

Refinements of the Six-Layer Structures of the *R*-Type Hexagonal Ferrites $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ and $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$

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The structures of $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ and $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$ have been determined from neutron powder diffraction data collected at 300 K using the Rietveld profile refinement. The compounds were found to be isostructural, space group $P6_3/mmc$. $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$: $a = 5.8470(2) \text{ \AA}$, $c = 13.6116(9) \text{ \AA}$, $V = 403.01(5) \text{ \AA}^3$, $M = 632.6$, $Z = 2$, $D_{\text{calc.}} = 3.09 \text{ Mg m}^{-3}$, final R -factor = 3.77. $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$: $a = 5.9624(5) \text{ \AA}$, $c = 13.7468(14) \text{ \AA}$, $V = 423.23(10) \text{ \AA}^3$, $M = 774.2$, $Z = 2$, $D_{\text{calc.}} = 3.66 \text{ Mg m}^{-3}$, final R -factor = 2.41. The structure consists of h-stacked BaO_3 and O_4 layers in the ratio 1 : 2. The BaO_3 layers contain a mirror plane. Between the O_4 layers three octahedral sites are occupied, and between the BaO_3 and O_4 layers an octahedral site and a tetrahedral site are occupied. Because of the mirror plane in the BaO_3 plane the latter sites both share faces in the BaO_3 plane. The octahedral sites are occupied by Fe and Ti or Sn, the pair of tetrahedral sites is occupied by one Fe atom. This Fe atom may hop between these two tetrahedral sites. The structure is considered to be constructed by two R -blocks of the $\text{BaFe}_{12}\text{O}_{19}$ (M) structure. Unit-cell dimensions are given of a number of isostructural compounds of general formula $A^{\text{II}}B_2^{\text{IV}}C^{\text{III}}C_3^{\text{III}}\text{O}_{11}$. Mössbauer experiments on some of these compounds were focused on the tetrahedral positions that show an unusual quadrupole splitting. A brief review is given of the observed magnetic properties of some compounds with the R -structure.

Introduction

The structure of the hexagonal ferrite $\text{BaFe}_{12}\text{O}_{19}$ (M), an important material for permanent magnets, has been described as a stacking of two spinel-blocks and two so-called R -blocks (I), the notation becomes $(RS)_2$. The ferrites $\text{BaFe}_{18}\text{O}_{27}$ (W) and $\text{BaFe}_{15}\text{O}_{23}$ (X) can be described as $(RS)_2$ and R_2S_3 (I , 2). The occurrence of these structures suggested the existence of a compound with a structure R_2 , of which a probable formula is $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$. This compound was reported (3) and the unit-cell dimensions were found to be in good agreement with the expected ones.

A structure determination of $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ based on the X-ray powder diffraction pattern was reported later (4), and the structure suggested by Gorter (3) was almost completely confirmed. Fe and Ti were supposed to be randomly distributed over the available octahedral and tetrahedral sites. The atomic parameters were not refined. Using the results of Mössbauer spectroscopy a refinement of the cation-distribution was carried out for several samples of $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$, that were sintered at different temperatures (5).

During investigations in the $\text{BaO-SnO}_2\text{-Fe}_2\text{O}_3$ system (6) and related systems we found several compounds with unit-cell di-

mensions comparable to those of BaTi₂Fe₄O₁₁. Because of our interest in the completely refined structures of these compounds, we decided to a structure determination from neutron powder diffraction data using the Rietveld profile refinement, as single crystals of these compounds are hard to obtain. Moreover the cation distribution can be determined using neutron diffraction because of the different scattering lengths of Fe, Ti, and Sn.

Experimental

BaTi₂Fe₄O₁₁ and BaSn₂Fe₄O₁₁ were prepared by mixing appropriate ratios of BaCO₃, TiO₂ (anatase) or SnO₂, and Fe₂O₃ in an agate mortar and heating the mixture at 1470 K for several days with repeated grindings. The reaction mixtures were examined using X-ray diffraction. After a heating time of a few hours the title compounds were the main product in the reaction mixture. The heating time had to be extended to almost a week in order to obtain an X-ray powder diffraction pattern of only the pure compound. The heating temperature was chosen at 1470 K because at more elevated temperatures the reduction of Fe³⁺ to Fe²⁺ took place and as a result Fe₃O₄ was found in the reaction product. Fe₃O₄ as an impurity was detected by the Curie-temperature.

When initially lower heating temperatures were applied, the heating time at 1470 K had to be increased considerably to obtain the same results. Both reaction mixtures were air-quenched from 1470 K. The isomorphs were prepared in the same way, but sometimes other preparation techniques were necessary (see below). Unit-cell parameters were obtained from the X-ray powder diffraction patterns using a least-squares refinement program (7).

Neutron diffraction data have been collected at 4.2 and at 300 K for both com-

pounds, in view of the magnetic properties of BaTi₂Fe₄O₁₁ (5) and BaSn₂Fe₄O₁₁ (see below), using the powder diffractometer of the Petten High Flux Reactor (The Netherlands). A wavelength of 2.5788(3) Å from the (111) plane of a copper monochromator was used with a 30' collimation. The angular range $5.4^\circ < 2\theta < 140.4^\circ$ was scanned in steps of 0.144°. Absorption was small and no correction was made. The background points were estimated at regions of the diffraction pattern where reflections were known to be absent. It was decided to make the correction for a probable preferred orientation with aid of the computer program and not to try to prepare a randomly oriented sample using glue, since its hydrogen content would cause a considerable higher background in the diffraction pattern. Crystallites of hexagonal compounds have a preference for a horizontal orientation of their (001) planes.

The Mössbauer measurements at 300 K were performed using an Elscint MVT-2 constant acceleration drive with a 400-channel analyzer. The temperature stability was better than 1 K for indefinite periods. Velocity calibration was obtained by the spectrum of a 0.001-in. iron foil. The initial intensity of the source was 10 mC ⁷⁵Co, diffused into a 6-μm rhodium foil.

The measurements below 77 K were performed by a constant acceleration drive, with the sample in a helium-flow cryostat. The temperature accuracy was about 1 K.

Magnetic susceptibility measurements above 80 K, for the detection of Curie points were carried out with a Faraday balance, equipped with a temperature control (8). Magnetization measurements at 4.2 K and susceptibility measurements below 80 K were performed by means of a P.A.R. vibrating sample magnetometer Model 150 (9). For fields above 56 kOe up to 220 kOe the pulsed field magnet of the Kamerling Onnes Laboratory at Leiden was used (10).

TABLE I

STARTING PARAMETERS FOR THE REFINEMENT OF THE STRUCTURE OF $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ AND $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$, SPACE GROUP $P6_3/mmc$

Atom	Position	x	y	z
Ba	2a	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$
Fe	2d	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$
Oc(1), Ti, Sn	4e	0	0	$\frac{1}{6}$
Oc(2), Fe	6g	$\frac{1}{2}$	0	0
O(1)	4f	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{7}{12}$
O(2)	6h	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{4}$
O(3)	12k	$\frac{1}{6}$	$\frac{2}{6}$	$\frac{1}{12}$

Structure Determination

(a) $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$. The diffraction data collected at 300 K have been refined in the following way. The ideal atomic parameters of the R -structure, space group $P6_3/mmc$ (4) were used as starting parameters with Fe at the 2d and 6g position and Ti at the 4e position (Table I). This occupation has been chosen because an occupation of Ti at the 2d position seemed unlikely in presence of Fe.

The variables in the first refinement were a scale factor, three half-width parameters defining the Gaussian line shape, the counter zero error, the unit-cell dimensions, and an overall temperature factor. After the first runs, the atomic parameters, a preferred orientation parameter, and an asymmetry parameter below $2\theta = 40^\circ$ were introduced. Next, the occupation of Fe and Ti in the octahedral sites 6g and 4e were varied within the overall formula and with the limitation that the total occupation rate of a site remained 100%. Finally, the Fe in the 2d position was changed to a 4f position with an occupation of 50%. The 5-coordination of Fe changed to 4-coordination. The R_1 dropped from 5.82 to 4.29 in this stage of the refinement. The same procedure for the 2d position was used in the structure refinement of $\text{BaFe}_{12}\text{O}_{19}$ (11). Refinements with

Ti at the 4f position yielded higher R -factors. Isotropic temperature factors for three groups of atoms, Ba, the remaining cations and the O-atoms, were used in order to keep the number of parameters as low as possible.

The final R -factors are $R_1 = 3.77$, $R_p = 7.72$, $R_{wp} = 8.87$, and R_{wp} expected = 2.10. For the definition of the R -factors see Ref. (12). The coherent scattering lengths assumed were Ba 5.25, Ti -3.38, Fe 9.54, O 5.805, and Sn 6.228 fm (13). The maximum atomic parameter shift on the last cycle was 0.06 times its esd. The value of the preferred orientation parameter was 0.05(1). The final atomic parameters are presented in Table II. Table III shows the relevant distances and angles in $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$. The diffraction pattern collected at 4.2 K showed almost no differences with the one collected at 300 K. Only some diffuse diffraction lines indicated a magnetic structure with a c -axis of twice the nuclear c -axis, and with the same a -axis. Because of the diffuse character of the magnetic reflections no attempt was made to determine the magnetic structure of this compound.

(b) $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$. The diffraction pattern collected at 300 K was refined in the same way as that of $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$. The final R -factors are $R_1 = 2.41$, $R_p = 5.33$, $R_{wp} = 6.80$, R_{wp} expected = 2.76. The maximum atomic parameter shift on the last cycle was 0.02 times its esd. The final atomic parameters are presented in Table II. Table IV shows the important distances and angles in $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$.

Figure 1 shows the agreement between observed and calculated profiles of both compounds, the (110) plane of the R -structure is shown in Fig. 2, a three-dimensional picture of the unit-cell of the R -structure is given in Fig. 3.

The diffraction pattern collected at 4.2 K also showed some diffuse reflections due to the magnetic structure of $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$. Just like in the case of $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ no attempts

TABLE II
 ATOMIC POSITIONS, OCCUPATION RATES, ISOTROPIC TEMPERATURE FACTORS, AND CHARGE COMPENSATION
 IN THE STRUCTURES OF BaTi₂Fe₄O₁₁ AND BaSn₂Fe₄O₁₁, SPACE GROUP *P6₃/mmc*

Compound	Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	Occupation rate (%)	<i>B</i> (Å ²)	Charge compen- sation
BaTi ₂ Fe ₄ O ₁₁	Ba	2 <i>a</i>	0.3333	0.6667	0.25	100	-0.05(30)	
	Fe	4 <i>f</i>	0.3333	0.6667	0.7322(8)	50	0.62(10)	
	Oc(1) _{Fe} Ti	4 <i>e</i>	0.0	0.0	0.1435(8)	52(1) 48(1)	0.62(10)	
	Oc(2) _{Fe} Ti	6 <i>g</i>	0.5	0.0	0.0	65(1) 35(1)	0.62(10)	
	O(1)	4 <i>f</i>	0.3333	0.6667	0.5783(5)	100	0.21(11)	2.27
	O(2)	6 <i>h</i>	0.8495(5)	0.6990(10)	0.25	100	0.21(11)	2.09
	O(3)	12 <i>k</i>	0.1714(5)	0.4328(9)	0.0810(3)	100	0.21(11)	1.87
BaSn ₂ Fe ₄ O ₁₁	Ba	2 <i>a</i>	0.3333	0.6667	0.25	100	0.02(24)	
	Fe	4 <i>f</i>	0.3333	0.6667	0.7297(5)	50	0.34(6)	
	Oc(1) _{Fe} Sn	4 <i>e</i>	0.0	0.0	0.1409(3)	39(1) 61(1)	0.34(6)	
	Oc(2) _{Fe} Sn	6 <i>g</i>	0.5	0.0	0.0	74(1) 26(1)	0.34(6)	
	O(1)	4 <i>f</i>	0.3333	0.6667	0.5811(4)	100	0.29(8)	2.23
	O(2)	6 <i>h</i>	0.8493(5)	0.6985(10)	0.25	100	0.29(8)	2.13
	O(3)	12 <i>k</i>	0.1759(5)	0.3518(9)	0.0806(2)	100	0.29(8)	1.86

Note. The esd's of the last figure are included in parentheses.

were made to determine the magnetic structure of BaSn₂Fe₄O₁₁.

Discussion of the Structures

The structures found consist of a hexagonal close-packed stacking of two BaO₃- and four O₄-layers. A BaO₃-layer is followed by two O₄-layers. The BaO₃-layer contains a mirror plane in the structure just as reported for the *R*-block in BaFe₁₂O₁₉ (*I*). Ba has a 12-coordination, Ti or Sn and 75% of Fe a 6-coordination, the remaining Fe a 4-coordination.

The most important differences from the starting model are the shift of the atom from the 2*d* position, which means 5-coordination, to the 4*f* position (two separated tetra-

hedral sites), the *z*-parameter of the 4*e* position, and the possibility that Ti or Sn occupy both types of octahedral sites.

The shift from the 2*d* position to the 4*f* position has been proposed already at the refinement of the structure of BaFe₁₂O₁₉ (*II*). The 5-coordinated site is split into a pair of tetrahedral sites, of which the tetrahedra share faces. Of course it is impossible to occupy both tetrahedral sites, the Fe-Fe distance would become too short, thus only one site of a pair can be occupied by Fe. The Fe-Fe distances reported in Tables III, IV, and VI are the distances between both sites of a pair of tetrahedral sites, and will not occur in the structures. These distances have increased compared to the one found in BaFe₁₂O₁₉, 0.312 Å (*II*). It is assumed that both sites of a pair are separated by a

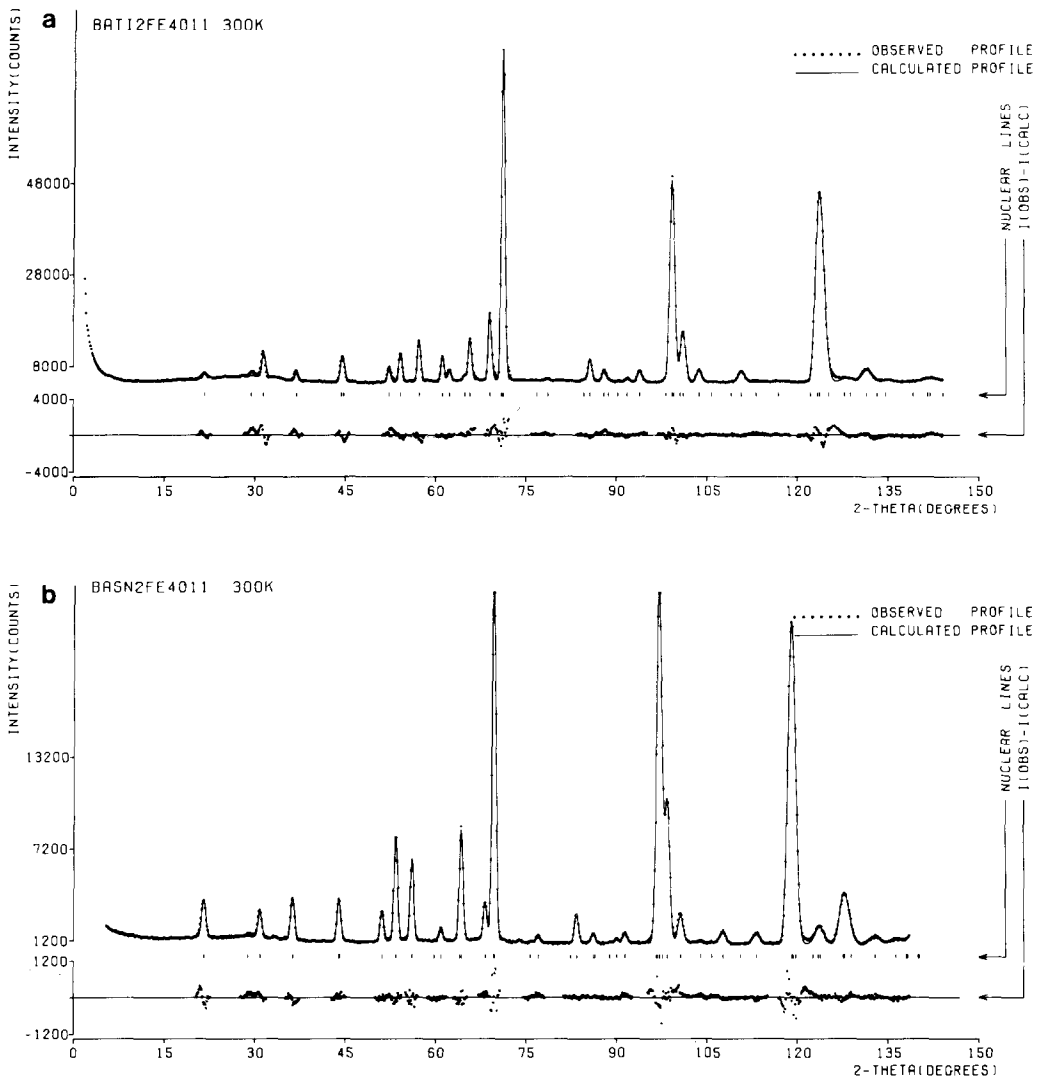


FIG. 1. Observed (dots) and calculated (full line) neutron diffraction profile of $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ at 300 K and $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$ at 300 K. A difference curve (observed - calculated) appears at the bottom of the figure. Thick marks below the profile indicate the positions of the Bragg reflections included in the calculation.

potential barrier. At sufficient high temperature the Fe-atom has enough energy to pass over this barrier. In $\text{BaFe}_{12}\text{O}_{19}$ this temperature was determined to be 150 K, using Mössbauer spectra recorded at different temperatures (14). In $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ and isomorphs this temperature will be comparable but somewhat higher because the Fe-

Fe distance has increased and the face-sharing tetrahedra are more regular than in $\text{BaFe}_{12}\text{O}_{19}$.

By decreasing the z -parameter of the $4e$ position (Oc(1)), the distance between the two cations of the face-sharing octahedra has increased. The Oc(1) octahedron is distorted by this increased distance, and the

TABLE III
RELEVANT DISTANCES (Å) AND ANGLES (°) IN
BaTi₂Fe₄O₁₁

Ba -O(2)	2.928(4)	6×	Ba -Fe	3.384(1)
Ba -O(3)	2.828(4)	6×	Fe -Fe	0.485(24)
Fe -O(1)	2.098(14)	1×	Oc(1)-Oc(1)	2.904(22)
Fe -O(1)	2.583(14)	1×	Oc(2)-Oc(2)	2.923(0)
Fe -O(2)	1.867(5)	3×	O(1)-O(2)	2.984(6)
Oc(1)-O(2)	2.105(8)	3×	O(1)-O(3)	2.924(4)
Oc(1)-O(3)	1.933(7)	3×	O(2)-O(2)	2.640(9)
Oc(2)-O(1)	1.997(4)	2×	O(2)-O(3)	2.828(5)
Oc(2)-O(3)	1.997(4)	4×	O(3)-O(3)	2.840(8)
O(2)-Ba-O(2)	53.6(2)	3×		
O(2)-Ba-O(2)	66.4(2)	3×		
O(2)-Ba-O(2)	120.0(0)	6×		
O(2)-Ba-O(2)	173.6(2)	3×		
O(2)-Ba-O(3)	58.8(1)	12×		
O(2)-Ba-O(3)	91.9(1)	12×		
O(2)-Ba-O(3)	119.0(1)	12×		
O(3)-Ba-O(3)	60.3(2)	6×		
O(3)-Ba-O(3)	109.1(2)	3×		
O(3)-Ba-O(3)	146.3(1)	6×		
O(1)-Fe-O(1)	180.0(0)	1×		
O(1)-Fe-O(2)	82.5(4)	3×		
O(1)-Fe-O(2)	97.5(4)	3×		
O(2)-Fe-O(2)	118.3(2)	3×		
O(2)-Oc(1)-O(2)	77.7(4)	3×		
O(2)-Oc(1)-O(3)	88.8(2)	6×		
O(2)-Oc(1)-O(3)	162.5(5)	3×		
O(3)-Oc(1)-O(3)	102.1(4)	3×		
O(1)-Oc(2)-O(1)	180.0(0)	1×		
O(1)-Oc(2)-O(3)	85.9(2)	4×		
O(1)-Oc(2)-O(3)	94.1(2)	4×		
O(3)-Oc(2)-O(3)	89.4(3)	2×		
O(3)-Oc(2)-O(3)	90.6(3)	2×		
O(3)-Oc(2)-O(3)	180.0(0)	2×		

relatively short Oc(1)-O(3) distance compensates the low charge compensation of O(3). These observations are in good agreement with the structure of BaFe₁₂O₁₉ (11).

The possibility that Ti or Sn occupy both types of octahedral sites is found in almost all quaternary compounds in the BaO-SnO₂-Fe₂O₃ system and related systems (6, 15, 16). In this way it is possible to achieve better charge compensations.

The Oc(2) octahedron is slightly distorted; it is remarkable that the Oc(2)-O(1) distance is almost equal to the Oc(2)-O(3) distance, while the charge compensation of O(1) and O(3) differs noteworthy (Table II), and thus a shorter Oc(2)-O(3) distance than the Oc(2)-O(1) distance would be expected. The high charge compensation of

O(1) is apparently fully compensated by the distortions of the Oc(1) octahedron.

Isomorphs

A search for substitutions in the *R*-structure was made, because of the possibility of synthesizing compounds with interesting magnetic properties. A number of substitutions are possible and are reported below.

(a) *Substitution of Ba*. Only substitutions with Sr were successful, but the compound SrTi₂Fe₄O₁₁ could not be prepared, in this case we found a mixture of TiFe₂O₅, SrTiO₃, and Fe₂O₃. Attempts to substitute with Pb and ($\frac{1}{2}$ La + $\frac{1}{2}$ Na) met with no success.

TABLE IV
RELEVANT DISTANCES (Å) AND ANGLES (°) IN
BaSn₂Fe₄O₁₁

Ba -O(2)	2.987(4)	6×	Ba -Fe	3.455(1)
Ba -O(3)	2.842(4)	6×	Fe -Fe	0.559(17)
Fe -O(1)	2.044(10)	1×	Oc(1)-Oc(1)	3.002(8)
Fe -O(1)	2.603(10)	1×	Oc(2)-Oc(2)	2.982(0)
Fe -O(2)	1.907(5)	3×	O(1)-O(2)	2.993(5)
Oc(1)-O(2)	2.163(4)	3×	O(1)-O(3)	2.756(6)
Oc(1)-O(3)	1.998(5)	3×	O(2)-O(2)	2.697(8)
Oc(2)-O(1)	2.052(3)	2×	O(2)-O(3)	2.886(4)
Oc(2)-O(3)	2.010(3)	4×	O(3)-O(3)	2.817(8)
O(2)-Ba-O(2)	53.7(2)	3×		
O(2)-Ba-O(2)	66.3(2)	3×		
O(2)-Ba-O(2)	120.0(0)	6×		
O(2)-Ba-O(2)	173.7(2)	3×		
O(2)-Ba-O(3)	59.3(1)	12×		
O(2)-Ba-O(3)	91.8(1)	12×		
O(2)-Ba-O(3)	118.6(1)	12×		
O(3)-Ba-O(3)	59.4(1)	6×		
O(3)-Ba-O(3)	110.2(2)	3×		
O(3)-Ba-O(3)	146.7(1)	6×		
O(1)-Fe-O(1)	180.0(0)	1×		
O(1)-Fe-O(2)	81.6(3)	3×		
O(1)-Fe-O(2)	98.4(3)	3×		
O(2)-Fe-O(2)	117.9(1)	3×		
O(2)-Oc(1)-O(2)	77.1(2)	3×		
O(2)-Oc(1)-O(3)	87.8(1)	6×		
O(2)-Oc(1)-O(3)	160.6(2)	3×		
O(3)-Oc(1)-O(3)	104.0(2)	3×		
O(1)-Oc(2)-O(1)	180.0(0)	1×		
O(1)-Oc(2)-O(3)	85.6(2)	4×		
O(1)-Oc(2)-O(3)	94.6(1)	4×		
O(3)-Oc(2)-O(3)	89.0(2)	2×		
O(3)-Oc(2)-O(3)	91.0(2)	2×		
O(3)-Oc(2)-O(3)	180.0(0)	2×		

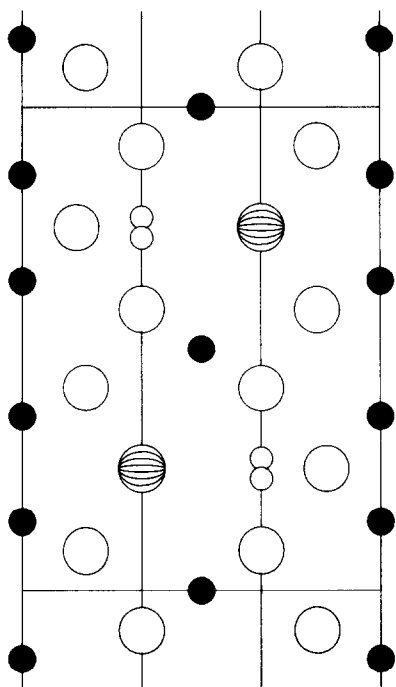


FIG. 2. Plane (110) of the structure of $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$.

(b) *Substitution of Ti.* As reported above, it is possible to replace Ti completely by Sn. It is also possible to replace Ti by Ru, Ir and Mn. In all these attempts an *R*-phase was found, but unfortunately no pure compounds could be obtained. Substitution with Ge and Zr was not observed.

The compounds with Ru and Ir were prepared by mixing BaCO_3 , RuO_2 or IrO_2 and Fe_2O_3 in the appropriate ratio's and heating the mixture in air at 1050 K to achieve reaction between BaCO_3 and Fe_2O_3 . The reaction mixture now was free of BaCO_3 (tested with HCl) and was ground and sealed in a platinum tube and heated at 1470 K for some days. The reaction product contained an *R*-phase, but also a phase with an X-ray diffraction pattern similar to $\text{BaFe}_{12}\text{O}_{19}$. The formation of the latter compound is due to reduction of Ru^{4+} to Ru^{3+} , that can be incorporated easily in the $\text{BaFe}_{12}\text{O}_{19}$ structure. The same difficulties occurred

with the preparation of Ru-containing hollandites (17).

The Mn substitution was carried out by preparing a mixture of BaMn_2O_8 and Fe_2O_3 in the appropriate ratio and sealing this mixture with a drop of water into a gold tube. The mixture was heated for 2 or 3 days at 970 K and at a pressure of 0.2 GPa, in a stainless-steel reaction vessel using a Tempress hydrothermal equipment. The reaction mixture contained an *R*-phase but always also a $\text{BaFe}_{12}\text{O}_{19}$ and a hollandite phase. This can be explained by the fact that BaMn_2O_8 is much more soluble in water than Fe_2O_3 , so the reaction mixture can easily become unhomogeneous. The samples prepared in this way were buffered

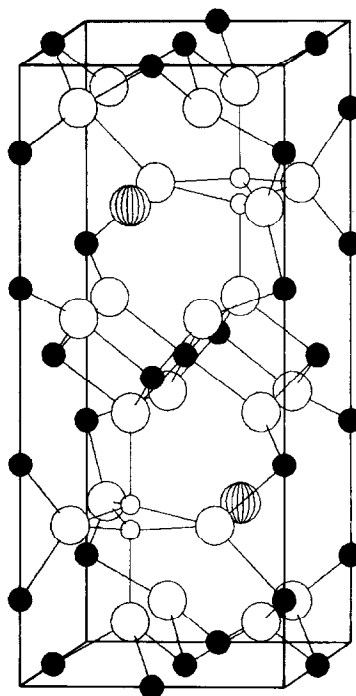


FIG. 3. Unit-cell of the structure of $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$. For Figs. 2 and 3: shaded circles: Ba; open circles: O; solid circles: octahedral sites occupied by Sn and Fe; small open circles: tetrahedral site occupied by Fe with an occupation rate of 50%. Both figures were generated using the crystallographic plotting program FIGATOM (20).

TABLE V
UNIT-CELL DIMENSIONS FROM X-RAY POWDER
DIFFRACTION AT 295 K OF THE OBSERVED
COMPOUNDS WITH THE *R*-STRUCTURE

Compound	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
BaTi ₂ Fe ₄ O ₁₁ , cooled, 1.2 K/h	5.8399(5)	13.6066(13)	401.88(9)
BaTi ₂ Fe ₄ O ₁₁ , quenched	5.8470(2)	13.6116(9)	403.01(5)
BaTi _{1.5} Sn _{0.5} Fe ₄ O ₁₁	5.8720(6)	13.6706(16)	408.21(13)
BaTiSnFe ₄ O ₁₁	5.9008(6)	13.7164(14)	413.62(11)
BaTi _{0.5} Sn _{1.5} Fe ₄ O ₁₁	5.9333(6)	13.7415(15)	418.94(12)
BaSn ₂ Fe ₄ O ₁₁	5.9624(5)	13.7468(14)	423.23(10)
BaMn ₂ Fe ₄ O ₁₁	5.7826(11)	13.4631(30)	389.88(22)
BaRu ₂ Fe ₄ O ₁₁	5.8531(7)	13.5876(16)	403.13(13)
BaSn ₂ In ₃ FeO ₁₁	6.1820(12)	13.9827(28)	462.78(25)
BaSn ₂ In ₃ GaO ₁₁	6.1831(12)	13.9931(22)	463.29(23)
BaSn ₂ In ₃ RhO ₁₁	6.1996(23)	13.8429(53)	460.74(48)
BaTi ₂ Rh ₃ FeO ₁₁	5.8927(31)	13.3494(60)	401.44(56)
SrSn ₂ Fe ₄ O ₁₁	5.9558(9)	13.5429(21)	416.03(18)
SrRu ₂ Fe ₄ O ₁₁	5.8387(11)	13.4063(19)	395.80(17)
SrTi ₂ Cr ₃ FeO ₁₁	5.7858(11)	13.1945(21)	382.52(19)
SrTi ₂ Rh ₃ FeO ₁₁	5.8697(18)	13.1555(57)	392.53(36)
SrRu ₂ Cr ₃ FeO ₁₁	5.7917(21)	13.1218(42)	381.19(37)
SrSn ₂ Cr ₃ FeO ₁₁	5.9071(11)	13.3341(33)	402.97(23)

Note. The esd's are given in parenthesis. High esd's indicate that the observed compound could not be obtained without impurities.

with MnO₂ grains inside the gold tube or in a second gold tube against reduction by H₂ that is formed by the reaction of water with the stainless steel of the reaction vessel.

Mixtures of BaCO₃, MnO₂, and Fe₂O₃ that were heated at once at 1470 K yielded a compound with an X-ray diffraction pattern similar to BaMnFe₆O₁₁ (Mn₂Y).

Attempts to replace Ti by V, Mo, and Nb met with no success; it is our impression that the combination Mo⁴⁺ and Fe³⁺ immediately changed to Mo⁵⁺ and Fe²⁺ at the reaction temperature, and that the same occurs with V⁴⁺ and Nb⁴⁺. The reaction mixtures were heated in a sealed platinum tube.

(c) *Substitution of Fe.* Complete substitution of Fe by another atom was not observed, but 75% of the Fe can be replaced by In, Rh, or Cr. Rh and Cr substitutions were made in several Ba and Sr compounds (see Table V); In substitution was only possible in BaSn₂Fe₄O₁₁. Attempts to replace

75% of Fe by Sc yielded *R*-phases, but the reaction products always contained impurities, mostly hollandite phases.

In BaSn₂In₃FeO₁₁ it is possible to replace the remaining Fe by Ga, and in this way an *R*-phase free of Fe can be obtained. It was assumed that in BaSn₂In₃FeO₁₁ all octahedral sites are occupied by In and the remaining Fe occupies the tetrahedral 4*f* position. Thus substitution of the remaining Fe is only possible by an atom that usually occupies tetrahedral sites in oxide structures. However, Mössbauer spectroscopy of BaSn₂In₃FeO₁₁ and SrTi₂Rh₃FeO₁₁ made it clear that the remaining Fe in this compound not only occupies the 4*f* position (see below). Attempts to replace the Fe of BaSn₂In₃FeO₁₁ by Rh, Mn, Co, and Ni yielded also *R*-phases, but in the reaction products always considerable amounts of BaSnO₃ and In₂O₃ were found.

All reactions were carried out at 1470–1320 K. A list of all observed *R*-phases with unit-cell dimensions is presented in Table V.

Mössbauer Spectroscopy

Because the Mössbauer spectra of ⁵⁷Fe in BaTi₂Fe₄O₁₁ are known (5, 18), Mössbauer spectroscopy was used only to determine the different positions of Fe, especially in the compounds with 75% of Fe replaced by other atoms. With Mössbauer spectroscopy it is possible to detect whether all Fe-atoms are at the 4*f* position or some Fe-atoms occupy octahedral sites in this compounds. The Fe at the 4*f* position can be easily detected since the Mössbauer peaks corresponding to this site show a considerable quadrupole splitting, e.g., Δ*E*_Q = 1.70(3) mm sec⁻¹ in BaTi₂Fe₄O₁₁ (18) and in the comparable 4*e* position in BaFe₁₂O₁₉ Δ*E*_Q = 2.12(5) mm sec⁻¹ (14).

Mössbauer experiments with BaSn₂Fe₄O₁₁ yielded almost the same results as reported for BaTi₂Fe₄O₁₁ (5), only the

TABLE VI
QUADRUPOLE SPLITTINGS (mm sec^{-1}) AND Fe-Fe
DISTANCES (\AA) OF THE $4f$ SITE IN SEVERAL
R-PHASES AND OF THE COMPARABLE $4e$ SITE
IN $\text{BaFe}_{12}\text{O}_{19}$

Compound	ΔE_Q (300 K)	Fe-Fe distance	Reference
$\text{BaFe}_{12}\text{O}_{19}$	2.12(5)	0.312(20)	(11, 14)
$\text{BaTi}_2\text{Fe}_4\text{O}_{11}$	1.70(3)	0.485(24)	(15), This work
$\text{BaSn}_2\text{Fe}_4\text{O}_{11}$	1.42(4)	0.559(17)	This work
$\text{BaSn}_2\text{In}_3\text{FeO}_{11}$	1.95(3)		
$\text{SrSn}_2\text{Fe}_4\text{O}_{11}$	1.44(4)		
$\text{SrSn}_2\text{Cr}_3\text{FeO}_{11}$	1.46(3)		
$\text{SrTi}_2\text{Cr}_3\text{FeO}_{11}$	1.72(3)		
$\text{SrTi}_2\text{Rh}_3\text{FeO}_{11}$	1.84(3)		

quadrupole splitting of the $4f$ site has decreased (Table VI), because the coordination of Fe is more regular in $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$.

At 4.2 K a spectrum was observed that points to a magnetically ordered structure, at 46 K already an unstructured spectrum was observed almost identical to the spectrum of $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ at 77 K (5), and at 300 K a spectrum consisting of at least two dou-

plets was found, comparable to the spectrum reported of $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$. In the compounds with 75% of the Fe-atoms replaced by In, Rh, or Cr, always a doublet with a considerable quadrupole splitting corresponding to the $4f$ position is observed (Table VI). In addition doublets with a smaller quadrupole splitting corresponding to the octahedral sites are observed. In $\text{BaSn}_2\text{In}_3\text{FeO}_{11}$ these doublets even have the highest intensity (Fig. 4), in the Sr compounds the doublets corresponding to the $4f$ position have the highest intensity. This means that in $\text{BaSn}_2\text{In}_3\text{FeO}_{11}$ a considerable part of the In-atoms has occupied the $4f$ position. This is in agreement with the results reported for In substitution in $\text{BaFe}_{12}\text{O}_{19}$ (19). A list of quadrupole splittings of the $4f$ position in different compounds is given in Table VI. The spectra were not completely analyzed because of the difficulties with the two available octahedral sites that give doublets with almost the same parameters (19). The lowering of the quadrupole splitting from $\text{BaFe}_{12}\text{O}_{19}$ to $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ and $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$ means that the coordination of Fe at the $4f$ position is more regular than that of Fe in

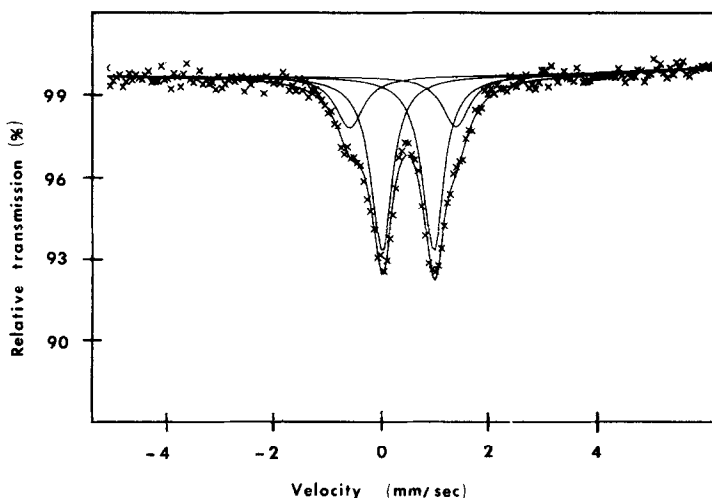


FIG. 4. Mössbauer spectrum of $\text{BaSn}_2\text{In}_3\text{FeO}_{11}$ at 300 K, with fits to the $4f$ tetrahedral site ($\Delta E_Q = 1.95 \text{ mm sec}^{-1}$) and an octahedral site ($\Delta E_Q = 0.87 \text{ mm sec}^{-1}$).

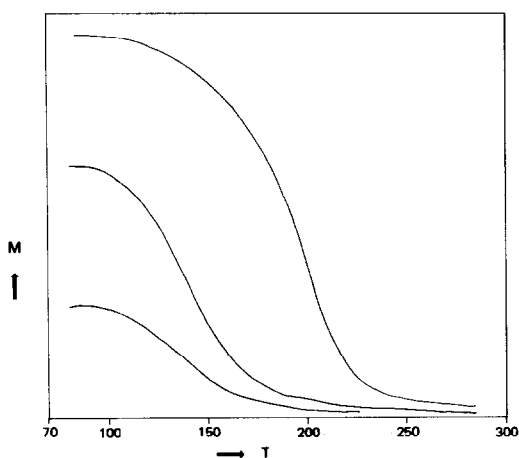


FIG. 5. Magnetization (M) in arbitrary units of BaTi₂Fe₄O₁₁ samples with different cooling rates, versus temperature (T) in K. Respectively, water quenched, $T_c = 221(3)$ K, cooling rate 12K/hr, $T_c = 174(3)$ K and cooling rate 1.2 K/hr, $T_c = 171(3)$ K. The applied field was about 1 kOe.

BaFe₁₂O₁₉ at the $4e$ position, consequently the Fe–Fe distance has increased.

Magnetic Properties of some R -Phases

BaTi₂Fe₄O₁₁ was reported to possess a ferrimagnetic behavior, with a magnetic transition point between 120 and 200 K, depending on the sintering temperature of the sample (5). The magnetic transition point is also influenced by the cooling rate of the sample. A sample cooled from 1470 K to room temperature with a cooling rate of 1.2 K/hr showed a T_c of 171(3) K, whereas the same sample, water-quenched, showed a T_c of 221(3) K (Fig. 5).

As indicated (5), this difference in T_c is due to ordering effects of the cations. Ti has a slight preference for the $4e$ site, so the occupation of Ti in the $4e$ site will be high in a slowly cooled sample and lower in a quenched sample. A high occupation of Ti in the $4e$ site hampers the magnetic exchange between the parts of the structure that are bounded by the BaO₃-layer, thus a

lower T_c is found. Moreover the unit-cell dimensions change with the cooling rate, in the slowly cooled sample the a -axis has decreased more than the c -axis compared to the quenched sample (see Table V).

In BaSn₂Fe₄O₁₁ the occupation of Sn in the $4e$ position is higher than that of Ti in BaTi₂Fe₄O₁₁. So the T_c of quenched BaSn₂Fe₄O₁₁, 180(3) K, is lower than the T_c of quenched BaTi₂Fe₄O₁₁, and in a series with increasing Sn content T_c will decrease.

Magnetization curves at 4.2 K were measured for BaTi₂Fe₄O₁₁, BaSn₂Fe₄O₁₁, and SrSn₂Fe₄O₁₁, up to 56 kOe, but the compounds are not saturated at this field. A measurement carried out with a pulsed field magnet at 4.2 K up to 220 kOe showed a first saturation of BaTi₂Fe₄O₁₁ at 80 kOe, the saturation magnetization is 1.7 μ B per formula unit. The magnetization is still increasing with increasing fields, due to alignment to the field of anti-ferromagnetic coupled moment in the structure (see Fig. 6). High temperature magnetic measurements, carried out in order to trace magnetic impurities, revealed that in BaSn₂Fe₄O₁₁ and SrSn₂Fe₄O₁₁ a trace of BaFe₁₂O₁₉ and, respectively, SrFe₁₂O₁₉ is present, determined by the T_c of these compounds. The X-ray diffraction patterns did not even

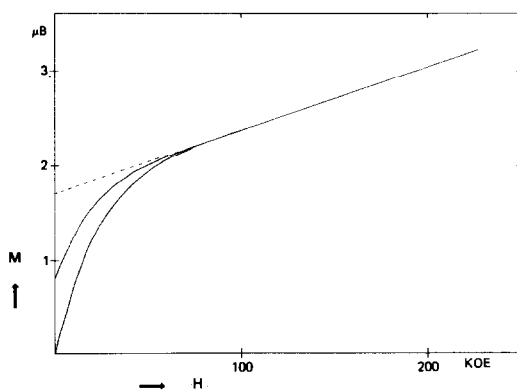


FIG. 6. Magnetization (M) at 4.2 K of BaTi₂Fe₄O₁₁ (quenched) in μ B per formula unit versus the magnetic field (H) in kOe. The magnetic fields were obtained using a pulsed field magnet.

show a trace of these compounds. Compounds with 75% of Fe replaced by In, Rh, or Cr showed a paramagnetic behavior with ordering points below 2 K. $\text{SrRu}_2\text{Cr}_3\text{FeO}_{11}$ shows a slight ferrimagnetic behavior, $T_c = 148(5)$ K. The compounds with an ion with a magnetic moment substituted for Ti showed a ferrimagnetic behavior with high magnetic transition points T_c , $\text{BaMn}_2\text{Fe}_4\text{O}_{11}$: $T_c = 524(5)$ K and $\text{BaRu}_2\text{Fe}_4\text{O}_{11}$: $T_c = 493(5)$ K. Because both compounds could not be obtained pure, further measurements were not carried out. If these compounds can be obtained pure further investigations on magnetic behavior and magnetic structure should prove interesting.

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