Structural characterization of mineral with rutile inclusions (TiO₂) and manganocolumbite (MnNb₂O₆) by means of X-ray

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Abstract. A sample of mineral obtained in the department of Vichada was characterized by the technique of X-ray diffraction in powder samples, in order to determine the crystallographic phases present. After analyzing diffraction patterns, as a result, the mineral had inclusions of Rutile (86.3%) and Manganocolumbita (13.7%). Next, a simulation of the crystal structure of these minerals from the data entered in the databases was carried on. Later, the Rietveld method was used, from this refinement, the new diffraction pattern and the new network parameters were obtained. For the Rutile it was obtained a tetragonal structure, and for the Manganocolumbita an orthorhombic structure was obtained. The characterization is justified among other aspects due to the important applications of these materials in industry and technology, such as Rutile is used in welding rod coatings, in Industries cardboard paper and ink impression among many other uses, the Manganocolumbita is used in special alloys resistant to high temperatures, it also is directly related to the tantalite in coltan formation.

1. Introduction

W. L Bragg accounted for this by regarding a crystal as made out of parallel planes of ions, spaced a distance d apart. The conditions for a sharp peak in the intensity of the scattered radiation were: that the X rays should be specularly reflected by the ions in any one plane and that the reflected rays from successive planes should interfere constructively. The path difference between the two rays is just 2d sin θ where θ is the angle of incidence. For the rays to interfere constructively, this path difference must be an integral number of wavelengths, leading to the Bragg condition: λ = 2d sin θ.

The integer n is know as the order of the corresponding reflection [1]. The Bragg law is a consequence of the periodicity of the lattice [2].

The interatomic distances in crystals and molecules amount to 0.15 - 0.4 nm, which correspond in the electromagnetic spectrum with the wavelength of X-rays having photon energies between 3 and 8 keV. Accordingly, phenomena like constructive and destructive interference should become observable when crystalline and molecular structures are exposed to X-rays. To produce X-rays used in diffraction is need a voltage of about 35 kV [3].

In the powder method we put a crystal in an X-ray beam to observe any diffraction: The crystal has to be placed in the beam so as to fulfill the Bragg condition for diffraction. The Bragg-Brentano geometry is the most commonly used geometry for powder diffractometers. The source and the detector are each moved by an angle θ, while the sample is fixed horizontally. Alternatively the source is fixed and the sample is rotated by θ and the detector by 2θ. The sample is used in reflection mode and a comparably large amount of sample is needed, typically 0.5cm³. Due to the large irradiated sample surface. The standard version uses filtered radiation and a monochromator in the diffracted beam. In this way fluorescence radiation is effectively removed, and in general the background level is
very low. The secondary monochromator will not remove the $K_{\alpha 2}$ contribution and the peaks gradually split up in two at higher $2\theta$-angles. The Bragg-Brentano geometry is very good with medium to highly absorbing samples [3].

The Rietveld Method is a method of refining powder diffraction data to find the crystal structure. The practical reason to perform Rietveld refinement is that solving an unknown crystal structure, calculating the amount disorder or mixing on a Wyckoff site, quantitatively determining the percentages and determining the crystallite sizes in the samples. The method fits the whole pattern at once and refines: atomic positions, disorder or mixing between atomic sites, lattice, profile and background parameters. Some factors that affecting peak intensities are: Structure factors, multiplicity, lorentz factor, polarization factor, temperature factor or atomic displacement, absorption or preferred orientation [4].

2. Experimental Procedure
To make an Analysis of crystallographic periods of our mineral, the measurements of the diffraction patterns were done by means of X-ray diffraction, a diffractometer brand X-Pert PRO MPD Panalytical was used. Working at a voltage of acceleration of 45 kV and a current intensity of 40 mA, with monochromatic line $K\alpha$ of copper (Cu-K wave length 1.540598 Å), With a time of 8 s per step and a step size of 0.020 degrees $2\theta$ in continuous mode, from 10 degrees to 90 degrees $2\theta$.

The sample was obtained in an agreement with the Departamento de Geologia de la Universidad Nacional de Colombia, this sample had been found in the Department of Vichada embedded in a stone. When it was given to us it was in a solid status and was amorphous, by means of a hammering procedure (using an agate stone) it was obtained a sample in powder of this material that finally was obtained and given to the specialized technician in order to get the diffraction patterns.

3. Results Analysis
Below we will present the main results derived from X-ray characterization, it is important to note that the motivation for the exploitation of this kind of minerals depends on how evident it is, on its inclusions, and also on its possible applications such as technological and industrial applications. In this case, lies essentially the agreement, so the characterization within its purposes shall clarify the useful components, without leaving aside of the interest scientific. The figure 1 related the diffractogram obtained.

![Figure 1](image)

Using X-Pert program it could be established that the characterized mineral had Rutile ($TiO_2$) and Manganocolumbita ($MnNb_2O_6$) inclusions and determines that the sample has 85% Rutile and 15%
Manganocolumbite. These values were obtained by means of a comparison of patterns on each inclusion on program data base.

When minerals were determined by means of mineral database AMCSRD it was carried on the crystallographic structure simulation as its diffraction pattern with the PCW program. Next, it is present the Rutile structure and its Manganocolumbite respectively.

A tetragonal structure of Rutile was obtained, the characteristics of this structure are shown below: $\alpha = \beta = \gamma = 90^\circ$ and $a = b \neq c$.

![Figure 2](image2.png)

**Figure 2.** Crystal structure of rutile and the diffractogram simulated.

For Manganocolumbta we got an orthorhombic structure, the relationship of angles and sides, and it is the following one: $\alpha = \beta = \gamma = 90^\circ$ and $a \neq b \neq c$.

The refinement Rietveld was done in order to get our sample was obtained and the definitive diffraction pattern was obtained (see figure 4).

![Figure 3](image3.png)

**Figure 3.** Crystal structure of manganocolumbite and the diffractogram simulated.
Finally presents abstract the lattice parameters in the next data table:

**Table 1.** The lattice parameters.

|                | Rutile (TiO$_2$) | Manganocolumbite (MnNb$_2$O$_6$) |
|----------------|------------------|-----------------------------------|
|                | Experimental     | Database                          | Rietveld R | Experimental | Database | Rietveld R |
| a(Å)           | 4.6255           | 4.593                             | 4.6373     | 14.246       | 14.352   | 14.306     |
| b(Å)           | 4.6255           | 4.593                             | 4.6373     | 5.726        | 5.74     | 5.728      |
| c(Å)           | 2.959            | 2.959                             | 2.9854     | 5.093        | 5.09     | 5.08       |

Since we know the components isolated from the mineral, we can conclude that the characterization among other concepts is justified by the important applications of these materials in industry and technology, for example Rutile is used in welding rod coatings, in Industries cardboard paper and ink, impression among many other uses, the Manganocolumbite is used in special alloys resistant to high temperatures, it also is directly related to the tantalite in coltan formation.

Due to these materials different applications, it will be of great interest, firstly the exploitation of this mineral, and on the other hand, the separation into its components, for the separation of the material we suggest to take advantage of the magnetic properties of each inclusion.

### 4. Conclusions and remarks

After Rietveld refinement, the following lattice for the Rutile parameters were obtained $a = 4.6373$ Å, $b = 4.6373$ Å, $c = 2.9854$ Å. The Manganocolumbite parameters were $a = 14.306$ Å, $b = 5.728$ Å, $c = 5.08$ Å. For other hand the characterization is justified among other concepts by the important applications of these materials in the industry and technology, also is possible to think about the magnetic separation as one separation option in components of our material.

**References**

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