NEUTRON DIFFRACTION PATTERNS MEASURED WITH A HIGH-RESOLUTION POWDER DIFFRACTOMETER INSTALLED ON A LOW-FLUX REACTOR

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Abstract

A powder diffractometer has been recently installed on the IEA-R1 reactor at IPEN-CNEN/SP. IEA-R1 is a light-water open-pool research reactor. At present it operates at 4.5 MW thermal with the possible maximum power of 5 MW. At 4.5 MW the in-core flux is ca. 7×10^{13} $cm^{-2}s^{-1}$. In spite of this low flux, installation of both a position-sensitive detector (PSD) and a double-bent silicon monochromator has turned possible to design the new instrument as a high-resolution powder diffractometer. In this work, we present results of the application of the Rietveld method to several neutron powder diffraction patterns. The diffraction patterns were measured in the new instrument with samples of compounds having different structures in order to evaluate the main characteristics of the instrument.

1. INTRODUCTION

The first neutron diffractometer, installed on the 'beam hole' no. 6 at the IEA-R1 reactor [1], was constructed in the middle of the sixties under an IAEA project named 'Neutron Diffractometry.' It was a multipurpose instrument with a single wavelength and a single boron-trifluoride (BF_3) neutron detector. Owing to the low flux in the reactor core and consequent low flux in the monochromatic beam the old instrument was used mainly in measurements with single crystalline samples [2–7]. In general, with the old diffractometer a neutron powder pattern took several weeks to be measured. It should be noted that at the time the old diffractometer was installed the reactor was being operated at 2 MW in a discontinuous schedule (8 hours a day, 3 days a week).

The new instrument [8] was designed as an extensive upgrade of the old multipurpose neutron diffractometer and installed on the same 'beam hole' used for the old one. The main modifications introduced in the old instrument were the installation of a position sensitive detector (PSD) [9,10] and a focusing silicon monochromator [11,12]. Placed at a distance of 1600 mm from sample, the PSD spans an angular range of 20º of a diffraction pattern measuring 400 intensity points all at once in a step of 0.05º. An extensive powder diffraction pattern can be obtained by collecting data in contiguous 20º segments with the 2θ angle ranging from 5 to 130^0. The double-focusing perfect single crystal silicon monochromator, installed in a take-off angle of 84°, can be positioned to produce 4 different wavelengths, namely 1.111, 1.399, 1.667 and 2.191 Å (nominal values). Due mainly to the installation of the PSD and the monochromator the new instrument could be designed as a high-resolution powder diffractometer (HRPD). To the new diffractometer was given the name 'Aurora'. The

HRPD Aurora was constructed under a financial support of FAPESP[1]. Figure 1 shows photographs of the HRPD Aurora and the three racks where the instrumentation for control and data acquisition are installed.

(a) (b)

Fig.1. The HRPD Aurora (a) and the three racks with the associated electronics and control modules used in control and data acquisition (b).

The PSD, the monochromator and a rotating-oscillating collimator (ROC) [13] were acquired from Instrumentation Associates (IA)[2].The ROC is an essential component for the operation of the new instrument. The electronic instrumentation for neutron detection as well as a personal computer and the software used in control and data acquisition were also acquired from IA. Some parts of Aurora were constructed at the IPEN machine shop as, for example, the main neutron shield, the PSD shield, the in-pile and the monochromatic-beam collimators and the beam shutter. Other parts as the control modules for the ROC and the 2θ movement were developed and constructed at the IPEN electronics department [8]. It should be noted that, except for the ROC which is placed at the entrance to the PSD shield, both in-pile and monochromatic-beam collimators are open, i.e. without plates.

In what follows, we present several neutron powder diffraction patterns measured at room temperature in the HRPD Aurora. They serve here to give an idea of the resolution achieved in the new instrument. For all patterns, we applied the Rietveld Method [14] using the program GSAS [15]. With this program we refined the structural and thermal parameters of the crystalline phases found in the patterns. However, in this work, we only present as results of the refinement three of the often-used numerical criteria of fit: R-pattern (R_p), R-weighted pattern (R_{wp}) [14] and the reduced chi-square (χ^2) [15]. We do not present tables listing refined parameters since this is beyond the scope of the work. Time required for the measurement of the pattern and the reactor power during the measurement are both mentioned.

The neutron wavelength during the measurements was λ = 1.4119 Å (1.399 nominal) which resulted of a calibration process where a silicon standard sample was employed [8]. Three different vanadium sample cans are available: 0.125 in. and 0.250 in. internal diameter (i. d.), both 3.0 in. long; 0.375 in. i. d. x 2.0 in. long. In all measurements we used the 0.250 in. i. d. can, except for the three resolution curves, where all three sample cans were used, and BaY_2F_8 doped with 2% of neodymium, where the 0.375 i. d. can was used. Due to the low flux in the reactor a pattern suitable to be analyzed by the Rietveld method, including

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[2]Instrumentation Associates, 2 Davis Drive, Research Triangle Park, Durham, NC 27709, USA.

refinement of positional and thermal parameters for different phases, takes no less than 15 hours of reactor time to be measured with the reactor at 4 MW. As a matter of fact, in general time required depends on the irradiated volume, the scattering power of the material and the symmetry of the space-group associated to its structure.

2. RESOLUTION CURVES

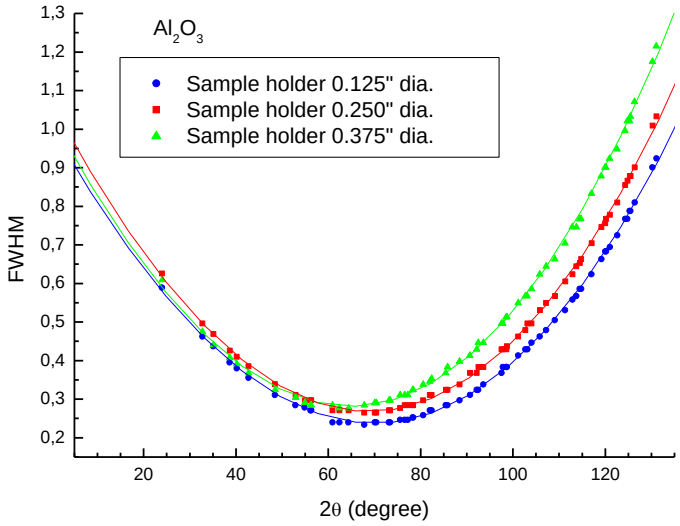


Fig. 2. Resolution curves FWHM vs. 2θ for the HRPD Aurora obtained with Al_2O_3 in three different sample holders.

The three resolution curves in Figure 2 were obtained from powder diffraction patterns of a standard sample of alumina (Al_2O_3) in the three different vanadium sample cans. The full width at half maximum (FWHM) of the peaks, as a function of the scattering angle 2θ, give the resolution curve for a determined sample can. In order to obtain the values of the FWHM, each experimental Al_2O_3 pattern was fitted by a theoretical pattern which resulted from the application of program GSAS. The FWHM values used in the curves were those obtained from the theoretical peaks.

2.1. Rietveld refinement of hematite (Fe_2O_3).

Figure 3 is an example of the results that can be obtained with the new instrument. It corresponds to the Rietveld refinement of the powder pattern of Fe_2O_3. At room temperature this oxide has an antiferromagnetic structure and crystallizes according to the trigonal space group $R\bar{3}c$ [16]. Time required to measure the pattern in Figure 3 was 48 hours with the reactor operating at 4 MW. R_p, R_{wp} and χ^2 resulted equal to 0.047, 0.060 and 3.4, respectively.

2.2. Rietveld refinement of NiO

NiO crystallizes according to the cubic space group Fm3m [17]. This oxide is antiferromagnetic at room temperature with the magnetic moments lying in the (111) planes [18]. Figure 4 shows the fitting obtained in the Rietveld refinement of NiO. The experimental pattern was measured in 48 hours with the reactor operating at 4 MW. R_p, R_{wp} and χ^2 resulted equal to 0.041, 0.051 and 2.9, respectively.

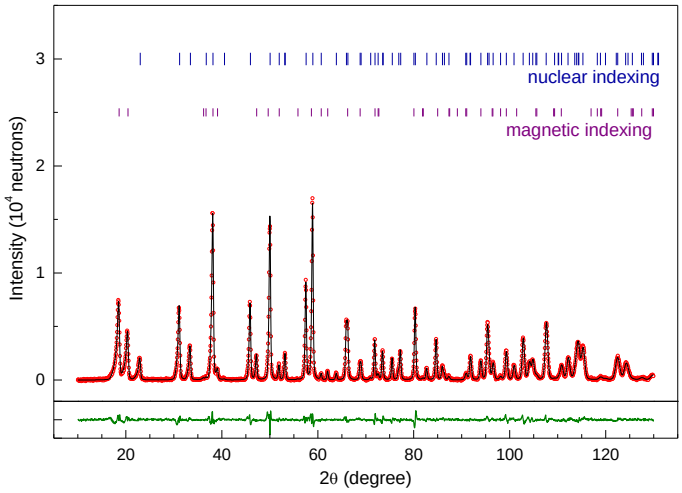


Fig. 3. Rietveld refinement of Fe_2O_3.

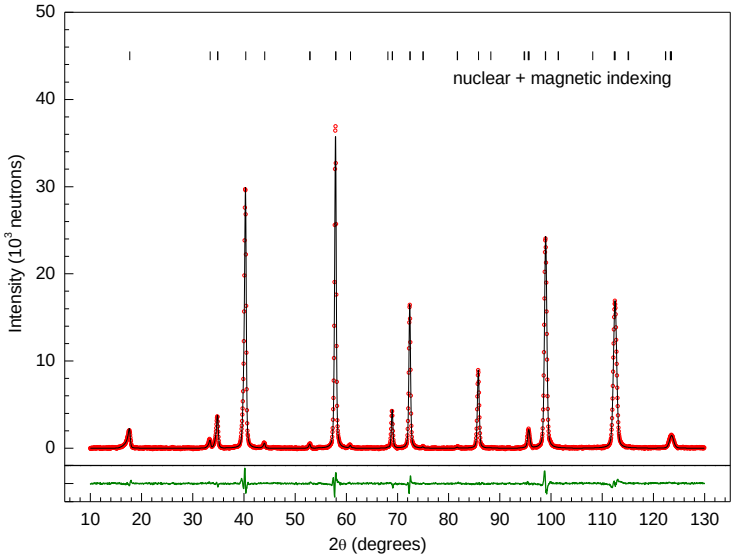


Fig. 4. Rietveld refinement of NiO.

2.3. Rietveld refinement of yttrium-barium fluoride (BaY_2F_8) doped with 2% of neodymium

Figure 5 shows the fitting obtained in the Rietveld refinement of BaY_2F_8 doped with 2% neodymium [19]. This fluoride crystallizes according to the monoclinic space group C2/m. Due to the low symmetry of the monoclinic space groups the density of peaks in the pattern is high. Indexing above the pattern shows this fact. However, in spite of the large number of peaks, R_p, R_{wp} and χ^2 resulted equal to 0.040, 0.051 and 1.2, respectively. It is noteworthy in Figure 4, by observing the difference plot, how good is the agreement between experimental and theoretical peaks. Time required to measure the pattern was 24 hours at 2 MW.

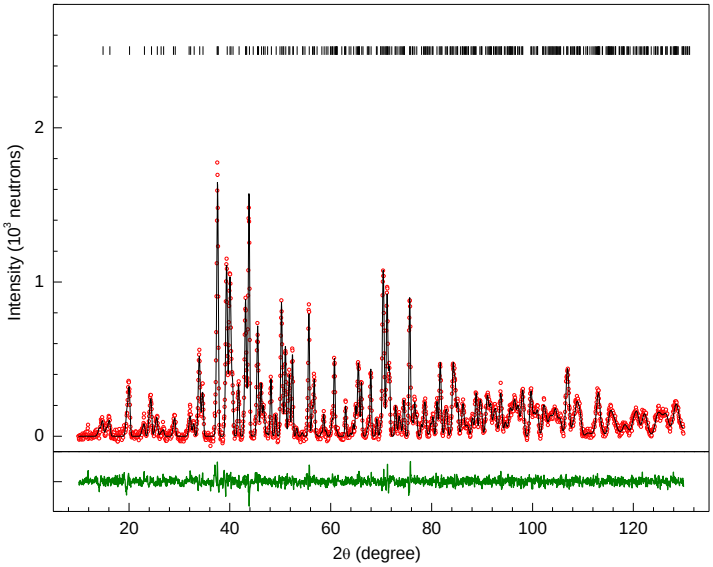
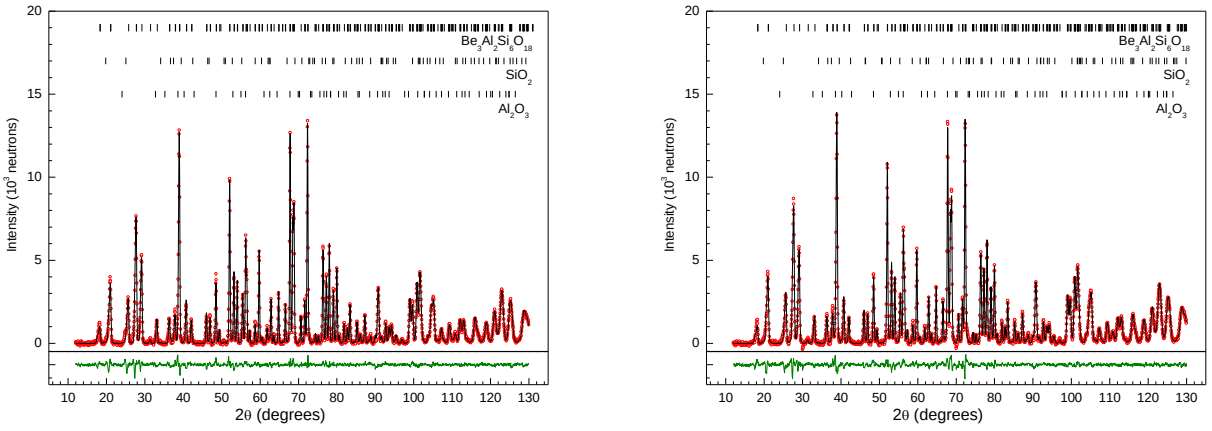


Fig. 5. Rietveld refinement of BaY_2F_8:Nd (2%).

2.4. Rietveld refinement of mineral beryl

A structural study of beryl was made using mineral samples from Teófilo Otoni, Minas Gerais, Brazil. One of the mineral samples was blue in color. It was identified as an aquamarine. The other, that was pale-blue in color, was simply called beryl. Powder samples were prepared by pulverizing the natural gemstones of both minerals.

Beryl, with the approximate formula $Be_3Al_2(SiO_3)_6$, crystallizes according to the hexagonal space group P6/mcc [20]. Rietveld quantitative phase analyses of both mineral samples showed a main phase together with two trigonal minor phases Al_2O_3 ($R\bar{3}c$) and SiO_2 ($P3_221$). The final compositions for the main phases of mineral beryl and aquamarine resulted, respectively, $Be_3Al_{1.89}Fe_{0.11}Na_{0.25}(SiO_3)_6$ and $Be_3Al_{1.83}Fe_{0.17}Na_{0.03}(SiO_3)_6$ where Fe is a substitutional atom for Al and Na an interstitial atom. Phase concentrations resulted equal to 96.94 wt% for the main phase, 2.70 wt% for SiO_2 and 0.36 wt% for Al_2O_3 in the beryl sample. For aquamarine they resulted, respectively, 97.87, 1.75 and 0.38 wt%. Concerning R_p, R_{wp} and χ^2, they resulted 0.022, 0.032 and 4.0, for beryl, and 0.024, 0.034 and 4.7, for aquamarine.



(a) (b)

Fig. 6. Rietveld refinement of beryl (a) and aquamarine (b).

In this particular study the quality of the experimental patterns was very good so that anisotropic thermal parameters could be refined instead of isotropic ones. Time required to measure each one pattern was 54 hours with the reactor at 3.5 MW.

2.5. Rietveld refinement of tantalum oxide (Ta_2O_5)

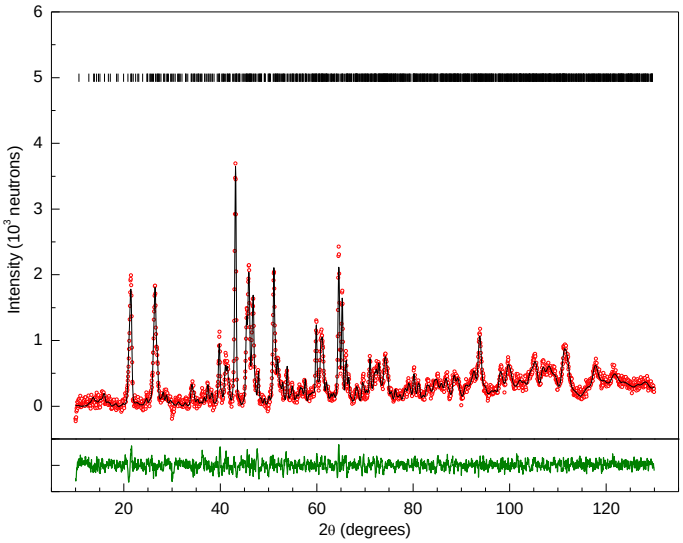


Fig. 7. Rietveld refinement of Ta_2O_5.

Ta_2O_5 crystallizes according to the orthorhombic space group Pmm2 [21]. Figure 7 shows the result obtained for the refinement of this oxide. Time required in the measurement was 57 hours at 3.5 MW. R_p, R_{wp} and χ^2 resulted equal to 0.021, 0.027 and 1.9, respectively.

2.6. Rietveld refinement of rhenium oxide (ReO_2)

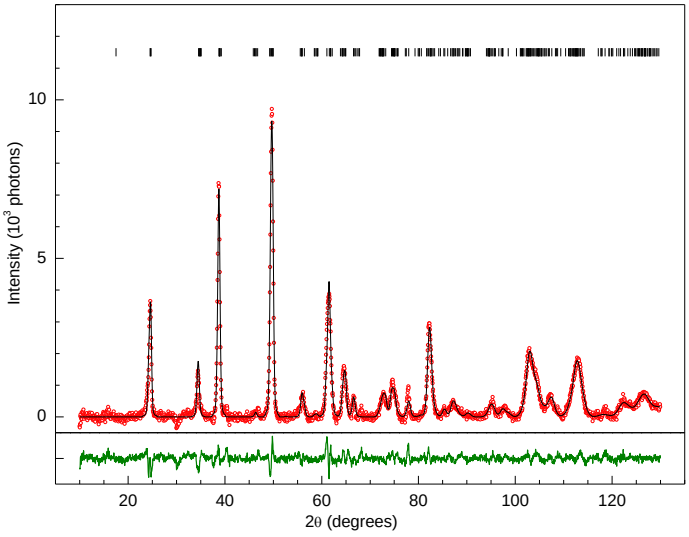


Fig. 8. Rietveld refinement of ReO_2.

ReO_2 is monoclinic crystallizing according to the space group $P2_1/c$ [17]. Figure 8 shows the fitting obtained in the refinement of this oxide. R_p, R_{wp} and χ^2 resulted respectively equal to 0.019, 0.025 and 2.7. The measurement of the experimental pattern took 54 hours with the reactor at 3.5 MW.

3. FINAL REMARKS

In this work, we present seven experimental patterns measured with the HRPD Aurora. Taking into account the results attained in the Rietveld analyses of such patterns one can easily evaluate how good they are for the application of this type of analysis. In particular, high resolution is essential to obtain better results in the Rietveld method.

The open collimators together with the focusing monochromator and the PSD, all three installed during the upgrading of the first IPEN neutron diffractometer, made it possible to construct the new diffractometer as an HRPD. From our point of view, construction of this type of diffractometer in a low flux reactor without the installation at least of a multidetector system is a rash decision. It should be noted that one of the drawbacks of installing an HRPD in a low-flux reactor is the long time needed to measure a pattern of good quality. That is the price to be paid for such an installation.

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