concluded only that these distances represent full metal bonds. In addition, the Ni(1), Ni(2) and Ni(4) sites are related to adjacent Ni sites by distances of 2·6 to 2·9 Å, and these must represent weaker, but still significant, metal–metal interactions. The complete nearest-neighbour environments about the Ni sites are indicated for selected sites in Fig. 1. Because of the incomplete occupancy of all of the sites, the actual nearest-neighbour environment of any of the Ni atoms cannot be predicted.

The Ni_7S_6 composition is transitional between that of heazlewoodite (Ni_3S_2) and millerite (NiS). The Ni environment in the structures of both of these minerals is indicated in Fig. 2(*a*) and (*b*). The relevant interatomic distances are given in Table 4 for which the sources of the data are as follows: heazlewoodite, cell parameters: Peacock (1947), positional parameters: Westgren (1938); millerite: Alsén (1925). The Ni in heazlewoodite is coordinated to four S atoms, tetrahedrally arranged, and four Ni atoms. The Ni in millerite is coordinated to five S atoms, and two Ni atoms; the S polyhedron approximates a pyramidal configuration in which the fifth S is offset. The Ni–S bonds for α-Ni_7S_6 are within the range exhibited by millerite and heazlewoodite and the Ni–Ni distances suggest full metal bond formation. Allowing for the uncertainty in predicting the exact coordination of the Ni in α-Ni_7S_6, it is apparent that there is a good correlation between the configurations of the pyramidal and tetrahedral Ni sites in α-Ni_7S_6 and the Ni sites in millerite and heazlewoodite respectively. Clearly, me tallic (Ni–Ni) bonding has been significant in stabilizing all three of these structures.

Table 4. *Nearest-neighbour interatomic distances* (Å) *in heazlewoodite and millerite*

Heazlewoodite		Millerite	
Ni–S	2·29	Ni–S	2·19
Ni–S′	2·27	Ni–S′	2·39
Ni–Ni′	2·49	Ni–S″	2·43
Ni–Ni″	2·52	Ni–Ni′	2·53

This work was supported by a National Research Council of Canada operating grant.

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Acta Cryst. (1972). B**28**, 1241

Polymorphism of Barium Monoferrite, $BaFe_2O_4$

BY S. MERIANI

Istituto di Chimica Applicata dell'Università di Trieste, via Valerio 2, *Trieste*, *Italy*

(*Received* 6 *January* 1971 *and in revised form* 11 *October* 1971)

$BaFe_2O_4$ undergoes polymorphic transitions at 800 °C and 1000 °C. The resulting phases are: γ-$BaFe_2O_4$, stable up to 800 °C, orthorhombic with $a=5·387$, $b=19·056$ and $c=8·458$ Å; β-$BaFe_2O_4$, stable from 800 °C to 1000 °C, orthorhombic pseudo-hexagonal with $a=5·463$, $b=9·461$ ($a\sqrt{3}$) and $c=8·710$ Å; α-$BaFe_2O_4$, stable above 1000 °C, hexagonal with $a=5·458$ and $c=9·016$ Å, space group $P6_322$ with two formula units per unit cell, isomorphous with $BaAl_2O_4$. By quenching the β phase a new metastable β' phase, orthorhombic, with $a=5·442$, $b=9·325$ and $c=8·670$ Å, has been obtained at room temperature.

Introduction

Interest in the phase equilibrium diagrams of the alkaline earth ferrites prompted us to examine previously reported data concerning both symmetry and cell dimensions of barium monoferrite, $BaFe_2O_4$.

Single-crystal data (Okazaki, Mori & Mitsuda, 1963) showed that the actual unit cell is orthorhombic, with $a=19·05$, $b=5·398$ and $c=8·448$ Å; these results were confirmed also in an investigation of $BaAl_{2-x}Fe_xO_4$ solid solutions (Do Dinh & Bertaut, 1965).

A hexagonal symmetry, with $a=5·51$ and $c=8·44$ Å, was suggested by other authors (Winkler, 1965; Glasser & Dent Glasser, 1963; Okazaki, Mori & Kanamaru, 1961).

Differential thermal analysis (Ziolowski, 1962) suggested that $BaFe_2O_4$ undergoes plymorphic transitions in the temperature ranges 850 to 920°C and 1050 to 1100°C, but no further information has been derived on this phenomenon.

The present investigation was undertaken to ascertain the suspected polymorphism of this compound by observation of powder patterns of materials, both at high and room temperature, in order to deduce lattice parameters and symmetry of the different phases and to study the structure of the high temperature phase in more detail.

Experimental

Powder specimens of the compound were obtained by solid state reaction of a pressed pellet mixture of 1 $BaCO_3$:1 Fe_2O_3, which was heated on a platinum strip in a resistance furnace at temperatures ranging from 750 to 1420°C, which is the congruent melting point. The resulting microcrystalline black material was reground and refired to assure complete reaction. Polished fragments of the sintered pellets were checked by reflexion microscopy to ascertain that the sample was a single phase. The powder patterns herein reported were obtained using the high-temperature attachment of the Material Research Corp. mounted on a Philips diffractometer, which was also used for room temperature registrations. Intensities were recorded with a proportional counter in conjunction with a pulse height analyser. Temperatures were measured with a Pt/Pt–Rh 10% thermocouple and were manually controlled. Densities were measured by pycnometric methods.

Results

Starting from room temperature with a sample obtained by grinding a pellet quenched from 1200°C, two transition points were detected, by X-ray analysis, at 800 and 1000°C (both ±10°C). These results are in a fair agreement with the DTA measurements (Ziolowski, 1962). The high-temperature powder patterns of the forms, which we named β-$BaFe_2O_4$ in the range 800 to 1000°C and α-$BaFe_2O_4$ above 1000°C, are summarized in Tables 1 and 2.

Quenched samples showed the existence of two phases at room temperature. The stable form (Okazaki *et al.*, 1963; Do Dinh & Bertaut, 1965), which we now call γ-$BaFe_2O_4$, was obtained by quenching the compound from temperatures either below 800°C or above 1000°C, whereas a new and different β' form, more closely related to the β form, was obtained by quenching from temperatures between 800 and 1000°C. The powder pattern of this new phase is reported in Table 3. In order to check the stability of the β' form and to prove that it is a metastable form at room temperature, a sample of β' was heated above room temperature. The X-ray diffraction patterns demonstrate that the β' form turns into the stable γ form within few hours, even at temperatures as low as 400°C

The lattice parameters of the various forms are collected in Table 4.

Table 1. *Debye–Scherrer diagram of* β-$BaFe_2O_4$ *at* 950°C

*h k l**	*h k l*†	d_{obs}	d_{calc}	I_{obs}
	0 2 0		4·731	
1 0 0		4·725		12
	1 1 0		4·731	
	1 1 2		3·204	
1 0 2		3·203		100
	0 2 2		3·204	
	2 0 0		2·731	
1 1 0		2·732		46
	1 3 0		2·731	
	0 4 0		2·365	
2 0 0		2·368		5
	2 2 0		2·365	
	2 0 2		2·314	
1 1 2		2·316		8
	1 3 2		2·314	
0 0 4	0 0 4	2·177	2·177	15
	0 4 2		2·078	
2 0 2		2·076		24
	2 2 2		2·078	
	1 1 4		1·978	
1 0 4		1·978		9
	0 2 4		1·978	
	2 0 4		1·702	
1 1 4		1·701		18
	1 3 4		1·702	
	1 5 2		1·654	
2 1 2	2 4 2	1·654	1·654	15
	3 1 2		1·654	
	0 4 4		1·602	
2 0 4		1·601		6
	2 2 4		1·602	
	3 3 0		1·577	
3 0 0		1·576		10
	0 6 0		1·577	

* $a=5·463$, $c=8·710$ Å, hexagonal axes of reference.

† $a=5·463$, $b=9·461$ $(a\sqrt{3})$ and $c=8·710$ Å, orthorhombic axes of reference.

Table 2. *Debye–Scherrer diagram of* α-$BaFe_2O_5$ *at* 1100°C

h k l	d_{obs}	d_{calc}	I_{obs}	I_{calc}
1 0 0	4·726	4·727	13	16
0 0 2	–	4·508	<2	<1
1 0 1	4·185	4·186	11	15
1 0 2	3·264	3·262	100	100
1 1 0	2·730	2·729	48	61
1 1 1	2·613	2·612	7	4
1 0 3	2·538	2·536	14	9
2 0 0	2·363	2·363	9	4
1 1 2	2·335	2·334	9	9
2 0 1	–	2·268	2	3
0 0 4	2·254	2·254	9	10
2 0 2	2·092	2·093	28	26
1 0 4	2·033	2·034	14	11
1 1 3	–	2·020	<2	1
2 0 3	1·857	1·858	4	3
2 1 0	–	1·786	<2	3
1 1 4	1·738	1·738	13	12
1 0 5	1·685	1·685	7	6
2 1 2	1·661	1·661	22	26
2 0 4	1·632	1·631	3	6
3 0 0	1·576	1·576	20	17

Table 3. *Debye–Scherrer diagram of* β'-$BaFe_2O_4$ *at* 20°C

h k l	d_{obs}	d_{calc}	I_{obs}
1 1 0	4·706	4·700	18
0 2 0	4·692	4·662	10
0 1 2	3·857	3·931	16
1 2 0	3·532	3·540	4
1 1 2	3·180	3·187	100
0 2 2		3·175	
2 0 0	2·720	2·721	28
1 3 0	2·699	2·699	50
2 2 0	2·352	2·350	2
2 0 2	2·307	2·305	4
1 3 2	2·288	2·291	2
2 1 2	2·220	2·237	4
0 0 4	2·169	2·167	10
2 2 2	2·066	2·066	18
0 4 2	2·053	2·053	10
1 1 4	1·973	1·968	9
3 1 0	1·785	1·780	3
2 0 4	1·696	1·695	4
3 2 0	1·690	1·690	8
1 3 4		1·690	
2 4 2	1·638	1·639	5
1 5 2	1·634	1·633	5
3 3 0	1·566	1·567	5

Structure determination of α-$BaFe_2O_4$

In a previous work on the crystal chemistry of AB_2O_4 compounds, $BaFe_2O_4$ was assumed to be of the same 'stuffed tridymite structure' as $BaAl_2O_4$, just on the basis of related unit-cell parameters, (Glasser & Dent Glasser, 1963). To test the structure of $BaAl_2O_4$ as a model for α-$BaFe_2O_4$, a computer program (Smith, 1963) to compare theoretical and experimental intensities was used. The atomic parameters herein reported are practically those of the $BaAl_2O_4$ model (Do Dinh & Bertaut, 1965). They yield the best agreement between calculated and measured intensities which are reported in Table 2. The final agreement index of the form $R=\sum|I_{obs}-I_{calc}|/\sum I_{obs}$, is 0·16. Atoms are located in the following positions of the $P6_322$ space group: two barium atoms in 2(*b*) $(0,0,\frac{1}{4};\ 0,0,\frac{3}{4})$; four iron atoms in 4(*f*) $(\frac{1}{3},\frac{2}{3},z$ with $z=0{\cdot}055)$; two oxygen atoms in 2(*c*) $(\frac{1}{3},\frac{2}{3},\frac{1}{4};\ \frac{2}{3},\frac{1}{3},\frac{3}{4})$ with the remaining six oxygen atoms in 6(*g*) (*x*,0,0; *etc.* with $x=0{\cdot}343$). The interatomic distances calculated are Ba–O, 2·93 Å; Fe–O, 1·86 Å; O–O, 2·88 Å and Ba–Fe, 3·61 Å.

Conclusions

On the basis of our results it can be stated that $BaFe_2O_4$ undergoes a first structural rearrangement at 800°C from the γ-$BaFe_2O_4$ form, stable at room temperature, into a β-$BaFe_2O_4$ form stable up to 1000°C. A second transition occurs at 1000°C. Above this temperature the structure was found to be similar to that of $BaAl_2O_4$. Symmetry and lattice parameters of the γ form agree with previously reported values (Okazaki *et al.*, 1963; Do Dinh & Bertaut, 1965). For comparison purposes with high-temperature forms the *a* and *b* axes have been interchanged.

The powder pattern of the high-temperature form could be indexed with a hexagonal metric, with $b=a\sqrt{3}$, within the uncertainty of the standard error. It should be noted however that the alternative orthorhombic unit cell of the β form is comparable with the unit cell of the metastable β′ form, which has an orthorhombic symmetry closely related to the stable γ form, except for a doubling of the *b* axis in the latter. On this basis it can be suggested that the structural rearrangement which occurs at 800°C is probably a transformation from a superstructure into the simpler β form with a halved unit cell. In this case the β form is more efficiently described in terms of an orthorhombic pseudohexagonal unit cell. In a previous work on the chemistry of AB_2O_4 compounds, $BaFe_2O_4$ was considered to have hexagonal symmetry and be related to $BaAl_2O_4$, (Glasser & Dent Glasser, 1963). Our investigation has proved that $BaFe_2O_4$ can be considered of the 'stuffed tridymite type', *i.e.* isomorphous with $BaAl_2O_4$, only above 1000°C, and the structures of the β and β′ forms, found below that temperature, should be considered as orthorhombic deviations of the basic hexagonal structure. Finally the γ form, stable at room temperature, can be looked upon as a superstructure of the β form along the *b* axis.

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Table 4. *Lattice parameters – symmetry and cell content of* $BaFe_2O_4$

Phase	Temperature (°C)	Symmetry	*a* (Å)	*b* (Å)	*c* (Å)	*Z*	D_x (g.cm^{-3})	D_m (g.cm^{-3})
α	1100	hexagonal	5·458 (1)		9·016 (2)	2	4·46	–
β	950	hexagonal*	5·463 (3)		8·710 (5)	2	4·62	–
			5·463 (3)	9·461 (5)	8·710 (5)	4	4·62	–
β′	20	orthorhombic	5·442 (3)	9·325 (6)	8·670 (5)	4	4·73	4·69
γ	20	orthorhombic	5·387 (2)	19·056 (6)	8·458 (3)	8	4·79	4·71

* Possibly pseudohexagonal. Parameters for hexagonal axes of reference are given in the first line, for orthorhombic axes in the second.