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Synthesis, structure and properties of a double potassium–yttrium vanadate

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The double vanadate $K_3Y(VO_4)_2$, which is a unique compound in the YVO_4–K_3VO_4 pseudo-binary system, was prepared and characterised.

The aim of this study was to synthesise and characterise $K_3Y(VO_4)_2$.† Previously,[1,2] double vanadium oxides were prepared by a solid state method of synthesis. K_2CO_3, Ln_2O_3 and V_2O_5 were used as initial reagents. The annealing of samples was carried out at 100–1000 °C. The final product, however, frequently contained admixture phases of polyvanadates and unreacted V_2O_5. The synthesis at melting temperatures (above 1000 °C) results in the formation of YVO_4 and evaporation of K_3VO_4. Double potassium–yttrium vanadate contained vanadium(IV). Therefore, for solid phase synthesis, we used ammonium metavanadate instead of vanadium oxide since in this case fairly pure $K_3Y(VO_4)_2$ is formed with an impurity concentration lower than 0.5%.

The interaction of initial components K_2CO_3, Y_2O_3 and NH_4VO_3 was investigated by thermal analysis. At low temperatures (100 °C), sorbed water leaves and then up to 250 °C NH_4VO_3 transforms in potassium polyvanadate with the complete removal of ammonia at 350 °C. The main mass loss occurs up to 450 °C and is due to the removal of CO_2 and NH_3. These processes take place under dynamic conditions (heating ratio of 10 K min^{-1}), at which it is impossible to receive a pure product. To achieve the evolving of main gaseous products, at each temperature stage it is necessary to perform long annealing (24 h). On the X-ray diagram for the product of reaction (600 °C), there are reflexes of $K_3Y(VO_4)_2$, and also other phases (initial components and intermediate products of reaction). Even long annealing (approximately 120 h) does not change essentially the X-ray diagram. For obtaining pure well-crystallised $K_3Y(VO_4)_2$, it is necessary to perform long time annealing at 750–770 °C (120 h) with grinding through every 24 h. Only in this case, a well-crystallised compound is formed without other phases.

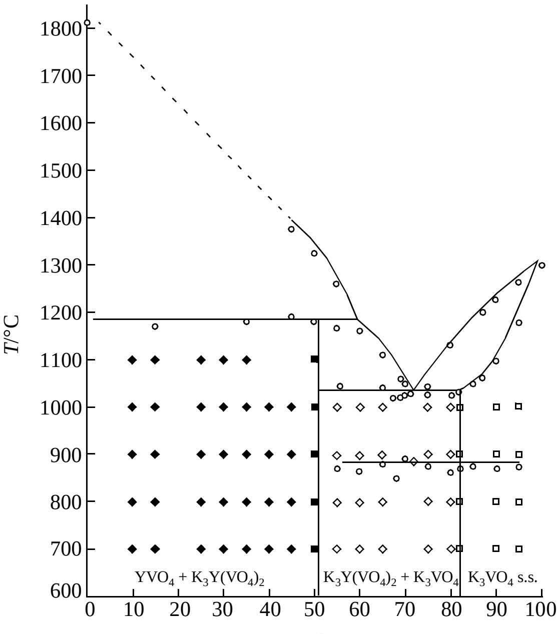

Figure 1 Phase diagram of the YVO_4–K_3VO_4 system.

The interval of temperatures for the existence of $K_3Y(VO_4)_2$ and the possibility of double potassium–yttrium vanadate formation with other composition was established during an investigation of phase formation in the YVO_4–K_3VO_4 system at 600–1400 °C. The study of phase equilibrium in the system was made for samples with 33, 68, 71–73, 82, 83, 87 and 92 mol% K_3VO_4. The sample quenching was carried out from 600, 800, 900, 1000 and 1100 °C to 20 °C in air. The duration of heating was tested by X-ray analysis. The phase diagram of the YVO_4–

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† Powder diffraction data were obtained using DRON-3M (CoKα radiation, λ = 1.79021 Å) and SIEMENS D500 (CuKα_1 radiation, λ = 1.5406 Å, primary SiO_2 monochromator) powder diffractometers. IR spectra were recorded on a PE 1600 FTIR spectrometer in the range 400–4000 cm^{-1}. Thermal analysis was performed with an OD-103 derivatograph.

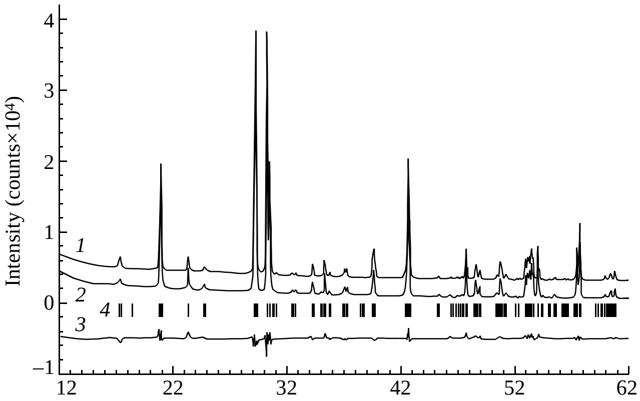

Figure 2 Portion of the Rietveld refinement profiles for $K_3Y(VO_4)_2$: (*1*) calculated, (*2*) observed, (*3*) difference X-ray powder diffraction pattern, (*4*) Bragg reflections.

K_3VO_4 binary system (Figure 1) is constructed based on the X-ray and thermal analysis data.

In this system, one compound $K_3Y(VO_4)_2$ is formed, which decomposes by peritectic reaction at 1170±5 °C. There is a biphase area in the interval of concentrations 50–100 mol% YVO_4 and at temperatures lower than 1170 °C, in which YVO_4 (structure of the zircon type) and $K_3Y(VO_4)_2$ (structure derivative from the glazerite type) crystallise. The parameters of the crystal lattice of YVO_4 in the investigated interval of concentrations and at the change of quenching temperatures were practically constant (to within the measurement error): $a = 7.117(4)$ Å, $c = 6.289(4)$ Å, which is in agreement with the published data $a = 7.1193$ Å, $b = 6.2892(4)$ Å.[3] The solid solutions are formed on the basis of cubic α-K_3VO_4 in an area with high K_3VO_4 contents (more than 82 mol%). The presence of $K_3Y(VO_4)_2$ stabilises the high-temperature cubic modification α-K_3VO_4. The formation of solid solutions on the basis of K_3VO_4 is possible due to cation vacancies at the replacement of K^+ by Y^{3+}. The lattice parameter a in solid solutions in biphase and single-phase areas are close. The slight tendency of diminution of mean parameter a with increasing concentration of K_3VO_4 is observed. For solid solutions, the polymorphic transition was revealed at 860 °C. The eutectic temperature is 1025±10 °C, and the composition of an eutectic point is 71 mol% K_3VO_4. The partial decomposition of samples with 50 mol% K_3VO_4 is observed in a dynamic mode (15 K min^{-1}) above 1300 °C, the last is accompanied by a constant mass loss. Thus, with increasing K_3VO_4 contents of solid solutions, the mass loss is more significant and it is fixed already at ≥ 1200 °C.

The phase diagram of the YVO_4–K_3VO_4 system belongs to a characteristic type of systems with incongruent formation (latent maximum). It is complicated by the existence of the limited region of solid solutions on the basis of the cubic form α-K_3VO_4.

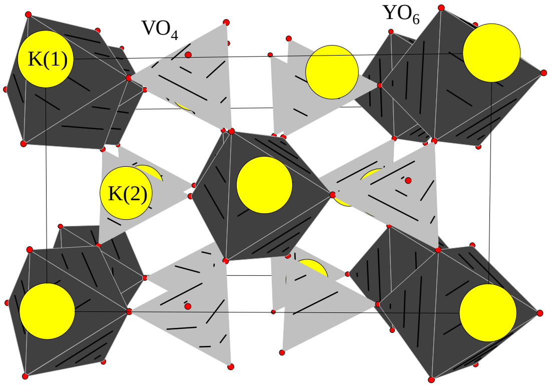

Figure 3 Projection of the structure of $K_3Y(VO_4)_2$ along the direction [001].

The structure of $K_3Y(VO_4)_2$ was studied for a polycrystal sample. This compound crystallises in a structural type of glazerite. Structure refinement based on powder diffraction data was performed by the Rietveld method. The experimental X-ray diffraction patterns were in good agreement with calculated data (Figure 2). In $K_3Y(VO_4)_2$ the atom K(1) is surrounded by 10 oxygen atoms with distances of 2.77–3.06 Å, and the atom K(2), by 9 ones with distances of 2.726–3.477 Å. The average V–O distance in VO_4 tetrahedra is 1.70 Å. Cations Y^{3+} occupy positions in $Y^{3+}O_6$ polyhedra with Y–O distances of 2.17–2.37 Å (Figure 3). The compound $K_3Y(VO_4)_2$ crystallises in a monoclinic system (glazerite type), space group $C2/c$; $Z = 4$ with unit cell parameters $a = 10.253(1)$ Å, $b = 5.8586(3)$ Å, $c = 15.230(1)$ Å, $\beta = 90.274(5)°$, $V = 913.8(1)$ Å^3, $R_{wp} = 6.35$; $R_p = 4.70$; $R_I = 6.55$; $R_F = 5.09$.

The sensitivity of $K_3Y(VO_4)_2$ to moisture was investigated by a gravimetric method and IR spectroscopy (at 16–95% relative humidity of air) at 25 °C. The conductivity (nSm) was measured at change of humidity in an interval of 16–75%. The tablets of powder $K_3Y(VO_4)_2$ with a diameter of 5 mm and a height of 2 mm with silver contacts were prepared for the measurement of conductivity. At the relative humidity of air 16–75%, the adsorption degree was small (up to 2%). Its value is maximal (7.14%) at 90% relative humidity of air. Sample spreads out at 95% relative humidity of air. Note that even insignificant water adsorption essentially influences the conductivity. At 16, 26, 33, 52, 60 or 75% relative humidity of air the conductivity is equal to 33, 165, 700, 3800, 6000 or 20000 nSm, respectively. The character of conductivity for compounds changes with humidity. At small values of humidity 16, 26, 33% the constant value of conductivity is established quickly (7–17 min) and the time for regeneration of a tablet at blow by dry air makes 10 min. The fast establishment of equilibrium indicates that only the superficial layer participates in conductivity. At an increase of the humidity of air up to 52–75% the equilibrium is established slowly or is not established at all. It reveals that at an increase of the humidity of air the adsorption of water occurs not only in a superficial layer but also in the volume of the sensor element and diffusion of water molecules proceeds in deep pores. The similar situation is observed at drying of the sensor. Vapours of organic solvents (benzene and acetone) have not an effect on the electrical properties of the sensor $K_3Y(VO_4)_2$. Adsorption of these solvents practically is equal to zero.

The IR spectra demonstrate the presence of H_2O molecule vibration bands. Its intensity depends on water vapour pressure and, therefore, increases when the relative humidity of air rises and the amount of H_2O sorbed on the surface augments.

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