

ON THE CRYSTAL AND HYPERFINE PARAMETERS OF THE HEXAGONAL $BaCa_xSr_{1-x}Fe_4O_8$ MONOFERRITES

By

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ABSTRACT

The alkaline earth monoferrites $BaCa_xSr_{1-x}Fe_4O_8$ with $X = 0, 0.5$ and 1 , were studied by Mossbauer spectroscopy and neutron diffractometry over a wide range of temperatures (78 - 900 K). The lattice constants were obtained from X-ray powder patterns. The nuclear intensities of coherent Bragg reflections above the magnetic transition temperatures were successfully interpreted according to the space group $P31m$ with one formula unit per unit cell. Neutron magnetic intensities and magnetically split Mossbauer spectra showed that all compositions to be antiferromagnetic due to interactions between nearest neighbour Fe^{3+} ions with magnetic unit cell has the same periodicity as the crystallographic one. The reduced hyperfine magnetic fields of the Fe^{3+} ions were found to follow the Brillouin curve for $S = 5/2$. Crystallographic and Mossbauer parameters were reported and relationships between structural and magnetic properties were discussed.

INTRODUCTION

The alkaline-earth monoferrites have been studied in much less detail than the spinel-type double oxides of the general formula $A^{2+}B_2^{3+}O_4^{2-}$. The spinel structures are obtained when the divalent ions are small. When the size of the divalent ion increases, as in the case of the alkaline-earth ferrites, many variations in the structure occur. For instance, $CaFe_2O_4^{(1)}$ and $BaFe_2O_4^{(2)}$ crystallize in the orthorhombic system with the spin free trivalent iron in octahedral and tetrahedral coordination respectively. These two monoferrites give rise to a new intermediate phase with the composition $BaCaFe_4O_8$. The magnetic properties and the structural modifications, brought about by substitution in this ferrite, draw deal of attention. To study magnetic ordering in such compounds as $BaCa_xSr_{1-x}Fe_4O_8$, it has become necessary to determine at first their crystallographic parameters.

The role of substitution of the alkaline-earth ions on the structure arose from the fact that these ions have significantly different ionic radii ($Ca^{2+} = 1.00$ $Sr^{2+} = 1.16$ and $Ba^{2+} = 1.36A^\circ$)⁽³⁾ and as a result can be expected to modify the structures, as shown for instance in the case of alkaline earth tungstates by X-ray diffraction analysis⁽⁴⁾.

The crystal structure of the stoichiometric compound $BaCaFe_4O_8$ and the substitution of Ca^{2+} by Sr^{2+} , i.e. $BaSrFe_4O_8$, was studied by using X-ray diffraction techniques. (5,6) However, neutron diffraction methods are more sensitive tools for the determination of the atomic parameters, since the neutron scattering length of the atoms involved are of the same order of

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magnitude. Moreover, such methods can also give a corresponding view in terms of the magnetism of the constituent atoms in these compounds. On the other hand, Mossbauer effect technique can provide information on the Mossbauer atom site and the magnetic ordering temperature of these materials by measuring the temperature variation of the internal magnetic field. Therefore, samples of the system BaCa_xSr_{1-x}Fe₄O₈ with $x = 0, 0.5$ and 1 , have been synthesized and then studied by neutron diffraction and Mossbauer effect techniques.

EXPERIMENTAL

Three powder samples with the composition BaCa_xSr_{1-x}Fe₄O₈ with $x = 0, 0.5$ and 1 were synthesized using ceramic sintering method⁽⁷⁾. Well ground stoichiometric powders of BaCO₃, CaCO₃, SrCO₃ and α -Fe₂O₃ were mixed in the appropriate equivalent weights and fired in air at 900°C for 24 hours. The resulting powder was pressed into pellets and heated again at 1100°C for 24 hours then left to cool slowly. X-ray diffraction measurements were carried out, using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). Analysis of the obtained spectra showed the samples with one phase and no extra lines, indicating the starting materials or any other impurities, were observed. A representative example is shown in Figure 1. The lattice constants of the prepared samples were determined and collected in table 1, together with the previously published data. Neutron diffraction patterns for all prepared compounds at 300 and 900 K were taken on the neutron spectrometer placed at the beam hole No. 5 of the ET-RR₁ reactor⁽⁸⁾. The neutron wave length was $1.016 \pm 0.01 \text{ \AA}$. All measurements were repeated twice. The observed intensities of reflections were obtained in the usual way and corrected for the aluminium contamination due to the container. Representative neutron diffraction patterns are given in Figure 2.

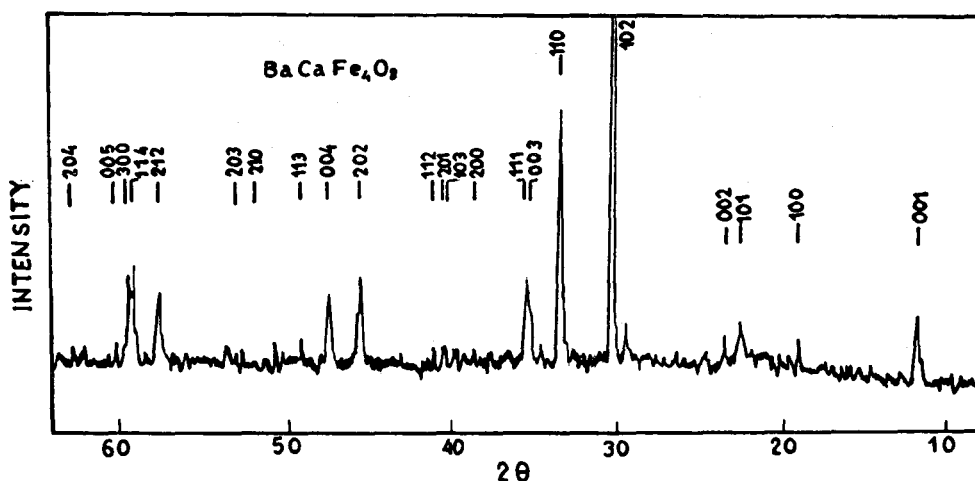


Figure 1. X-ray diffraction pattern of the hexaferrite BaCaFe₄O₈ at room temperature.

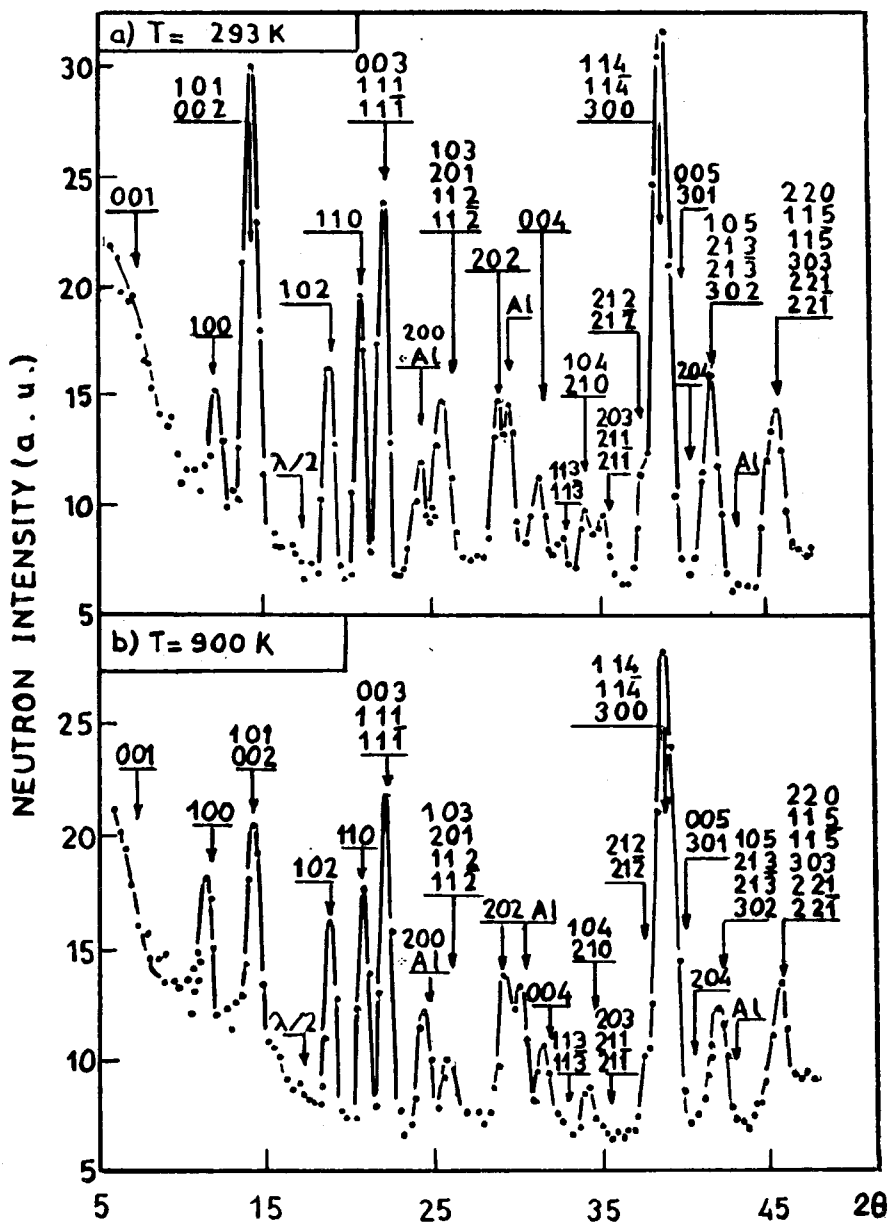


Figure 2. Neutron diffraction patterns of BaCa - hexaferrite at 300 and 900 K.

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Table 1
Unit cell dimensions of the hexaferrite $BaCa_xSr_{1-x}Fe_4O_8$ system

Composition	aÅ°	cÅ°	Reference
BaCaFe ₄ O ₈	5.4059	7.7023	Herman <i>et al</i> ⁽⁵⁾
BaSrFe ₄ O ₈	5.448	8.091	Lucchini <i>et al</i> ⁽⁶⁾
BaCaFe ₄ O ₈	5.388±0.001	7.6669±0.001	present work
BaCa _{0.5} Sr _{0.5} Fe ₄ O ₈	5.3900±0.001	7.8300±0.001	present work
BaSrFe ₄ O ₈	5.4123±0.001	8.0675±0.003	present work

Mossbauer effect measurements on the studied compounds were performed on a constant acceleration spectrometer with a laser velocity calibration. The source was 50 mCi CO⁵⁷ diffused in Pd matrix. A Mossbauer absorber of about 10 mg/cm² was prepared from fine powder of each ferrite. The spectra were measured with the source kept at room temperature, while the absorbers were maintained at various temperatures ranging from 78 to 800 K. Representative examples are given in Figures 3 and 4.

RESULTS AND DISCUSSION

The neutron coherent Bragg reflections, obtained at high temperatures for all samples, could be successfully indexed using a primitive hexagonal unit cell belonging to the space group $P\bar{3}1m^{(9)}$. The atomic positions of the stoichiometric compounds for the different crystallographic sites are given in Table 2. The determined z parameter of the iron ions and the x and z parameters of oxygen ions in (6k) positions, were obtained by comparing the observed and calculated nuclear intensities (see Table 3 for the simple hexaferrite BaCaFe₄O₈). The unit cell of this compound (Fig. 5) has the layer sequence BaO₂, O₃, Ca □ □, O₃ and BaO₂ (the symbol □ means an oxygen vacancy). The layers are hexagonal close stacked. The iron ions are between the BaO₂ and the O₃ layers in a tetrahedron of O²⁻ ions. All the tetrahedrons are similar. Three iron-oxygen distance are equal and have the value 1.9802Å°. The fourth distance is slightly shorter and has the value 1.8125Å°. The above obtained layer sequence in BaCaFe₄O₈ resembles the layer sequence of KAl(SO₄)₂ described by Manoli *et al.*⁽¹⁰⁾. The shortest interatomic distance, as obtained from the final parameters, are listed in Table 4.

Neutron diffraction patterns at room temperature for the system $BaCa_xSr_{1-x}Fe_4O_8$ do not reveal any additional reflections, but the intensities of some of the reflections were increased with respect to their values at 900 K, due to magnetic ordering. Thus, the magnetic unit cell is identical to the chemical one and the propagation vector of the magnetic structure is zero $K = [000]$. With four iron ions per unit cell (Figure 5), four collinear configurations are possible: (F = + + + +), (C = + + - -), (G = + - + -) with the signs referring respectively to the Fe positions 1/3, 2/3, z; 1/3, 2/3, x; 2/3, 1/3, z and 2/3, 1/3, z in the hexagonal unit cell. The magnetic intensity is given by:

$$I_M = P \langle \sin^2\alpha \rangle |F_M|^2$$

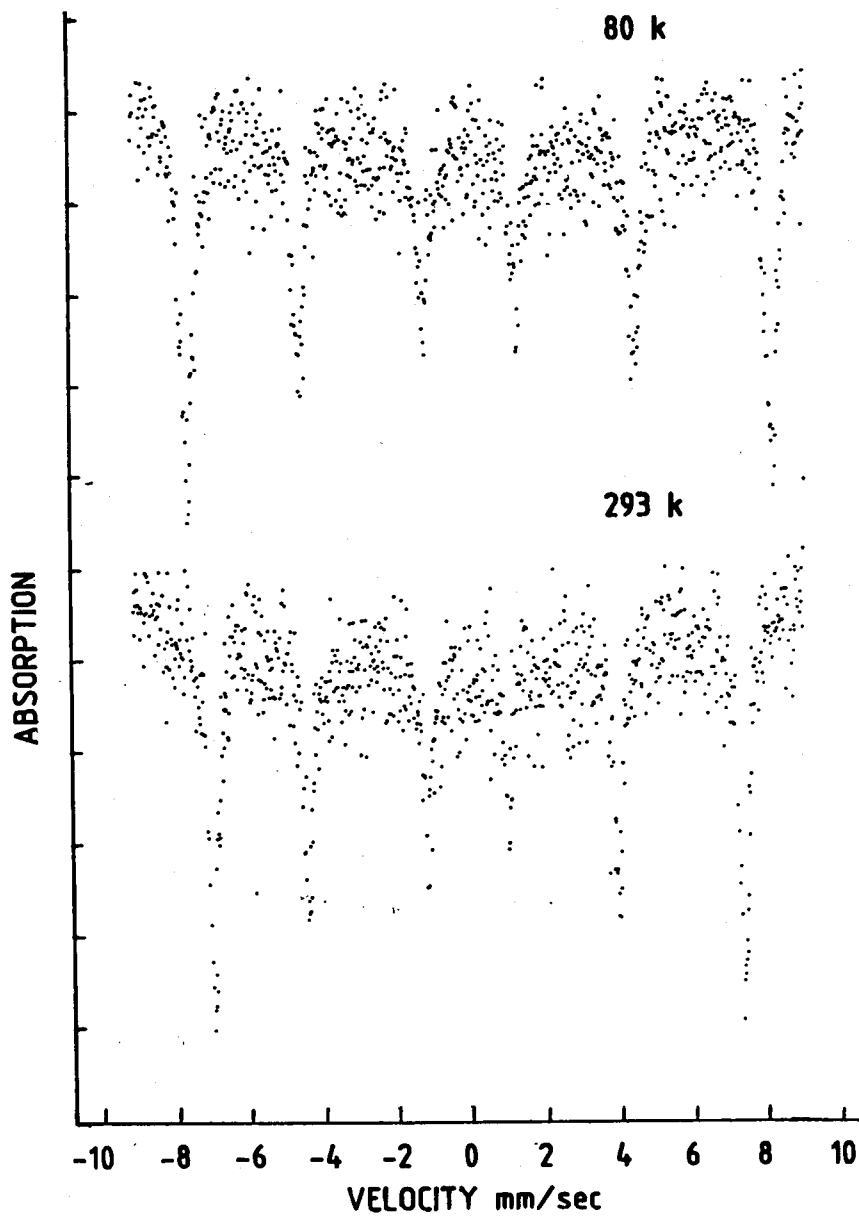


Figure 3. γ -ray resonance absorption spectra of BaCaFe₄O₈ at liquid nitrogen and room temperatures.

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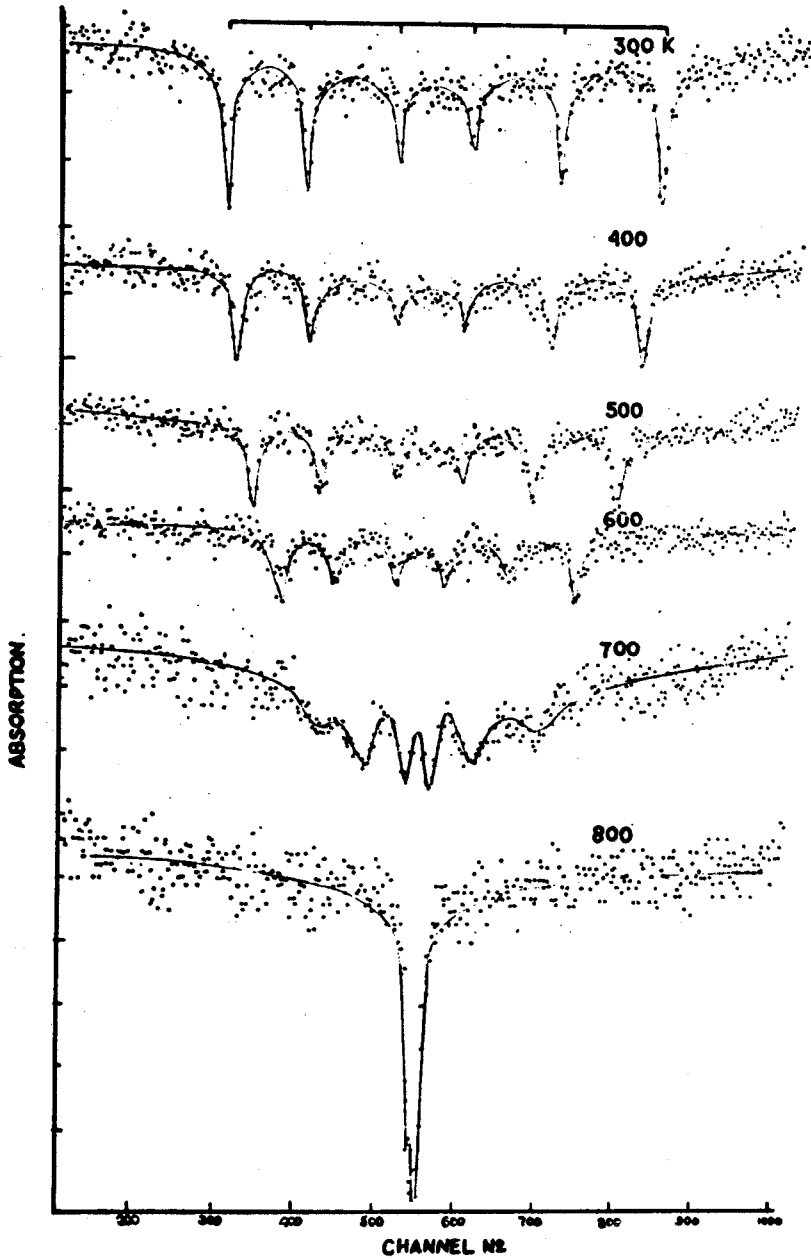


Figure 4. Mössbauer effect patterns of the compounds $BaSrFe_4O_8$ at the temperature range 300 - 800 K.

Table 2
Atomic parameters of BaCaFe₄O₈ and BaSrFe₄O₈ unit cells.

No. of atoms	No. of positions	Wyckoff notation	Coordinates of equivalent BaCaFe ₄ O ₈	positions BaSrFe ₄ O ₈
1 Ba	in 1	(a)	0, 0, 0;	0, 0, 0;
1 Ca or Sr	in 1	(b)	0, 0, ½;	0, 0, ½;
4 Fe	in 4	(h)	1/3, 2/3, ±z; z = 0.236 (2)	1/3, 2/3, ±z; z = 0.224 (2)
2 O _I	in 2	(c)	1/3, 2/3, 0; 2/3, 1/3, 0;	1/3, 2/3, 0; 2/3, 1/3, 0;
6 O _{II}	in 6	(k)	x, u, z; o, x, z; x, x, z; o, x, z; x, x, z; x, o, z; x = 0.328 (2) z = 0.309 (2)	x, o, z; o, x, z; x, x, z; o, x, z; x, x, z; x, o, z; x = 0.346 (2) z = 0.297 (2)

Standard deviation are given in parantheses.

Table 3
Comparison between observed and calculated structure factors for the hexaferrite BaCaFe₄O₈

hkl	jF _O ²	jF _e ²
001	0	0.13
100	12	11.59
(101-002)	47	40.02
102	69	63.54
110	113	109.70
(003-111-111 ⁻)	172	158.73
200	contaminated with Al	
103-201 } 112 - 112 }	53	56.20
202	contaminated with Al	
004	82	68.10
(113-113)	7	4.71
(104-210)	49	44.11
(203-211-211)	12	15.87
212-212-114 } 114-300-005 } 301 }	1116	1159.70

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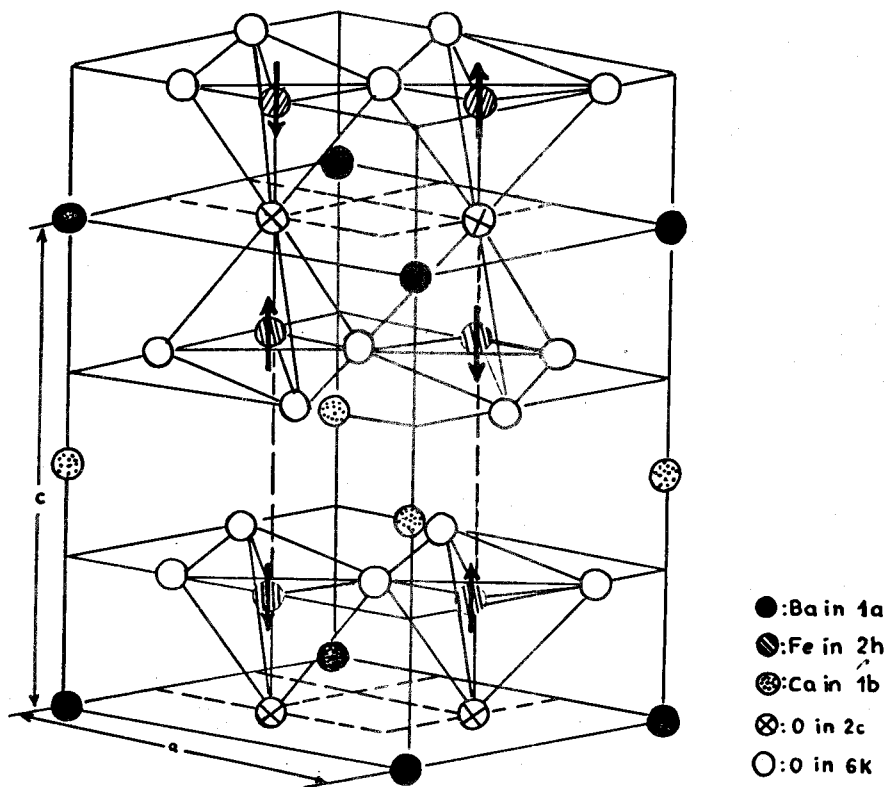


Figure 5. The hexagonal unit cell of the compounds $BaCaFe_4O_8$ (arrows represent the spin direction of the iron atoms).

Table 4
Interatomic distances (in Å°) in the unit cell of $BaCaFe_4O_8$

Fe	Ca	Ba	O_I	O_{II}	
3.1108	3.7096	3.6003	1.8125	1.8902	Fe
	5.3881	3.8335	4.9369	2.3013	Ca
		5.3881	3.1108	2.9624	Ba
			3.1108	2.9801	O_I
				1.7764	O_{II}

Errors in all values within 0.0001 Å°

where P is the multiplicity of the reflection (hkl), α is the angle between the scattering vector and the magnetic moment direction, and F_M is the magnetic structure factor. It is found that the room temperature diffraction diagram is in accordance with the magnetic configuration of type A = (+ - - +). For example, we do not observe any magnetic contribution for the (100) reflection plane which should be present for the configuration (C = + + - -). The configuration (G = + - + -) is not present either, since this would require the presence of the magnetic reflection plane (110) for example. The configuration F = (+ + + +) refers to ferromagnetic ordering which must be discarded on the ground of other physical measurements⁽¹¹⁾. The best fit to the neutron diffraction data corresponds effectively to an antiferromagnetic structure of type-A with the moment direction along the c-axis of the crystallographic unit cell. Good agreement between observed and calculated magnetic intensities at room temperature for the compound BaSrFe₄O₈ was obtained for a magnetic moment of Fe³⁺ = 4.25 ± 0.1⁽¹³⁾ (Table 5).

Table 5
Comparison of observed and calculated neutron magnetic intensities at 300 K for BaSrFe₄O₈

hkl	I _o	I _c
101	106.84	108.18
102	4.48	5.32
103	95.72	{ 17.13 }
201		{ 76.51 }
202	6.02	5.26
104	3.34	3.36
203	110.66	{ 23.22 }
211		{ 43.77 }
211		{ 43.77 }
212	7.06	{ 3.77 }
212		{ 3.77 }

Reliability factor R = $|I_o - I_c| / I_o = 1.7 \%$

The magnetic structure of BaCa ferrite is very similar to that of isostructural BaSrFe₄O₈, except for a small change in the magnetic moment value (the magnetic moment for BaCaFe₄O₈ was found to be 4.5 ± 0.1 Bμ). This means that the exchange interactions, which are of the same nature in the two compounds, are stronger in the case of BaCa ferrite where the distance between iron ions is smaller.

The measured Mossbauer absorption spectra of the Fe⁵⁷ 14.4 Kevγ-rays for the polycrystalline studied sample BaCa_xSr_{1-x}Fe₄O₈ showed simple six lines magnetically split Zeeman patterns.

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The hyperfine parameters for all studied compositions, calculated from the positions of the Lorentzian lines and fitted to the experimental spectra, are listed in table 6; they revealed that the magnetic hyperfine fields in these hexaferrites are related to Fe³⁺ ions in tetrahedral sites. The obtained spectra at 78 K for all samples did not change dramatically, compared with that at room temperature (Figure 3), and confirmed the stability of the magnetic structure of such compounds at low temperatures. Figure 4 shows Mossbauer effect spectra of the composition BaSrFe₄O₈ in its magnetically ordered state. At low temperatures, i.e. up to about 600K, the spectra exhibit well defined absorption lines, related to the tetrahedral ferric ions. At higher temperatures, the absorption lines become very broad. Above 700K, the spectra show a rather peculiar shape which may a priori be ascribed to relaxation effects⁽¹²⁾ or to broad magnetic hyperfine field distributions⁽¹³⁾. The transition temperature, at which all possible hyperfine fields in each ferrite are no longer observable with the Mossbauer effect (see Table 6), was in good agreement with that obtained by measuring the disappearance of the magnetic scattering by neutrons. The thermal variation of the hyperfine magnetic field for the compound BaSr Fe₄O₈ was given in Figure 6. The obtained curve shows closer agreement with the theoretical curve computed from Brillouin function for S = 5/2 on the basis of the Weiss molecular field theory.

Table 6

Mossbauer effect parameters of the hexaferrite BaCa_xSr_{1-x}Fe₄O₈ system at room temperature

Composition	Isomer shift δ relative to metallic iron	Quadrupole interaction ΔE_q	Hyperfine magnetic field Heff	Magnetic transition temperature
	mm/s	mm/s	KOe	K
BaCaFe ₄ O ₈	0.17	0.21	434	769
BaCa _{0.5} Sr _{0.5} Fe ₄ O ₈	0.22	0.18	420	775
BaSrFe ₄ O ₈	0.29	0.16	403	780

Errors ± 0.02 ± 0.02 ± 2 ± 5

The observed spectrum recorded above the magnetic transition temperature at 800K consisted of a broad absorption line with a poorly resolved asymmetrical quadrupole split doublet.

Mossbauer patterns for line positions and derived parameters from X-rays and neutron diffraction data for all compositions, establish that the alkaline-earth ferrites BaCa_xSr_{1-x}Fe₄O₈ (X = 0,0.5 and 1) are isomorphous with a single type of ferric ions surrounded by four oxygen ions in the tetrahedral geometry.

Our attempts to prepare ferrites with replacing Ba²⁺ by Ca²⁺ or Sr²⁺ have not succeeded, thus the possible partial or total substitution retaining isomorphism with BaCaFe₄O₈ is that Ca²⁺ by Sr²⁺. Such conclusion is also in accordance with the observed trends in the a and c values obtained for the system (Table 1). The replacement of Ca²⁺ by Sr²⁺ with larger ionic radius, may be expected to result in an increase of c value, leaving the value unchanged. Moreover, the

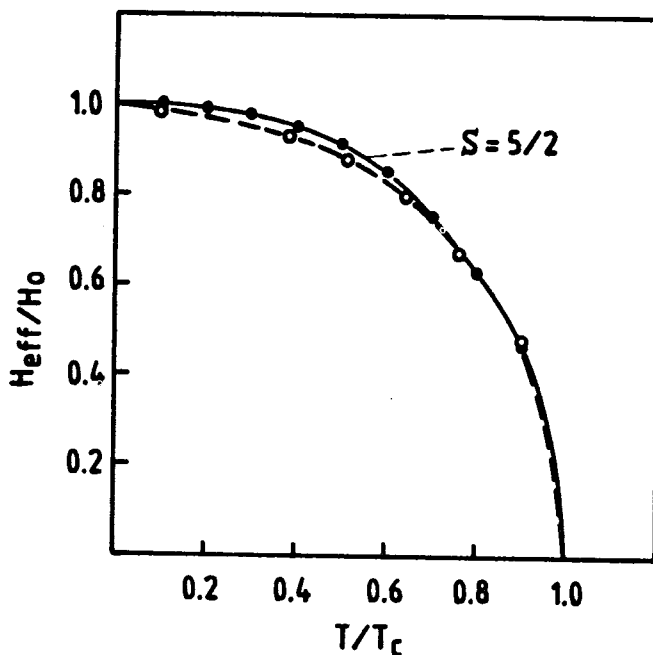


Figure 6. Reduced hyperfine field H_{eff}/H_0 versus T/T_c for the compound $BaSrFe_4O_8$. The solid line represents the Brillouin curve for Fe^{3+} .

possible structural variations, due to the substitution of Ca^{2+} by the relatively bigger Sr^{2+} , may be expected for the following reasons: the $Ca - O$ distance for the near neighbour oxygen atoms has been found to be 2.3013 \AA (Table 4). This value is quite close to the sum of the Ca^{2+} and O^{2-} ionic radii (2.40 \AA), indicating that the Ca^{2+} ion is in close contact with the O^{2-} ion, which forms one of the apices of the oxygen tetrahedra around the Fe^{3+} ion. Substitution of Ca^{2+} by a bulkier ion should therefore bring about a change in the extent of distortion of these tetrahedra from cubic symmetry. This distortion is given in the order $BaCaFe_4O_8 > BaCa_{0.5}Sr_{0.5}Fe_4O_8 > BaSrFe_4O_8$.

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البارامترات البلورية والدقيقة للحديدات السداسية

يحيى عباس

حسام صلح

محمد خورشيد فايق

مصطفى النمر

تم دراسة المركبات الحديدية ذات التركيب الكيميائي باكاست ح أ
س ١ - س ٨٤
بواسطة ظاهرتهى الموسباور وحيود النيوترونات في المدى الحراري (٧٨ - ٩٠٠ درجة مطلقه) . وقد
أمكن حساب ثوابت الخلية لهذه المركبات من نماذج حيود الأشعة السينية لها . كذلك أظهرت الشدة
النوية لانعكاسات براج البناء أن هذه الحديديات تنتمي إلى التركيب البلورى ذي التنظيم P3Lm
وتحتوى على جزء لكل وحدة خلية . وأوضحت قياسات البعثة المغناطيسية للنبوترونات والانقلاقات
المغناطيسية لنماذج موسباور أن هذه المركبات ذات ترتيب انتيفيرو مغناطيسى داخل خلية
مغناطيسية مساوية للخلية البلورية وذلك نتيجة التفاعلات المغناطيسية لأيونات الحديد الثلاثية مع
جيرانها والتي تبعت قيم مجالاتها المغناطيسية الدقيقة منحنى بريلون . هذا وقد نوقشت الخواص
البلورية والمغناطيسية لهذه الحديديات السداسية في ظل النتائج العملية التي تم الحصول عليها .