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 thermochromical reactions could be observed. The phase compositions at different temperatures were determined with standard quantitave 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 out. The reaction paths were observed to be distinctly different when samples preheated at lower temperatures were ground. The influence of the substantions on the reaction kinetics was clarified in systems with compositions corresponding to garnets Y₁₋ₓFeₓ₂₋ₓAlₓFe₃O₁₂ and YₓCaₓFe₂₋ₓZrₓFe₃O₁₂ in the range x=0 to 1.0 for x 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 x₁. The Zr was found to be able to substitute Fe of octahedral coordination completely, but no In substitution could be reached for x₁. The


PS11.04.12 KINETICS OF MUSCOVITE DEHYDRATION IN MICA GLASS COMPOSITIONS. T.I.Shishelova, L.V.Chilikanova, T.I.Sozhina, A.V.Stecherbakov, Irkutsk Technical University, Irkutsk, Russia

The kinetic aspect of muscovite hydroxylation in a softened glass medium is of primary importance in the formation of optical 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 sandine 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 sandine 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 sandine and aluminum oxide isolated as independent phases. Aluminum oxide can either occur in an amorphous form or react fast with aluminoborosilicate glass components to form sillimanite.

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

Not long ago there was found a new family of superprotonic MeH₂O₄ (Me= Ca, NH₄, Rb; A=S, Se). Soon we found other families of superprotonics: Mo₆H₂(O₄)₂ (Me= Ca, NH₄, Rb; A=S, Se) and Cs₂H₂O₄ (A=P, As). Later family Cs₃H₂(O₄)₄·2H₂O (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 ferroelastic one.
3) Conductivity jumps increase 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 quantity of equivalent sites for protons increases in several times therefore protons on H-bonds system are dynamically disordered.

Such situation and high conductivity are realized even in ideal crystals. Crystals Cs₃H₂(O₄)₄ have else unique properties. Dynamical disorder of protons and H-bonds existing at high T freezes below room T and crystal turns 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 researchers from different institutions.


We planned to study the behavior of the Ni and Mo in the process of the NiMoO₄ 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 Ni-NiMoO₄. EXAFS and XANES also used for the investigation of the crystal position of the Ni and Mo near NiO/MoO₃ 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 Na₂MoO₄, MoO₃ and NiMoO₄ and intermediate phase.

The diffraction data from Mo oxides near K-edge Ni received by the STEAS method during the solid state chemical reaction NiO/MoO₃ 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(000) of the MoO₃ 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 MoO₂/NiO, than very quickly NiO₄/MO₃ solution and then β-NiMoO₄.