

Note on the Monoxide Region in the Vanadium-Oxygen System

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In two previous communications^{1,2} from this Institute, the existence, at $\sim 800^\circ\text{C}$, of a body-centered tetragonal phase of approximate composition $\text{VO}_{1.27}$ was reported. This finding has subsequently been challenged by Gel'd *et al.*³ The purpose of the present investigation was to establish the stability conditions for this phase and to study, at the same time, the range of homogeneity of the cubic VO_x phase at elevated temperatures.

Experimental. Vanadium metal (Fairmount Chemical Co. 99.7% V) and V_2O_5 obtained by hydrogen reduction of V_2O_5 (LKB-produkter, *pro analysi*) or ammonium vanadate (Kebo, *purum*) were weighed out and arc-melted together in an argon atmosphere to produce specimens of the desired compositions. The samples, resting on a water-cooled copper base, were rapidly cooled to room temperature. Part of the samples were subsequently crushed and heat treated in vacuum (sealed, evacuated silica tubes) at $760 \pm 10^\circ$, at $785 \pm 5^\circ$, and at $810 \pm 10^\circ\text{C}$ for periods of 2–3 weeks. One sample, of composition $\text{VO}_{1.26}$, was more carefully investigated, the heat treatments being conducted at $760 \pm 10^\circ$, $780 \pm 5^\circ$, $790 \pm 5^\circ$, and $805 \pm 5^\circ\text{C}$.

The oxygen content of the samples was determined by Ce^{4+} titration.²

Guinier photographs⁴ taken with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54051 \text{ \AA}$) and with KCl ($a = 6.2919 \text{ \AA}$) as an internal standard were used for phase analysis and for the determination of accurate lattice parameters. During exposure, the X-ray film was covered with Al foil (0.014 mm) which absorbed the fluorescent radiation from vanadium.

Several tiny fragments picked from a sample of composition $\text{VO}_{1.27}$ were, in turn, mounted on a General Electric X-ray Diffractometer, equipped with a Single Crystal Orienter. The diffraction of Ni-filtered $\text{CuK}\alpha$ radiation from these fragments was analyzed with a narrow receiving slit in front of the scintillation counter.

The calculations of lattice parameters and diffractometer settings were carried out with

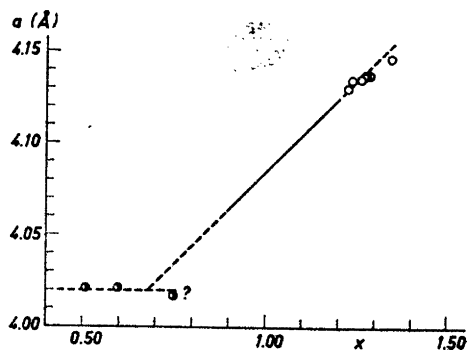


Fig. 1. Lattice parameter a (\AA) of the cubic monoxide phase in as-cast arc-melted VO_x samples. The unshaded circles represent single-phase, and the partially shaded circles, two-phase preparations. The solid line indicates the relationship between a and x within the one-phase region at 800°C , reported by Westman and Nordmark.³

computer programs written at this Institute for use with the IBM 1800 computer located here.

Results. The equilibrium in the as-cast arc-melted samples appears to have been frozen in at varying temperatures, and several different estimates of the limit of solubility of oxygen in the cubic, defect NaCl type, monoxide phase were obtained. The lattice parameters of the specimens which were single phase are presented in Fig. 1 as a function of the composition (x in VO_x). The longest unit cell edge observed was $a = 4.147 \text{ \AA}$ for $\text{VO}_{1.34}$.

The lattice parameter of the monophasic samples with $x > 1$, fall approximately on a continuation of the straight line representing the relationship between a and x .^{5,6} A previous study³ of the solubility mechanism for V and O in the structure indicated that the oxygen sites should be 100% filled at $x \approx 1.27$. Thus, the rate of removal of V with increasing x should change at this composition, and a change in the a versus x slope might be observed. Actually, the experimental point for $\text{VO}_{1.34}$ lies the furthest from the extrapolated line but not very much outside the observational scatter, which is quite large in the present case.

The a versus x line has previously been found to extend down to $x = 0.89$ at 800°C ⁵ and to $x = 0.78$ at 900°C .^{5,6}

Three arc-melted (as-cast) samples were obtained which appeared to contain only the two phases VO_x (cub.) + V_2O_5 . A constant lattice parameter, $a = 4.020 \pm 2 \text{ \AA}$, was measured in these three cases. Extrapolation of the a versus x line to the above a value yields an estimate of $x = 0.68$ for the vanadium-rich homogeneity limit of the phase. One of the three samples, however, had an analyzed oxygen content appreciably higher than this limit, *viz.* $x = 0.75$. Since, in the analysis, the rate of dissolution of the oxide is rather sluggish at low oxygen contents, this single piece of evidence for a behaviour of the a versus x graph at high temperatures, which is substantially different from that at lower temperatures, must be regarded with some caution. It should be pointed out, though, that Vol'f *et al.*⁷ have determined a solubility limit of $x \approx 0.86$ at 1600°C , from a series of measurements which yielded lattice parameter values appreciably lower than those reported in the present investigation and in Refs. 2, 5, and 6. A review by Stringer⁸ summarizes previous work in this area.

The samples heat-treated at $810 \pm 10^\circ\text{C}$ were those with $x > 1.26$. All were two-phase, containing V_2O_5 and cubic VO_x with a cell edge of $a = 4.135 \pm 1 \text{ \AA}$ which corresponds to a solubility limit of $x = 1.26$, if it be assumed that a changes only with composition and not with the temperature of heat-treatment, which appears fairly certain judging from the existing data.

At all temperatures below 800°C , a body-centered tetragonal phase (the " $\text{VO}_{1.37}$ " phase of Refs. 1 and 2) was observed to be present in samples with gross compositions given by $1.17 \leq x \leq 1.34$, the latter being the highest oxygen content investigated. Equilibrium is established very slowly, so that several specimens were found to contain three phases even after a heating period of three weeks.

It was found possible, though, to select two representative samples, one in which the tetragonal phase was in equilibrium with cubic VO_x and one in which it was in equilibrium with V_2O_5 , both at 780°C . The analyzed compositions and lattice parameters were:

$$\begin{aligned} \text{VO}_{1.33 \pm 1} \quad a &= 16.613 \pm 2 \text{ \AA} \quad c = 16.497 \pm 3 \text{ \AA} \\ \text{VO}_{1.26 \pm 1} \quad a &= 16.608 \pm 2 \text{ \AA} \quad c = 16.496 \pm 3 \text{ \AA} \end{aligned}$$

The indexing of the powder patterns was identical with the one published by Westman and Nordmark² who, however, found both a and c to be of the order of 0.02 \AA

longer. In the present investigation, the measured lattice parameters of several other specimens, prepared below 800°C , were found to vary randomly with gross composition over ranges of 0.02 \AA . Thus, a difference between samples, such as the one existing between $\text{VO}_{1.33}$ and $\text{VO}_{1.36}$ in the lattice parameters, cannot be taken to signify a difference in oxygen content.

The results indicate that the tetragonal phase has a very narrow range of homogeneity. Its probable composition, then, is $\text{VO}_{1.35 \pm 0.01}$, which corresponds exactly to the stoichiometric formula $\text{V}_{204}\text{O}_{255}$ proposed by Westman and Nordmark.²

For the $\text{VO}_{1.35}$ sample, which was heat-treated at a series of temperatures up to $805 \pm 5^\circ\text{C}$, the measured lattice parameters varied unsystematically with the temperature over ranges of approximately 0.01 \AA .

As mentioned previously, the tetragonal phase was not formed in any of the samples prepared at $810 \pm 10^\circ\text{C}$ or above that temperature.

In all attempts to isolate a single crystal of the tetragonal phase, the fragments mounted on the diffractometer were observed to be twinned. The twins were plate-shaped, with two of the crystallographic axes lying in the plane of the plate and the third axis at right angles to it.

The axial reflexions at $2\theta \approx 44^\circ$ were all found to consist of an 800 component, with its maximum at $2\theta = 43.60^\circ$, and an 008 component peaking at $2\theta = 43.90^\circ$. When the X-ray beam was reflected off the face of the plate, in the case most carefully investigated, the 800 component dominated. When the diffracted beam passed through the plate (the diffraction vector lying in the plane of the plate), the two components were equally strong.

The effect may be interpreted to signify that the plate was built up of single crystal slabs, with the [001] and the [100] directions alternately at right angles to the face of the plate.

With the narrow receiving slit in front of the X-ray detector exchanged for the ordinary beam tunnel used in measuring integrated intensities it was no longer possible, for any reflexion, to resolve the components diffracted from different crystals within the twinned aggregate. Consequently, the attempts to record data for a refinement of the crystal structure were discontinued.

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Animal Carotenoids

2.* Actinioerythrin and Related Compounds — Novel Nor-carotenoids with Ring Contraction

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Actinioerythrin, first isolated by Lederer¹ in 1933 from the sea anemone *Actinia equina* has only been partly characterized.¹⁻³ Following alkali treatment this red pigment was converted to the blue-coloured violerythrin.² It has been questioned whether these compounds belong to the carotenoid series.⁴

We now conclude that actinioerythrin is a 2,2'-bis-nor-astaxanthin diester (1) and violerythrin the corresponding tetraketone (2), the extraordinary light absorption properties of the latter being caused by the conjugated cyclopentenedione rings. Simple cyclopent-3-en-1,2-dione derivatives are yellow compounds.^{5,6}

Actinioerythrin, m.p. 91°C, λ_{\max} 505 and (536) $m\mu$ (all visible light absorption maxima refer to acetone solutions), ν_{\max} (KBr disc) 1740, 1695, 1528 cm^{-1} ; τ 7.97 (4 Me), 8.08 (2 Me), 8.57 (2 Me), and 8.83 (2 Me), methyl signals only are quoted; $M > 800$, gave a mono- and dioxime, no product under conditions for acetal formation and no product with o-phenylenediamine, acetylating, silylating, or methylating reagents. Sodium borohydride reduction furnished a mono-ol (3), a diol (4), a triol (5), and a tetraol (6, 3 *trans* stereoisomers). The mono-ol (3, λ_{\max} 489 and (525) $m\mu$) gave a monoacetate and was oxidized with air in the presence of iodine⁷ (subsequent oxidations refer to this method) to actinioerythrin (1). The diol (4, λ_{\max} (444), 470 and 499 $m\mu$) gave a mono- and a diacetate and was oxidized to the mono-ol (3) and actinioerythrin (1). Both the diol (4) and the triol (5, λ_{\max} (444), 470 and 499 $m\mu$) on further treatment with lithium aluminium hydride or alkali were transformed to the tetraol (6). The triol (5) furnished on oxidation two products more polar than

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