

projection of the C(5)C(6)C(7)-moiety (the 't-Bu' group) along the C(4)C(3) bond is given in Fig. 2(b). An average twist from the perfectly staggered position of  $17.4^\circ$  is observed.

The molecular strain is relieved by an overall flattening of the chair and not by adopting a 'twist' conformation. The distortion of the ring and the observed twist of the 't-Bu' group may be due to non-bonded contacts between the methyl-hydrogen atoms and ring-hydrogen atoms. Relevant contacts, smaller than  $2.50 \text{ \AA}$ , are shown in Fig. 4. As far as we know this is the first 1,2-diaxially substituted cyclohexane chair thus far reported.

The C(4)C(7)O(1)O(2)-group is planar within experimental error. The atoms C(5) and C(8) are  $0.155$  and  $0.128 \text{ \AA}$  at either side from this plane. The C=O and C(4)-C(5) bonds deviate  $6.2^\circ$  from being eclipsed [Fig. 2(c)]. This orientation is in excellent agreement with the situation usually found in aliphatic carboxylic acids (Kanters, Kroon, Peerdeman & Schoone, 1967) and with the conformation of an axial carboxyl group in cyclohexanecarboxylic acids (van Koningsveld, 1972 and references cited therein). The orientation of the methyl groups is shown in Fig. 3. The large H(82)C(8)H(83) angle ( $136^\circ$ ) cannot be conclusively explained.

The packing of the molecules in the crystal is illustrated in Fig. 4. The cyclohexane rings form strings along the [110] direction. The strings are held together by non-bonding contacts between the 2-carboxymethyl-2-propyl groups. Some short hydrogen-hydrogen distances ( $< 2.50 \text{ \AA}$ ) are given in the figure.

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#### References

- ALLINGER, N. L. & FREIBERG, L. A. (1960). *J. Amer. Chem. Soc.* **82**, 2393-2394.  
 ALLINGER, N. L., HIRSCH, J. A., MILLER, M. A., TYMINSKI, I. J. & VAN-CATLEDGE, F. A. (1968). *J. Amer. Chem. Soc.* **90**, 1199-1210.  
 ALLINGER, N. L., MILLER, M. A., VAN-CATLEDGE, F. A. & HIRSCH, J. A. (1967). *J. Amer. Chem. Soc.* **89**, 4345-4357.  
 ALTONA, C. & SUNDARALINGAM, M. (1970). *Tetrahedron*, **26**, 925-939.  
 BEKKUM, H. VAN., HOEFNAGEL, M. A., DE LAVIETER, L. & VAN VEEN, A. (1967). *Rec. Trav. Chim. Pays-Bas*, **86**, 1363-1371.  
 GRAAF, B. VAN DE (1972). Work in progress. Delft University of Technology, Delft.  
*International Tables for X-ray Crystallography* (1968). Vol. III, p. 202. Birmingham: Kynoch Press.  
 KANTERS, J. A., KROON, J., PEERDEMAN, A. F. & SCHOONE, J. C. (1967). *Tetrahedron*, **23**, 4027-4033.  
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849-859.  
 KONINGSVELD, H. VAN (1972). *Acta Cryst.* **B28**, 1189-1195.  
 REMIJNSE, J. D. (1971). Thesis, Delft University of Technology, Delft.  
 STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY-70 System. Univ. of Maryland, College Park Md.  
 STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, pp. 454-457. New York: Macmillan.  
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151-152.

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## An X-ray Study of Two Phases of $\text{BaFeO}_{3-x}$

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$\text{BaFeO}_{3-x}$  shows several phases depending upon the iron valence. In  $\alpha\text{-BaFeO}_{2.5}$ , which is orthorhombic, with  $a = 5.911 \pm 0.003$ ,  $b = 16.450 \pm 0.008$ ,  $c = 11.037 \pm 0.006 \text{ \AA}$ , the iron atom is strictly trivalent.  $\text{BaFeO}_{2.67}$ , which is hexagonal with  $a = 5.683 \pm 0.002$ ,  $c = 13.916 \pm 0.005 \text{ \AA}$ , space group  $P6_3/mmc$ , is isomorphous with  $\text{BaTiO}_3$ .

### Introduction

The compound  $\text{BaFeO}_{3-x}$ , barium orthoferrate, has been examined by many authors (Erchak, Fankuchen & Ward, 1946; Malinofsky & Kedesdy, 1954; Brisi, 1955; Gallagher, MacChesney & Buchanan, 1965; MacChesney, Potter, Sherwood & Williams, 1965; Mori, 1966) to determine its phase equilibrium diagram and structural properties.

The valence of the iron atom and the crystal structure of barium orthoferrate depend upon temperature, firing atmosphere and cooling rate.

The present investigation was undertaken to ascertain the isomorphism between hexagonal  $\text{BaFeO}_{3-x}$  and  $\text{BaTiO}_3$ , suggested by Malinofsky & Kedesdy (1954), Brisi (1955), Gallagher *et al.* (1965), MacChesney *et al.* (1965), and Mori (1966) and to determine the crystal data of a phase quenched at

temperatures higher than 915°C and hereafter called  $\alpha$ -BaFeO<sub>2.5</sub>, with the iron atom strictly trivalent.

### Experimental

The  $\alpha$ -BaFeO<sub>2.5</sub> phase was obtained by sintering pressed pellet mixtures of BaCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in a 2:1 molecular ratio in air at 1300°C. The sintered product was quenched in air from 1300°C. Other samples were quenched from 950°C and from 1100°C respectively. Iodometric analysis of these samples showed that the percentage of Fe<sup>4+</sup> was lower than 1%.

Fragments of the compound quenched from 950°C were reheated in vacuum at 1100°C for several hours and then quenched in vacuum. These fragments did not reveal the presence of Fe<sup>4+</sup> on iodometric analysis. The reflexions from these samples were obtained with a Siemens diffractometer and a Guinier camera, using Co K $\alpha$  radiation. All the compounds exhibited the same values of interplanar spacings, which were indexed according to an orthorhombic symmetry.

The  $\alpha$ -phase was then ground and reheated at 900°C in air for several hours and slowly cooled. The product obtained exhibited a hexagonal symmetry and a formula BaFeO<sub>2.67</sub> on iodometric determination of the percentage of Fe<sup>4+</sup>. The structure of this phase, isomorphous with BaTiO<sub>3</sub>, was determined by recording reflexions with a scintillation counter in conjunction with a pulse-height analyser, using Co K $\alpha$  radiation on a Siemens diffractometer.

### X-ray analysis

MacChesney *et al.* (1965) reported the data of a phase of barium orthoferrate, with trivalent iron, and suggested it to be orthorhombic ( $a=5.83$ ,  $b=16.38$ ,  $c=5.54$  Å). However, the values of the spacing calculated with these parameters did not completely reproduce the X-ray pattern of our compound  $\alpha$ -BaFeO<sub>2.5</sub>. Duplication of the  $c$  axis permitted us to index all the reflexions of our pattern. The least-squares refined lattice parameters of this  $\alpha$ -phase are:  $a=5.911 \pm 0.003$ ,  $b=16.450 \pm 0.008$ ,  $c=11.037 \pm 0.006$  Å at room temperature ( $Z=16$ ,  $D_{\text{obs}}=5.7$  g cm<sup>-3</sup>,  $D_{\text{calc}}=5.77$  g cm<sup>-3</sup>). Systematic extinctions occurred for  $h00$  reflexions with  $h \neq 2n$  and  $0k0$  with  $k \neq 2n$ ; no extinction was observed for the general reflexions  $hkl$ . The proposed space group is  $P2_12_12$ , No. 18 of *International Tables for X-ray Crystallography* (1952). The final data for the observed and calculated interplanar spacings are reported in Table 1.

The lattice dimensions of BaFeO<sub>3-x</sub>, hexagonal phase, are a function of the percentage of Fe<sup>4+</sup> (Mori, 1966). Our product, BaFeO<sub>2.67</sub>, gave the least-squares refined lattice parameters  $a=b=5.683 \pm 0.002$ ,  $c=13.916 \pm 0.005$  Å ( $Z=6$ ,  $D_{\text{obs}}=5.9$  g cm<sup>-3</sup>,  $D_{\text{calc}}=6.03$  g cm<sup>-3</sup>). The BaTiO<sub>3</sub> structure, hexagonal, space group  $P6_3/mmc$  (No. 194 of *International Tables for*

Table 1. *Debye-Scherrer diagram of  $\alpha$ -BaFeO<sub>2.5</sub>, orthorhombic phase, at 20°C*

* For a formula BaFeO <sub>3</sub> .						
$h$	$k$	$l$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{obs}}$	
0	0	1	11	11.037	w	
0	4	0	4.125	4.113	w	
1	0	2	4.041	4.035	m	
0	0	3	3.675	3.679	vw	
0	4	2	3.303	3.297	vw	
1	1	3	3.070	3.069	vw	
1	2	3	2.928	2.920	s	
2	1	0	2.906	2.909	s	
1	5	0	2.876	2.879	vs	
2	2	0	2.786	2.782	s	
2	2	1	2.704	2.700	vw	
0	6	1	2.653	2.660	vw	
2	3	0	2.601	2.602	vw	
1	5	2	2.552	2.550	vw	
0	3	4	2.463	2.464	w	
1	2	4	2.394	2.393	m	
2	0	3	2.303	2.304	w	
1	3	4	2.276	2.275	vw	
1	7	0	2.185	2.184	w	
0	5	4	2.110	2.114	vw	
1	0	5	2.067	2.068	m	
0	8	1	2.021	2.021	m	
2	1	4	2.003	2.002	vw	
0	7	3	1.982	1.980	vw	
1	3	5	1.935	1.935	vw	
2	3	4	1.900	1.893	w	
3	1	2	1.845	1.845	w	
0	5	5	1.834	1.834	vw	}
1	8	2	1.834	1.833		
0	9	1	1.803	1.803	vw	
2	0	5	1.772	1.769	vw	
3	0	3	1.739	1.738	vw	
2	3	5	1.684	1.683	m	
2	8	1	1.668	1.668	w	
3	3	3	1.656	1.656	w	
0	9	3	1.635	1.637	w	
2	4	5	1.624	1.625	w	}
2	6	4	1.624	1.624		
2	7	4	1.531	1.531	vw	
3	7	0	1.510	1.510	vw	

Intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

*X-ray Crystallography*, 1952), was reported by Burbank & Evans (1948). The structure of BaTiO<sub>3</sub> was tested as a model of BaFeO<sub>2.67</sub> by means of a computer program (Smith, 1967). The final agreement index  $R = \sum ||I_o| - |I_c|| / \sum |I_o|$  is 0.095. The structure of BaFeO<sub>2.67</sub> is therefore considered to be of the same type as that of BaTiO<sub>3</sub>.

In terms of the positions of the space group  $P6_3/mmc$  the proposed atomic positions are:

2 Ba(1) in (b):	0	0	$\frac{1}{4}$	
4 Ba(2) in (f):	$\frac{1}{3}$	$\frac{2}{3}$	$z$ , $z=0.097$	
2 Fe(1) in (a):	0	0	0	
4 Fe(2) in (f):	$\frac{1}{3}$	$\frac{2}{3}$	$z$ , $z=0.845$	
*6 O(1) in (h):	$x$	$2x$	$\frac{1}{4}$ , $x=0.522$	
*12 O(2) in (k):	$x$	$2x$	$z$ , $x=0.836$ , $z=0.076$	

Table 2. Debye-Scherrer diagram of BaFeO<sub>2.67</sub>, hexagonal phase, at 20°C

<i>h k l</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>obs</sub>	<i>I</i> <sub>calc</sub>
0 0 2		6.958	<1	<1
1 0 1	4.635	4.640	3	2
1 0 2	4.023	4.018	15	10
0 0 4		3.479	<1	1
1 0 3	3.378	3.376	33	40
1 1 0		2.842		100
1 0 4	2.841	2.841	170	70
1 1 2		2.631	<1	<1
2 0 1		2.423		3
1 0 5	2.420	2.422	5	4
2 0 2		2.320		10
0 0 6		2.319		6
1 1 4	2.199	2.201	2	3
2 0 3	2.175	2.174	23	22
2 0 4	2.007	2.009	36	33
2 1 1		1.844	<1	1
2 0 5		1.8435		4
1 0 7	1.843	1.843	13	11
2 1 2		1.797		3
1 1 6	1.798	1.796	11	6
0 0 8		1.739	<1	1
2 1 3	1.727	1.727	7	9
3 0 0		1.641		17
2 1 4	1.641	1.6404	43	24
1 0 8		1.640		2
2 1 5		1.547		2
2 0 7	1.548	1.546	8	7
1 1 8	1.485	1.487	12	5
1 0 9	1.478	1.479		4
2 0 8		1.422		3
2 2 0	1.420	1.419	19	14

The significant interatomic distances are:

Ba(1)-Ba(2)	3.913 Å	Ba(2)-O(1)	2.824 Å
Ba(1)-Fe(1)	3.479	Ba(2)-O(2)	2.854
Ba(1)-Fe(2)	3.539	Fe(1)-Fe(2)	3.928
Ba(1)-O(1)	2.850	Fe(2)-O(1)	1.945
Ba(2)-Fe(1)	3.549	O(1)-O(2)	2.880

The best final data for the observed and calculated intensities and interplanar spacings are reported in Table 2.

## References

- BRISI, C. (1955). *Ann. Chim. (Rome)*, **45**, 431-438.  
 BURBANK, R. D. & EVANS, H. T., JR (1948). *Acta Cryst.* **1**, 330-336.  
 ERCHAK, M., JR, FANKUCHEN, I. & WARD, R. (1946). *J. Amer. Chem. Soc.* **68**, 2085-2093.  
 GALLAGHER, P. K., MACCHESNEY, J. B. & BUCHANAN, D. N. E. (1965). *J. Chem. Phys.* **43**, 516-520.  
*International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.  
 MACCHESNEY, J. B., POTTER, J. F., SHERWOOD, R. C. & WILLIAMS, H. I. (1965). *J. Chem. Phys.* **43**, 3317-3322.  
 MALINOVSKY, W. W. & KEDESZY, H. (1954). *J. Amer. Chem. Soc.*, **76**, 3090-3091.  
 MORI, S. (1966). *J. Amer. Ceram. Soc.* **49**, 600-605.  
 SMITH, D. K. (1967). UCRL-50264. 12 June 1967. Lawrence Radiation Laboratory, Livermore, California.

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## The Crystal Structure of 1*H*,3*H*-Naphtho[1,8]thiopyrane

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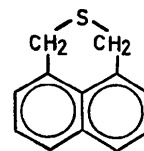
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Crystals of 1*H*,3*H*-naphtho[1,8]thiopyrane, C<sub>12</sub>H<sub>10</sub>S, are monoclinic (*P*2<sub>1</sub>/*c*) with *a* = 15.2305, *b* = 9.0518, *c* = 14.6491 Å and β = 108.37°. There are two molecules in the asymmetric unit. No individual bond lengths deviate by more than three standard deviations from the corresponding average values. The lengths of the differently located bonds in the aromatic system agree well with those reported earlier for the naphthalene nucleus. The hetero-atom is 0.94 Å out of the plane of the rest of the molecule.

### Introduction

In connexion with studies on ring systems containing sulphur and selenium atoms Biezais-Zirnis & Fredga (1971) prepared some compounds with the hetero-atoms attached to a 1,8-dimethylnaphthalene nucleus. The crystal structure of 1*H*,4*H*-naphtho[1,8]diselenepine was earlier determined at this research unit (Aleby, 1972). In this connexion it was also considered desirable to perform an X-ray analysis of 1*H*,3*H*-naphtho[1,8]thiopyrane (NTP, I).



(I)

### Experimental

Recrystallization of NTP from petroleum spirit gave colourless crystals with a rhombic shape. The