mirror plane that exists in **4**, so that, in principle, both **1** and **5** ought to display three separate lines for this $M(CO)_3$ group. The lack of any qualitative difference or any significant quantitative difference in the structures of **1** and **5** leaves us at a loss to explain the observations. Evidently, a very subtle effect is involved.

The change from Mo to W in going from **1** and **5** has essentially no effect on the ease of the carbonyl scrambling processes in this case. This is not particularly surprising, but at the same time, no valid generalization can be based on this one case.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant A494. We also thank Drs. B. A. Frenz and J. M. Troup of the Molecular Structure Corporation for assistance and Dr. John R. Kolb for helpful comments.

Registry No. **1**, 12320-70-6; **4**, 60295-03-6; **5**, 60306-24-3; $(CH_3CN)_3W(CO)_3$, 16800-47-8; ^{13}C, 14762-74-4.

Supplementary Material Available: Listing of structure factor amplitudes (10 pages). Ordering information is given on current masthead page.

References and Notes

(1) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Organomet. Chem.*, **87**, C42, (1975).
(2) F. A. Cotton, P. Lahuerta, and B. R. Stults, *Inorg. Chem.*, **15** 1866 (1976).
(3) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).
(4) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **7**, 1545 (1968).
(5) All computations were performed on a PDP 11/45 computer at the Molecular Structure Corporation, College Station, Tex. 77840, using software from the Enraf-Nonius structure determination package.
(6) Unfortunately the crystal structure of $(azl)Mo_2(CO)_6$ is disordered[7] and therefore the molecular structure is not precisely known.
(7) M. R. Churchill and P. H. Bird, *Chem. Commun.*, 746 (1967).
(8) (a) A study[8b] has been made of rotational barriers of substituents on an azulene ring. Although activation parameters are not given, coalescence temperatures between −70 and −95 °C are reported for rotation of $-C(CH_3)_2$ and $-CH(OH)CH_3$ groups occupying the 1 position in 4,6,8-trimethylazulene. (b) M. Oki and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **44**, 1880 (1971).
(9) D. S. Ginley and M. S. Wrighton, *J. Am. Chem. Soc.*, **97**, 3533 (1975).

Contribution from the Materials Research Laboratory,
The Pennsylvania State University, University Park, Pennsylvania 16802

Effects of $M^{III}_2TeO_6$ Substitutions on the Crystal Structure and Transition Temperature of VO_2

R. R. NEURGAONKAR and RUSTUM ROY*

Received May 5, 1976 AIC603347

The $V_{1-x}M^{III}_{2x/3}Te_{x/3}O_2$, where M = Fe, Cr, or Al, series of solid solutions have been prepared and studied by x-ray diffraction and DTA methods. It has been shown that all the substitutions are partial. Further, the phase transition sequences $M_1 \rightarrow M_2 \rightarrow M_4$ for $V_{1-x}M^{III}_{2x/3}Te_{x/3}O_2$, M = Fe or Cr, and $M_1 \rightarrow M_2$ for $V_{1-x}Al_{2x/3}Te_{x/3}O_2$ have been examined at the VO_2 end. It is interesting to report that the T_{tr} shifts toward higher temperatures with increasing amounts of $M^{III}_2TeO_6$ in all the systems.

Introduction

The system VO_2–$M^{III}_2M^{VI}O_6$ has been the subject of several investigations in recent years. Bernier and Poix[1] were first to recognize the trirutile V_2WO_6 solid solution in the VO_2–WO_2 system and soon after Bernigaud, Bernier, and Michel[2] reported that V_2WO_6 dissolves in all proportions in VO_2. Further it has been shown that the rutile structure exists over a large composition range and the T_{tr} shifts toward lower temperatures. More recently Neurgaonkar and Roy[3] showed that complete solid solution also exists between VO_2 and Cr_2WO_6 and demonstrated the existence of the monoclinic (M_2) and the rutile (R) structures, at room temperature, as a function of composition. They also reported that the T_{tr} first decreased and then increased with increasing amounts of Cr_2WO_6 in VO_2. These results suggest that the T_{tr} should shift toward a higher temperature, if both W^{6+} and V^{3+} are replaced by the smaller cations. The present investigation has been undertaken to study the effects of replacing V_2WO_6 by $M^{III}_2TeO_6$, where M = Fe, Cr, or Al, on solid solubility, on structural changes, and finally on the transition temperature.

Experimental Section

The starting materials used were V_2O_5 (Research Organic/Inorganic Chemical Corp.), TeO_2 (Johnson Mathey Chemical), Cr_2O_3, Al_2O_3, and Fe_2O_3 (Fischer Scientific Co.). V_2O_3 was prepared by hydrogen reduction of V_2O_5 at 800 °C for 8–10 h. $M^{III}_2TeO_6$ phases were first prepared at 750 °C and then samples were weighed by mixing the appropriate amounts of V_2O_5, V_2O_3, and $M^{III}_2TeO_6$. Detailed experimental techniques have been described elsewhere.[3] The reaction temperature was raised 100 °C/day and kept at 750–800 °C for 2–8 days, after which the samples were quenched and analyzed.

Room- and high-temperature x-ray powder data were obtained by using a Picker diffractometer with nickel-filtered Cu Kα radiation. For phase identification a scanning speed of 1° in 2θ/min was used.

Table I. Synthesis Conditions and Phase Analyses for $V_{1-x}M_{2x/3}Te_{x/3}O_2$ Systems

System	Compn	Reacn temp, °C	Structure[a]
$V_{1-x}Al_{2x/3}Te_{x/3}O_2$	$0 \leq x \leq 0.01$	760 °C/8 days	M_1
	$0.012 \leq x \leq 0.12$	760 °C/8 days	M_2
	$0.13 \leq x \leq 0.69$	760 °C/8 days	$M_2 + T_R$
	$0.70 \leq x \leq 1.0$	760 °C/8 days	T_R
$V_{1-x}Cr_{2x/3}Te_{x/3}O_2$	$0 \leq x \leq 0.01$	800 °C/8 days	M_1
	$0.015 \leq x \leq 0.08$	800 °C/8 days	M_2
	$0.09 \leq x \leq 0.21$	800 °C/8 days	M_4
	$0.22 \leq x \leq 0.69$	750 °C/8 days	$M_2 + Cr_2O_3$
	$0.70 \leq x \leq 1.0$	750 °C/8 days	T_R
$V_{1-x}Fe_{2x/3}Te_{x/3}O_2$	$0 \leq x \leq 0.01$	760 °C/2 days	M_1
	$0.015 \leq x \leq 0.08$	760 °C/2 days	M_2
	$0.09 \leq x \leq 0.30$	760 °C/2 days	M_4
	$0.31 \leq x \leq 0.64$	750 °C/2 days	Unknown
	$0.65 \leq x \leq 1.0$	750 °C/2 days	T_R

[a] M_1 = monoclinic; M_2 = monoclinic; M_4 = monoclinic; T_R = trirutile.

Results and Discussion

Synthesis of $V_{1-x}M^{III}_{2x/3}Te_{x/3}O_2$. The phase $V_{1-x}M^{III}_{2x/3}Te_{x/3}O_2$, where M = Fe, Cr, or Al, has been prepared by substituting M_2TeO_6 (trirutile) for VO_2 as in

$$(1-x)VO_2 + (x/3)M_2TeO_6 \rightarrow V_{1-x}M^{III}_{2x/3}Te_{x/3}O_2$$

Table I summarizes the synthesis conditions and phase analyses for the different phases which have been prepared in the present study. It has been shown that all of the substitutions are partial.

The synthesis of Te^{6+}-containing phases was difficult due to the volatilization of Te^{6+} from $V_{1-x}Cr_{2x/3}Te_{x/3}O_2$, while $V_{1-x}Fe_{2x/3}Te_{x/3}O_2$ phases melted at ~800 °C.

The volatilization of Te^{6+} was a great problem in the system $V_{1-x}Cr_{2x/3}Te_{x/3}O_2$ when the samples were heated to 800 °C in 1 day. When the firing temperature was lowered to 750 °C, a considerable portion of Cr_2TeO_6 would remain unreacted. This suggests that Te^{6+} volatilizes at about 750 °C. Samples with compositions where $0 \leq x \leq 0.21$ have been found to be single phase and the loss of Te^{6+} by volatilization was negligible when all of the batches were heated very slowly from 400 to 800 °C in 6–8 days. Beyond this composition limit, however, small amounts of Te^{6+} escaped and the monoclinic (M_4) and Cr_2O_3 phases were identified in the composition region $0.22 \leq x \leq 0.69$. The stoichiometry of each phase was established by gravimetric oxidation to V_2O_5–Cr_2TeO_6 and by x-ray diffraction. Attempted synthesis of $V_{1-x}Cr_{2x/3}Te_{x/3}O_2$ in sealed platinum or gold capsules was completely unsuccessful since Te^{6+} was reduced to metallic tellurium and formed Pt–Te or Au–Te alloys. The resulting phase was a mixture of the monoclinic phase (M_2) and Cr_2O_3 indicating Te^{6+} was completely lost.

It is interesting to note that the volatilization of Te^{6+} was almost eliminated when Cr^{3+} was replaced by Al^{3+} or Fe^{3+}. The solubility of Al_2TeO_6 in VO_2, however, was very limited, 12 mol %. Two phases, the monoclinic (M_2) and Al_2TeO_6, coexist in the composition range $0.13 \leq x \leq 0.70$. The solubility of Fe_2TeO_6 in VO_2 was 30 mol %. Beyond this limit the samples with compositions $0.31 \leq x \leq 0.64$ melted at ~800 °C and were poorly crystallized. For this reason, each batch mixture was first heated to 750 °C in silica tubes followed by reaction above the melting temperature for 1–2 h. After the mixture was cooled back to 750 °C and after it was annealed for 1–2 days, the sample was quenched. Although the x-ray powder patterns showed a few reflections of the structure (M_4), complete analysis was difficult due to the limited number of reflections. Further experiments are needed to characterize the system in this area. It seems, however, reasonable that this is a two-phase region ($M_4 + T_R$).

At the other end, the behavior of VO_2 in $M^{III}{}_2TeO_6$, M = Fe, Cr, or Al, was more or less similar and the limit of solubility was 30 mol %.

X-Ray Results

When a trirutile is made to react with the monoclinic VO_2, an undistorted rutile structure usually results over a large composition range. Such are the findings by Bernigaud, Bernier, and Michel[2] and Neurgaonkar and Roy.[3] The results of the present investigation on VO_2–$M^{III}{}_2TeO_6$ systems, however, are exceptions to the rule. The results of the x-ray measurements, at room temperature, confirmed the existence of the intermediate structures at the VO_2 end. Further, the sequences $M_1 \rightarrow M_2 \rightarrow M_4$ for $V_{1-x}M^{III}{}_{2x/3}Te_{x/3}O_2$, where M = Fe or Cr, and $M_1 \rightarrow M_2$ for $V_{1-x}Al_{2x/3}Te_{x/3}O_2$ have been identified. Although the results of this work on $V_{1-x}Fe_{2x/3}Te_{x/3}O_2$ in the region $0.31 \leq x \leq 0.65$ are not conclusively established, it would appear that there exists no rutile solid solution in the $V_{1-x}M^{III}{}_{2x/3}Te_{x/3}O_2$ systems.

The M_2 and M_4 structures which have been identified in the present work have already been characterized and reported in the VO_2–$M^{III}VO_4$ systems,[4-14] where M = Fe, Cr, Ga, or Al. It has been shown that the displacement of the smaller cations M^{3+} and V^{5+} from the centers of coordination octahedra causes the distortion of the monoclinic (M_1) to intermediate structures. Further, it can be seen that the smaller the ions, the higher the distortion of the monoclinic (M_1) structure. Since the ionic radii of Te^{6+} and V^{5+} are similar and Te^{6+} is coupled with Fe^{3+}, Cr^{3+}, or Al^{3+}, it was expected that $M^{III}{}_2TeO_6$ should stabilize the intermediate structures and at the same time rule out the rutile solid solution in the VO_2–$M^{III}{}_2TeO_6$ systems. The observations are in excellent agreement with the experimental results with only one exception. The expected highly distorted triclinic (T) phase in $V_{1-x}Al_{2x/3}Te_{x/3}O_2$ and the monoclinic (M_3) structure in $V_{1-x}M^{III}{}_{2x/3}Te_{x/3}O_2$, M = Cr or Fe, did not appear.

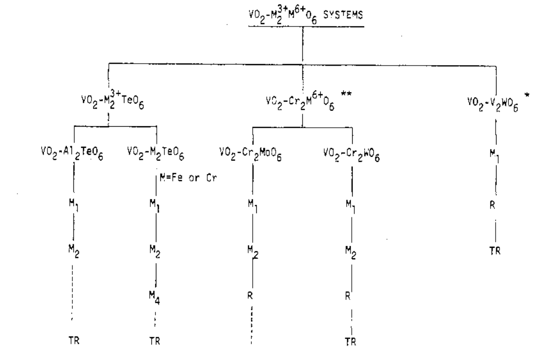

Figure 1. Compositional dependence of structure in VO_2-$M^{III}{}_2$-$M^{VI}O_6$ systems.

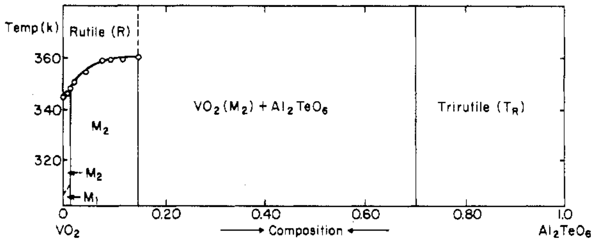

Figure 2. Phase diagram for $V_{1-x}Al_{2x/3}Te_{x/3}O_2$.

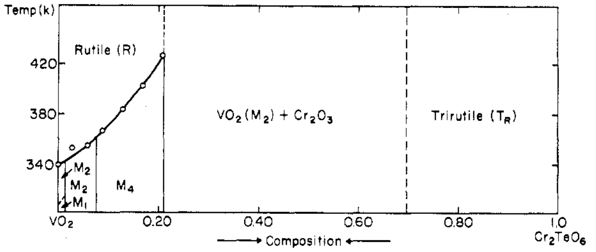

Figure 3. Phase diagram for $V_{1-x}Cr_{2x/3}Te_{x/3}O_2$.

Figure 1 summarizes the crystallographic changes for the entire VO_2–$M^{III}{}_2M^{VI}O_2$ systems. The results are grouped into three different categories according to the structural changes observed in the various systems. The classification has mainly been made on the basis of mean ionic radii[19] of doping ions and it is interesting to note that it fits nicely for the VO_2–$M^{III}{}_2M^{VI}O_6$ systems except for VO_2–Fe_2TeO_6.

Temperature Dependence of Structures

DTA studies were performed in the temperature range 300–480 K using a Du Pont 990 thermal analyzer. The DTA data obtained are the average values collected from three or four measurements. For all of the measurements the T_{tr} change was ±2 K. Figures 2–4 show the variation of T_{tr} as a function of $M^{III}{}_2TeO_6$ content and also represent a generallized phase diagram for the $V_{1-x}M^{III}{}_{2x/3}Te_{x/3}O_2$ systems. It is interesting to report that the T_{tr} shifts toward the higher temperatures with increasing amounts of $M^{III}{}_2TeO_6$ for all of the systems. The $V_{1-x}Al_{2x/3}Te_{x/3}O_2$ solid solution shows a saturation at ~357 K. The results are in excellent agreement with results of Kitahiro and Watanabe[13] on the $V_{1-2x}V^{V}{}_xAl_xO_2$ system. They found saturation for

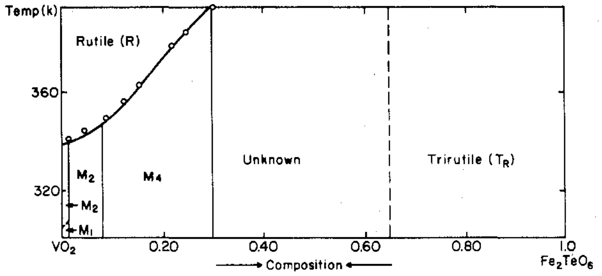

Figure 4. Phase diagram for $V_{1-x}Fe_{2x/3}Te_{x/3}O_2$.

$AlVO_4$-substituted VO_2 at ~354 K.

High-temperature x-ray results show that the rutile (R) structure forms in all of the compositions above the T_{tr}. In the particular compositions where $0 \leq x \leq 0.015$, a sequence $M_1 \rightarrow M_2 \rightarrow R$ has been reported with increasing temperature. The $M_1 \rightarrow M_2$ transition is indicated by a dotted line in Figures 2–4. Precise DTA and x-ray work is needed to characterize the $M_1 \rightarrow M_2$ transition temperature, since it lies close to room temperature.

The overall effect of composition on T_{tr} has been surveyed in other rather comprehensive investigations.[9,11,12,15–17] It appears that cations with ionic radii smaller than that of V^{4+} shift the T_{tr} toward higher temperatures, and vice versa. It is interesting to note that the present results follow this trend for smaller (e.g., Al + Te, Cr + Te, Cr + V, Ge^{4+}, etc.) and larger ($V^{3+} + W^{6+}$, Mo^{4+}, Nb^{4+}, etc.) cations, but they hold poorly for cations ($Cr^{3+} + Mo^{6+}$, $Cr^{6+} + W^{6+}$, $Fe^{3+} + Te^{6+}$) having mean ionic radii close to but slightly higher than that of V^{4+}. Although the results of the $V_{1-x}Cr_{2x/3}M_{x/3}O_2$, M = W or Mo, solid solution[3] are not sufficient to generalize, it was tentatively suggested that the character of each ion should be considered separately, where more than one ion is introduced for V^{4+}. The DTA measurements on $V_{1-x}Fe_{2x/3}Te_{x/3}O_2$ solid solution clearly signify that both Fe^{3+} and Te^{6+} support the T_{tr} shift toward a higher temperature. There exists, however, a controversy on Fe^{3+} substitutions on the transition temperature of VO_2. Futaki and Aoki[12] claimed that when Fe^{3+} was added to VO_2 the T_{tr} shifted to a lower temperature. According to the results obtained by McChensney and Everhart[10] the T_{tr} shifts toward a higher temperature for Fe^{3+}-doped VO_2. The present work as well as our unpublished data on the system $V_{1-2x}Fe_xNb_xO_2$[18] favors the T_{tr} shift toward higher temperatures.

Hence, in surveying all of the experimental results reported on VO_2–$M^{III}{}_2M^{VI}O_2$ systems to date, it is remarkable that the structural changes can be predicted so consistently on the basis of ionic size, but no consensus has yet been reached concerning the mechanism responsible for the transition in VO_2.

Acknowledgment. The authors extend their thanks to Professor I. R. Harrison for providing the DTA facilities for this work.

References and Notes

(1) J. C. Bernier and P. Poix, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **265**, 1247 (1967).
(2) A. Bernigaud, J. C. Bernier, and A. Michel, *Rev. Int. Hautes Temp. Refract.*, **8**, 261–268 (1971).
(3) R. R. Neurgaonkar and R. Roy, *Mater. Res. Bull.*, **11**, 361–368 (1976).
(4) G. Villeneuve, A. Bordet, A. Casalot, and P. Hagenmuller, *Mater. Res. Bull.*, **6**, 119–130 (1971).
(5) M. Marezio, D. B. McWhan, J. P. Remeika, and J. P. Dernier, *Phys. Rev. B*, **5**, 2541–2551 (1972).
(6) G. Villeneuve, M. Drillon, and P. Hagenmuller, *Mater. Res. Bull.*, **8**, 1111–1122 (1973).
(7) J. Galy, A. Casalot, J. Darriet, and P. Hagenmuller, *Bull. Soc. Chim. Fr.*, 223 (1967).
(8) K. Kosuge, *J. Phys. Soc. Jpn.*, **22**, 551 (1967).
(9) T. Mitsuishi, *Jpn. J. Appl. Phys.*, **6**, 1060 (1967).
(10) C. R. Everhart and J. B. McChensney, *J. Appl. Phys.*, **39**, 2872 (1968).
(11) J. Umeda, S. Ashida, M. Kusumoto, and K. Narita, *J. Phys. Soc. Jpn.*, **21**, 1461 (1966).
(12) H. Futaki and M. Aoki, *Jpn. J. Appl. Phys.*, **8**, 1008–1013 (1969).
(13) J. Kitahiro and A. Watanabe, *Jpn. J. Appl. Phys.*, **6**, 1023–1024 (1967).
(14) M. Drillon and G. Villeneuve, *Mater. Res. Bull.*, **8**, 1199–1208 (1974).
(15) J. B. McChensney and H. J. Guggenheim, *J. Phys. Chem. Solids*, **30**, 225–234 (1969).
(16) J. Umeda, H. Kusumoto, K. Narita, and E. Yamada, *J. Chem. Phys.*, **42**, 1461 (1965).
(17) J. B. Goodenough, *J. Solid State Chem.*, **3**, 490–500 (1971).
(18) R. R. Neurgaonkar and R. Roy, submitted for publication.
(19) Ionic radii used in the present classification are taken from the work R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969); **26**, 1046 (1970).

Contribution from the Institute of Scientific and Industrial Research,
Osaka University, Suita, Osaka 565, Japan

Synthesis and Characterization of the Organic Derivatives of Zirconium Phosphate[1]

SHOJI YAMANAKA[2]

Received March 4, 1976 AIC60164Y

When γ-zirconium phosphate is immersed in an aqueous solution of ethylene oxide, it is converted into new phases with enlarged basal spacings. Unlike usual intercalated complexes, the resulting phases are very stable to heating up to about 200 °C and to washing with various solvents. In alkaline solution, they are hydrolyzed into the phosphoric ester of ethylene glycol and zirconium hydroxide gel. Analysis by infrared spectroscopy and hydration studies on the new phases indicate that ethylene oxide is not merely adsorbed but suffers ring scission upon reaction with the phosphate groups on the interlamellar surfaces of γ-zirconium phosphate. The amount of reacted ethylene oxide and the basal spacing of the organic derivative vary depending upon the reaction conditions, and there is a linear relation between the two. A possible structural model for the organic derivative is proposed on the basis of this linear relation.

Introduction

Many inorganic substances with a layered structure form intercalated complexes with polar organic molecules. Such complexes have been reported on clay minerals,[3–5] transition metal chalcogenides,[6,7] hydroxy salts,[8,9] iron(III) oxychloride[10] and others.[11] In most of these complexes adsorbed species are loosely bound to the host layers and are easily removed by evacuation or may be exchanged with other polar molecules, such as water in the atmosphere. If adsorbed molecules were linked by a covalent bond to the interlamellar surfaces, however, more stable complexes would be formed. These are considered to belong to the class of organic derivatives rather than to the class of sorption complexes of layer crystals. In the organic derivatives, the interlamellar surfaces as well as the outer surfaces of the layer crystals react with organic molecules. Therefore, they are considered as organic derivatives of inorganic sheet polymers or as grafting products of organic chains onto inorganic sheet polymers.