JOURNAL OF SOLID STATE CHEMISTRY 55, 314–319 (1984)

Pressure–Products Diagram of $Fe_xV_{1-x}O_2$ System ($0 \leq x \leq 0.5$)

Y. HOTTA,* Y. UEDA, N. NAKAYAMA, K. KOSUGE, AND S. KACHI

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto, Japan

AND M. SHIMADA† AND M. KOIZUMI

The Institute of Scientific and Industrial Research, Osaka University, Osaka 565, Japan

Received December 22, 1983; in revised form April 20, 1984

The pressure–products diagram of the $Fe_xV_{1-x}O_2$ system ($0 \leq x \leq 0.5$) was investigated under the conditions of 5 ~ 55 kbar and 800°C. In high-pressure synthesis, FeV_3O_8 phase (monoclinic), which is stable under ambient pressure, was converted to the O phase (orthorhombic) and the region of O phase was extended from $x = 0.1$ up to ~0.3. The O phase so obtained, showed the characteristic reversible temperature-induced phase transition to the high-temperature rutile phase under ambient pressure, prior to the decomposition to an ambient pressure form. At $x = 0.5$, successive transformations, $FeVO_4$–I (monoclinic) → –II (orthorhombic) → –III (α-PbO_2 type) → –IV (wolframite type), were observed with increasing pressure.

1. Introduction

Much work done on the $Fe_xV_{1-x}O_2$ system ($0 \leq x \leq 0.5$) can be classified into two groups according to the purpose of the study. One is a study on the impurity effect of the phase transition of VO_2, which was discovered by Morin (*1*). The substitution of V ion by trivalent ions, such as Cr (*2–6*), Fe (*7, 8*), Al (*9, 10*), etc., leads to a complex phase diagram with several new insulating phases. For iron ion, two of the present authors reported (*11*) that six phases, $M_1 \rightarrow T \rightarrow M_2 \rightarrow M_4 \rightarrow O \rightarrow X$, appear in the composition range $0 \leq x \leq 0.25$ of the $Fe_xV_{1-x}O_2$ system with increasing x at room temperature (M_1, M_2, M_4: monoclinic, T: triclinic, O: orthorhombic, X: unknown, see Refs. (*6, 11*) about the detailed structure). All of these insulating phases show a temperature-induced phase transition to the high-temperature rutile phase (R). This transition is characteristic of the phases belonging to this group. Muller *et al.*, subsequently, found the new phase FeV_3O_8 (*C2/m*, monoclinic) near $x = 0.27$ in the $Fe_xV_{1-x}O_2$ system (*12*).

The second set of studies pertain to the modification of $FeVO_4$ ($x = 0.5$ in $Fe_xV_{1-x}O_2$ system) under high pressure. A low-pressure form, hereafter denoted

---

* Present address: Toyobo Research Center, Ohtsu, Shiga 520-02, Japan.

† Present address: Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai 980, Japan.

0022-4596/84 $3.00

$FeVO_4$–I, was reported by Levinson and Wanklyn (*13*), and the structure ($P\bar{1}$, triclinic) was analyzed by Rovertson and Kostiner (*14*). Kanamaru *et al.* (*15*) synthesized $FeVO_4$–II (orthorhombic) at 800°C and 20 kbar, and Young and Schwartz (*16*) $FeVO_4$–III (*Pbcn*, orthorhombic, α-PbO_2 type) at 750°C and 60 kbar. Muller and Joubert (*18*), further, synthesized $FeVO_4$–IV ($P2/c$, monoclinic, wolframite $NiWO_4$ type) at 800°C and 80 kbar, and $FeVO_4$–III, at 1100°C and 80 kbar.

Thus, the phase relations of the $Fe_xV_{1-x}O_2$ system are very complex. We attempted to determine the pressure–product diagram of the overall composition for the $Fe_xV_{1-x}O_2$ system ($0 \leq x \leq 0.5$).

2. Experimental

The starting compounds for the high-pressure experiments were prepared by the ceramic method, i.e., the weighed mixture of V_2O_3, V_2O_5, and Fe_2O_3 was pressed into a pellet, heated for 3 days at 600°C, and for 4 days at 1000°C ($0 \leq x \leq 0.2$) or at 800°C ($0.2 \leq x \leq 0.5$), in an evacuated silica tube, and then quenched in cold water.

The materials so prepared were pressed into a BN capsule, heated for a few hours at 800°C under various pressures, then quenched to room temperature, prior to the release of applied pressure. The apparatus employed was a piston-cylinder type for use below 20 kbar and a cubic-anvil type one for use in the 20 ~ 55 kbar pressure range. The pressure was calibrated by observing the resistance discontinuities at the transition points of Bi and Ba.

Phase identification of the products and the measurement of the lattice parameters were accomplished by X-ray powder diffraction with Cu$K\alpha$ radiation at room temperature. The phase transition was investigated by the high-temperature X-ray and DSC measurements in the temperature range up to 600°C. For these measurements, the samples were sealed in an evacuated silica capillary or capsule to prevent oxidation.

3. Results and Discussion

3.1. Synthesis Under High Pressure

Prior to the investigation under high pressure, the starting materials for high-pressure experiment were synthesized by the ceramic method to attain an overall composition of the $Fe_xV_{1-x}O_2$ system. The phase diagram so obtained was mostly in agreement with the results reported in previous work (*11*), except that the unknown X phase was a mixture of the O phase and FeV_3O_8 phase. The homogeneous region ($0.27 \leq x \leq 0.3$) of the FeV_3O_8 phase was shifted from the stoichiometric composition $x = 0.25$ to the iron-rich side. In the range of $0.3 \leq x \leq 0.5$, the FeV_3O_8 phase coexisted with $FeVO_4$–I. M_1, M_2, M_4, and O phases exhibited a reversible phase transition induced by temperature to the rutile phase, but FeV_3O_8 and $FeVO_4$–I phases underwent no phase transition up to 800°C.

A high-pressure synthesis was carried out at constant temperature at 800°C for several hours under pressures of 5 ~ 55 kbar. The phase identification of the products was done at atmospheric pressure and room temperature. The pressure–product diagram so obtained is shown in Fig. 1.

(*1*) *Composition range* $0 \leq x \leq 0.3$. In this composition range, all samples treated at 20 and 30 kbar showed an orthorhombic X-ray diffraction pattern similar to the O phase prepared by the ceramic method. The lattice parameters were affected by iron content but not significantly by the pressure. Figure 2 shows the curves of composition x vs lattice parameters of the orthorhombic phase obtained in the high-pressure synthesis ($0.12 \leq x \leq 0.27$) with those of the O phase prepared by the ceramic method ($0.07 \leq x \leq 0.10$). The lattice parameters show a continuous change with

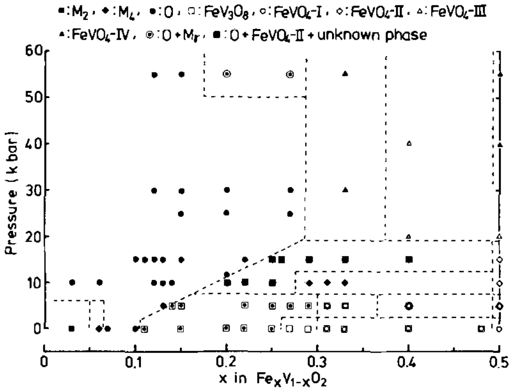

FIG. 1. Pressure–products diagram of $Fe_xV_{1-x}O_2$ system ($0 \leq x \leq 0.5$). Single and multiple symbols denote a single phase and two or three phase mixture, respectively. The position of the phase boundary is not clear.

composition x. These results suggest that the FeV_3O_8 phase with a loose structure was converted to the O phase with a more dense packing, and the region of the O phase was extended up to $x \sim 0.3$ by high-pressure synthesis. The pressure needed for obtaining the single O phase tended to increase with increasing iron content. Under lower pressure, two or three phases (O, FeV_3O_8, and an unknown phase) were encountered in the range $0.1 \leq x \leq 0.3$.

(*2*) *Composition range* $0.3 \leq x \leq 0.5$. The high-pressure synthesis of the composition $FeVO_4$ was reported by many workers. Three high-pressure forms were found: $FeVO_4$–II (orthorhombic) (*15*), $FeVO_4$–III (α-PbO_2 type, Fe and V disordered) (*16*), and $FeVO_4$–IV (wolframite type, Fe and V ordered) (*17*). In the present study, three successive transformations, $FeVO_4\text{–I} \rightarrow \text{II} \rightarrow \text{III} \rightarrow \text{IV}$, were observed with increasing pressure, as shown in Fig. 1. These transformations are consistent with a trend toward a denser structure with increasing pressure (the densities of $FeVO_4$–I, –II, –III, and –IV are approximately 3.63 (*17*), 4.15 (*15*), 4.63 (*17*), and 4.69 $g \cdot cm^{-3}$ (*17*), respectively). In the composition range $0.4 \leq x \leq 0.5$, only the $FeVO_4$–III type phase was obtained at higher pressure. In the range $0.3 \leq x \leq 0.4$, the O phase coexisted with $FeVO_4$–III at higher pressure. Under lower pressure, X-ray powder pattern showed two- or three-phase mixture in the composition range $0.3 \leq x \leq 0.5$.

The $FeVO_4$–IV type phase was obtained only at $x = 0.5$, but the $FeVO_4$–III type phase in a wider composition range below $x = 0.5$, under higher pressure. This result may be understood as follows. $FeVO_4$–IV type has an atomic-ordered structure of Fe and V atom, and so is stable in the atomic ratio Fe/V = 1 ($x = 0.5$). $FeVO_4$–III type with an atomic disordered structure, on the other hand, becomes more stable in the composition range below $x = 0.5$, where the ratio Fe/V is less than 1.

3.2. *Phase Transition*

As mentioned above, the stable region of the O phase was extended up to approxi-

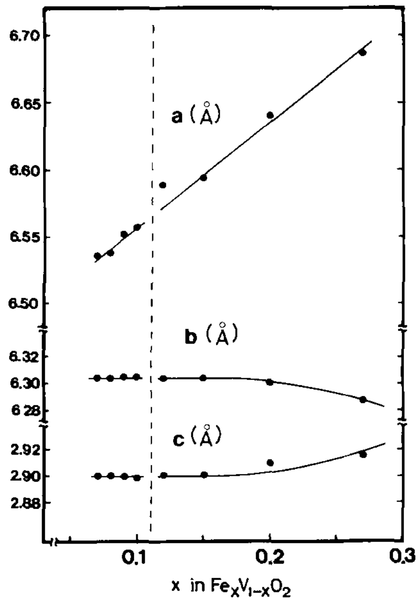

FIG. 2. Composition vs lattice parameter curves of O phase synthesized by high pressure (right zone, $0.12 \leq x \leq 0.27$) and by ceramic method (left zone, $0.07 \leq x \leq 0.10$) in $Fe_xV_{1-x}O_2$.

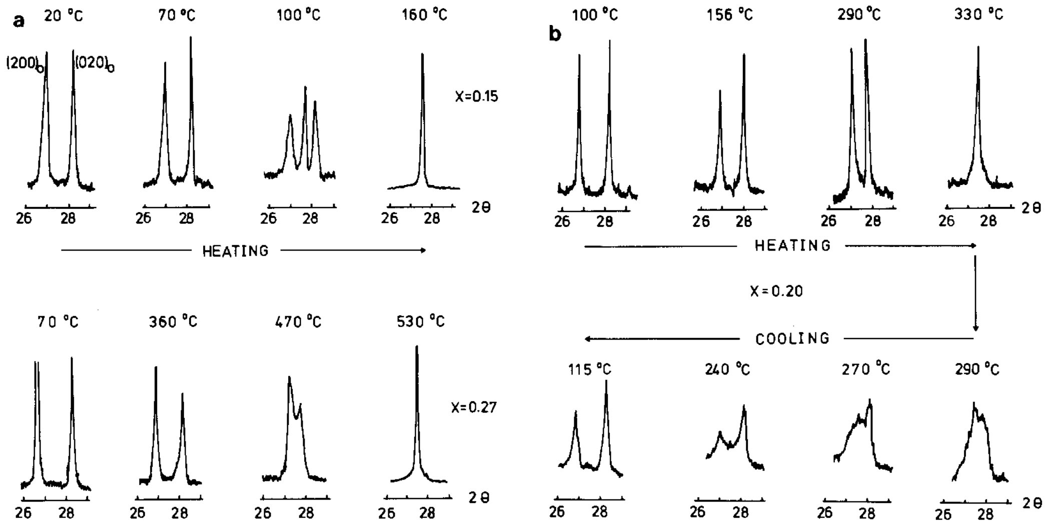

FIG. 3. (a) Temperature dependence of X-ray diffraction peaks $(200)_O$ and $(020)_O$ of synthesized O phase by high pressure, on heating under ambient pressure, for the samples $x = 0.15$ and 0.27 in $Fe_xV_{1-x}O_2$. Both samples show the phase transition to rutile phase and the two peaks merge to form the single peak $(110)_R$ of rutile phase at high temperature. (b) Temperature dependence of $(200)_O$ and $(020)_O$ peak on heating and cooling under ambient pressure for the sample $x = 0.20$ in $Fe_xV_{1-x}O_2$. The transition to the rutile phase is reversible.

mately $x = 0.3$ by high-pressure synthesis. A characteristic of the M_1, M_2, M_4, and O phases prepared by the ceramic method is the temperature-induced phase transition to the high-temperature rutile phase. This transition is of first order and reversible. The high-temperature rutile phase is not quenchable on temperature. It was examined by high-temperature X-ray and DSC measurements as to whether or not the O phase obtained by high-pressure synthesis also shows a similar transition under ambient pressure. Figures 3a and b show the temperature dependence of X-ray diffraction peaks, $(200)_O$ and $(020)_O$, of the O phase on heating or cooling for the samples $x = 0.15$ (synthesized at 25 kbar), 0.20 (12 kbar), and 0.27 (25 kbar). In all samples, the two diffraction peaks of the O phase changed to a single $(110)_R$ peak of rutile structure at high temperature, showing that a phase transition to the rutile phase had occurred. The feature of the temperature dependence is somewhat different among three samples. Figure 4 shows the temperature dependence of the difference $\Delta(2\theta)$ between the $(200)_O$ and $(020)_O$ peaks in the respective samples. In the sample with $x =$

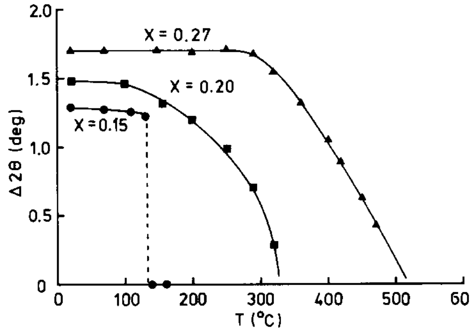

FIG. 4. Temperature dependence of the difference $\Delta(2\theta)$ between $(200)_O$ and $(020)_O$ diffraction peak for the sample $x = 0.15$, 0.20 and 0.27 in $Fe_xV_{1-x}O_2$. The $\Delta(2\theta) = 0$ coincides with the phase transition to rutile phase. The phase transition is first order for $x = 0.15$ and second order for $x = 0.20$ and 0.27.

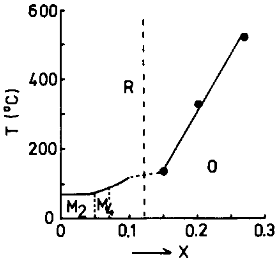

FIG. 5. Composition dependence of transition temperature from O to rutile phase. Right zone (above $x = 0.10$) for the samples synthesized by high pressure and left zone (below $x = 0.10$) by ceramic method.

0.15, $\Delta(2\theta)$ is little dependent on temperature, and the intensity of two peaks decreases toward zero with increasing temperature through the coexistence of the three peaks (the original two: the $(200)_O$ and $(020)_O$ peaks of the O phase, the other: the $(110)_R$ peak of the rutile phase) (see Fig. 3). In the samples with $x = 0.20$ and 0.27, two peaks of the O phase approach to form a single peak $(110)_R$ of the rutile phase with increasing temperature, as shown in Figs. 3 and 4. In DSC measurement, the heat of transition was detected in the sample with $x = 0.15$ but was not detectable in the samples with $x = 0.20$ and 0.27. This suggests that the transition from the O phase to the rutile phase gradually changes from first order to second order, with increasing iron content. The transition temperature rose with increasing iron content, as shown in Fig. 5. Further, it should be noted that this transition was reversible under ambient pressure, as shown in Fig. 3b. These results can be interpreted as showing that the O phase, synthesized under high pressure, exhibits a reversible phase transition to the rutile phase, which is characteristic of the phases belonging to this group, by heating or cooling. This occurs even under ambient pressure prior to the decomposition, since the decomposition rate to structure normal for its composition is not very rapid. This suggests that the material has the rutile structure at the high temperature and high pressure under which it was synthesized.[1] Of course, if the material is maintained at high temperature under ambient pressure for longer time, the O phase or rutile phase decomposes to the ambient pressure form in equilibrium.

4. Conclusions

A pressure-products diagram for $Fe_xV_{1-x}O_2$ system ($0 \leq x \leq 0.5$) was obtained. The phases which appear at room temperature under ambient pressure are $M_1 \rightarrow M_2 \rightarrow M_4 \rightarrow O$ ($0 \leq x \leq 0.1$), FeV_3O_8 ($0.27 \leq x \leq 0.3$), and $FeVO_4$–I ($x = 0.5$). In high-pressure synthesis, the FeV_3O_8 phase was suppressed and the O phase was obtained in a wide composition range up to $x \sim 0.3$. Such an O phase showed the characteristic reversible phase transition induced by temperature to the high-temperature rutile phase under ambient pressure, prior to decomposition to an ambient pressure form. The transition changed from first order to second order and the transition temperature rose with increasing iron content.

At $x = 0.5$, the successive transformations $FeVO_4$–I → II → III → IV were observed with increasing pressure. These high-pressure forms showed no phase transition induced by temperature and decomposed to the ambient pressure form by heating under ambient pressure.

References

1. F. J. MORIN, *Phys. Rev. Lett.* **3**, 34 (1959).
2. G. VILLENEUVE, A. BORDET, A. CASALOT, AND P. HAGENMULLER, *Mater. Res. Bull.* **6**, 119 (1971).

---

[1] In preliminary resistivity measurement under high pressure, we observed a discontinuity in O phase synthesized under high-pressure close to the transition temperature observed under ambient pressure. This suggests that the phase transition takes place even under high pressure. Therefore, we believe that the material has the rutile structure at high temperature and high pressure.

3. M. Marezio, D. B. McWhan, L. P. Remeika, and P. D. Dernier, *Phys. Rev. B* **5,** 2541 (1972).
4. J. W. Pierce and J. B. Goodenough, *Phys. Rev. B* **5,** 4104 (1972).
5. J. B. Goodenough and H. Y.-P. Hong, *Phys. Rev. B* **8,** 1323 (1973).
6. G. Villeneuve, M. Drillon, and P. Hagenmuller, *Mater. Res. Bull.* **8,** 1111 (1973).
7. C. Blaauw and F. van der Woude, *J. Phys. C* **7,** 4361 (1974).
8. C. Blaauw, F. Leenhouts, and F. van der Woude, *Solid State Commun.* **17,** 559 (1975).
9. M. Drillon and G. Villeneuve, *Mater. Res. Bull.* **9,** 1199 (1974).
10. M. Ghedira, H. Vincent, M. Marezio, and J. C. Launay, *J. Solid State Chem.* **22,** 423 (1977).
11. K. Kosuge and S. Kachi, *Mater. Res. Bull.* **11,** 255 (1976).
12. J. Muller, J. C. Joubert, and M. Marezio, *J. Solid State Chem.* **27,** 191 (1979).
13. L. M. Levinson and B. M. Wanklyn, *J. Solid State Chem.* **3,** 131 (1971).
14. B. Rovertson and E. Kostiner, *J. Solid State Chem.* **4,** 29 (1972).
15. F. Kanamaru, M. Shimada, M. Koizumi, and T. Asai, "Proceedings, 4th International Conference on High Pressure, Kyoto," p. 180 (1974).
16. A. P. Young and C. M. Schwartz, *Acta Crystallogr.* **15,** 1305 (1962).
17. F. Laves, A. P. Young, and C. M. Schwartz, *Acta Crystallogr.* **17,** 1476 (1964).
18. J. Muller and J. C. Joubert, *J. Solid State Chem.* **14,** 8 (1975).