

(II) Keggin related anions: (1)  $[\text{AsV}_{12}\text{O}_{40}(\text{As}^{\text{III}}\text{OH})_2]^{11-}$ , space group  $P\bar{4}3m$ ,  $a=10.72(2)\text{\AA}$ ,  $V=1231.8(9)\text{\AA}^3$ ,  $Z=1$  R factor is 0.057; (2)  $[\text{AsV}_{12}\text{O}_{40}(\text{VO})_2]^{6-}$ , space group  $F\bar{4}3d$ ,  $a=24.707(7)$ ,  $b=14.983(7)$ ,  $c=24.455(8)\text{\AA}$ ,  $V=15732(7)\text{\AA}^3$ , and  $Z=4$ , R factor is 0.059.

(III) Strandberg-type anion:  $[\text{Se}_2\text{Mo}_6\text{O}_{21}]^{4-}$ , space group  $P\bar{2}_1/n$ ,  $a=9.851(2)\text{\AA}$ ,  $b=23.224(5)\text{\AA}$ ,  $c=10.456(3)\text{\AA}$ ,  $\beta=114.13(2)^\circ$ ,  $V=2183\text{\AA}^3$ , and  $Z=4$ , R factor is 0.069.

(IV) Dawson-type anion:  $[\text{H}_2\text{V}_2\text{W}_{10}\text{O}_{62}]^{4-}$ , space group  $R\bar{3}m$ ,  $a=37.613(11)$ ,  $c=12.972(7)\text{\AA}$ ,  $V=15901(13)\text{\AA}^3$ , and  $Z=9$ , R factor is 0.063.

(V) New type of high-nuclearity anions: (1)  $[\text{Mo}_{27}\text{V}_6\text{O}_{183}(\text{NO})_6(\text{H}_2\text{O})_{18}]^{6-}$  (Zhang, Huang, Shao & Tang, J. Chem. Soc., Chem. Commun., 1993, 1, 37-38); (2)  $[\text{H}_6\text{Mo}_{27}\text{Fe}_6\text{O}_{183}(\text{NO})_6(\text{H}_2\text{O})_{18}]^{6-}$ , space group  $P\bar{6}_3/mmc$ ,  $a=23.847(4)$ ,  $c=27.797(9)\text{\AA}$ ,  $V=13685(7)\text{\AA}^3$ , and  $Z=2$ , R factor is 0.049; (3)  $[\text{H}_6\text{Mo}_{27}\text{Fe}_6\text{O}_{183}(\text{NO})_6(\text{H}_2\text{O})_{18}(\text{MoO})_2]^{6-}$ , space group  $P\bar{6}_3/mmc$ ,  $a=23.868(6)$ ,  $c=27.612\text{\AA}$ ,  $V=13577\text{\AA}^3$ , and  $Z=2$ , R factor is 0.058.



Fig. 1. Bright field micro - graph of amorphous Pb-oxides in  $\text{Pb}_2\text{MoO}_5$  crystals.

Fig. 2. Bright field micro - graph of  $\text{PbO}_{1.57}$  particle (1.5x0.4 microns). SAED from it -  $[\bar{3}15]$  zone axis.

Fig. 3. Bright field micro - graph of  $\text{Pb}_3\text{MoO}_8$  particle (0.7x0.7 microns). SAED from it -  $[100]$  zone axis.

#### PS-08.04.40 PHASE INHOMOGENEITY OF $\text{Pb}_2\text{MoO}_5$ SINGLE CRYSTALS.

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The existence of  $\text{PbO}_{1.57}$  and  $\text{Pb}_3\text{MoO}_8$  microphases in  $\text{Pb}_2\text{MoO}_5$  crystals was not explained earlier (Nihtianova et al, SPOC, 1989, Budapest, Booklet, p.19). Pale yellow  $\text{Pb}_2\text{MoO}_5$  crystals, obtained by Czochralski 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 state microinclusions in them. While searching for the optimal conditions of obtaining  $\text{Pb}_2\text{MoO}_5$  nutrient in a solid state reaction of initial oxides  $2\text{PbO} + \text{MoO}_3$  we found out by PDA, STA and EDAX, that: 1/ the synthesis of  $\text{Pb}_2\text{MoO}_5$  is not carried out to the end; 2/ in some experiments the system is 2-phase: predominant  $\text{Pb}_2\text{MoO}_5$  phase and PbO (massicot) and in others 3-phase: predominant  $\text{Pb}_2\text{MoO}_5$ , PbO and  $\text{Pb}_3\text{MoO}_8$ . These data indicated unambiguously, that the appearance of amorphous Pb-oxides (Fig. 1),  $\text{PbO}_{1.57}$ , (Fig. 2) and  $\text{Pb}_3\text{MoO}_8$  (Fig. 3) in  $\text{Pb}_2\text{MoO}_5$  crystals is directly connected with the phase composition of the starting nutrient.

#### PS-08.04.41

THE STRUCTURAL AND PHASE TRANSFORMATIONS OF GLAUCONITES IN Na-, Ca- AND Mg-CHLORIDE MEDIA UNDER HYDROTHERMAL CONDITIONS. By E.A.Giolo, K.A.Nauruzbaev, N.V.Kotov 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 octahedron layer compositions have been carried out in the presence of Na, Ca and Mg under pressure of  $P(\text{H}_2\text{O}) = 1$  kbar at temperatures of 200-600°C under hydrothermal conditions in the three-days experiment. What is observed is that Fe and Fe-Mg-glaucanites are very similarly formed under any experimental conditions except the appearance of Ca-trioctahedral montmorillonite at  $T=500^\circ\text{C}$  in the presence of  $\text{CaCl}_2$  and of amphibole at  $T=600^\circ\text{C}$  in the presence of NaCl. Therefore, it is interesting to compare the Al- and Fe-glaucanite behaviour. At the minimum experimental temperature  $T=200^\circ\text{C}$ , glaucanites are not changed. However, at the temperature  $T=300^\circ\text{C}$  and in the presence of NaCl,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  Fe- and Fe-Mg-glaucanites, unlike Al-glaucanites, start to become unstable and they transform into trioctahedral montmorillonite. The following conclusions can be drawn from the crystallochemical analysis of the initial, intermediate and final phases under the experiment conditions: First of all, the composition of octahedral layer of glaucanites definitely influence the transformational features under the mineralized hydrothermal condition. Fe- rich glaucanites are transformed at a lower temperature, beginning from  $T=300^\circ\text{C}$ . But at this temperature, the glaucanites rich in Al are characterized by higher stability, which start to transform only at  $T=400^\circ\text{C}$ . Secondly, the important features of structural transformation of glaucanites 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 stabiliser. Thirdly, with the

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increase of experiment temperature, biatization 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, Si and Mg. The fourth conclusion is that to some extent the following transformational rows can be picked out from the structural continuity of transformational phases: a) with a maximal structural continuity: glauconite - trioctahedral montmorillonite - disordered mixed-layer intermediates - biotite. Glauconite - talc - serpentine. b) with partial destruction of structure: glauconite - feldspars, 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 raises the interchange 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 ferruginous 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- $\text{Ca}_2\text{FeWO}_6$ . 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- $\text{Sr}_2\text{CdWO}_6$ " (Fu Zheng-min, SCIENCE IN CHINA (Series A), 1991, 34, 455-466) and "Phase Transition and Crystal Structure of A New Compound- $\text{Sr}_2\text{FeWO}_6$ " (to be published), we have described the phase transition mechanism of  $\text{Sr}_2\text{CaWO}_6$  (Fu Zheng-min, Li Wen-xiu and Liang Dong-cai, SCIENTIA SINICA (Series A), 1983, 26, 835-847) and  $\text{Sr}_2\text{FeWO}_6$ . When  $\text{Sr}^{2+}$  ion in  $\text{Sr}_2\text{FeWO}_6$  is replaced by  $\text{Ca}^{2+}$  ion, the volume of the crystal cell will reduce further, because the ionic radius of  $\text{Ca}^{2+}$  is smaller than that of  $\text{Sr}^{2+}$ . So the level squeezed of  $\text{Fe}^{2+}$  ion increases. As a result, the crystal structure of  $\text{Ca}_2\text{FeWO}_6$  changes again from cubic to orthorhombic structure, because its distortion degree increases further.

The phase transition of a new compound  $\text{Ca}_2\text{FeWO}_6$  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  $\alpha$ - $\text{Ca}_2\text{FeWO}_6$  belongs to the orthorhombic crystal system with space group  $\text{Pmm}2$ . Its lattice parameters at room temperature are:  $a=5.5172\text{\AA}$ ,  $b=5.4042\text{\AA}$  and  $c=7.7104\text{\AA}$ , the measured density is  $D_m=6.04\text{g/cm}^3$ , and each unit cell contains two formula weights. The high-temperature phase  $\beta$ -

$\text{Ca}_2\text{FeWO}_6$  belongs to the cubic system, with space group  $\text{Fm}\bar{3}\text{m}$  and lattice parameter  $a=7.808\text{\AA}$  at  $750^\circ\text{C}$ , and  $Z=4$ .

The crystal structures of  $\alpha$ - $\text{Ca}_2\text{FeWO}_6$  and  $\beta$ - $\text{Ca}_2\text{FeWO}_6$  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- $\text{Sr}_2\text{FeWO}_6$ . 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- $\text{Sr}_2\text{CdWO}_6$ " (Fu Zheng-min, SCIENCE IN CHINA (Series A), 1991, 34, 455-466) we have described the phase transition mechanism of  $\text{Sr}_2\text{CaWO}_6$  (Fu Zheng-min, Li Wen-xiu and Liang Dong-cai, SCIENTIA SINICA (Series A), 1983, 26, 835-847) and distortion degree. When  $\text{Ca}^{2+}$  ion in  $\text{Sr}_2\text{CaWO}_6$  is replaced by  $\text{Cd}^{2+}$  ion, the distortion degree of  $\text{Sr}_2\text{CdWO}_6$  is slightly smaller than of  $\text{Sr}_2\text{CaWO}_6$  because the ionic radius of  $\text{Cd}^{2+}$  is slightly smaller than that of  $\text{Ca}^{2+}$ . If  $\text{Ca}^{2+}$  ion in  $\text{Sr}_2\text{CaWO}_6$  is replaced by an ion with the ionic radius of less size for example,  $\text{Fe}^{2+}$  ion, will its distortion degree decrease further? In this case, the crystal structure of  $\text{Sr}_2\text{FeWO}_6$  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  $\text{Sr}_2\text{FeWO}_6$  has been investigated by means of differential scanning calorimetry (DSC), X-ray powder diffraction, precise measurement of lattice parameters and other method. It has been discovered that the compound has a first-order displacive phase transition. The low-temperature phase  $\alpha$ - $\text{Sr}_2\text{FeWO}_6$  belongs to the tetragonal crystal system with space group  $\text{I4/m}$ . Its lattice parameters at room temperature are:  $a=b=5.5652\text{\AA}$  and  $c=7.9024\text{\AA}$ , the measured density is  $D_m=6.94\text{g/cm}^3$ , and each unit cell contains two formula weights. The high-temperature phase  $\beta$ - $\text{Sr}_2\text{FeWO}_6$  belongs to the cubic system, with space group  $\text{Fm}\bar{3}\text{m}$  and lattice parameter  $a=7.939\text{\AA}$  at  $400^\circ\text{C}$ , and  $Z=4$ .

The crystal structure of  $\alpha$ - $\text{Sr}_2\text{FeWO}_6$  and  $\beta$ - $\text{Sr}_2\text{FeWO}_6$  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 THIOCUPRATES WITH  $\text{ThCr}_2\text{Si}_2$  STRUCTURE. By M. V. Savelyeva, S. A. Gromilov, V. I. Alekseev', Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Novosibirsk, Russia.