ABSTRACT — The aim of the study was to gain more information about the structural changes during the dewatering reactions of the above compounds. The paper is focus on the low-temperature absorption of hopeite clay mineral, afterward the phases are examined for the dependence of temperature at different pressures. Hopeite shows signs of a phase transformation. Their use for the dental cement industry as a lubricant for cold-rolling mills is to be emphasized, such as coating with phosphate mineral or carbonaceous crystal. This is shown by the appearance of the new reflexes. The observed changes take place below the dewatering known from the literature. The phase change was investigated using a neutron scattering experiment. A temperature-pressure phase diagram of the de-watering could be set up in the range of 275 K to 380 K and 10⁻³ mBar to 10³ mBar with the temperature-dependent powder diffractometer at different pressures and the temperature-dependent neutron scattering experiment. In this work, it has been proved that the dewatering of the hopeite is dependent on pressure and that the dewatering process of the hopeite is a reversible process.

Keywords— Phase transformation, temperature-dependent powder diffractometer at different pressures, temperature-dependent neutron scattering, phosphate coating, clay mineral.

1. INTRODUCTION

The chemical classification of the minerals is based on the mineralogical tables of Strunz (1957,1978) in 9 classes. The phosphate mineral class, which also contains arsenates and vanadates, is particularly rich in arsenic due to its diadochi (mutual replacement of the individual ions). The phosphates consist of compounds which can be derived from the phosphoric acid H₃PO₄. The structures are predominantly determined by PO₄ tetrahedra and are mostly water-containing. The water-free phosphates include apatite (Ca₅[OH, F, Cl] [PO₄]₃), pyromorphite (Pb₅[Cl] [PO₄]₃), ambylygonite (LiAl[F] [PO₄]) and lazulite ((Mg, Fe) Al₂[OH] [PO₄]₂).

Hopeite belongs to the water-containing phosphates. These minerals can be assigned to the general formula with A₃(PO₄)₂⋅4H₂O. A is mainly a divalent cation, such as Zn, Fe, Co, Cu and Ca, for n there are characteristic values from 0 to 10.

The aim of the study was to gain more information about the structural changes during the dewatering reactions of the above compounds. Here the phases are investigated as a function of temperature at different pressures. Hopeite shows signs of a phase transformation. This is expressed by the appearance of the new reflexes. The observed dewatering takes place below the dewatering known from the literature (Hopeite's first dewatering takes place at about 100° C, the second dewatering at about 200° C (Shechegov LN, 1986). The cause of the phase transformations was investigated by a neutron scattering experiment. The research conducted at the Hahn Meitner Institut Berlin.

In the automotive industry, Hopeite is an important material. They are grown to act as a layer protector on the body of the car of corrosion (Yoshihara and Okita, 1983). Hopeite is also used as a dental cement and as a lubricant for steel production in cold rolling mills.
2. MATERIAL AND METHODS

The measurements were performed on a Guinier Low Temperature Diffractometer G645 Huber. The Guinier diffractometer offers a relatively high resolution due to its focusing layout. The device is equipped with a closed helium cryostat CTI Cryogenic Model 22C. The Guinier Low Temperature Diffractometer G645 is designed for the temperature range from 10K to 350K and angle range from 0° to 50° Theta. The freezing of the cooling systems is avoided by a vacuum. The vacuum was controlled by adjusting the vacuum valves. The negative pressure could be varied from 10-3 mbar to room pressure. The full-pattern analysis method of Rietveld programs, Foolproof, Hill (1992) was used to analyze the Roentgen data. The sample comes from Hagendorf-Süd Bayern, Germany. The syntheses were conducted at Technische Universität Berlin.

3. RESULTS

According to Whitker (1975), the orthorhombic hopeite (Zn3(PO₄)2.4H₂O) has the space group Pnma with the lattice constants a = 10.629 Å, b = 18.333 Å, c = 5.040 Å. Thermodiffractograms from Hopeite were recorded between 270 K and 335 K in 2 K steps of 2θ-20θ Theta and a vacuum pressure of 10⁻³ mbar. The appearance of new reflexes and the disappearance of reflexes of orthorhombic hopeite indicate a phase transformation (Figure 1).

Roentgen imaging has shown that phase transformations take place. The critical temperatures of the phase transformations under vacuum pressure of 10⁻³ mbar (here starting at 273 K and finished at 288.1 K) do not correspond to that from the literature value. The trend of the d-value of the reflex (020) between the temperature from 270 K to 350 K shows that in the initial phase the crystal behaves normally, the lattice expands with the rising temperature (Figure 2).

The relationship of the spacing d between adjacent (hkl) and the lattice plane parameters a, b, c, α, β, γ is in an orthorhombic axis system is:

\[ \frac{1}{d_{hkl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \]

for the reflex (020) is also:

\[ b = 2d_{020} \]

Figure 1. Thermodiffractograms of Hopeite between 270 K and 335 K steps of 2°-20° theta and vacuum pressure of 10⁻³ mbar.

Figure 2. The Trend of the reflex (020) between 350K and 270K in 2K steps from 4.2° to 6° Theta and at a pressure of 10⁻³ mbar.
4. DISCUSSION

The Thermodiffractogram results were confirmed by a temperature-dependent neutron scattering experiment at a pressure of 4.5 mbar. Here, on the one side, the structural changes can be observed and on the other side, the water loss can be determined by the decrease of the incoherent scatter contribution. From the results of the neutron scattering experiment that the transformation at about 300 K and the pressure at about 4.5 mbar (Figure 4) are connected with the dewatering, it follows that the dewatering of hopeite is dependent on the vacuum at low temperatures.

5. CONCLUSIONS

It is affirmed in the process of the study that the transformation of hopeite is very sensitive towards to low pressure. Measurements with different negative pressures showed, on the one side, that the starting and ending temperatures of the dewatering decrease with increasing negative pressure, and on the other side, the coexistence field from completely to intermediary hydrated hopeite becomes smaller. The summarization of the results for the dewatering temperatures of hopeite shows Fig.5.

By logarithmic application of the pressure, a linear relationship with temperature can be assumed. The slope of the start and the end of the dewatering is different; at higher temperatures, the range of transitions between tetra- and dihydrate hopeit is larger.
Figure 4. A: The d-values of the reflex (020) over the temperature of 270 to 350 K at 10^{-3} mbar. And B: Thermodiffractograms of the neutrons scattering experiments of hopeite between 300 K and 500 K in 5 K steps at a pressure of 4.5 mbar.

Figure 5. A: Graphical presentation of the transformation temperature of the hopeite as a function of pressure. B: Comparison-Diagram of the same sample between an orthorombic-Hopeite and the dihydrat-Hopeite and the Hopeite after 18 days.

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