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Phase Relations in the WO_2–V_2WO_6 System

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This work constitutes part of a systematic study of the crystallographic changes in $M^{4+}O_2$–$M^{3+}{}_2M^{6+}O_6$ systems, where M^{4+} = W or V, M^{3+} = V, Fe, Cr, or Al, and M^{6+} = W, Mo, or Te.

The VO_2–$M^{3+}{}_2M^{6+}O_6$ system, where M^{3+} = V, Fe, Cr, or Al and M^{6+} = W, Mo, or Te, has been studied extensively by a number of workers.[1-3] The recent paper by Neurgaonkar and Roy[3] gives a fuller description of the crystallographic changes and the variation of the transition temperature as a function of size of the dopant ions in the VO_2–$M^{3+}{}_2M^{6+}O_6$ system. In the present note, the work on VO_2–V_2WO_6 has been extended by replacing V^{4+} by W^{4+}, and the effects of such replacement on crystalline solubility and structural changes have been studied.

Experimental Section

The starting materials used were WO_3,W (Research in Organic and Inorganic Chemistry Corp.), and V_2O_5 (Fisher Scientific Co.). V_2O_3 was prepared by hydrogen reduction of V_2O_5 for 8 h at 800 °C. The phase $W^{4+}{}_{1-x}V_{2x/3}W^{6+}{}_{x/3}O_2$ has been prepared by substituting vanadium tungstate for WO_2

$$(1-x)WO_2 + \frac{x}{3}V_2WO_6 \rightarrow W_{1-x}V_{2x/3}W_{x/3}O_2 \qquad (1)$$

For the study of the homogeneity range for the different structures, about 25–30 specimens of gradually varying compositions were prepared by mixing WO_3, W, and V_2O_3. The pressed pellets were heated to the desired temperature ranging from 1000 to 1200 °C in evacuated silica tubes. X-ray powder data were obtained using a Picker diffractometer with nickel-filtered Cu Kα radiation. For phase identification a scanning speed of 1° 2θ/min was used. The stoichiometry of each phase was checked by simple gravimetric oxidation to WO_3–V_2WO_6.

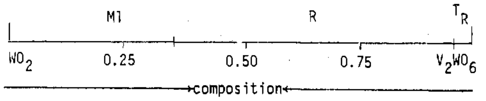

Figure 1. Phases in the system $W_{1-x}V_{2x/3}W_{x/3}O_2$ as observed at room temperature.

Results

A series of these $W_{1-x}V_{2x/3}W_{x/3}O_2$ crystalline solutions exists between the monoclinic WO_2 and the trirutile V_2WO_6 phases. Three structurally related phases have been identified. The results of phase analysis are shown in Figure 1. Here M1 stands for the monoclinic WO_2-type structure, R for the tetragonal rutile structure, and T_R for the trirutile structure. At room temperature, the homogeneity range of the M1 structure is $0.0 \le x \le 0.33$, while the R structure appears over a wide compositional range estimated to extend between $0.34 \le x \le 0.985$. Only in the samples where $0.985 \le x \le 1.0$, superstructure lines indicating the formation of the trirutile solid solution are found.

This study did not find any new phase in the range $W_{1-x}V_{2x/3}W_{x/3}O_2$. WO_2[4] and VO_2[5] are isostructural at room temperature and possess the monoclinically distorted rutile structure. Vanadium dioxide, however, undergoes a structural transformation to the tetragonal rutile at ~67 °C. This fact suggests that the systems WO_2–V_2WO_6 and VO_2–V_2WO_6 should exhibit similar crystallographic changes at room temperature. It is interesting to note that, although the structural changes (M1 → R → T_R) are identical for both the systems, the crystalline solubility of V_2WO_6 in "MO_2" or "MO_2" in V_2WO_6 is entirely different depending on whether "M" is V or W. Recent work on the VO_2–V_2WO_6 system[1] shows that approximately 5 mol % V_2WO_6 dissolves in VO_2. On the other hand, VO_2 dissolves to a large extent in V_2WO_6. It has been shown that 30 mol % of VO_2 can easily be accommodated in V_2WO_6. This interchange of the crystalline solubility in these systems can be explained simply on the basis of the differences in the ionic radii of W^{4+} (0.79 Å) and V^{4+} (0.73 Å).[6]

A notable feature in this system is the occurrence of an undistorted tetragonal rutile-type phase, over a wide range of composition, despite the fact that neither WO_2 nor V_2WO_6 possesses the rutile structure. This large tetragonal rutile crystalline solution field has been reported previously for VO_2–V_2WO_6, VO_2–Cr_2WO_6,[1,2] and some other systems, e.g., VO_2–WO_2, VO_2–MoO_2, and NbO_2–ReO_2, etc.[7,8,9] However, the VO_2–$M^{3+}{}_2TeO_6$ system[3], where M = Fe, Cr or Al, has been shown to be an exception to this rule. No rutile solid solution exists on these binary joins. A comparison between the two systems WO_2–V_2WO_6 and VO_2–V_2WO_6 shows that the homogeneity range of the rutile crystalline solution is exactly similar for the two systems. However, this range does not occur at the same compositional region. For WO_2–V_2WO_6 the rutile solid solution extends in the region $0.34 \le x \le 0.985$, while the rutile solid solution is shown to occur in the region $0.06 \le x \le 0.70$ in the VO_2–V_2WO_6 system.

Figure 2 gives unit cell parameters, at room temperature, as a function of composition for the rutile-type phase $W_{1-x}V_{2x/3}W_{x/3}P_2$, $0.34 \le x \le 0.985$. As shown in Figure 2, the *a* parameter decreases while the *c* parameter increases with increasing amounts of V_2WO_6 in WO_2. It is interesting to note

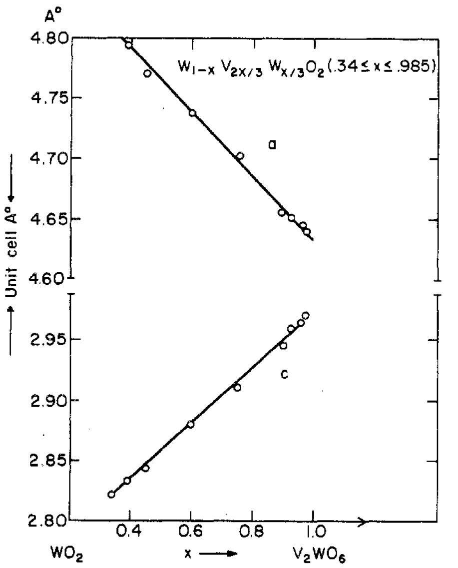

Figure 2. Unit cell parameters, at room temperature, as a function of composition for the rutile crystalline solution $0.34 \leq x \leq 0.985$.

that similar situations have also been reported for $V_{1-x}Mo_xO_2$ and $V_{1-x}W_xO_2$ crystalline solutions. The VO_2–V_2WO_6 system, however, is an exception to this rule. Both *a* and *c* parameters increased with increasing amounts of V_2WO_6 in VO_2.

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Some Anomalous Properties of Oxygen and Nitrogen

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It has been shown that the interaction energies of a fluorine atom with a variety of other species are anomalously low, relative to the trends among the other halogens.[1] Perhaps the best known example is F_2, but the same situation has been found for HF, CH_3F, and the alkali fluorides. In all of these cases the experimental dissociation energy of the fluorine-containing bond is lower than would be anticipated on the basis of the strengths of the analogous bonds in the other hydrogen halides, methyl halides, and alkali halides. The deviation is always approximately 26 kcal/mol of fluorine atoms.[1] In fact, the electron affinity of fluorine, corresponding to the interaction $F(g) + e^- \rightarrow F^-(g)$, is also lower than expected (less than that of chlorine!), and again by the same amount, 26 kcal/mol.

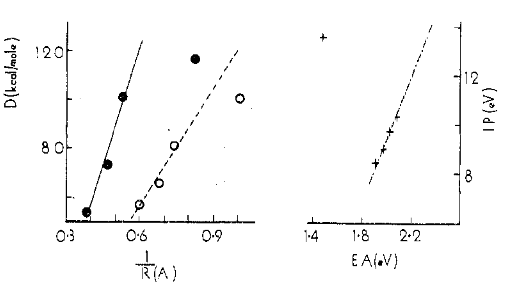

Figure 1. (Left) Relationships between the dissociation energies, *D*, and the reciprocals of the bond lengths, $1/R$, for the molecules X_2 (●) and XH (○) (X = S, Se, and Te). O_2 and OH are seen to deviate. (Right) Relationship between electron affinity and ionization potential for the atoms S–Po; again oxygen deviates.

These anomalous properties of the fluorine atom have been attributed to its very small size, which causes its electronic charge to be very highly concentrated and to consequently exert an exceptionally strong repulsive force upon any external electron that enters its outer shell, whether in forming a negative ion or a covalent bond.[1] This interpretation is not inconsistent with the highly reactive and electronegative nature of the fluorine atom; the point is simply that its electron-attracting and reactive strengths are not quite as great (by about 26 kcal/mol) as the trend among the other halogens implies.

Cotton and Wilkinson have suggested that "a similar effect may account for the low bond energies in H_2O_2 and N_2H_4".[2] They refer to the O–O and N–N bonds. The average energies of O–O and N–N single bonds are only 35 and 38 kcal/mol, respectively, whereas the values for S–S and P–P single bonds are 54 and 50 kcal/mol.[3] More specifically, the dissociation energy of H_2O_2 to two OH radicals is 51.1 kcal/mol, while the corresponding energy for H_2S_2 is 65 kcal/mol.[4] In this paper will be presented evidence supporting Cotton and Wilkinson's suggestion and indicating that there is indeed an anomalous repulsive effect, analogous to that of fluorine, operating in the cases of oxygen and probably also nitrogen. The line of approach will be similar to that used in the fluorine investigation.[1]

Just as for the halogens, the experimentally determined electron affinities of the group 6 elements show a gradual increase in going from polonium (1.9 eV) to sulfur (2.0772 eV), but then a sharp *decrease* for oxygen (1.462 eV).[5] In contrast, the ionization potentials increase monotonically through the same series, including oxygen.[6] For the elements Po–S, there is an excellent linear relationship between electron affinities and ionization potentials, as shown in Figure 1; the correlation coefficient is 0.995. Oxygen deviates very markedly from this relationship. Extrapolation of the line to the ionization potential of oxygen yields a corresponding electron affinity of 2.37 eV, which is 0.91 eV (21 kcal/mol) greater than the observed value. This is the first indication of an anomalous destabilizing effect associated with the interaction of an oxygen atom with an electron.

Further evidence is found when the dissociation energies of the X_2 and XH molecules (X = S, Se, Te) are plotted against the reciprocals of their bond lengths (see Figure 1).[7] Again following the pattern of the halogens, very good linear relationships are obtained (correlation coefficient = 0.988 for the X_2 molecules, 0.978 for the XH molecules), from which both O_2 and OH deviate. Extrapolation to the $1/R$ values of the latter shows that both of their dissociation energies are too low, by 77 kcal/mol for O_2 and 25 kcal/mol for OH. When the