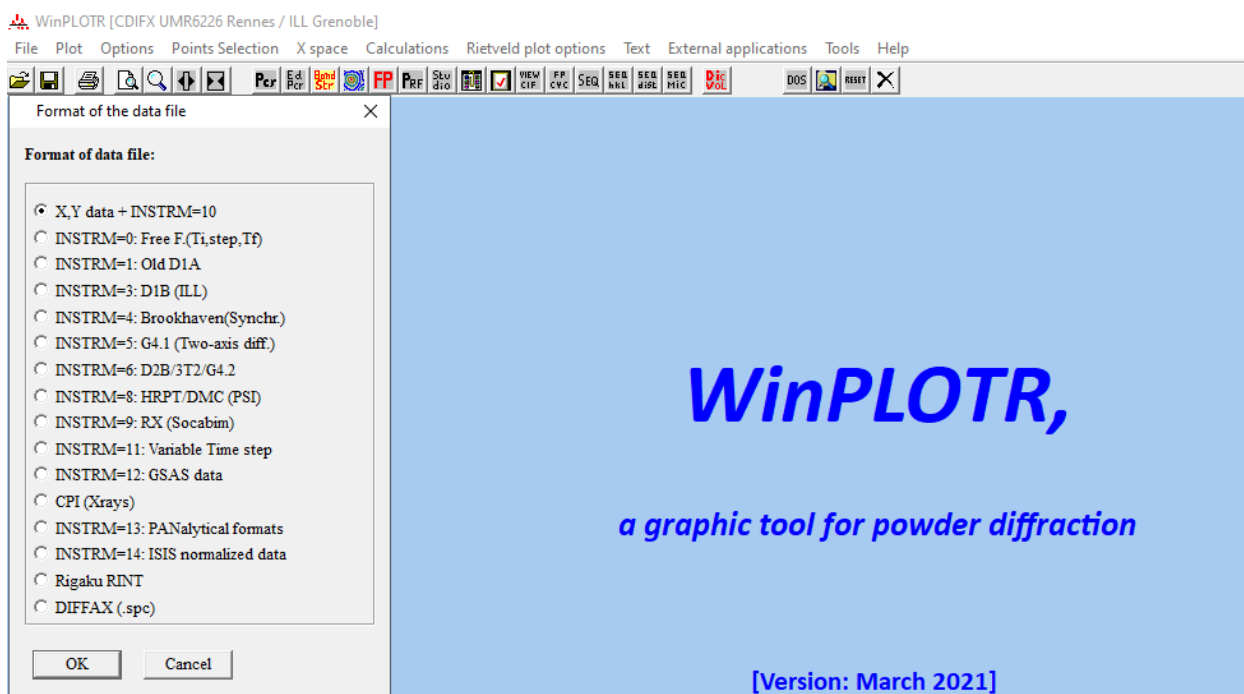
**Figure 1.** Different formats for input files for WinPLOTR

The graphic has been build up with Lahey Fortran 95. There are different formats of data input files that can originate from diffraction pattern, Rietveld files or microstructural files (**Figure 1**).

After adequate choice, for example .xy file, we get a diffraction pattern that was obtained experimentally. This was presented on **Figure 2**.

Figure 2. Diffraction pattern

As WinPLOTR is program for visualization of different patterns, it can manipulate with visual features of plots. In the menu *Text* one can change text font, text color, legend and text positions, graduations etc. In *Plots* menu are also different options for visual features where one can change focus, add error bars, do 3D plots etc. Example of those changes are represented on **Figure 3**.
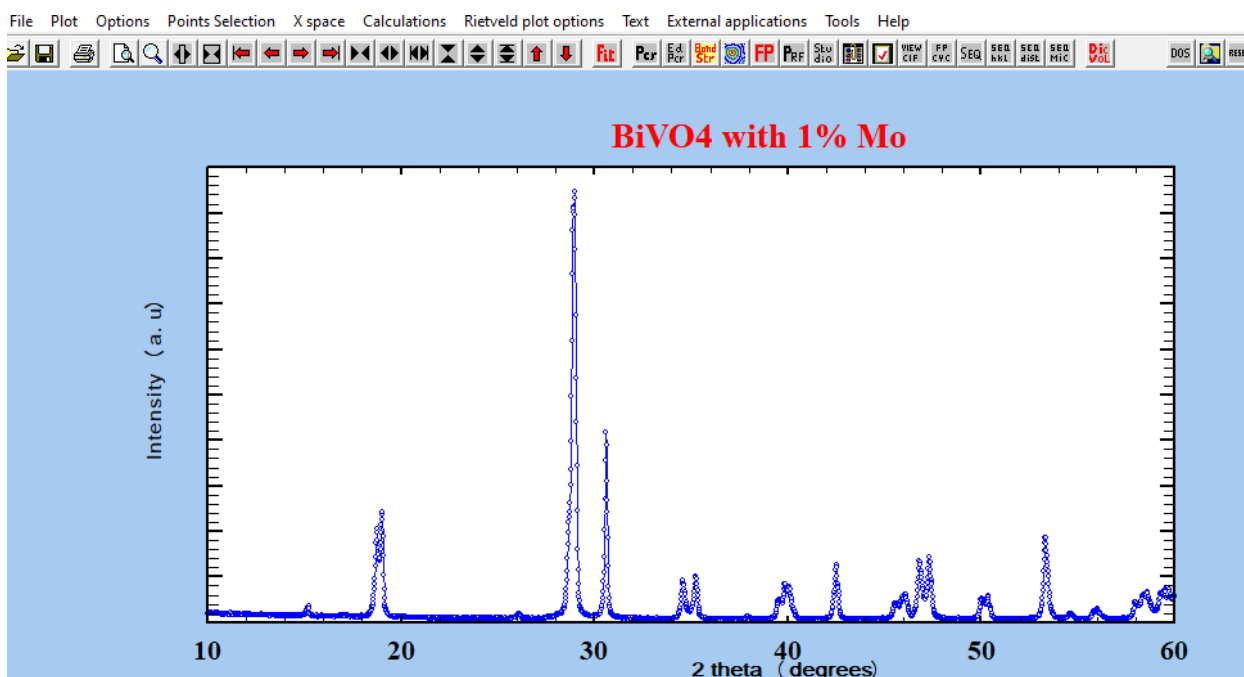
Figure 3. Different visual representation of pattern from Figure 2 using *Text* and *Plot* menu

Besides visual changes, different calculations can be done in WinPLOTR. After uploading another pattern, difference between the two is calculated and result is presented on **Figure 3**. Other than difference between diffractograms there are different types of calculation that can be done, like summation, integration, derivative etc. In the menu *Point Selection* there is an option for automatic peak and background search. After search, one can add missing peaks/background points or delete the unwanted peaks/background points. Information about peak or/and background positions, intensities and number of peak/background points is automatically pops up in new window. One example is presented in **Figure 4**. Obtained information can be saved in different formats like .dicvol, .ito etc. These files can be used as input PCR files for Rietveld analyisis or profile fitting using FullProf. After uploading this file in PCR editor, Fullprof calculation is started and profile fitting after initial cycle is presented in **Figure 5**. X^2 value is 28.3 which is not good enough so refinement should continue until this value as close to 1 as possible (on **Figure 6** is presented result with much better fitting). Other than X^2 there are also parameters R_p, R_{wp} and R_{exp} which also indicate quality of Rietveld refinement. As a result, one can get many output files (which were chosen before calculation) where can be found different crystallographic information.
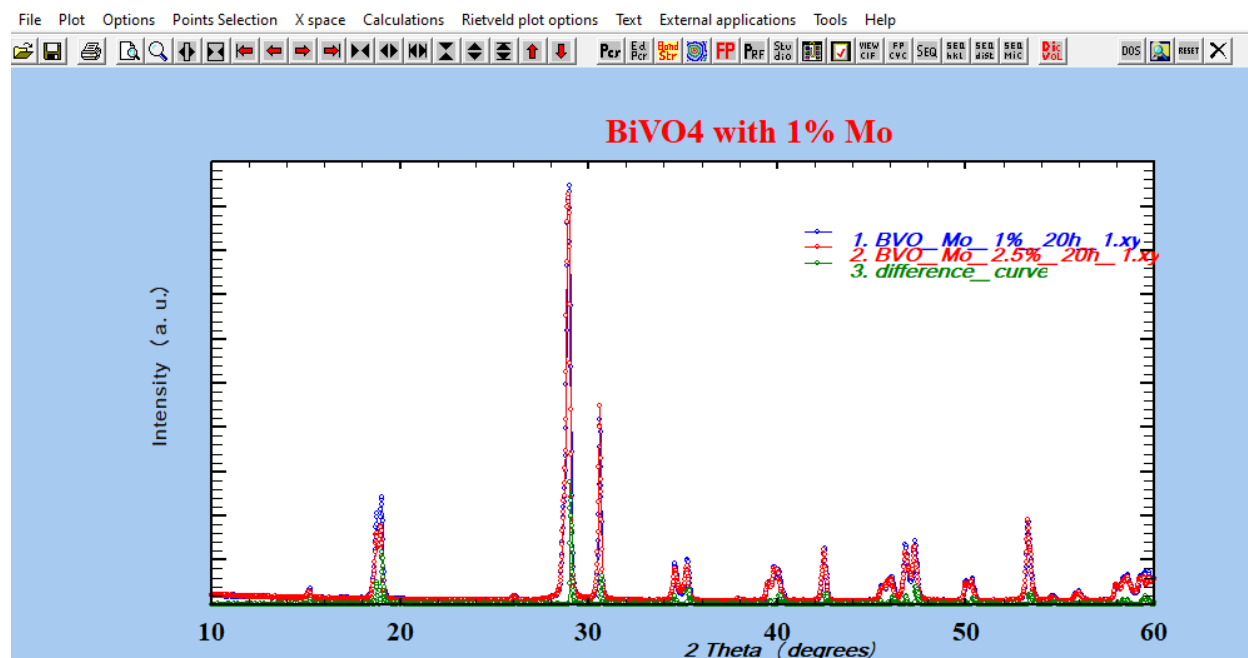
Figure 3. Plot that contains two different plots (blue and red) and their calculated difference (green)
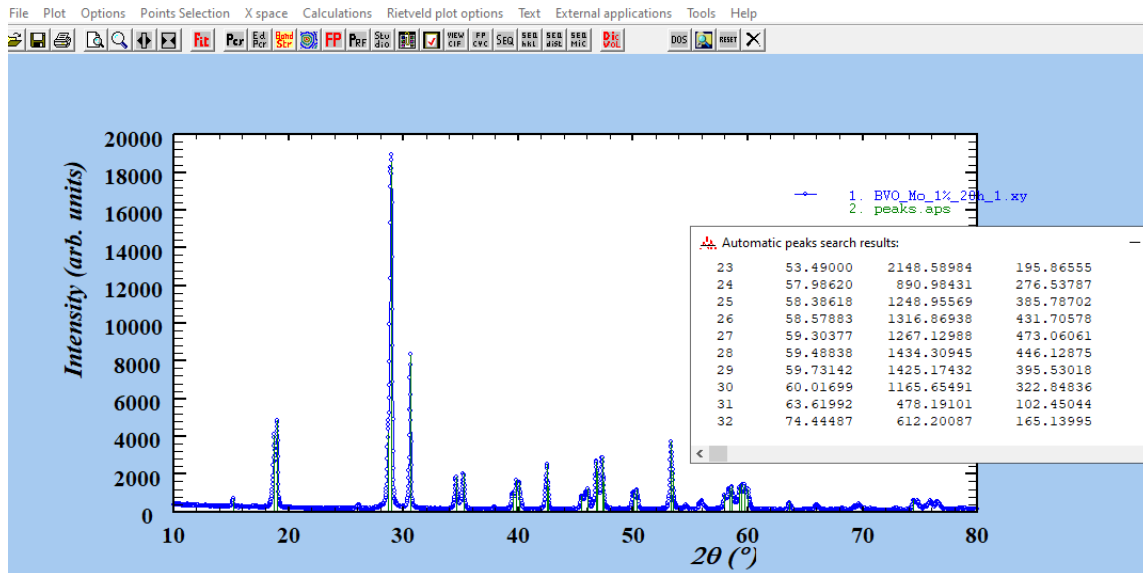
Figure 4. Automatic peak search

```
=> Rp:  29.4     Rwp:  36.0     Rexp:    6.76                    Chi2:  28.3
    => Global user-weigthed Chi2 (Bragg contrib.):    30.72
    => ---------> Pattern#       1
    => Phase:        1
    =>    Bragg R-factor:   4.997
    =>    RF-factor    :    4.465
=> Normal end, final calculations and writing...


=> CPU Time:     7.645 seconds
=> 0.127 minutes

=> END    Date:17/10/2021   Time => 19:26:26.960
```
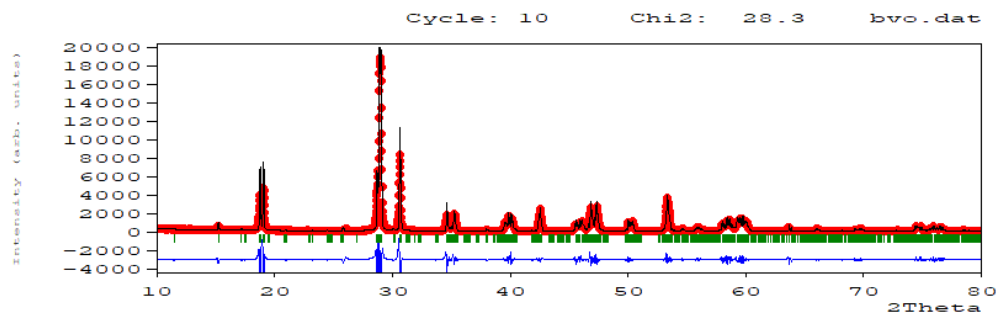

Figure 5. Profile fitting with bad refinement

```
Load  Edit PCR  Mode  Run  Exit
=> Rp:  11.5      Rwp:  14.3      Rexp:    6.75                          Chi2:   4.47
   => Global user-weigthed Chi2 (Bragg contrib.):   4.518
   => ---------> Pattern#      1
   => Phase:      1
   =>     Bragg R-factor:   2.065
   =>     RF-factor    :   2.387
=> Normal end, final calculations and writing...


=> CPU Time:     9.438 seconds
=> 0.157 minutes

=> END    Date:18/10/2021  Time => 19:29:51.427
```
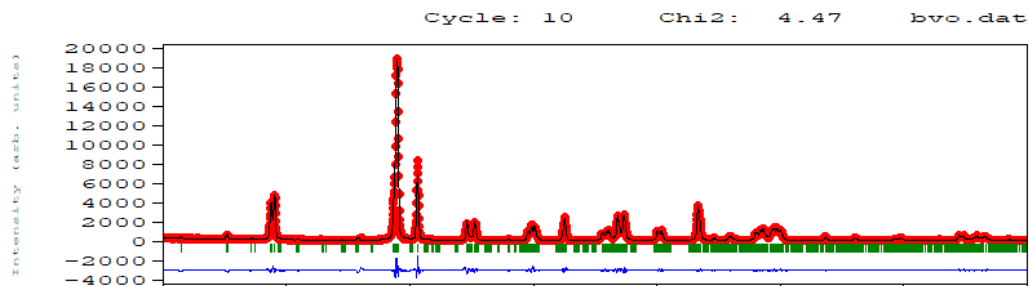

**Figure 6**. Profile fitting after much better refinement

3. Example of the proposal for neutron scattering experiment at large scale facilities

Classic proposal consist of several parts: aim of the proposed experiment and description of the scientific background, results of the previous own work at the facility that proposal was sent, details of the neutron/X-ray experiment (experimental methods with specific information about instrument of interest, justification for the use of neutrons/X-rays, justification of the amount of experimental time needed, any issues related to safety, special technical difficulties), description of the results expected and their scientific relevance, related own publications.
In the following is one example of proposal.

Aim of the proposed experiment and description of the scientific background

Bismuth vanadate ($BiVO_4$) is a promising n-type semiconducting material for photoelectrochemical water splitting devices due to its ability to absorb visible light (band-gap energy $\sim$ 2.4 eV), a favorable conduction band edge position (just below the water reduction potential), and its relative stability in near-neutral aqueous environments. Moreover, it is made of cheap, non-toxic, earth-abundant elements and can be easily produced on a large scale. $BiVO_4$ occurs naturally as pucherite mineral having an orthorhombic crystal structure. Although this form has not been prepared by normal laboratory routes of ceramic synthesis such as precipitation or solid state reaction, three other polymorphs of the compound can be prepared. Low temperature synthesis results in a tetragonal zircon-type structure whereas high temperature preparation produces monoclinic form. On heating above 255°C (528 K), monoclinic

BiVO$_4$, (space group 12b) undergoes a reversible transition to a tetragonal scheelite type structure (space group 14$_1$/a) which is known as a ferroelastic transition. For water-splitting application it is desirable to obtain pure monoclinic phase, not only on surface, but throughout the whole material. In this experiment, five different routes of hydrothermal synthesis of BiVO$_4$ material is proposed with the aim of finding the one with the purest monoclinic phase. Besides raw material, doping with molybdenum (Mo), tungsten (W) and copper (Cu) was done in order to analyze the effect of dopant on the structural properties of material. XRD spectra of the pure monoclinic phase before doping and the tetragonal after doping with W is presented in **Figure 7**. The picture indicates that route for synthesis of W-doped BiVO$_4$ should be changed.
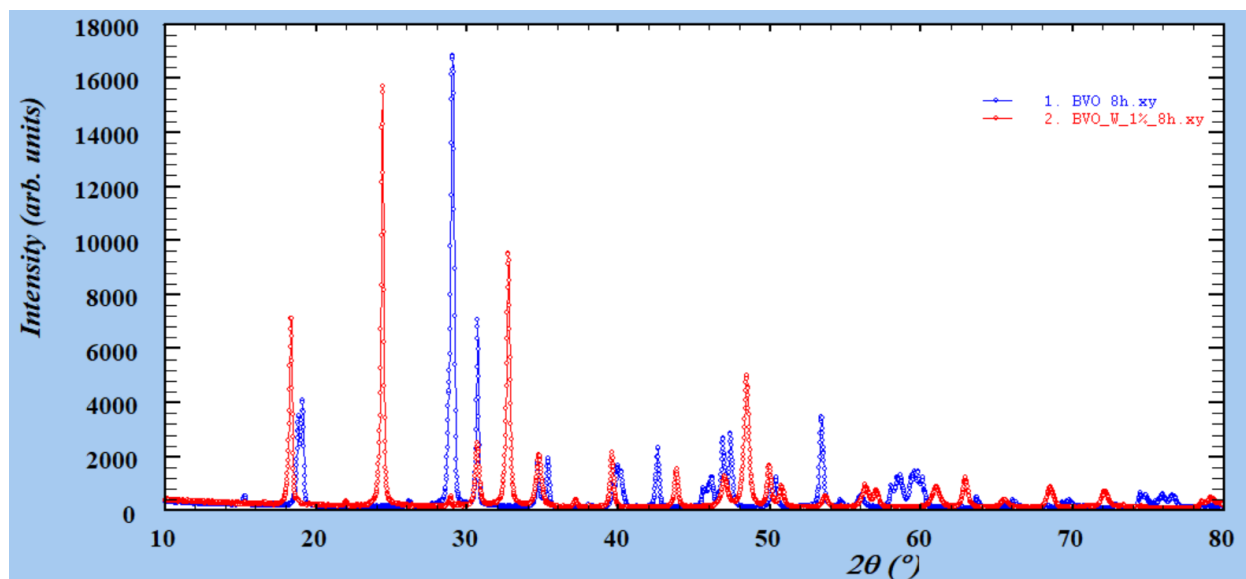
Figure 7. Two different phases of BiVO$_4$ (with and without doping)

Details of neutron experiment

Instrument: D1B - High intensity two-axis powder diffractometer with incident neutron beam of λ=2.52 nm in the range 10-90 degrees. Temperature scan between 1.5-300 K can be done to investigate thermal phase transitions. Mass of the sample is 1.5 g.

Neutrons with optimal wavelength are very useful because they can give a detailed insight into the crystallographic properties of material. Neutron diffraction was preferred to X-ray diffraction because of the greater sensitivity of neutrons to the oxygen atoms (bismuth and oxygen have similar neutron scattering lengths, 0.860 and 0.580 x 10^{-12} cm respectively) and can give information about bulk properties of material.

Diffraction pattern is collected in 1-5 minutes and complete thermal variation for one sample can be obtained in 3-5 h. There are five different routes of synthesis plus three different dopants for every synthesis which equals 60 h of beam time.

Description of the results expected and their scientific relevance

We expect to get different phase purities for five proposed synthesis routes which will help us to determine the one that gives the purest monoclinic phase. Also, structural changes are expected after doping with Mo, W and Cu. Doping has proven to be a suitable strategy to overcome the

inherent limitations that $BiVO_4$ has because in this way dopants, which are characterized by a different ionic radius relative to bismuth and vanadium, take their places and lead to distortion in the structure which creates suitable environment for improvement of charge separation and conduction.

Related publications

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