

Crystal Structure of Mongolian Phosphorite Minerals and Mechanochemistry

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Abstract We have carried out crystal structure investigations of natural and mechanochemically activated samples of Burenkhan, Tsakhir uul and Aldarkhan phosphorite deposits (The North Mongolia) by x-ray, neutron and synchrotron powder diffraction techniques. We have determined the exact mineral contents of the phosphorite ore and crystallochemical formula of each mineral. It was established that natural samples of Tsakhir uul and Aldarkhan phosphorite deposits contain fluorite (CaF_2) among the main ore minerals ($(\text{Ca})_5(\text{PO}_4)_3\text{F}$ and SiO_2). The amount of CaF_2 , in the sample of Tsakhir uul is more than in the Aldarkhan sample. It was shown that as a result of mechanochemical activations any new crystal phases formed. Strong distortion in the crystal lattice of fluorapatite, especially, in the PO_4 -tetrahedrons that possibly lead to increasing of the lattice energy and more solubility of apatite after mechanochemical activation.

Keywords Mongolian phosphorite, Crystal structure, Mechanochemistry, X-ray diffraction, Rietveld method

1. Introduction

According to the survey of A.I.Ilyin and B.Z. Blyskovskii (1984), the Khuvsgul phosphorite basin spans from the northeast Ukhaa river deposit with square of 30000 km^2 to southern Burenkhan deposit along a longitude of 300 km and covers more than 50 deposits, ranking at the first place in Asia by large resources of high-quality phosphate of 4.5 billion tonnes [1].

As geological structure, the Aldarkhan phosphorite deposit is rather simply located on the territory of Zavkhan aimag. Today it is estimated that this deposit has ore of 465 thousand tonnes. The Tsakhir uul phosphorite deposit is located in Yaruu sum, Zavkhan aimag and covers the north-western hills of Tsakhir uul, which is at 12-20 km north-westward from the Alagiin davaa deposit [1].

The phosphorite mainly occurs in the lower parts of carbonate layer of Vendian-Cambrian age. Its lithological and paleogeographic features are the same for all deposits.

Our objectives in this work are to study the crystal structure of natural and mechanochemically activated samples of phosphorite deposits in Tsakhir uul, Aldarkhan of Zavkhan aimag, Burenkhan of Khuvsgul aimag of Mongolia by x-ray, neutron and synchrotron powder diffraction techniques and to summarise the results.

2. Experiment and Results

The phosphate of Burenkhan phosphorite deposit, Khuvsgul, Mongolia, has been studied by X-ray diffraction and the mechanochemical activation's effect in the structural parameters of fluorapatite has been determined (figures 1, 3, 4 and table 1) [1, 2].

In the result of comparative studies in dependence crystalline structures of natural minerals of phosphorite in Zavkhan and Khuvsgul aimags by X-ray diffraction method, it is proved that the natural samples of Tsakhir uul and Aldarkhan, Zavkhan, consist of the phases of fluorapatite $(\text{Ca})_5(\text{PO}_4)_3\text{F}$, quartz SiO_2 and the fluorite (CaF_2). The sample of Tsakhir uul, Zavkhan, contains relatively more fluorite phase (CaF_2) than the sample of Aldarkhan (table 2) [3].

In addition, the position sorts, chemical bonds and electronic density of divalent cations (Sr^{2+} , Ba^{2+}) in the fluorapatite of activated and unactivated samples from the Burenkhan phosphorite deposit, Khuvsgul, have been studied depending on mechanochemical process by X-ray diffractometer and fourier synthesis methods. And it is explained that the electronic density growth in the anion's position has more ionic characteristic than their forming bonds; that $\text{F} \leftrightarrow \text{OH}$ occupation occurs in the same time of the formation of hydrogen bonds, so this destabilizes the crystal lattice of apatite. Furthermore, it may be a reason that its solubility is increased as the result of mechanochemical activation [4, 5].

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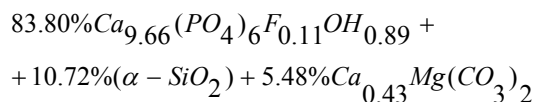
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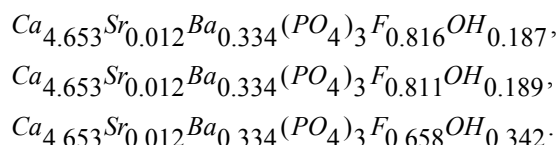
The studies of crystal structure of natural phosphorite from Burenkhan, Mongolia, by synchrotron powder diffraction (SR) method show that the phosphorite consists of three minerals: hydroxylflourapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}, \text{OH})$, quartz ($\alpha\text{-SiO}_2$) and dolomite $\text{Ca}_{0.43}\text{Mg}(\text{CO}_3)_2$ [5, 6].

For hydroxylflourapatite and dolomite, the calcium content is strongly deviated from stoichiometry.

In the refinement of diffraction spectrum, the composition of minerals contained in the samples of phosphorite is determined and the exact formula can be written:



The OH content in crystal structure of phosphorite of Burenkhan, Khuvsgul, Mongolia, is determined by the TOF-neutron diffraction method, and the chemical formulas of each sample are:



The results of this research work are briefly shown as integrated form in figures 1, 2, 3 and 4 and tables 1

and 2 [2-6].

Table 1. Numeric values of change of bond length and angles of PO_4 tetrahedron in the apatite crystal of Burenkhan's phosphorite deposit

Bond length and angles	a)	b)	c)
P-O ₁	1.58	1.57	1.38
P-O ₂	1.58	1.58	1.49
P-O ₃	1.58	1.66	1.56
O ₁ -P-O ₂	109.5°	108.7°	110.68°
O ₁ -P-O ₃	109.5°	104.62°-111.97°	107.97°-112.95°

Table 2. Phase contents for samples of Khuvsgul (Burenkhan) and Zavkhan (Aldarkhan and Tsakhir uul)

No	Type of samples	Structural formula	Phase contents, wt %
1	Natural phosphorite of Burenkhan	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	84.84
		SiO_2	15.16
		$\text{Ca}_5(\text{PO}_4)_3\text{F}$	42.53
2	Natural phosphorite of Aldarkhan	SiO_2	56.73
		CaF_2	0.74
		$\text{Ca}_5(\text{PO}_4)_3\text{F}$	47.86
3	Natural phosphorite of Tsakhir uul	SiO_2	50.73
		CaF_2	1.41

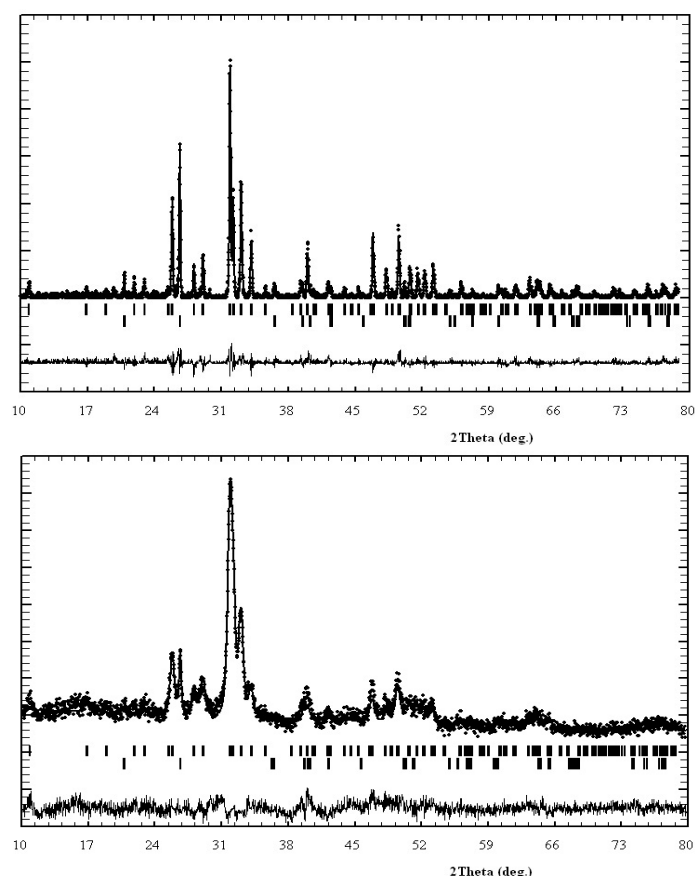


Figure 1. Observed (open circles) and calculated (line) x-ray diffraction patterns for unactivated and activated phosphorite from Burenkhan deposit, Khuvsgul refined by the Rietveld method. The vertical bars indicate the angular positions of the allowed Bragg reflections. Lower curve shows difference between theoretical and experimental data

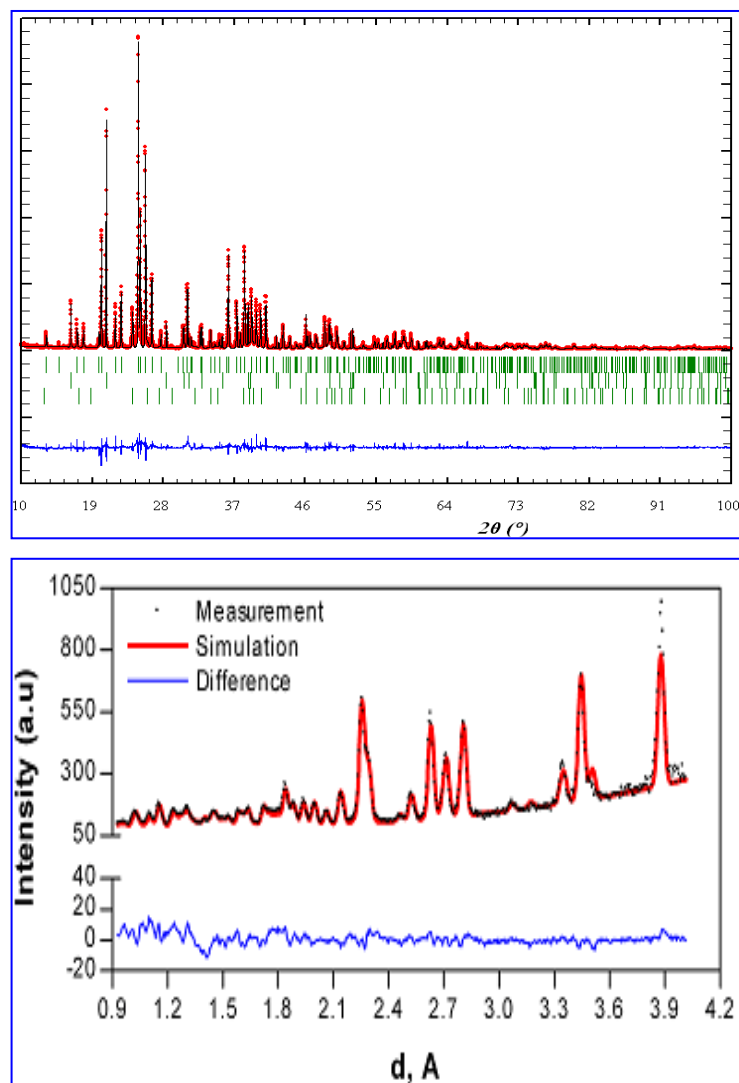


Figure 2. Diffractogram (KEK, 3L-3A, Japan) of synchrotron radiation and TOF-neutron diffraction pattern (IBR-2, DN-2, Dubna, Rusia) of Burenkhan's phosphorite deposit, Khuvsugul refined by the Rietveld method

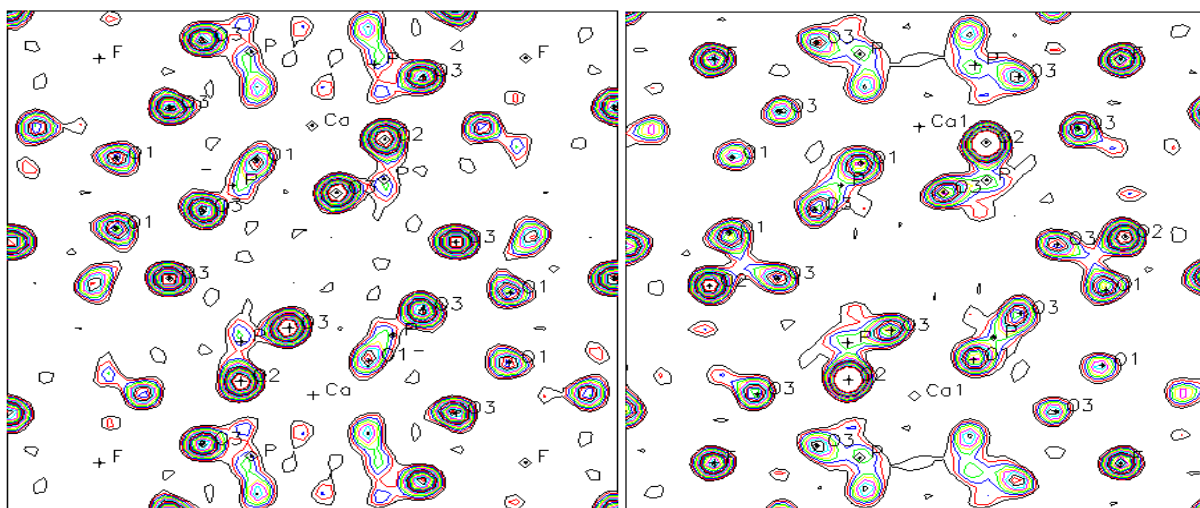


Figure 3. Distributions of electron density in the plane (110) of hexagonal structure of the fluorapatite of unactivated and activated Burenkhan's phosphorite deposit, Khuvsugul 10x10Å fragments with (0,0,0) coordinate center. Numerals indicate levels of electron densities

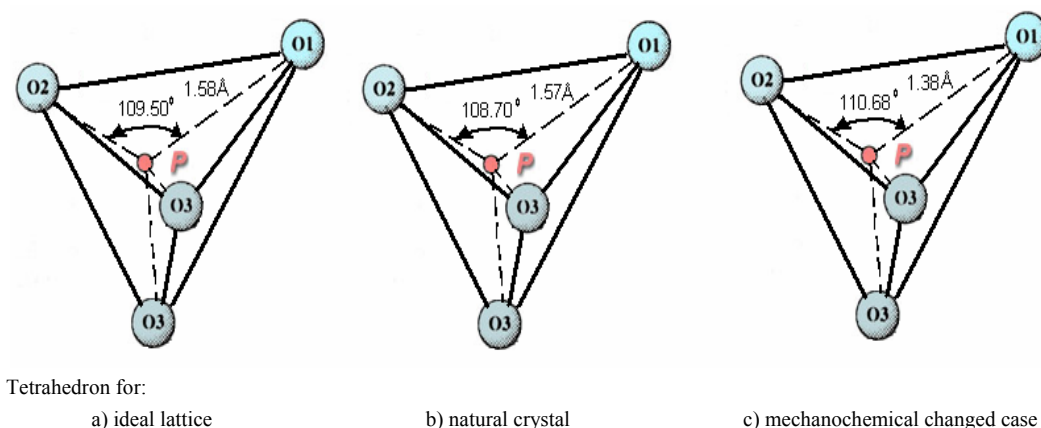


Figure 4. Change of bond length and angles of PO_4 -tetrahedron in the apatite crystal lattice

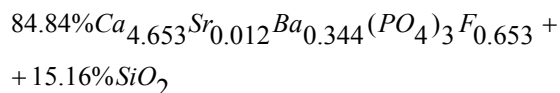
X-ray fluorescence and ICP analysis have shown that on spectra are observed two intensive peaks, which refers to Sr and Br atoms.

It was found out that in positions of Ca1 and Ca2 atoms in the structures of flourapatite for all natural samples exists isomorphic substituting of Sr^{2+} and Ba^{2+} cations and is exactly calculated the occupations of each atom in the positions.

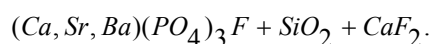
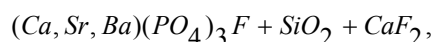
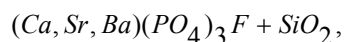
As seen from table 2, the sample 1 (Burenkhan deposit) contains 84.84% flourapatite and 15.16% quartz while the sample 2 (Aldarkhan deposit) and sample 3 (Tsakhir uul deposit) consist of 42.53% and 47.86% flourapatite, 56.73% and 50.73% quartz and 0.74% and 1.41% fluorite phases, correspondingly. So, the samples 2 and 3 have more quartz and less flourapatite in comparison with the sample 1. The main feature of the samples 2 and 3 are: they contain fluorite phases in small quantities.

3. Conclusions

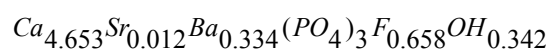
In the result of X-ray diffraction research, the formula of mineral structure of phosphorite (Burenkhan) is written as follows:



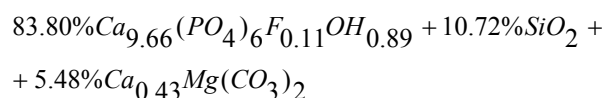
In phosphorites of Burenkhan, Aldarkhan and Tsakhir uul deposits the main phosphorite mineral is flourapatite $(Ca)_5(PO_4)_3F$ with the space group $P6_3/m$. The mineral compositions of phosphorite can be expressed for the three deposits as the next:



As the result of TOF-neutron diffraction technique, the coordinate and component of phosphorite anion (OH) of Burenkhan are determined:



In the result of synchrotron radiation diffraction, the formula of the structure of phosphorite mineral of Burenkhan is as follows:



It is explained that $F \leftrightarrow OH$ occupation occurs in same time of formation of hydrogen bonds, so this destabilizes the crystal lattice of apatite, furthermore, it may be a reason that its solubility has increased as the result of mechanochemical activation.

The mechanochemical activation hadn't any result the observation of any new crystalline phases. However, that the amorphisation occurs in crystal lattice of the apatite, for example, by observation of amorphisation of PO_4 tetrahedron the energy of crystal lattice has increased and it could lead to be increased the solubility of the apatite.

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