PS11.04.11 REACTION KINETICS ON FORMATION OF In- AND Zr,Ca- SUBSTITUTED YIGs BY "IN SITU" POWDER XRD. A.Preisinger, K.Mereiter and L.Petrás. Institute of Mineralogy, Crystallography and Structural Chemistry Tech. University of Vienna, A-1060 Vienna, Getreidemarkt 9, AUSTRIA.

Solid state reactions taking place during formation of differently substituted Yttrium-Iron Garnets (YIG) from the corresponding oxides were studied with high temperature X-ray powder diffraction method up to 1400°C. The measurements were carried out in a newly developed high temperature chamber PMP1600 which provided good temperature uniformity in the sample, and reduced the recrystallization caused grain size effects by spinning the samples of compacted pellets. Reaction kinetic studies were based on Rietveld refinements of „in situ" high temperature diffraction patterns. Different diffusion processes and thermochemical reactions could be observed. The phase compositions at different temperatures were determined with standardless quantitative analysis, the substitution rates were concluded from both refinement of the site occupancy factors and unit cell volume changes, subtracting thermal expansions. In this way the distribution of all cations in the numerous phases (starting oxides, intermediate phases and end-products) could reasonably be traced on. The reaction paths were observed to be distinctly different when samples presintered at lower temperatures were ground. The influence of the substituents on the reaction kinetics was clarified in systems with compositions corresponding to garnets $Y_3Fe_{2-x}In_xFe_3O_{12}$, and $Y_{3-x}Ca_xFe_{2-x}Zr_xFe_3O_{12}$ in the range x=0 to 1.0 for In, and x=0 to 2.0 for the Zr,Ca substitution resp. Zr was found to be able to substitute Fe of octahedral coordination completely, but no In substitution could be reached for x 1. The angular dependencies of peak broadenings have special composition dependent behaviours: Garnets with Zr,Ca substitution close to x=0, 1 and 2 gave sharp reflections also at high 2θ angles, while those with substitution rates in between showed reflections highly broadening with 2θ angles. An attempt was made to explain these peculiarities with the phenomenon of paracrystallinity [1].

1. H. Ludwiczek, A. Preisinger, A. Fischer, R. Hosemann, A. Schönfeld, W. Vogel: J. Catalysis, 51 (1978) 326-337

PS11.04.12 KINETICS OF MUSCOVITE DEHYDROXYLATION IN MICAGLASS COMPOSITIONS. T.I.Shishelova, L. V.Chilikanova, T.I.Sozinova, A.V.Shcherbakov, Irkutsk Technical University, Irkutsk, Russia

The kinetic aspect of muscovite hydroxylation in a softened glass medium is of primary importance in the formation of optimal technological conditions of production of mica-glass compositions. Kinetic studies of the phases formed in the process of muscovite-glass sintering were carried out by x-ray diffraction and UV spectroscopy. Heating of the mica-glass composition leads to the dehydroxylation of muscovite with the release of molecular water and the formation of sanidine and sillimanite. The rate of dehydroxylation and formation of these phases depends on muscovite size, glass composition, and temperature. The dehydroxylation of muscovite occurs at a temperature lower than that of the formation of sanidine and sillimanite, especially, in the presence of glass. Therefore, their appearance in the sintering products at~ 1100 K should be considered as a result of the interaction of the glass with mica dehydroxylate rather than with the initial mica. The dehydroxylate formed seems to be a supersaturated solid solution relative to sanidine and aluminum oxide isolated as independent phases. Aluminum oxide can either occur in an amorphous form or react fast with alumoborosilicate glass components to form sillimanite.

PS11.04.13 PHASE TRANSITIONS INTO SUPERPROTONIC STATE IN SOME HYDROGEN SULPHATES, SELENATES AND PHOSPHATES. L.A.Shuvalov, Inst. of Crystallography of RAS, Moscow, Russia

Not long ago there was found a new family of superprotonic $MeHAO_4$(Me = Cs,NH_4, Rb; A = S, Se). Soon we found other families of superprotonics: $Me_3H(AO_4)_2$ (Me= Cs, NH_4, Rb; A=S,Se) and CsH_2AO_4 (A=P,As). Later family $Cs_5H_3(AO_4)_4{\bullet}2H_2O$(A=S,Se) was found. All crystals have common features therefore we can unite them in new class of superprotonics.

1) They have phase transition (PT) at Tsp in high temperature superprotonic phase. 2) The PT is the first order improper feroelastic one.

3) Conductivity jumply increases at Tsp in several orders and with further growth of T reaches conductivity of melt.

4) The PT is accompanied by the anomalies of many physical properties.

5) In some crystals where melting point Tm<Tsp PT in superprotonic phase can be realized only at high hydrostatic pressure.

6) In low symmetry phase all possible sites for protons are occupied and all H- bonds are ordered.

7) Above Tsp quantaty of equivalent sites for protons increases in several times therefore protons on H-bonds system are dynamicaly disordered.

Such situation and high conductivity are realized even in ideal crystals. Crystals $Cs_5H_3(AO_4)_4$ have else unique properties. Dynamical disorder of protons and H-bonds existing at high T frezes below room T and crystal turnes to glassy state with static disorder of structure. In the paper we consider structures of crystals ,mechanism of high conductivity and other results obtained by big informal group of recearchers from different institutions.

PS11.04.14 "*In situ*" INVESTIGATION OF THE INTERMEDIATE STATE FORMED AT THE NiO/MoO_3 REACTION INTERFACE. Boris P. Tolochko, Alexei V Bessergenev, Nikolay Z. Lyakhov, Vladimir Boldyrev, Sergei V.Chernov, Sergei G. Nikitenko*, Institute of Solid State Chemistry, Novosibirsk128, Russia, *Institute of catalysis, Novosibirsk-90, Russia.

We planned to study the behavior of the Ni and Mo in the process of the $NiMoO_4$ synthesis by new method - Simultaneous two energies anomalous scattering method [1]. We planned to receive information about position of the Ni in the Mo oxide at the initial stage of the reaction, about structure forming at the next stage and how it transforms to the α-$NiMoO_4$.

EXAFS and XANES methods also used for the investigation of the crystal position of the Ni and Mo near NiO/MoO_3 interface at the high temperature. The computational programs on the base of the self-consisting field Xa-multiple scattering wave method used for calculating of the XANES structures of Mo in the Na_2MoO_4, MoO_3 and $NiMoO_4$ and intermediate phase.

The diffraction date from Mo oxides near K-edge Ni received by the STEAS method during the solid state chemical reaction $NiO+MoO_3$ at T=600-800 C. This method gives an anomalous scattering signal when the Ni atoms appear in the molybdenum oxide phase. At first stage of the interaction (at the interface) the small increasing d(060) of the MoO_3 was observed. The kinetics of formation of intermediate phase obtained. At different temperatures the Ni atoms occupied different positions in the new structure, at 650 C they were at the sites of the crystal lattice, at 690 C they were in the interstitial positions.

The experimental data received by STEAS, EXAFS and XANES have show, that at the first stage is forming solid solution MoO_3/NiO, than very quickly Mo_4O_{11}/NiO solution and then β-$NiMoO_4$.

1. A.V.Bessergenev, B. P.Tolochko, et al, in Nuclear Instruments and Methods in Physics Research, A 359(1995), pp 160-164.