JOURNAL OF SOLID STATE CHEMISTRY **72**, 218–224 (1988)

Crystal Structure of Strontium Hexaferrite $SrFe_{12}O_{19}$

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Received November 14, 1986

The room temperature structure of $SrFe_{12}O_{19}$ hexagonal ferrite has been refined from X-ray single-crystal data. Structural isomorphism of the title compound with the hexagonal ferrite $BaFe_{12}O_{19}$ has been demonstrated. In particular, it is corroborated that the bipyramidal Fe ions have a fast diffusional motion within a quasiharmonic double-well potential as in $BaFe_{12}O_{19}$. Some structural

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0022-4596/88 $3.00

differences within the R-block are found among Ba and Sr magnetoplumbites which may account for the different dynamic, magnetic, and crystallochemical behavior of both compounds.

Introduction

In a recent work (*1*) some of us reported an accurate study of the crystal structure and dynamic characteristics of the M-type hexagonal ferrite $BaFe_{12}O_{19}$. In this work we concentrated on the elucidation of two different models for the structural and dynamic hehavior of 5-coordinate Fe ions in the M structure. For instance, from previous Mössbauer spectroscopy measurements (*2, 3*) and our own X-ray diffraction results, it was concluded that the 5-coordinate Fe ions undergo a fast diffusional motion between two pseudotetrahedral sites lying at each side of the trigonal bipyramid base (Fig. 1).

Strontium hexaferrite $SrFe_{12}O_{19}$ is isomorphous with the magnetoplumbite $BaFe_{12}O_{19}$ (space group *P*6_3*/mmc*) (*4, 5*), but its dynamical and magnetic properties differ slightly from those of $BaFe_{12}O_{19}$.

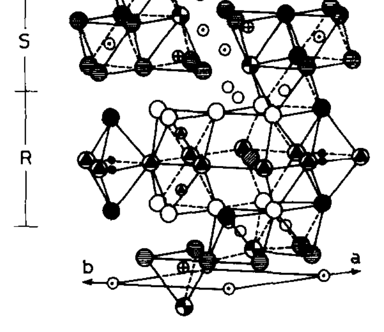

FIG. 1. Crystallographic structure of $SrFe_{12}O_{19}$.

Mamalui *et al.* (*3*) showed that the Lamb–Mössbauer factors of the 5-coordinate Fe ions are quite different in SrM and BaM hexagonal ferrites. For instance, the low-temperature freezing of the Fe diffusion motion occurs at a slightly higher temperature. Moreover, the ^{57}Fe quadrupole splitting of these 5-coordinate Fe ions is very sensitive to the replacement of the neighboring alkaline earth cation (*6–8*). In fact, the structural and dynamic characteristics of bipyramidal Fe ions in M- and R-type hexagonal ferrites seem to be very sensitive to the distortions of the neighboring polyhedra (*9–11*).

It has been experimentally proved that several magnetic properties, such as the Curie temperature and magnetocrystalline anisotropy, are also modified by the replacement of Ba ions with Sr or Pb ions (*12, 13*). As a matter of fact, these modifications are relevant to the technological applications of hexagonal ferrites, such as in production of permanent magnets.

Finally we must point out that the replacement of Ba with Sr in hexagonal ferrites has important crystallochemical consequences. For instance, Albanese *et al.* (*7*) showed that in cationic substituted M-type hexagonal ferrites, the distribution of metallic ions among the different sublattices is greatly modified with the replacement of Ba with Sr. These crystallochemical effects could be as well the origin of the drastic modification of the magnetic structure observed in $(Ba,Sr)Zn_2Y$ and $(Ba,Sr)Zn_2Z$ hexagonal ferrites (*14–16*).

The aim of the present work is to study the structural differences among Sr and Ba M-type hexagonal ferrites to gain a deeper understanding of the role played by the alkaline earth cation in the dynamic, crystallochemical, and magnetic properties of the hexagonal ferrites.

Experimental and Results

Single crystals of $SrFe_{12}O_{19}$ hexagonal ferrite were grown by the flux method using $NaFeO_2$ as solvent. The procedure and melt composition used in this work were the same used in a previous investigation (*1*), except for the substitution of $SrCO_3$ for $BaCO_3$ in the initial mixture. Good-quality single crystals up to 4 cm^3 were obtained by this method.

To study the crystal structure of $SrFe_{12}O_{19}$ a sphere of radius $r = 0.07$ mm was prepared and mounted in a Philips PW 1100 four-circle X-ray diffractometer. The radiation used for the measurement of Bragg reflections was Mo*Kα* and a total of 2952 reflections were measured in the interval 2–36° by the ω-scan method. After the equivalent reflections were averaged according to the $6/mmm$ Laue class, 346 independent reflections remained. These intensities were converted to structure factors by applying Lorentz polarization and absorption ($\mu R = 1.049$) corrections. Finally, 339 reflections with $|F_{obs}| > \sigma(F_{obs})$ were retained. Scattering factor curves for neutral Sr, Fe, and O atoms given by Doyle and Turner (*17*) and anomalous dispersion data of Cromer and Liberman (*18*) were used in the crystal structure refinement.

The crystal structure refinement was carried out with the SHELX program (*19*), and the $BaFe_{12}O_{19}$ atomic positions (*1*) were used as starting parameters in the least-squares refinement. The hexagonal lattice parameters obtained for $SrFe_{12}O_{19}$ at room temperature were $a = 5.8844(6)$ Å and $c = 23.050(3)$ Å.

In Table I we report the positional and thermal parameters obtained after a fit giving R factors of $R = 0.022$ and $R_w = 0.023$. Further crystal structure refinements placing Sr ions in the $6h$ Wyckoff position with $\frac{1}{3}$ occupancy, as has been proposed for some M-type lanthanum hexaluminates (*20, 21*), led to negative results. In the same way, similarly to $BaFe_{12}O_{19}$ (*1*), the increase of R factors when Fe2 ion is placed in the $2d$ position ($R = 0.024$ and $R_w = 0.025$) gives a high level of statistical significance to the new z parameter (*22*). The interatomic distances and angles corresponding to the atomic positions reported in Table I are quoted in Table II; in Table III the thermal

TABLE I

POSITIONAL AND THERMAL ANISOTROPIC (× 10^5) PARAMETERS

Position		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sr	$2d$	$\frac{2}{3}$	$\frac{1}{3}$	0.25	856(7)	856	23(1)	428	0	0
Fe1	$2a$	0	0	0	303(6)	303	0(1)	152	0	0
Fe2	$4e(\frac{1}{2})$	0	0	0.2542(3)	144(6)	144	58(4)	72	0	0
Fe3	$4f$	$\frac{1}{3}$	$\frac{2}{3}$	0.0272(1)	197(6)	197	4(1)	99	0	0
Fe4	$4f$	$\frac{1}{3}$	$\frac{2}{3}$	0.1909(1)	273(6)	273	2(1)	137	0	0
Fe5	$12k$	0.1689(1)	0.3378	−0.1093(1)	242(6)	174(5)	7(1)	87	0	0(6)
O1	$4e$	0	0	0.1516(1)	205(16)	205	19(2)	103	0	0
O2	$4f$	$\frac{1}{3}$	$\frac{2}{3}$	−0.0552(1)	182(15)	182	6(2)	91	0	0
O3	$6h$	0.1817(1)	0.3634	0.25	727(24)	83(26)	23(2)	42	0	0
O4	$12k$	0.1565(1)	0.3130	0.0527(1)	386(17)	152(16)	10(1)	76	0	0(7)
O5	$12k$	0.5047(1)	1.0094	0.1508(1)	303(11)	379(17)	17(1)	189	0	0(6)

Note. $T = \exp[-\Sigma_{ij}\beta_{ij}h_ih_j]$, by symmetry $\beta_{11} = \beta_{22} = 2\beta_{12}$ and $\beta_{13} = \beta_{23} = 0$ for $2d$, $2a$, $4e$, and $4f$ positions; $\beta_{22} = 2\beta_{12}$ and $\beta_{23} = 2\beta_{13}$ for $12k$ position; $\beta_{22} = 2\beta_{12}$ and $\beta_{13} = \beta_{23} = 0$ for $6h$ position.

ellipsoid data are given and compared with those observed for $BaFe_{12}O_{19}$ at the same temperature (*1*).

TABLE II

COMPARISON OF INTERATOMIC DISTANCES (Å) AND ANGLES (°) OF $SrFe_{12}O_{19}$ WITH THOSE OF $BaFe_{12}O_{19}$

	Sr polyhedron	
Sr–O3	× 6 = 2.946(1)	(2.950)[a]
Sr–O5	× 6 = 2.820(2)	(2.868)
⟨Sr–O⟩	2.883	(2.909)
O3–O3	× 3 = 2.677(1)	(2.672)
O3–O3	× 3 = 3.208(1)	(3.220)
O5–O5	× 12 = 2.823(2)	(2.900)
O5–O5	× 6 = 2.859(1)	(2.850)
	Fe1 octahedron	
Fe1–O4	× 6 = 2.005(2)	(2.000)
O4–O4	× 6 = 2.763(1)	(2.766)
O4–O4	× 6 = 2.906(3)	(2.889)
	Fe2 bipyramidal	
Fe2–O1	× 1 = 2.171(7)	(2.128)
Fe2–O1	× 1 = 2.365(7)	(2.468)
Fe2–O3	× 3 = 1.854(1)	(1.867)
⟨Fe2–O⟩	2.020	(2.039)
Fe2–Fe2	× 1 = 0.194(10)	(0.340)
O1–O3	× 6 = 2.928(2)	(2.955)
O3–O3	× 3 = 3.208(1)	(3.220)
	Fe3 tetrahedron	
Fe3–O2	× 1 = 1.899(3)	(1.894)
Fe3–O4	× 3 = 1.896(2)	(1.894)
O4–O4	× 3 = 3.122(1)	(3.126)
O4–O2	× 3 = 3.072(3)	(3.058)
	Fe4 octahedron	
Fe4–O3	× 3 = 2.060(2)	(2.073)
Fe4–O5	× 3 = 1.976(2)	(1.969)
⟨Fe4–O⟩	2.018	(2.021)
O3–O3	× 3 = 2.677(1)	(2.672)
O3–O5	× 6 = 2.823(2)	(2.850)
O5–O5	× 3 = 3.025(1)	(2.992)
	Fe5 octahedron	
Fe5–O1	× 1 = 1.978(2)	(1.985)
Fe5–O2	× 1 = 2.089(2)	(2.092)
Fe5–O4	× 2 = 2.113(2)	(2.114)
Fe5–O5	× 2 = 1.919(2)	(1.932)
⟨Fe5–O⟩	2.022	(2.028)
O2–O4	× 2 = 2.945(1)	(2.949)
O2–O5	× 2 = 2.753(3)	(2.768)
O1–O4	× 2 = 2.782(3)	(2.796)
O1–O5	× 2 = 2.943(1)	(2.946)
O4–O4	× 1 = 2.763(1)	(2.766)
O4–O5	× 2 = 2.875(3)	(2.873)
O5–O5	× 1 = 2.859(1)	(2.850)
	Important distances and angles	
Sr–Fe4	= 3.660(1)	(3.673)
Sr–Fe2	= 3.399(1)	(3.406)
Sr–Fe5	= 3.651(2)	(3.691)
Fe2–Fe4	= 3.697(3)	(3.740)
Fe2–Fe5	= 3.758(7)	(3.862)
Fe2–Fe5	= 3.587(7)	(3.560)
Fe4–Fe4	= 2.725(3)	(2.768)
Fe5–Fe5	= 2.903(1)	(2.911)
Fe5–Fe5	= 2.982(1)	(2.982)
Fe2–Fe4	= 3.625(3)	(3.612)
Fe1–O4–Fe3	= 124.6(2)	(126.3)
Fe1–O4–Fe5	= 95.6(1)	(95.4)
Fe2–O1–Fe5	= 119.6(5)	(119.9)
Fe2–O3–Fe4	= 135.6(3)	(132.9)
Fe2–O3–Fe4	= 141.6(3)	(143.3)
Fe3–O2–Fe5	= 126.7(3)	(126.5)
Fe3–O4–Fe5	= 121.4(2)	(121.3)
Fe4–O3–Fe4	= 82.8(1)	(83.8)
Fe4–O5–Fe5	= 127.4(2)	(128.1)
Fe5–O1–Fe5	= 97.8(1)	(97.3)
Fe5–O2–Fe5	= 91.1(1)	(88.2)
Fe5–O5–Fe5	= 102.0(1)	(97.8)
Fe5–O4–Fe5	= 89.8(1)	(89.7)

[a] Values in parentheses are from Ref. (*1*).

Discussion

The first conclusion of the present X-ray diffraction (XRD) study is that structural isomorphism does indeed exist among $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ hexagonal ferrites. In particular, it may be concluded that the room-temperature dynamical behavior of 5-coordinate Fe2 ions observed in $BaFe_{12}O_{19}$, i.e., a fast diffusional motion between two pseudotetrahedral sites, is basically preserved in $SrFe_{12}O_{19}$. As in the $BaFe_{12}O_{19}$ XRD study, this conclusion can be extracted only by joint consideration of both XRD and Mössbauer spectroscopy results: the XRD study shows that Fe2 ions are not located within a single harmonic potential well centered at the SrO_3 mirror plane, while the Lamb–Mössbauer factor observed by Mamalui *et al.* (*3*) rules out the possibility of a static disorder among the two pseudotetrahedral sites forming the bipyramid.

TABLE III

THERMAL ELLIPSOID DATA

Atom	Symmetry	Root mean square (Å)[a]	Angles (°) with the hexagonal axes[a]		
			a	*b*	*c*
Sr	$\bar{6}m2$	0.11[b] (0.09)	0	0	90
		0.08 (0.09)	90	90	0
Fe1	$\bar{3}m$	0.06[b] (0.08)	0	0	90
		0.01 (0.06)	90	90	0
Fe2	$3m$	0.12 (0.09)	90	90	0
		0.04[b] (0.08)	0	0	90
Fe3	$3m$	0.05[b] (0.07)	0	0	90
		0.03 (0.07)	90	90	0
Fe4	$3m$	0.06[b] (0.08)	0	0	90
		0.02 (0.07)	90	90	0
Fe5	m	0.06 (0.08)	0(0)	120(120)	90(90)
		0.05 (0.07)	30(90)	90(33)	90(105)
		0.04 (0.10)	90(90)	90(90)	0(0)
O1	$3m$	0.07 (0.10)	90	90	0
		0.05[b] (0.08)	0	0	90
O2	$3m$	0.05[b] (0.09)	0	0	90
		0.04 (0.06)	90	90	0
O3	mm	0.11 (0.11)	0	120	90
		0.08 (0.08)	90	90	0
		0.03 (0.07)	90	30	90
O4	m	0.08 (0.09)	0(0)	120(120)	90(90)
		0.04 (0.09)	90(90)	150(55)	90(41)
		0.05 (0.08)	90(90)	90(49)	0(131)
O5	m	0.06 (0.11)	0(90)	120(51)	90(47)
		0.07 (0.09)	90(0)	150(120)	90(90)
		0.07 (0.07)	90(90)	90(53)	0(137)

[a] Values in parentheses are those for $BaFe_{12}O_{19}$ from Ref. (*1*).

[b] Circular section perpendicular *z* due to symmetry.

Despite the structural isomorphism among Ba and Sr M-type hexagonal ferrites, significant differences are observed in the interatomic distances and thermal parameters reported in Tables II and III, respectively. Let us then discuss the significance of these modifications on the magnetic, dynamic, and crystallochemical properties of $SrFe_{12}O_{19}$ as compared with $BaFe_{12}O_{19}$.

As may be observed in Table II the polyhedra in which significant differences do exist are those pertaining to the R-block where Sr ions are located, namely, the Sr, Fe2, and Fe4 polyhedra (Fig. 1). The 12-fold Sr coordination is formed by two sets of Sr–O distances: six longer Sr–O3 bonds within the mirror plane and six shorter Sr–O5 distances within the neighboring layers (Fig. 1). As is reported in Table II, while the Sr–O5 distances have been reduced, accordingly with the smaller ionic radius of Sr^{2+}[$r^{XII}(Sr^{2+}) = 1.44$ Å, $r^{XII}(Ba^{2+}) = 1.61$ Å (*23*)], the Sr–O3 distances are not modified. This leads to an anisotropic thermal vibration of Sr ions, with a greater amplitude within the mirror plane which was not observed in $BaFe_{12}O_{19}$. Furthermore, this unequal reduction of the Sr–O distances enhances the axial compression of the polyhedron (reduction of O3–O5 distances), which, of course, will have important consequences for the neighboring Fe2 and Fe4 polyhedra. First, in the (Fe_2O_9) group, made up of two Fe4 octahedra sharing a face (Fig. 1), the Fe4–Fe4 distance has been shortened (2.725 × 2.768 Å) through a slight distortion of the $Fe4O_6$ octahedron matching the axial compression of Sr polyhedron. It is, however, amazing that the octahedron distortion is made with hardly any change in the O3–O3 distance of the sharing face (2.677 × 2.672 Å) and in the corresponding O3–O3 distance of the bipyramidal base (3.208 × 3.220 Å). Meanwhile, in the Fe2 trigonal bipyramid the structural distortion is due mostly to the reduction of the interlayer SrO3–O4 distances [*d*(O1–O3) = 2.928 × 2.955 Å]. In this way, the flattening of the tetrahedra forming the trigonal bipyramid (Fig. 1) leads to displacement of the double-well minima where Fe2 ions lie [*d*(Fe2–Fe2) = 0.194 × 0.340 Å]. The fact that the modification of the double-well potential is made without a reduction of the basal plane opening (O3–O3 distances) may be understood as an effect of Fe2 diffusional motion. Actually, the minimum opening of the Fe2 passageway (1.852 Å) must remain compatible with the Fe^{3+} ionic radius. It is likely, however, that the observed slight reduction of the bipyramidal base opening lies at the origin of the different diffusional motion freezing temperatures observed in BaM and SrM by means of Mössbauer spectroscopy (*3*).

Summarizing, we state that the substitution of Ba^{2+} ions with a smaller ion like Sr^{2+} in the R-block of hexagonal ferrites produces a reduction of the mean distance between the SrO3 mirror plane layer and the neighboring O4 layers but no corresponding reduction of distances within the SrO3 layer. Thus, the final atomic configuration within the SrO3 plane is determined mostly by the diffusional motion of Fe2 ions together with the electrostatic repulsion among O^{2-} ions.

Let us now look at the consequences of the observed structural features on the magnetic properties of $SrFe_{12}O_{19}$. Exchange interactions among ferric ions in $BaFe_{12}O_{19}$ arise from the superexchange mechanisms for all intersublattice and intrasublattice interactions except the Fe4 intrasublattice interaction where, besides the superexchange interaction, some direct exchange contributions also exist (*24*). Therefore, on the grounds of exchange and superexchange theory (*25, 26*), it is likely that a significant increase in the J_{44} antiferromagnetic exchange interaction does occur, because the reduction in Fe4–Fe4 distance enhances their direct atomic orbital overlap, which in turn strengthens the J_{44} exchange integral. The remaining Fe–O distances and Fe–O–Fe angles are only very slightly modified; therefore it is expected that the remaining exchange interactions are similar to those of $BaFe_{12}O_{19}$ (*24*).

Finally, from the present XRD results on $SrFe_{12}O_{19}$ some clues may be anticipated concerning the different crystallochemical behavior of Ba and Sr hexagonal ferrites. For instance, it is likely that the structural distortions observed in the metallic polyhedra surrounding the Sr polyhedron are significant enough to modify, for example, the relative sublattice preference of substituting ions such as Al^{3+} (*7*). Moreover, similar distortions probably occur in Y- and Z-type hexagonal ferrites containing the T-block formed by two adjacent BaO_3 layers (*27, 28*). These structural modifications could modify the distribution of nonmagnetic Zn^{2+} ions in Y-type $(Ba,Sr)_2Zn_2Fe_{12}O_{22}$ and Z-type $(Ba,Sr)_3Zn_2Fe_{24}O_{41}$ hexagonal ferrites which, in turn, would produce a transition from a collinear ferrimagnetic structure to complex helimagnetic structures (*14, 16*).

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