JOINT INSTITUTE FOR NUCLEAR RESEARCH

Frank Laboratory of Neutron Physics

FINAL REPORT ON THE

START PROGRAMME

"Crystal and magnetic structure of advanced oxide materials: neutron diffraction studies"

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Contents

1) Abstract.

This report investigates the effect of temperature on crystal and magnetic structures, as well as the Rietveld refinement method using foolproof program. Through the refinement process, in which we create a calculated pattern that is being worked on to make it compatible with the measured pattern, we can extract all the information about the changes that happened to the **$PbFe_{0.67}W_{0.33}O_3$ (PFW)** compound, like lattice parameters, interatomic distance, and magnetic moment.to know to what extent the compound affected by increasing the temperature.

2) Introduction:

Neutron diffraction is a kind of techniques that used to investigate the solid materials to determine its crystal and magnetic structure, neutron interacts with the nucleus of atoms is the main idea of neutron diffraction analysis on the contrary of X-ray diffraction analysis which based on the interaction between the incident X-ray and the electronic atomic cloud. Although neutrons are uncharged, they carry a spin, and therefore interact with magnetic moments, including those arising from the electron cloud around an atom. Neutron diffraction can therefore reveal the microscopic magnetic structure of a material.in these report we are going to explain the work that have been done in the Project on "*Crystal and magnetic structure of advanced oxide materials: neutron diffraction studies*" which include the treatment of some neutron diffraction data for samples of **$PbFe_{0.67}W_{0.33}O_3$ (PFW)** compound which has been investigated under different temperatures (12K,50K,100K,150K,190K,200K,220K,230K, 250K,280K,300K,310K, 320K).these data has been subjected to Rietveld refinement until we get acceptable values of **chi-squared (χ^2)** and **R-factor.** PFW is of significant interest in materials science research due to its complex structure and properties. Understanding and optimizing these properties can lead to the development of new materials with tailored functionalities for specific applications. Overall, PFW's unique combination of ferroelectric and magnetic properties opens a wide range of possibilities for advanced technological applications, making it an important material in the field of multifunctional materials.as it is belonging to perovskite materials which attract the attention of the researchers due to its wide range of characteristics which means wide range of applications in many fields as many perovskites, including PFW, exhibit multiferroic behavior, meaning they have both ferroelectric and magnetic properties. this makes them useful in applications like sensors,

actuators, and memory devices, dielectric properties Perovskites often have high dielectric constants, making them suitable for use in capacitors and other electronic components, Photovoltaic Efficiency: Certain perovskites are highly efficient at converting light into electricity, which has led to their use in solar cells. These materials can achieve high power conversion efficiencies and are relatively easy to manufacture, Thermal Stability: Perovskites generally exhibit good thermal stability, which is important for applications that involve high temperatures, Magnetic Properties: The magnetic properties of perovskites can vary widely depending on the specific composition and structure. For example, PFW exhibits antiferromagnetic behavior at room temperature.

3) Method:

Our method in the processing of data included many steps, first of them is the preparation of the necessary files for the refinement process. Which are (Data file, IRF file, PCR file which converted from the CIF file), the CIF file can be obtained from the Crystallography Open Database (COD), or American Mineralogist Crystal Structure Open Database (AMCSD),the data file can be created with the values of time of flight (TOF) & intensity which measured by the DN-6 diffractometer in our project at JINR, The pulsed regime of the IBR-2 reactor operation provides neutron diffraction measurements at the DN-6 diffractometer using a time of flight (TOF) mode. There are two detector sections of the circular form installed at different scattering angles at the DN-6 diffractometer. The horizontal cryostat based on a closed-cycle helium refrigerator is used for the low- temperature experiments in the range 5-320 K. And the last necessary file which contains instrumental information can be found in Examples file which is attached with the program files and modify the parameters in accordance with the device used to measure the samples. Also, PCR file, and Data file can be obtained from Examples file. The next steps are the refinement process which starts by opening the data file by the pdf program then specify the background points, and save the

background points to be placed later in the PCR file. In the Pcr file a variety of parameters essential for conducting Rietveld refinement. Here are some key parameters typically found in a PCR file:

1. **Title and Comments**: Descriptive information about the refinement, often including the title and comments for clarity.
2. **Instrumental Parameters**: Details about the diffractometer, such as wavelength, zero shift, and resolution function, profile function, Background parameters, sample displacement, absorption correction.

3. **Phase Information**: Data about the crystal structures of the phases present, including lattice parameters, atomic positions, and occupancy factors, symmetry information, thermal parameters, phase scale factor.
4. **Profile Parameters**: Parameters that describe the shape and width of the diffraction peaks, such as Gaussian and Lorentzian components. U, V, W parameters which describes the variation of the peak width with the diffraction angle, asymmetry parameters, peak shape function, preferred orientation parameters, peak broadening parameters.
5. **Background Parameters**: Coefficients for the polynomial or other functions used to model the background intensity.
6. **Scale Factors**: Factors that scale the calculated intensities to match the observed data.
7. **Atomic Displacement Parameters**: Information about the thermal vibrations of atoms, often represented as isotropic or anisotropic displacement parameters.
8. **Constraints and Restraints**: Conditions applied to certain parameters to maintain physical or chemical plausibility during refinement.
9. **Refinement Instructions**: Commands that specify which parameters to refine and how to handle various aspects of the data, such as peak shapes and background.

   These parameters are organized in a structured format within the PCR file, allowing Foolproof to interpret and execute the refinement process effectively.

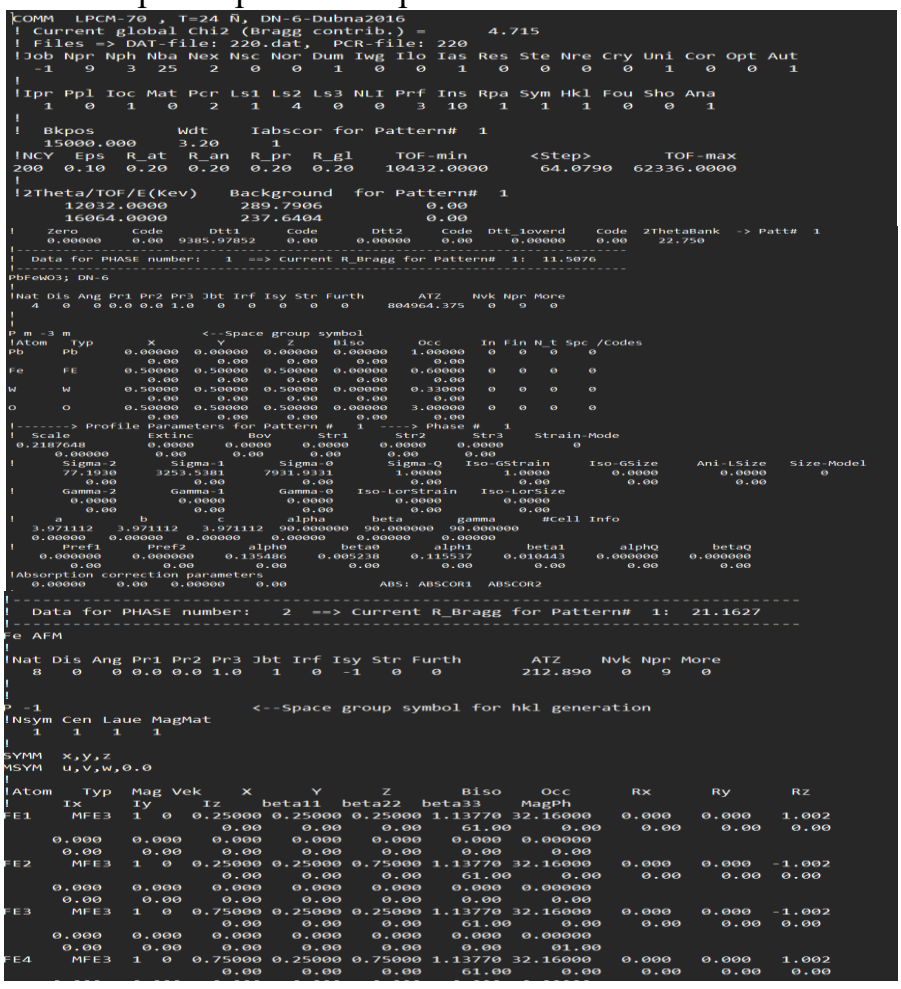

Figure (1): photos for the PCR file

4) Results:

First of wat we obtain is a good reining data as it appears in figure (2) which shows the refined data of some samples as example in the temperatures 12K,100K,200K,220K

And the way we can judge the efficiency of our refinement process is by looking at the red pattern which represents the observed data, the black pattern which represent the data calculated by the program and the compatibility between them which also be presented by the smoothness of the blue line. also, the most precise way is value of Chi-squared (χ^2) which is a statistical measure used to evaluate the goodness-of-fit between the observed diffraction data and the model calculated by the refinement process. Which calculated from equation (1).

$$\chi^2 = \sum\left(\frac{(y_{obs} - y_{calc})^2}{\sigma^2}\right) \qquad (1)$$

Where y_{obs} is the observed intensity, $y_{calc}$is the calculated intensity, and $\sigma^2$is the standard deviation of the observed intensity.

And these green lines represent Bragg position which refers to the specific angles or positions where Bragg reflections occur and Bragg low (equation (2)) satisfied

$$n\lambda = 2d\sin\ \theta \qquad (2)$$

The second step is to start to extract the data to determine to which extend the crystal and magnetic structure of (PFW) is affected by the temperature increments, so as we see in figure (3) the behavior of the magnetic moment is going to decrease rabidly at the range of low temperature then the decrement process start to decrease starting from 200K to 300K. which is caused by thermal agitation. When temperature rises, the thermal energy causes atoms to vibrate more vigorously. This increased movement disrupts the alignment of magnetic domains, magnetic domain misalignment as the misalignment of these domains weakens the overall magnetic field of the material. essentially, the more the atoms move, the harder it is for them to maintain a uniform magnetic direction. Figure (4) demonstrates the diffraction pattern intensity with the time of flight (TOF) for 13 samples, and it is clear that there is a small shift for the peaks to the left while the temperature increases. these shifts refer to an increase in the interplanar spacing of the crystal lattice which happens due to the increase in the thermal expansion where the atom of the crystal gains energy make her vibrations increase vigorously

which causes an expand in the crystal lattice and more spacing between atoms. Figures (5), and (6) demonstrate the behavior of the interatomic distance and lattice parameters with the increment of temperature and it's obvious that both graphs have the same behavior which seems to be as a stable in the less values of temperatures until 200, after this there is a sudden decrement in the interatomic distance, and lattice parameters with some aberration in some points. and coming to the magnetic phase demonstrated in figure (7) it is clear that (PFW) compound has an antiferromagnetic structure which means that the magnetic moments of the Fe ions are aligned in opposite directions, canceling each other out and resulting in no net magnetization. and finally reaching to the crystal structure which shown in figure (8) that the compound $PbFe_{0.67}W_{0.33}O_3$ (PFW) has a cubic crystal structure. This structure is characterized by a perovskite-type arrangement where $Fe^{3+}$and W^{6+} ions are randomly distributed at the octahedral B-site positions. a perovskite-type structure, which is a common structure for many oxides. The general formula for perovskites is ABX_3, where 'A' is a large cation, 'B' is a smaller cation, and 'X' is an anion (usually oxygen). In PFW, Pb^{2+}occupies the 'A' site, while Fe^{3+} and W^{6+} share the 'B' site positions.

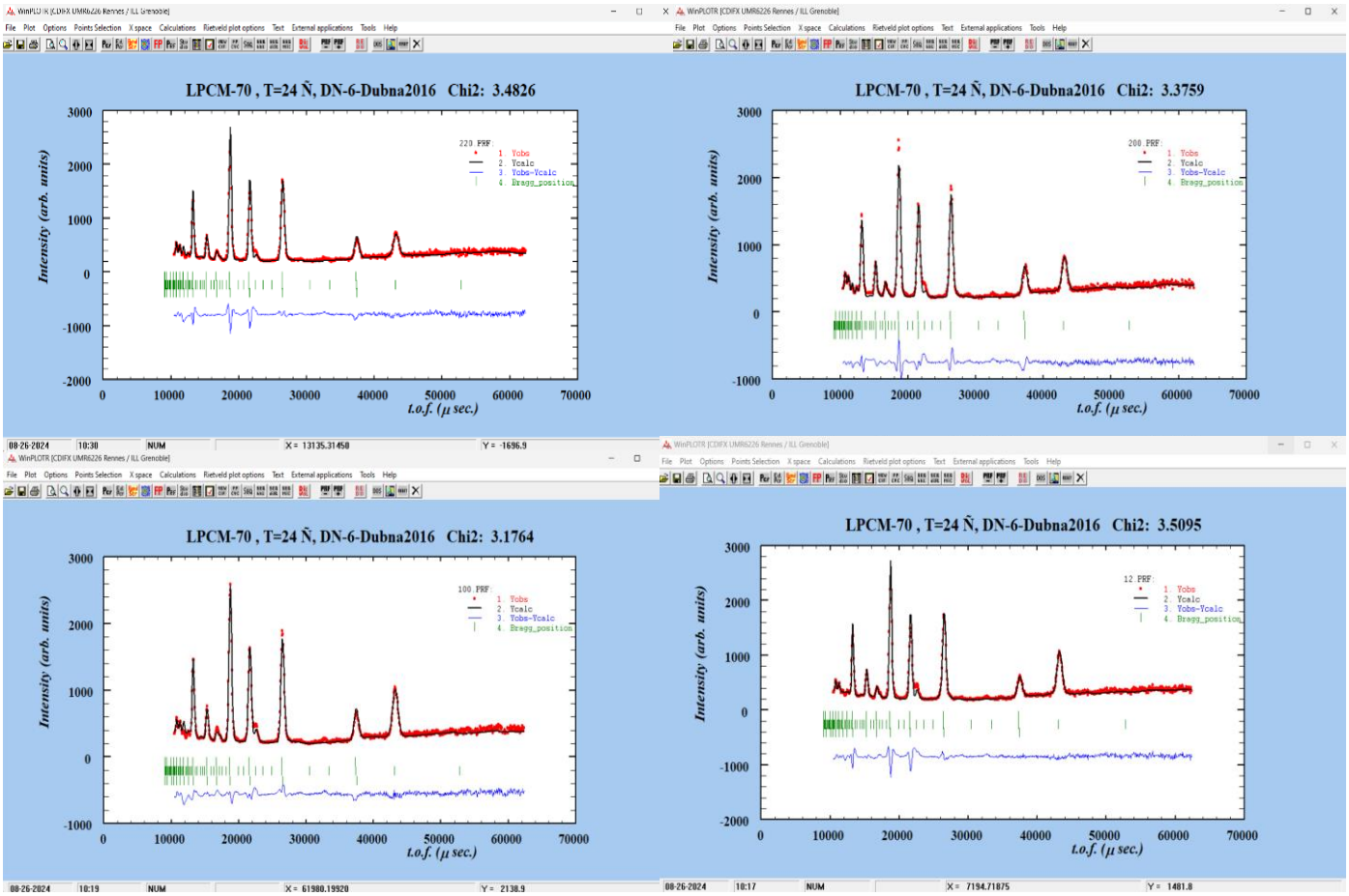

Figure (2): Example of some refined data

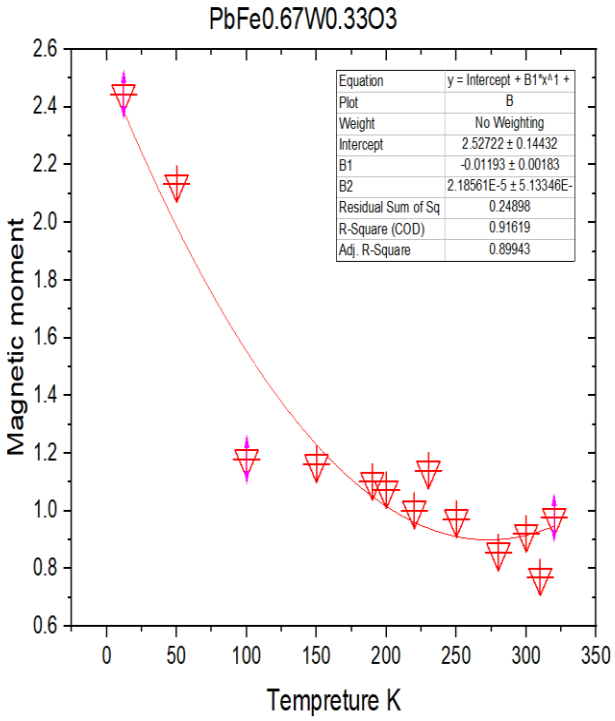

Figure (3): Magnetic moment dependence on temperature

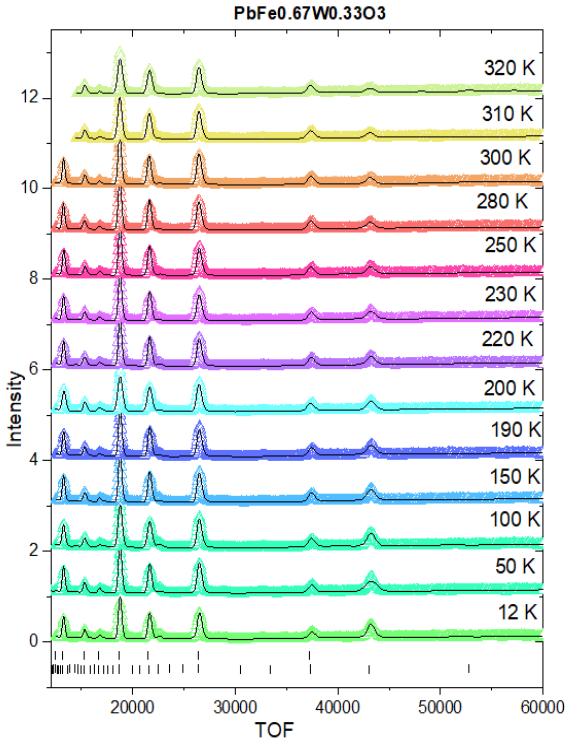

Figure (4): time of flight relation to the intensity

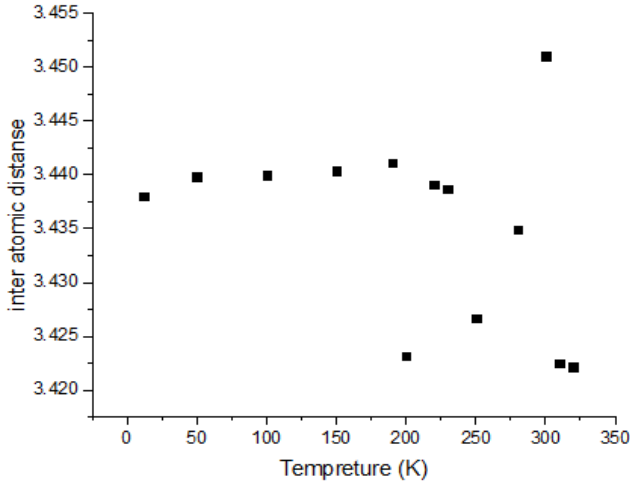

Figure (5): dependence of interatomic distance (Pb-Fe/W) on temperature.

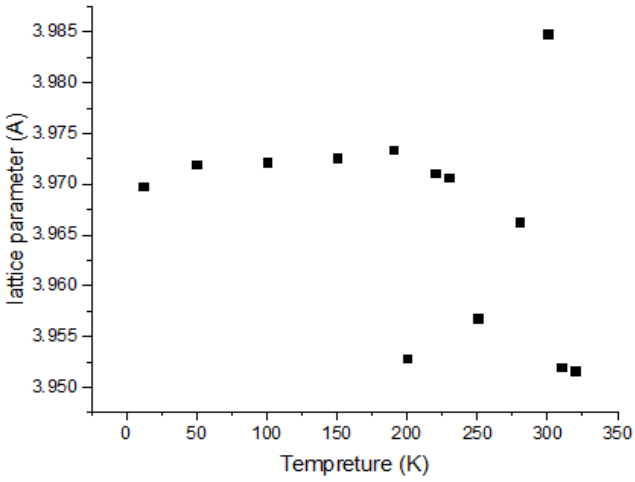

Figure (6): dependence of lattice parameters on temperature.

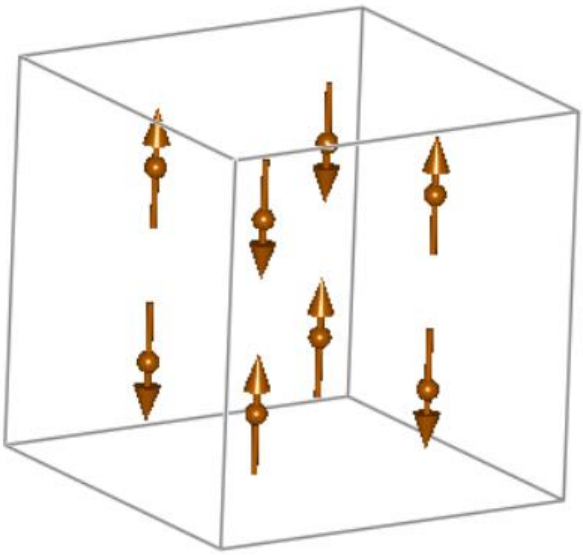

Figure (7): the magnetic moments of the atom inside the lattice.

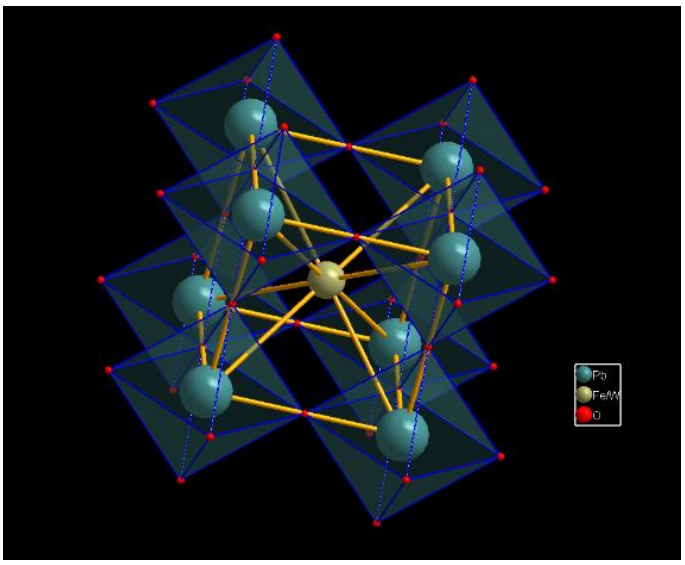

Figure (8): the atoms position.

5) Conclusion.

In summary, our project included the study of a compound belonging to perovskite materials which is PbFe0.67 W0.33O3 ,the study originally focused on how far the crystal structure and the magnetic phase of this compound will change under high temperature values, the way that has been used is the neutron diffraction analysis which can provide us with the necessary information of the crystal and magnetic structures, and by using Rietveld refinement process for the obtained data with full proof program we could extract the targeted parameters for each value of temperature, these parameters are magnetic moment, inter atomic distance (Pb-Fe/W),lattice parameters ,and the shape of the magnetic structure and crystal structure. and by using the Origin Lab program, we draw figures for the changes that happened to these parameters while the temperature increased.

6) References.

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