08-Inorganic and Mineralogical Crystallography

Fig. 1. Bright field micro - graph of amorphous Pb-oxides in PbMoO₄ crystals.

Fig. 2. Bright field micro - graph of Pb₃O₈ particle (1.5x1.4 microns). SAED from it - [315] zone axis.

Fig. 3. Bright field micro - graph of PbMoO₄ particle (0.7x0.7 microns). SAED from it - [100] zone axis.

PS-08.04.41 THE STRUCTURAL AND PHASE TRANSFORMATIONS OF GLAUCONITE IN Na-, Ca- AND Mg-GLAUCONIDE MEDIA UNDER HYDROTHERMAL CONDITIONS. By F.A. Goi-lo, K.A. Naurozbaev, N.V. Katov and V.A. Frank-Kamenetskii, Department of Crystallography, State University, St. Petersburg, Russia.

X-ray diffraction studies of the products of glauconite transformations with different octahedral layer compositions have been carried out in the presence of Na-, Ca- and Mg under pressure of P (H₂O) = 1 kbar at temperatures of 200-600°C under hydrothermal conditions in the three-days experiment. What is observed is that Fe and Fe-Mg-glaucirones are very similarly formed under any experimental conditions except the appearance of Ca-trioctahedral montmorillonite at T=500°C in the presence of CaCl₂ and of amphibole at T=600°C in the presence of NaCl. Therefore, it is interesting to compare the Al- and Fe-glaucirone behavior. At the minimum experimental temperature T=200°C, glauconites are not changed. However, at the temperature T=300°C and in the presence of NaCl, CaCl₂ and MgCl₂ Fe- and Fe-Mg-glaucites, unlike Al-glaucites, start to become unstable and they transform into trioctahedral montmorillonite. The following conclusions can be drawn from the crystallographical analysis of the initial, intermediate and final phases under the experiment conditions: First of all, the composition of octahedral layer of glauconites definitely influence the transformational features under the mineralized hydrothermal condition. Fe-rich glauconites are transformed at a lower temperature, beginning from T=200°C. But at this temperature, the glauconites rich in Al are characterized by higher stability, which start to transform only at T=600°C. Secondly, the important features of structural transformation of glauconites with the increase of the experiment temperature under hydrothermal conditions is the formation of expandable trioctahedral montmorillonites, this is connected with the existence of interchangeable Na, Ca, Mg in water medium, which functions as the expandable structural stabilizer. Thirdly, with the


The existence of Pb₅O₈ and PbMoO₄ microplates in PbMoO₄ crystals was not explained earlier (Nish-tanova et al., SPC. 1989, Budapest Booklet, p.19). Pale yellow PbMoO₄ crystals, obtained by Czechalski method at different conditions, were investigated by PDA (DRON 3M), STA (STA 1500) TEM (TEM 420 Philips) and SEM (SEM 515 Philips) in order to determine the origin of the additional solid microcrystals in them. While searching for the optimal conditions of obtaining PbMoO₄ nutrient in a solid state reaction of initial oxides ZrO₂ + 1MoO₃ we found out by STA, STA and EDAX, that: 1/ the synthesis of PbMoO₄ is not carried out to the end; 2/ in some cases the system is 2-phase, predominant PbMoO₄ phase and PbO (mass escort) and in others 3-phase, predominant PbMoO₄, PbO and Pb₂Mo₃O₁₀. These data indicated unmistakably, that the appearance of amorphous Pb-oxides (Fig. 1), PbO₁₅ (Fig. 2) and PbMoO₄ (Fig. 3) in PbMoO₄ crystals is directly connected with the phase composition of the starting nutrient.


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increase of experiment temperature, biotization of glauconites is taking place which topotactically passes through intermediate montmorillonite and irregular mixed-layer formations. In this case, the ferro of biotite increases with the increase of temperature, and feldspar and amphibole are formed from free Al, Bi and Mg. The fourth conclusion is that to some extent following the transformational rows can be picked out from the structural continuity of transformational phases: a) with a maximal structural continuity: glauconite - triotetrahedral montmorillonite - disordered mixed-layer intermediates - biotite, glauconite - talc - serpentine. b) with partial destruction of structure: glauconite - feldspar, amphibole, cordierite. Finally, data which have been got from the experiment are the result of crystallochemical model transformation of glauconites on their natural metamorphic and hydrothermal change in the presence of mineralized Na-, Ca-, Mg- chloridic environment. Formation of expandable montmorillonite phase considerably releases the interaction of cations in glauconites which needs to be taken into account in deciding the absolute age of glauconites according to the K-Ar method. In this case the most common mistakes in deciding the absolute age appear in more fettigenous glauconites in which the process of montmorillonitization is taking place more actively than in their Al - differences.

PS-08.04.42 PHASE TRANSITION AND CRYSTAL STRUCTURE OF A NEW COMPOUND - Ca5FeWO6, BY Zheng-min Fu and Wen-xiu Li, Institute of Physics, Academia Sinica, Beijing 100080, P.R.China.

In "Phase Transition and Crystal Structure of A New Compound - Sr2CaW6O20" (Fu Zheng-min, SCIENCE IN CHINA(Series A), 1993, 34, 435-464) and "Phase Transition and Crystal Structure of A New Compound - Sr2CaW6O20" (to be published), we have described the phase transition mechanism of Sr2CaW6O20 (Fu Zheng-min, Li Wen-xiu and Liang Dong-cai, SCIENCE IN CHINA(Series A), 1993, 26, 835-847) and Sr2FeWO6. When Sr2+ ion in Sr2CaW6O20 is replaced by Ca2+ ion, the volume of the crystal cell will reduce further, because the ionic radius of Ca2+ is smaller than that of Sr2+. So the level squeezed of Fe2+ ion increases. As a result, the structure of Sr2FeWO6 changes again from cubic to orthorhombic structure, because its distortion degree increases further.

The phase transition of a new compound Ca5FeWO6 has been investigated by means of differential thermal analysis (DTA), X-ray powder diffraction, precise measurement of lattice parameters and other methods. It has been discovered that the compound has a first-order displacive phase transition. The low-temperature phase a-Ca5FeWO6 belongs to the orthorhombic crystal system with space group Pmnm. Its lattice parameters at room temperature are a=5.517Å, b=5.482Å and c=7.714Å, the measured density is 1.86 g/cm3, and each unit cell contains two formula weights. The high-temperature phase B-

Ca5FeWO6 belongs to the cubic system, with space group Pm3m and lattice parameter a=7.408Å at 750°C, and Z=4.

The crystal structures of a-Ca5FeWO6 and B-Ca5FeWO6 have been determined by means of the X-ray polycrystal method. The phase transition mechanism and temperature are investigated.

PS-08.04.43 PHASE TRANSITION AND CRYSTAL STRUCTURE OF A NEW COMPOUND - Sr2CaW6O20" (Fu Zheng-min, SCIENCE IN CHINA(Series A), 1993, 34, 435-464) we have described the phase transition mechanism of Sr2CaW6O20 (Fu Zheng-min, Li Wen-xiu and Liang Dong-cai, SCIENCE IN CHINA(Series A), 1993, 26, 835-847) and distortion degree when Ca2+ ion in Sr2CaW6O20 is replaced by Ca2+ ion, the distortion degree of Sr2CaW6O20 is slightly smaller than of Sr2CaWO6 because the ionic radius of Ca2+ is slightly smaller than that of Ca2+. If Ca2+ ion in Sr2CaWO6 is replaced by an ion with the ionic radius of less size for example, Fe2+ ion. Will its distortion degree increase further? In this case, the crystal structure of Sr2CaW6O20 may not change from the cubic to the orthorhombic structure, but change to tetragonal structure. Therefore, it is worthy to study.

The phase transition of a new compound Sr2FeWO6 has been investigated by means of differential scanning calorimetry (DSC), X-ray powder diffraction, precise measurement of lattice parameters and other methods. It has been discovered that the compound has a first-order displacive phase transition. The low-temperature phase a-Sr2FeWO6 belongs to the tetragonal crystal system with space group 14/m. Its lattice parameters at room temperature are a=5.584Å and c=7.920Å, the measured density is 1.86 g/cm3, and each unit cell contains two formula weights. The high-temperature phase B-

Sr2FeWO6 belongs to the cubic system, with space group Fm3m and lattice parameter a=7.533Å at 400°C, and Z=4.

The crystal structure of a-Sr2FeWO6 and B-Sr2FeWO6 have been determined by means of the X-ray polycrystal diffraction method. The phase transition mechanism and temperature are investigated.

PS-08.04.44 SYNTHESIS AND PHYSICAL-CHEMICAL INVESTIGATIONS OF THIOCRUPATES WITH ThCr2Si2 STRUCTURE. By M. V. Savelyeva, S. A. Gromilov, V. I. Al'tsev, Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Novosibirsk, Russia.