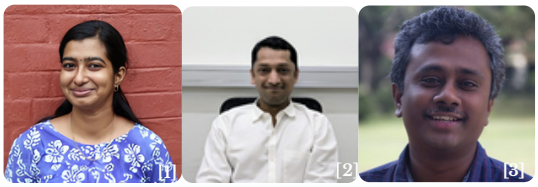
From Bragg to Rietveld: A century of X-Ray Diffraction and 50 years of structural refinement

KID: 20250103



Crystal structures define the properties of the materials, and characterising these structures is key to understanding their properties. X–Ray Diffraction (XRD) technique, often considered simple, is a vital characterization method and a powerful tool to understand a material's structural fingerprint – the crystal system, phases, strain, and defects.

XRD is primarily a coherent scattering of X-rays by electrons due to the ordered arrangement of atoms within a material. This periodicity in the arrangement of atoms gives rise to a phenomenon of diffraction that is unique to certain arrangements/crystallographic structures. This is absent in short-ranged, amorphous materials.

His seminal paper was published on "A Profile Refinement Method for Nuclear and Magnetic Structures" utilising algorithms with computers of that era, which allowed 33 refinement parameters. This program was distributed and was applied to XRD data also. Although it was coined as "Profile refinement method" by Rietveld himself, Terry Sabine and Ray Young proposed the name "Rietveld method" at the Neutron conference in Cracow to prevent confusion of using different terminologies.

Unlike traditional indexing methods that rely on peak positions alone, Rietveld refinement works by fitting an entire calculated diffraction pattern to the observed data—peak by peak, intensity by intensity.

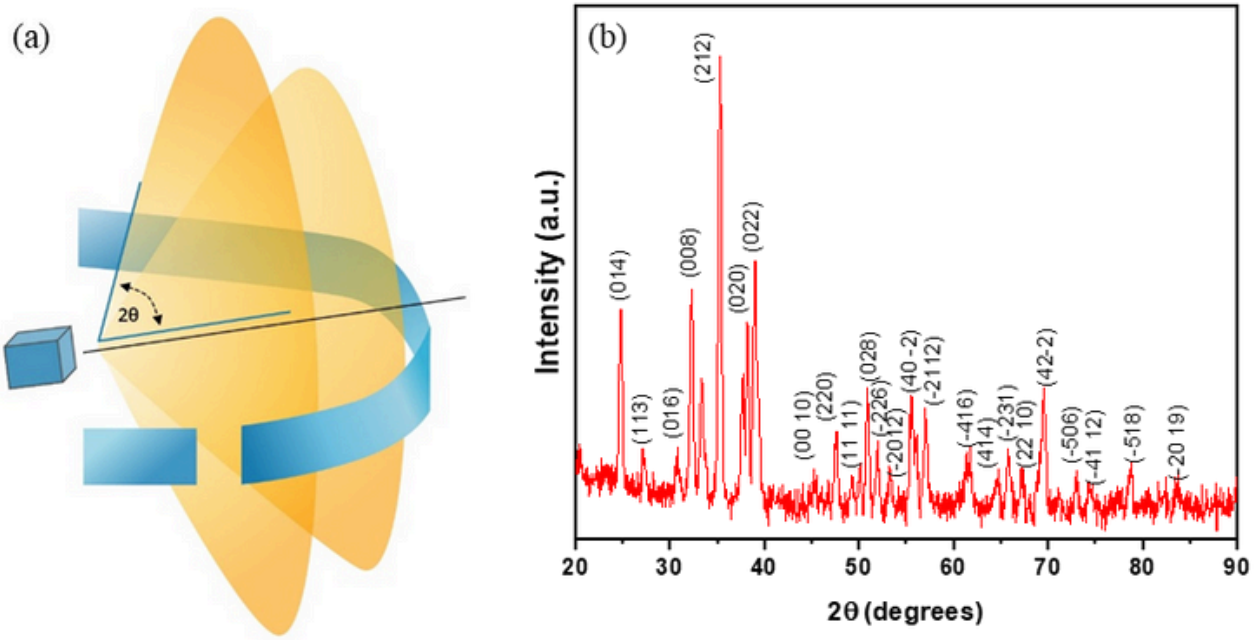


Figure 1. (a) Schematic explaining the Powder XRD (Source – MyScope – Microscopy training) and, (b) a diffractogram of a polycrystalline sample – $Nd_2Ti_2O_7$, of Monoclinic (low symmetry) structure

In powder XRD, all crystallites in a polycrystalline material contribute to the diffraction, and the three-dimensional reciprocal space is contained in one-dimensional data. While it is easier to index peaks for a single crystal, structural analysis studies in the case of polycrystalline samples are limited because of the peak overlap, especially in low-symmetry structures. This challenge highlights the necessity of refinement methods.

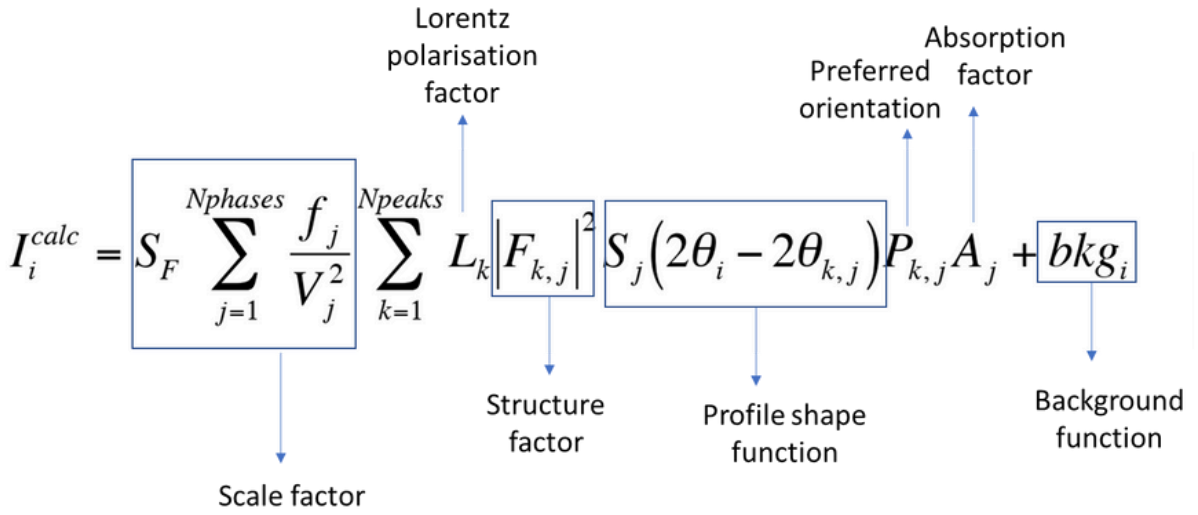
The Rietveld refinement method is a least-squares fitting approach to refine crystal structures. It is widely considered the best whole-pattern-fitting method of refinement, which revolutionised the application of powder diffraction in crystallography.

Originally developed by a Dutch scientist, Hugo Rietveld, in the 1960s, the method was designed for the refinement of neutron diffraction data.

The process begins with experimental diffraction data collected from a powdered sample. The next step involves generating a theoretical diffraction pattern based on an initial crystal structure model—usually obtained from database entries. Then, using software like FullProf, GSAS, or TOPAS, the model is refined iteratively.

Parameters such as lattice constants, atomic positions, occupancy factors, and thermal vibrations – as given in the equation below – are adjusted to minimize the difference between the observed and calculated patterns using a least-squares algorithm.

> *"XRD is primarily a coherent scattering of X-rays by electrons due to the ordered arrangement of atoms within a material."*



Rietveld refinement accounts for peak shapes, preferred orientation, background noise, and even microstructural factors like strain and crystallite size. A successful refinement depends on data quality and the initial model. Overfitting is a common pitfall, where the model appears perfect but lacks physical meaning. To avoid this, checking R-factors and residuals is a common practice.

As the pursuit of discovering new materials grows, XRD and refinement techniques will undoubtedly continue to play a crucial role in the field of materials characterization. What began with Laue's insightful realisation at a conference in Cologne, would continue to be an essential tool in the future of this pursuit.

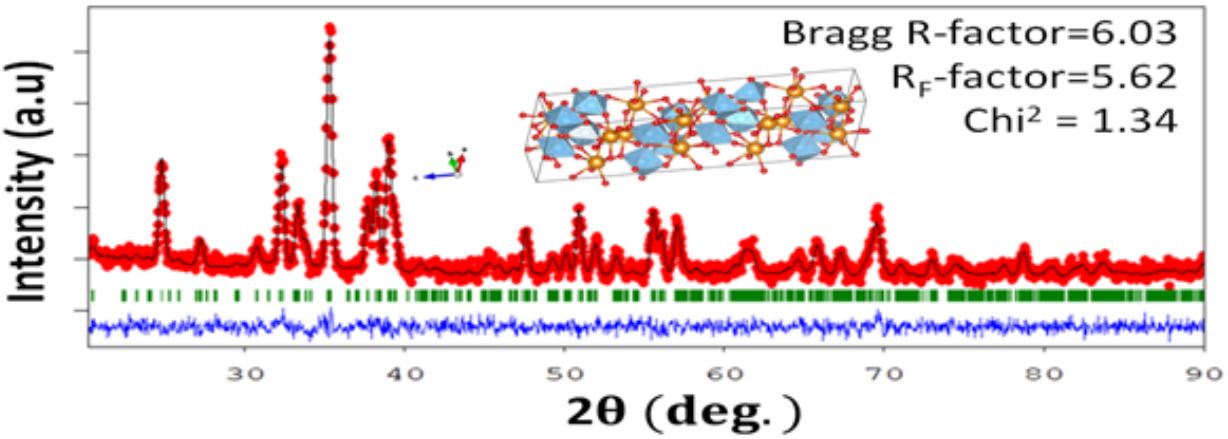


Figure 2. Rietveld refined - calculated data curve - the black line, that closely matches the measured data is fitted. The blue error curve at the bottom of the plot shows how well the calculated data fits the measured data, indicating a good match. Unit cell visualised from the data after the refinement is as an inset.

Alternative fitting approaches like Le Bail and Pawley are also used to do refinements without a need for an initial model focussing on peak positions and intensities. For amorphous materials, where long range order is absent, Pair Distribution Function (PDF) analysis is utilised. These techniques, each unique, offers a different perspective and are also used in tandem.

Rietveld method remains standalone, thanks to its flexibility and ability to evolve with the advancements in computational tools. In their commemorative article on half a century of the Rietveld refinement, the authors wrote, "Over the next 50 years, the Rietveld refinement will remain a cornerstone method in crystallographic studies and will provide the basis for understanding materials functions and applications".

Source - The Rietveld Refinement Method: Half of a Century Anniversary, Tomče Runčevski and Craig M. Brown, Crystal Growth & Design 2021 21 (9), 4821-4822

[1] Ms Sruti Muralikrishnan
PhD Scholar
[2] Mr Manish Chandra Joshi
PhD Scholar
[3] Prof Ranjith Ramadurai
Department of Materials Science And Metallurgical Engineering