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Acta Cryst. (1975). B31, 2012

The Crystal Structure of Hexagonal BaSrFe₄O₈

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(Received 23 October 1974; accepted 24 February 1975)

The structure of hexagonal BaSrFe₄O₈ was redetermined and found to be isostructural with BaCaFe₄O₈ (space group $P\bar{3}1m$). Mössbauer spectra and magnetic measurements showed BaCaFe₄O₈ and BaSrFe₄O₈ to be anti-ferromagnetic, with a Neél temperature higher than 1000 K. Ca²⁺ can be substituted by Sr²⁺ only, Fe³⁺ partially by Al³⁺ and Ga³⁺.

Introduction

Hexagonal BaSrFe₄O₈ was first reported by Kanamaru & Kiriya (1964). In a determination of the crystal structure (Lucchini, Minichelli & Meriani, 1973) a structure related to that of BaAl₂O₄ (Wallmark & Westgren, 1937) was found. The X-ray powder diffraction patterns of hexagonal BaSrFe₄O₈ prepared by us showed that this compound could be isostructural with BaCaFe₄O₈ (Herrmann & Bacmann, 1971). Comparison of the unit-cell dimensions supported this conclusion. Relating the structure of BaSrFe₄O₈ to the structure of BaAl₂O₄, the *c* axis is expected to be about 8.6 Å [mean value of the *c* axis of BaAl₂O₄ and SrAl₂O₄ (Glasser & Dent-Glasser, 1963)]. The unit-cell dimensions of these compounds are presented in Table 1.

Experimental

Commercially available BaCO₃, SrCO₃ and Fe₂O₃ (P. A.) were thoroughly mixed in an agate mortar under acetone and then fired at 1000°C for one day, reground and fired twice for several days and finally fired at 1000°C for two weeks. The X-ray powder diffraction pattern showed one phase and could be indexed as hexagonal with unit-cell dimensions $a=5.4464(9)$ and $c=8.0817(14)$ Å (the numbers in parentheses giving the standard deviation in units of the last decimal). No systematic absences were found. X-ray intensities were collected from a powder pattern of all reflexions between 5 and 110° in 2θ , recorded with a Philips diffractometer, using Cu $K\alpha$ radiation with a graphite monochromator.

Table 1. Unit-cell dimensions (Å) of some hexagonal AB₂O₄ compounds

Compound	<i>a</i>	<i>c</i>	Reference
BaAl ₂ O ₄	5.209	8.761	Wallmark & Westgren (1937)
SrAl ₂ O ₄	5.10	8.49	Glasser & Dent-Glasser (1963)
BaCaFe ₄ O ₈	5.407	7.703	Herrmann & Bacmann (1971)
BaSrFe ₄ O ₈	5.448	8.091	Lucchini, Minichelli & Meriani (1973)
BaSrFe ₄ O ₈	5.446	8.082	This publication
BaSrFe ₄ O ₈	5.15	8.62	Expected for BaSrFe ₄ O ₈ related to BaAl ₂ O ₄

Models

Five starting models of the BaSrFe₄O₈ structure were chosen for a least-squares refinement. The ion positions are shown in Fig. 1 and Table 2.

Model 1 (Fig. 1a) is isostructural with BaCaFe₄O₈, spacegroup $P\bar{3}1m$ with the layer sequence BaO₂, O₃, Sr◇◇,* O₃ and BaO₂. The layers are h.c.-stacked. The Fe³⁺ ions are between the BaO₂ and the O₃ layers, in a tetrahedron of O²⁻ ions. The Sr²⁺ ion is surrounded by six O²⁻ ions, forming an octahedron. The Ba²⁺ ion is surrounded by 12 O²⁻ ions.

* The symbol ◇ means an oxygen vacancy.

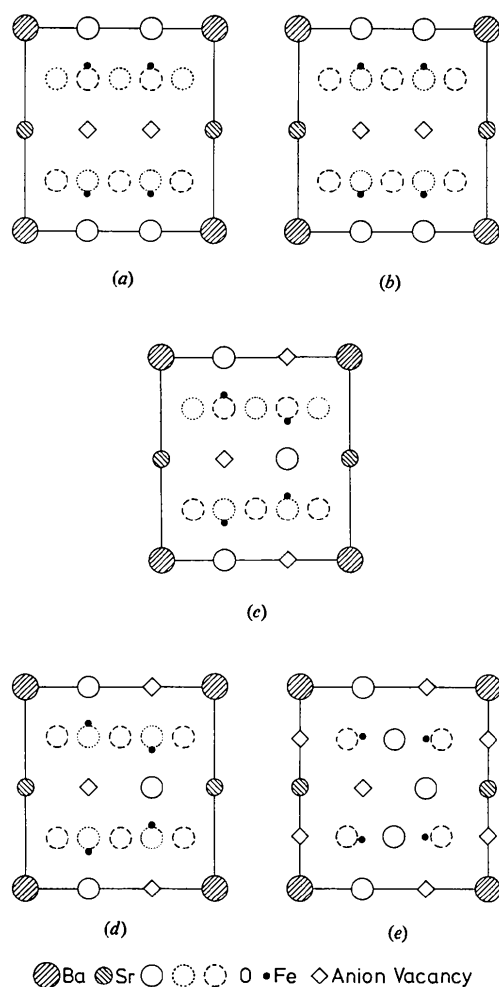


Fig. 1. Projections on the plane $(11\bar{2}0)$ of the relevant part of the five structure models of hexagonal $\text{BaSrFe}_4\text{O}_8$, used for the least-squares refinement. The oxygen ions indicated with broken circles are situated above the $(11\bar{2}0)$ plane, the oxygen ions indicated with dotted circles are situated below the $(11\bar{2}0)$ plane.

Model 2 (Fig. 1*b*) has the same cation positions as the first model, the layer sequence is: BaO_2 , O_3 , $\text{Sr}\diamond$, O_3 , and BaO_2 like the first model, whereas the layers are h.-stacked. The space group is $P\bar{6}2m$. The Sr^{2+} ion is surrounded by six O^{2-} ions, forming a trigonal prism.

Model 3 (Fig. 1*c*) is isostructural with BaAl_2O_4 ; Ba^{2+} and Sr^{2+} are placed in special positions (see Table 2), lowering the symmetry from $P6_322$ (space group of BaAl_2O_4), to $P312$. The layer sequence in this model is: $\text{BaO}\diamond$, O_3 , $\text{SrO}\diamond$, O_3 , and $\text{BaO}\diamond$; the layers are h.c.-stacked. Both Ba^{2+} and Sr^{2+} are surrounded by nine O^{2-} ions, three in their own layer, three in the lower and three in the upper layer, the latter six O^{2-} ions forming an octahedron. The Fe^{3+} ions are between the layers, surrounded by a tetrahedron of O^{2-} ions.

Model 4 (Fig. 1*d*) has the same cation positions as the third model and the same layer sequence, with h.-stacked layers. The space group is $P\bar{6}$. Ba^{2+} and Sr^{2+} are both surrounded by nine O^{2-} ions, like the third model, but the six O^{2-} ions in the O_3 layers are now forming a trigonal prism.

Model 5 (Fig. 1*e*) is the structure found by Lucchini, Minichelli & Meriani (1973). The space group is $P\bar{6}m2$, the layer sequence is: $\text{BaO}\diamond$, $\text{O}_3\diamond$, $\text{SrO}\diamond$, and $\text{BaO}\diamond$. The coordination of the Ba^{2+} ion and the Sr^{2+} ion is not easy to describe. The Fe^{3+} ions are lying between the layers, surrounded by a tetrahedron of O^{2-} ions. The Fe^{3+} ions are lying almost in the $\text{O}_3\diamond$ layers, the tetrahedra are strongly distorted.

Structure determination

For the least-squares refinement the computer program *T53* for overlapping powder reflexions was used (Rietveld, 1969). Atomic scattering curves were taken from Cromer & Waber (1965). The observed intensities were used without absorption correction.

The best agreement was found with model 1, the

Table 2. Ion positions of the five starting models of $\text{BaSrFe}_4\text{O}_8$

Model	Space group	Ba^{2+}	Sr^{2+}	$\text{Fe}^{3+}(1)$	$\text{Fe}^{3+}(2)$	$\text{O}^{2-}(1)$	$\text{O}^{2-}(2)$	$\text{O}^{2-}(3)$	
1. h.c. $\text{BaCaFe}_4\text{O}_8$	$P\bar{3}1m$	1 (a)	1 (b)	4 (h)		2 (c)	6 (k)		
		0	0	$\frac{1}{3}$		$\frac{1}{3}$	0.333	(x)	
		0	0	$\frac{2}{3}$		$\frac{2}{3}$	0	(y)	
		0	$\frac{1}{2}$	0.188		0	0.260	(z)	
		0	0	$\frac{1}{3}$		$\frac{1}{3}$	0	(x)	
2. h. $\text{BaCaFe}_4\text{O}_8$	$P\bar{6}2m$	1 (a)	1 (b)	4 (h)		2 (c)	6 (i)		
		0	0	$\frac{1}{3}$		$\frac{1}{3}$	0.333	(x)	
		0	0	$\frac{2}{3}$		$\frac{2}{3}$	0	(y)	
		0	$\frac{1}{2}$	0.188		0	0.260	(z)	
		0	0	$\frac{1}{3}$		$\frac{1}{3}$	0	(y)	
3. h.c. BaAl_2O_4	$P312$	1 (a)	1 (b)	2 (h)	2 (i)	1 (c)	1 (f)	6 (l)	
		0	0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	0.333	(x)
		0	0	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	0.001	(y)
		0	$\frac{1}{2}$	0.188	0.313	0	$\frac{1}{2}$	0.260	(z)
		0	0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	0.333	(x)
4. h. BaAl_2O_4	$P\bar{6}$	1 (a)	1 (b)	2 (h)	2 (i)	1 (c)	1 (f)	6 (l)	
		0	0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	0.333	(x)
		0	0	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	0.001	(y)
		0	$\frac{1}{2}$	0.188	0.313	0	$\frac{1}{2}$	0.260	(z)
		0	0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	0.333	(x)
5. Lucchini	$P\bar{6}m2$	1 (a)	1 (b)	2 (h)	2(i)	1 (c)	1 (f)	6 (n)	
		0	0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	0.515	(x)
		0	0	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	0.485	(y)
		0	$\frac{1}{2}$	0.245	0.255	0	$\frac{1}{2}$	0.260	(z)
		0	0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	0.333	(x)

final R value was 0.041 ($R = \sum |I_{\text{obs}} - I_{\text{calc}}| / \sum I_{\text{obs}}$). The final R value of model 2 was 0.058, which is understandable since the difference between the models is only in the positions of three O^{2-} ions. The other models generated very high R values. Hexagonal BaSrFe₄O₈ is thus found to be isostructural with BaCaFe₄O₈. The final parameters are listed in Table 3, with the final parameters of the refinement of model 2. Table 4 shows the shortest distances for the refinements of models 1 (see also Fig. 2) and 2, calculated by the computer program T172 (Rietveld, 1969). Table 5 shows the observed and calculated intensities and d values of the reflexions.*

A calculation with the computer program T53, using the reflexion data of Lucchini, Minichelli & Meriani (1973), showed better results using the final parameters of BaSrFe₄O₈, $P\bar{3}1m$ than using the final parameters published by Lucchini, Minichelli & Meriani. All calculations were carried out with the I.B.M. 370 computer of the University of Leiden.

Discussion of the structure

The final z parameter of the Fe^{3+} ions and the O^{2-} ions in the $6(k)$ position differs considerably from the starting parameters. In the models the Sr $\diamond\diamond$ layer is considered to be equivalent to the O_3 layers in the stacking. This of course is not true: the O_3 layers are situated nearer to the Sr $\diamond\diamond$ than to the BaO_2 layer, so the z parameter of the O^{2-} ions in the $6(k)$ position will increase. The Fe^{3+} ions are situated in a tetrahedron of O^{2-} ions, with an increasing z parameter too, as in the final structure the Fe^{3+} ions are situated in an almost ideal tetrahedron of O^{2-} ions. The same effect was found for BaCaFe₄O₈ (Herrmann & Bacmann, 1971). The Sr $\diamond\diamond$ layer, or in BaCaFe₄O₈ the

Ca $\diamond\diamond$ layer, is not very realistic but useful for the description of the structure. A more realistic description of the BaCaFe₄O₈ structure is a c.-stacked anion lattice with the layer sequence $\text{BaO}_2, \text{O}_3, \text{O}_3$ and BaO_2 with Ca^{2+} in an octahedron of O^{2-} ions between the two O_3 layers and the four Fe^{3+} ions in tetrahedra of O^{2-} ions between the BaO_2 and the O_3 layers. This structure resembles the structure of $\text{KAl}(\text{SO}_4)_2$, also a c.-stacked anion lattice, with layer sequence $\text{KO}_2, \text{O}_3, \text{O}_3$ and KO_2 with Al^{3+} in an octahedron of O^{2-} ions between the two O_3 layers and the two sulphur ions in tetrahedra of O^{2-} ions between the KO_2 and the O_3 layers (Manoli, Herpin & Pannetier, 1970).

Lattice Energy of BaSrFe₄O₈

The Madelung part of the lattice energy (MAPLE) (Hoppe, 1970) was calculated by the MADF computer program of the University of Giessen (West Germany). The MAPLE value of BaSrFe₄O₈, $P\bar{3}1m$, is somewhat higher than that of BaSrFe₄O₈, $P\bar{6}2m$, owing to the larger Ba–O(2) distances in BaSrFe₄O₈, $P\bar{6}2m$. The MAPLE balance of the formation of BaSrFe₄O₈, $P\bar{3}1m$, from the binary oxides is positive, owing to the lower coordination number of the O^{2-} ions (4.5 in the binary

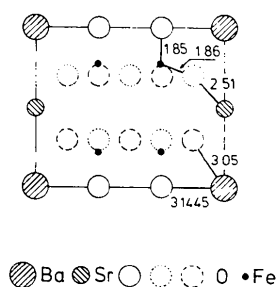


Fig. 2. Projection on the plane $(11\bar{2}0)$ of the relevant part of the structure of hexagonal BaSrFe₄O₈ with indicated shortest distances. The oxygen ions indicated with broken circles are situated above the $(11\bar{2}0)$ plane, the oxygen ions indicated with dotted circles are situated below the $(11\bar{2}0)$ plane.

Table 3. Final parameters of the refinements of models 1 and 2 of hexagonal BaSrFe₄O₈

Space-group $P\bar{3}1m$, model 1					Space-group $P\bar{6}2m$, model 2				
	x	y	z	B		x	y	z	B
Ba ²⁺ 1 (<i>a</i>)	0	0	0	1.03 (14)	Ba ²⁺ 1 (<i>a</i>)	0	0	0	0.97 (17)
Sr ²⁺ 1 (<i>b</i>)	0	0	$\frac{1}{2}$	0.14 (18)	Sr ²⁺ 1 (<i>b</i>)	0	0	$\frac{1}{2}$	0.20 (23)
Fe ³⁺ 4 (<i>h</i>)	$\frac{1}{3}$	$\frac{2}{3}$	0.2293 (9)	0.60 (14)	Fe ³⁺ 4 (<i>h</i>)	$\frac{1}{3}$	$\frac{2}{3}$	0.228 (1)	0.62 (18)
O ²⁻ (1) 2 (<i>c</i>)	$\frac{1}{3}$	$\frac{2}{3}$	0	1.6 (10)	O ²⁻ (1) 2 (<i>c</i>)	$\frac{1}{3}$	$\frac{2}{3}$	0	0.62 (110)
O ²⁻ (2) 6 (<i>k</i>)	0.347 (4)	0	0.296 (3)	0.70 (60)	O ²⁻ (2) 6 (<i>i</i>)	0.349 (5)	0	0.303 (3)	1.77 (84)

Table 4. Shortest distances (Å) from the final refinements of models 1 and 2 of hexagonal BaSrFe₄O₈

	Space-group $P\bar{3}1m$, model 1					Space-group $P\bar{6}2m$, model 2					
	Ba ²⁺	Sr ²⁺	Fe ³⁺	O ²⁻ (1)	O ²⁻ (2)	Ba ²⁺	Sr ²⁺	Fe ³⁺	O ²⁻ (1)	O ²⁻ (2)	
Ba ²⁺	5.4464 (0)	4.0409 (0)	3.650 (4)	3.1445 (0)	3.05 (2)	Ba ²⁺	5.4464 (0)	4.0409 (0)	3.646 (4)	3.1445 (0)	3.10 (3)
Sr ²⁺	4.0409 (0)	5.4464 (0)	3.830 (4)	> 4.0	2.51 (2)	Sr ²⁺	4.0409 (0)	5.4464 (0)	3.836 (5)	> 4.0	2.48 (3)
Fe ³⁺	3.650 (4)	3.830 (4)	3.1444 (6)	1.85 (1)	1.86 (1)	Fe ³⁺	3.645 (4)	3.836 (5)	3.1444 (6)	1.84 (1)	1.87 (2)
O ²⁻ (1)	3.1445 (0)	> 4.0	1.85 (1)	3.1440 (0)	2.98 (2)	O ²⁻ (1)	3.1444 (0)	> 4.0	1.84 (1)	3.1445 (0)	3.02 (2)
O ²⁻ (2)	3.05 (2)	2.51 (2)	1.86 (1)	2.98 (2)	3.08 (1)	O ²⁻ (2)	3.10 (3)	2.48 (3)	1.87 (2)	3.02 (2)	3.07 (2)

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oxides, 4.25 in BaSrFe₄O₈). The MAPLE value is within the range of 2% of the sum of the MAPLE values of the binary oxides (SrO, BaO, 2Fe₂O₃). This is an indication that the structure found is a realistic one (Vielhaber & Hoppe, 1971, 1972). The MAPLE value of model 5 is 9% higher than the sum of the binary oxides. The MAPLE values are shown in Table 6.

Table 6. MAPLE values in kcal mol⁻¹ of the BaSrFe₄O₈ models 1 and 2 and the constituting binary oxides

Ion	MAPLE	MAPLE	MAPLE
	binary oxides	BaSrFe ₄ O ₈ , P $\bar{3}1m$	BaSrFe ₄ O ₈ , P $\bar{6}2m$
Ba ²⁺	420.0	355.8	331.3
Sr ²⁺	449.5	508.1	536.0
Fe ³⁺	1200.3	1195.9	1183.6
O ²⁻ (BaO)	420.0		
O ²⁻ (SrO)	449.5		
O ²⁻ (Fe ₂ O ₃)	573.4		
O ²⁻ (gem.)	538.7		
O ²⁻ (1)		567.1	595.8
O ²⁻ (2)		546.9	532.8
O ²⁻ (gem.)		552.0	547.3
Total	9979.7	10062.6	9987.7

Magnetic properties

Mössbauer spectroscopy showed a strong magnetic order at room temperature ($H=425\text{kOe}$ for BaCaFe₄O₈ and $H=415\text{kOe}$ for BaSrFe₄O₈). Magnetic measurements carried out with a Faraday balance showed both compounds to be antiferromagnetic. The Neél temperature could not be detected, for it was out of the range of the apparatus, but is over 1000K, the upper limit of our measurements. Herrmann & Bacmann (1971) also found BaCaFe₄O₈ to be antiferromagnetic, with a Neél temperature of 779K, measured by the disappearance of the magnetic scattering by neutrons.

Substitutions in the BaCaFe₄O₈ structure

Several attempts to substitute Ca²⁺ by Pb²⁺ or Mn²⁺ met with no success. The Fe³⁺ ions could be substituted partly by Al³⁺ and Ga³⁺: the pure compounds BaCaFe₃AlO₈ and BaCaGa₂Fe₂O₈ were prepared at respectively 1000 and 1200°C with a firing time of

two weeks, the sample being reground several times. Attempts to substitute more Al³⁺ and Ga³⁺ were not successful, as other phases appeared. Because of the reported high-temperature phase of BaSrFe₄O₈ (Meriani & Slocardi, 1970), d.t.a. experiments were carried out in order to find other high-temperature phases and their melting points. The results are compiled in Table 7.

Table 7. Results of d.t.a. experiments

Compound	Transi-	Transi-	Melting	
	tion point I	tion point II	point	
BaCaFe ₄ O ₈			1220°C	Congruent
BaSrFe ₄ O ₈	1190°C	1220°C	1255	Incongruent
BaCaAlFe ₃ O ₈			1232	Incongruent
BaCaGa ₂ Fe ₂ O ₈			1255	Incongruent

I thank Dr D. J. W. Ydo and Dr A. B. A. Schippers for encouraging discussions, Drs E. C. Kruissink for the d.t.a. experiments, Drs Vermaas for the Mössbauer spectroscopy and Drs J. A. R. van Veen for the magnetic measurements.

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