A New Monoclinic Phase in the Fe_2O_3–TiO_2 System. I. Structure Determination and Mössbauer Spectroscopy

M. DROFENIK,* L. GOLIČ, D. HANŽEL, V. KRAŠEVEC,
A. PRODAN, M. BAKKER†, AND D. KOLAR

*Jožef Stefan Institute, E.Kardelj University, Jamova 39,
Ljubljana, Yugoslavia*

Single crystals with compositions within the Fe_2O_3–TiO_2 system were grown from a flux containing various amounts of the basic oxides. Apart from the known pseudobrookite (Fe_2TiO_5) and rutile (TiO_2) structures, a new monoclinic polytype of Fe_2TiO_5 was found, which was isostructural with V_3O_5. The structure was determined by X-ray analysis and Mössbauer spectroscopy contributed data on hyperfine parameters and the magnetic ordering temperature.

Introduction

The system Fe_2O_3–TiO_2 has been investigated by several authors (1–8) in the last few years. So far only one phase—pseudobrookite—has been found with the composition of Fe_2TiO_5. In all the investigations mentioned the samples were prepared by a solid-state reaction in air above 1570K.

Using the high-temperature-solution (HTS) method, we prepared a monoclinic phase with the Fe_2TiO_5 composition. In the present work we report on the X-ray structural determination and Mössbauer spectroscopy. The defect structure studied by electron microscopy will be described in part II of this paper (12).

Experimental Procedure

Compositions within the ternary diagram Fe_2O_3–TiO_2–SrO were mixed with an appropriate amount of flux. In all experiments, the amount of flux was kept constant at 80 wt%, while the composition of the flux was PbO–$2V_2O_5$ (9). The flux has low volatility and does not interact with the crucible appreciably. The chemicals used were at least 99.7% pure, and the samples were melted in platinum crucibles of 10- or 60-ml capacity. The furnaces were heated to the desired initial temperature of about 1620K followed by cooling at a rate between 7 and 10K/min. Finally, the crystals obtained were separated from the matrix with hydrochloric acid. Some experiments with CaO and BaO instead of SrO within region III (Fig. 1) were also performed, and similar results were obtained. The compositions of the crystals were determined chemically and with a microanalyzer. The con-
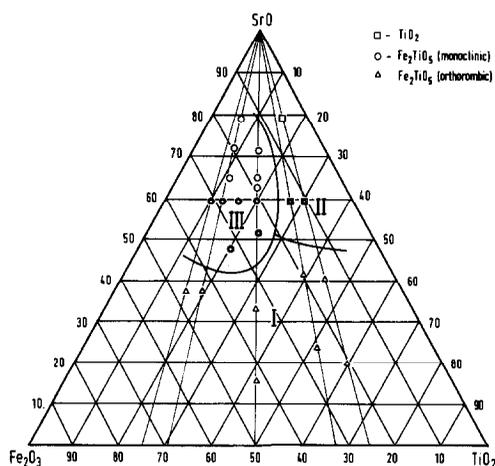
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* Author to whom correspondence should be addressed.

† On leave from Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands.

FIG. 1. The nominal composition diagram of the Fe_2O_3–TiO_2–SrO system. The amount of flux (PbO–$2V_2O_5$) was kept constant at 80 wt% in all the compositions studied.

tent of Fe^{2+} ions was found by dissolving the samples in dilute H_2SO_4 (1:1) acid under an inert atmosphere followed by titration with sodium dichromate.

The crystals were subjected to powder and single-crystal X-ray analysis and the unit-cell parameters were determined by the least-squares refinement of 45 reflections with the angle θ between 10 and 25°, using the graphite-monochromated Mo$K\alpha$ radiation. Intensity data were collected on an automatic computer-controlled CAD-4 diffractometer by use of the ω-2θ scan with a variable rate and the Mo$K\alpha$ radiation. After the absorption correction of 1830 reflections, 477 unique reflections were obtained after everaging with a discrepancy of 8.1%.

The absorbers for Mössbauer measurements were prepared by powdering single crystals. The source was ^{57}Co in Rh and the spectra were measured with a 512-channel analyzer (Promeda), operated in the time mode and using Elscint constant-acceleration equipment. The velocity scale was calibrated with metallic iron which was also used as a reference for the isomer shift parameters. The spectra were analyzed by a nonlinear least-squares program assuming Lorentzian line shapes.

Results and Discussion

(a) The Crystal Growth

Compositions of the melt from which the crystals were grown are plotted in a diagram, shown in Fig. 1. According to the crystals obtained, the system can be divided into the following three regions:

region I Fe_2TiO_5 (pseudobrookite) (*10*);
region II Fe_2TiO_5 (pseudobrookite), TiO_2 (rutile);
region III Fe_2TiO_5 (monoclinic), Fe_2TiO_5 (pseudobrookite).

In region III, besides pseudobrookite, a new monoclinic phase with apparently the same composition was found. It was also found that at slower cooling rates, which are normally used in crystal growth techniques, much fewer or no crystals of monoclinic Fe_2TiO_5 were observed. These monoclinic crystals were always in the form of thin platelets. They were magnetic and could be easily separated from the rest of the crystals by the use of a permanent
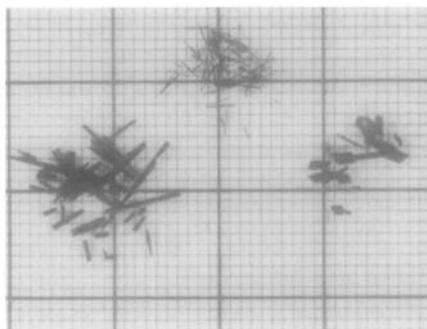

FIG. 2. Crystals obtained from regions II and III using a 60-cm³ crucible; small rods of pseudobrookite, needles of rutile, and black platelets of the monoclinic Fe_2TiO_5, respectively. The crystals are under the influence of a magnetic field (mm grid).

TABLE I

MEASURED AND CALCULATED COMPOSITION (wt%)
OF THE MONOCLINIC Fe₂TiO₅

	Chemical analysis	Electron probe analysis	Calculated values
Fe_2O_3	65.0	65.5	66.65
TiO_2	34.9	34.4	33.35

magnet. The very thin ones were transparent and of red-brown color.

Figure 2 shows the three different kinds of crystals mentioned above. Using single-crystal X-ray diffraction and electron transmission microscopy, it was found that crystals grown in the Fe_2O_3-rich part of region III were the best. But in general the perfection of the monoclinic crystals changed with the composition of the melt. The chemical analysis of these crystals and the calculated values for Fe_2TiO_5 are given in Table I.

The amount of Fe^{2+} ions as well as the amount of impurities found was less than 1 wt% (Pb < 0.03, Sr < 0.07, Pt < 0.1, V < 0.7 wt%). The pycnometrically determined crystal density (Table II) was found to be in a good agreement with the calculated one.

It is not known whether this structure is stabilized through some impurities incorporated in the lattice of these crystals, or whether it is just a result of the relatively rapid cooling rate. Furthermore, the

TABLE II

CRYSTAL DATA FOR THE
MONOCLINIC Fe₂TiO₅

$a = 10.101(3)$ Å
$b = 5.037(1)$ Å
$c = 7.024(2)$ Å
$\beta = 110.9(1)°$
$V = 333.8$ Å³
$D_o = 4.81$ g/cm³
$D_c = 4.774$ g/cm³
$Z = 4$
Space group $C2/c$

influence of alkaline earth oxides (CaO, SrO, BaO) on the growth of these crystals is not understood as yet.

(b) Structure Determination

The structure was solved by the Patterson methods and the refinement was undertaken using a full-matrix least-squares program with anisotropic temperature factors assigned to Ti, Fe, and O. Refinement was carried out (a) by putting the Ti atoms at the 4a and the Fe atoms at the 8f positions, and (b), by putting the Fe atoms at the 4a positions and the rest of the Fe and Ti atoms statistically distributed at 8f positions. For both models the R values were reduced to 0.11. Further refinement was not possible due to the presence of stacking faults, discussed in part II of this paper (12), as well as due to a relatively high amount of impurities.

From systematic absence (hkl; h + k = 2n and h0l; l = 2n) the space group C2/c was found and the crystal data are listed in Table II.

In Table III fractional coordinates and lengths for the first model are given. However, at least a partial population of 4a sites by iron atoms must exist.

Figure 3 shows the structure as seen along the b axis. The structure is built of slightly distorted TiO₆ and FeO₆ octahedra. Corner-connected successive (200) slabs alternate by b/2 along the [100] direction. Each slab consists of alternating single TiO₆ and double FeO₆ corner-connected octahe-

TABLE III

FRACTIONAL COORDINATES AND LENGTHS FOR THE
MONOCLINIC Fe₂TiO₅

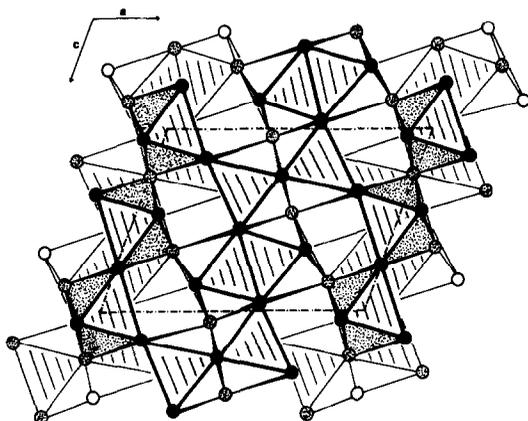| Fe	8f	0.3651(3)		0.0001(6)		0.2727(4)	
Ti	4a	0.0		0.0		0.0	
O₁	4e	0.1890(13)		0.1567(25)		0.1583(18)	
O₁₁	8f	0.4159(12)		0.1587(24)		0.5544(17)	
O₁₁₁	8f	0.0		0.2016(32)		0.7500	
Fe–O:	1.85(1)	2.26(1)	1.95(1)	2.02(1)	2.07(1)	1.92(1)	
Ti–O:	2.00(1)	×2 2.01(1)	×2 2.031(1)	×2			

FIG. 3. The structure of monoclinic Fe_2TiO_5 as seen along the b axis; TiO_6 octahedra dotted, FeO_6 octahedra empty.

dra chains, where the FeO_6 chains form face-sharing pairs.

This structure type has previously been found in a number of systems. Compounds with the same structure are V_3O_5 (7), Ti_3O_5 (8), and the compositionally closely related $FeCrTiO_5$ (5, 6).

(c) Mössbauer Spectroscopy

Mössbauer spectra of ^{57}Fe in monoclinic

TABLE IV

DATA COLLECTION SUMMARY

Temperature (K)	293(1)
Diffractometer	CAD-4 automatic, four-circle
Scan method	Co-2θ
2θ scan width (°)	0.6 0.3 tan θ
Aperture (mm)	2.4 0.9 tan θ
Radiation	Mo$K\alpha$ (0.71069 Å)
Size of crystal (mm)	(004)–(00-4) 0.02
	(200)–(-200) 0.12
	(01-3)–(0-13) 0.12
Linear absorption coefficient (mm^{-1})	10.782
Transmission	min 0.215 max 0.686
Measured reflections	1830
Averaged reflections	477
Observed reflections $I \geq 2\sigma$ (I)	440
Unobserved reflections	37
Isotropic temperature factors U_{iso}	
Fe	0.0038
Ti	0.0052
O(1)	0.0013
O(2)	0.0006
O(3)	0.0000

Fe_2TiO_5, obtained at 78 and 355K, are shown in Fig. 4.

At 78K a long-range magnetic order is evidenced with a resolved six-line pattern. This spectrum is consistent with a magnetic hyperfine field of $H = 480 \pm 5$ kG at the iron site and an isomer shift $\zeta = 0.52 \pm 0.02$ mm/sec relative to metallic iron.

With increasing temperature the absorption lines broaden, although the magnetic order persists. This might be explained by an electric field gradient of varying directions or by relatively broad hyperfine field distribution which could be due to partial disorder of the cation positions.

The transition from the magnetic ordered to paramagnetic state is not well defined due to the appearance of complex spectra near the phase transition. However, on the basis of the temperature dependence of the magnetic hyperfine splitting spectra, it can be deduced that the transition to the paramagnetic state takes place around 350K.

Above 355K all the spectra consist of symmetric quadrupole doublets with rather narrow absorption lines of Lorentzian shapes.
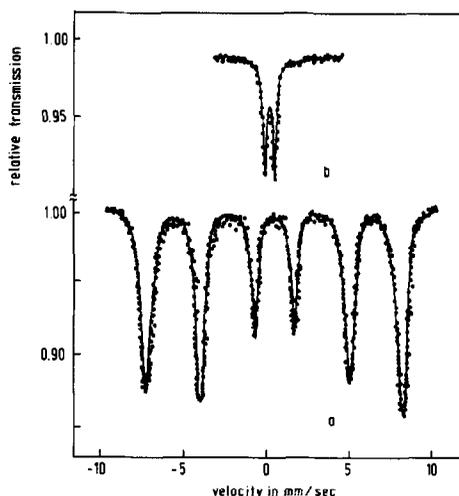
A good fit to the experimental data at

FIG. 4. ^{57}Fe Mössbauer spectra of monoclinic Fe_2TiO_5 at 78K (a) and at 355K (b).

355K is obtained with the isomer shift $\zeta = 0.32 \pm 0.02$ mm/sec relative to metallic iron, a quadrupole coupling parameter of $\Delta E_Q = 0.54 \pm 0.02$ mm/sec, and with absorption linewidths of 0.32 ± 0.02 mm/sec. All these parameters are weakly temperature dependent in the paramagnetic state.

The effective magnetic field and the isomer shift parameters indicate that the Fe ions are in the high-spin $3d^+$, $^6S_{5/2}$ state. Therefore, the measured quadrupole splitting parameters reflect the contribution of the surrounding ions to the electric field gradient tensor at the iron site. These parameters are typical for Fe ions located in distorted octahedra of O^{-2} ions. The relatively narrow absorption lines in the paramagnetic state further indicate that all iron ions are in the same valence state and that the influence of iron impurity phases is negligible.

Conclusions

—The structure of a new monoclinic phase within the Fe$_2$O$_3$–TiO$_2$ system was determined and found to be isostructural with V$_3$O$_5$.

—The growth of this phase was influenced by the presence of alkaline earth oxides and a relatively fast cooling rate.

—Two models for the monoclinic structure were proposed and it was concluded that at least a partial cation disorder must exist.

—The existence of cation disorder was confirmed by Mössbauer measurements.

—The lattice defects in the monoclinic phase studied by transmission electron microscopy are consistent with the above conclusions and will be discussed in the second part of this paper.

Acknowledgments

References

1. R. M. GIBB AND J. S. ANDERSON, J. Solid State Chem. 5, 212 (1972).
2. L. A. BURSILL, I. E. GREY, AND D. J. LLOYD, J. Solid State Chem. 16, 331 (1976).
3. I. E. GREY AND L. A. BURSILL, Acta Crystallogr. Sect. B 34, 2412 (1978).
4. I. E. GREY AND A. F. REID, Amer. Mineral. 60, 898 (1975).
5. I. E. GREY AND A. F. REID, J. Solid State Chem. 4, 186 (1972).
6. I. E. GREY, A. F. REID, AND J. G. ALLPRESS, J. Solid State Chem. 8, 86 (1973).
7. A. ÅSBRINK, S. FRIBERG, A. MAGNÉLI, AND G. ANDERSSON, Acta Chem. Scand. 13, 603 (1959).
8. G. ÅSBRINK, S. ÅSBRINK, A. MAGNÉLI, H. OKINAKA, K. KOSUGE, AND S. KACHI, Acta Chem. Scand. 25, 3889 (1971).
9. B. M. WANKLYN, J. Cryst. Growth. 7, 368 (1970).
10. R. W. WYCKOFF, "Crystal Structures," Vol. 3, p. 297. Wiley, New York (1964).
11. V. ATZMONY, E. GUREWITZ, M. MELAMUD, H. PINTO, H. SHAKED, G. GORODETSKY, E. HERMON, R. H. HORNREICH, S. SHTRIKMAN, AND B. WANKLYN, Phys. Rev. 43, 782 (1979).
12. V. KRAŠEVEC, A. PRODAN, M. BAKKER, M. DROFENIK, D. HANŽEL, L. GOLIČ, AND D. KOLAR, J. Solid State Chem. 40, 52 (1981).