

Gemischte Thio/Oxo-Orthovanadate $\text{Na}_3[\text{VS}_x\text{O}_{4-x}]$ ($x = 2, 3$): Darstellung – Strukturen – Eigenschaften

Mixed Thio/Oxo Orthovanadates $\text{Na}_3[\text{VS}_x\text{O}_{4-x}]$ ($x = 2, 3$): Synthesis – Crystal Structures – Properties

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Mixed sodium thio/oxo orthovanadates(V), dark red $\text{Na}_3[\text{VS}_3\text{O}]$ and orange red $\text{Na}_3[\text{VS}_2\text{O}_2]$, were synthesized *via* reactions in the melt starting from V, Na, Na_2S , Na_2O and sulfur. The structure of the low temperature phase of $\text{Na}_3[\text{VS}_3\text{O}]$ (space group *Pnma*, $a = 589.5(3)$, $b = 962.8(5)$, $c = 1186.6(6)$ pm, $Z = 4$, $R1 = 0.0494$) contains anions $[\text{VS}_3\text{O}]^{3-}$ almost identical to those known from the high temperature form, $\beta\text{-Na}_3[\text{VS}_3\text{O}]$ (space group *Cmc2₁*, $a = 968.4(4)$, $b = 1194.6(4)$, $c = 590.5(2)$ pm, $Z = 4$, $R1 = 0.0291$). The second order phase transition between these two forms at 536 °C was studied by temperature dependent powder diffraction and explained on the basis of a comparison of the anion packing in the two related structures. The packing of the dithiodioxovanadate anions in $\text{Na}_3[\text{VS}_2\text{O}_2]$ (space group *Pbca*, $a = 1162.7(2)$, $b = 592.71(12)$, $c = 1766.7(4)$ pm, $Z = 8$, $R1 = 0.0312$) is also closely related. The chemical bonding in the anions $[\text{VS}_3\text{O}]^{3-}$ and $[\text{VS}_2\text{O}_2]^{3-}$ of approximately ideal C_{3v} and C_{2v} symmetry is discussed on the basis of FP-LAPW band structure calculations and force constants obtained from Raman spectroscopy. The decrease of the calculated band gaps with increasing S content x in $\text{Na}_3[\text{VS}_x\text{O}_{4-x}]$ is in accordance with the optical properties showing a gradually deepening of the crystal and solution colour. Discernible trends in the chemical bonding in this series of mixed thio-oxo anions also include the amount of π bonding of the V-O and V-S bonds and the corresponding variation of force constants and V-O/V-S distances.

Key words: Vanadates, Thiooxovanadates, Raman Spectroscopy, Band Structure Calculation