

# Kalium-Thio/Oxo-Vanadate(V) $K_3[VS_xO_{4-x}]$ ( $x = 1-4$ ) und $Na_3[VSO_3]$ : Synthese, Strukturchemie, Eigenschaften

Potassium Thio/oxo-vanadates(V)  $K_3[VS_xO_{4-x}]$  ( $x = 1-4$ ) and  $Na_3[VSO_3]$ :  
Synthesis, Structural Chemistry, Properties

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The mixed potassium thio/oxo-orthovanadates(V) of the series  $K_3[VS_xO_{4-x}]$  ( $x = 1, 2, 2.6, 3.4-4$ ) and the sodium compound  $Na_3[VSO_3]$  have been prepared in evacuated silica ampoules at reaction temperatures of 450 to 600 °C starting from stoichiometric amounts of an alkali oxovanadate, the alkali sulfide and (where necessary) elemental vanadium and sulfur. The crystal structures (determined on the basis of X-ray single-crystal data) of the yellow compounds  $Na_3[VSO_3]$  (space group  $R3c$ ,  $a = 863.3(3)$ ,  $c = 1234.7(3)$  pm,  $Z = 6$ ,  $R1 = 0.0170$ ) and  $K_3[VSO_3]$  (space group  $P2_1/m$ ,  $a = 659.0(3)$ ,  $b = 589.5(3)$ ,  $c = 879.3(3)$  pm,  $\beta = 102.12(3)^\circ$ ,  $Z = 2$ ,  $R1 = 0.0907$ ) both contain isolated monothio-vanadate ions  $[VSO_3]^{3-}$ . The orange crystals of  $K_3[VS_2O_2]$  (space group  $P2_1/m$ ,  $a = 1056(2)$ ,  $b = 732.2(10)$ ,  $c = 1167(2)$  pm,  $\beta = 121.86(11)^\circ$ ,  $Z = 4$ ,  $R1 = 0.0977$ ) as well as the red phase  $K_3[VS_{2.6}O_{1.4}]$  (space group  $P2_1/c$ ,  $a = 1009.1(6)$ ,  $b = 681.2(4)$ ,  $c = 1190.1(8)$  pm,  $\beta = 93.55(1)^\circ$ ,  $Z = 4$ ,  $R1 = 0.0929$ ) also crystallize with new, singular, monoclinic structure types, which are nevertheless structurally related, as indicated by the similar lattice parameters. Starting from  $K_3[VS_4]$ , a phase width up to the composition  $K_3[VS_{3.4}O_{0.6}]$  (space group  $Pnma$ ,  $a = 909.5(3)$ ,  $b = 1035.6(5)$ ,  $c = 895.6(6)$  pm,  $Z = 4$ ,  $R1 = 0.0948$ ) is observed in addition. Structure and bonding in this new series of potassium compounds are discussed and compared with those in the respective sodium phases, including aspects like anion geometry and dynamics (as observed by Raman spectroscopy), packing in the crystals, UV/Vis spectroscopy and FP-LAPW band structure calculations.

*Key words:* Thiooxovanadates, Crystal Structure, Raman Spectroscopy, Band Structure Calculation