

Preparation et Etude Structurale des Spinelles (FeAl_{2-2z}Cr_{2z})O₄. F. CHASSAGNEUX AND A. ROUSSET. Laboratoire de Chimie Minerale, Universite Claude Bernard, 69621 Villeurbanne, France. Starting materials are either homogeneous finely crystallized metastable phases or single phase solid solutions of rhombohedral structure obtained by thermal decomposition in air of organic salts: (NH₄)₃[Fe $\frac{1}{3}$ Al_xCr_y(C₂O₄)₃·3H₂O(x + y = $\frac{2}{3}$). These oxides, reduced at ~700°C in H₂-H₂O atmosphere, give rise to the spinels (FeAl_{2-2z}Cr_{2z})O₄ (0 ≤ z ≤ 1). The miscibility gap previously reported by Cremer in the system FeAl₂O₄-FeCr₂O₄ is not observed. A crystallographic study of the system (FeAl_{2-2z}Cr_{2z})O₄ shows an increase of the lattice parameters with Cr³⁺ concentration and indicates that Al³⁺ ions occupy, as do Cr³⁺ ions, octahedral sites.

The Dioxide-Trioxide Region of the Vanadium-Tungsten-Oxygen System. T. EKSTRÖM. Department of Inorganic Chemistry, University of Stockholm, S 104 05 Stockholm, Sweden. AND R. J. D. TILLEY. School of Materials Science, University of Bradford, Bradford BD 7 1DP, West Yorkshire, England. The phases existing at 1373°K in the ternary vanadium-tungsten-oxygen system between the compounds WO₃, WO₂, VO₂ and V₂O₅ have been characterized by X ray diffraction and electron microscopy. In the region close to WO₃ no evidence of substantial substitution of vanadium into the tungsten trioxide structure was found and extensive formation of ternary CS phases was not found. In samples heated for 14 days the major ternary phase observed was a rutile phase (V,W)O₂ although some other less stable ternary compounds were also recorded in the V₂O₅ rich region of the phase field. Besides these, an orthorhombic modification of tungsten trioxide was found, coexisting with the usual monoclinic form, disordered W_nO_{3n-1}[102] crystallographic shear phases and the binary oxide W₁₈O₄₉. These results are summarized on a phase diagram. Samples heated for short periods of time contained, in addition to the compounds listed above, another unidentified phase and disordered W_nO_{3n-2}[103] crystallographic shear phases. A comparison of both sets of results allows a possible mechanism to be put forward for the reaction between the original tungsten and vanadium oxides.