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The Preparation and Structures of the Alkaline Earth Iron Oxyhalides

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The title compounds have been synthesized and crystallized in a variety of structure types. Three of these structure types have been identified via single crystal structure determinations. $CaFeO_2Cl$ is monoclinic; space group Am with $a = 8.712(5)$ Å, $b = 3.828(1)$ Å, $c = 9.999(4)$ Å, $\beta = 103.53(4)°$, and $Z = 4$. Ca_2FeO_3Cl is tetragonal; space group $P4$ with $a = 3.848(2)$ Å, $c = 13.65(1)$ Å, and $Z = 2$. $Sr_3Fe_2O_5Cl_2$ is also tetragonal; space group $I4/mmm$ with $a = 3.952(1)$ Å, $c = 23.807(3)$ Å, and $Z = 2$. In each of these structures, distinct layers can be identified. Mossbauer measurements of single crystals are presented.

Introduction

The high free energies and enthalpies of formation for most metal oxides and metal halides make the occurrence of metal oxyhalides somewhat unexpected. Indeed, most metal oxyhalides exist only over narrow temperature ranges and high halogen activities. However, the ability of iron oxyhalides to be formed from oxidation of the halides in air at moderate temperatures suggests that complex iron oxyhalides may also be sufficiently stable to form without resorting to exacting synthetic procedures. A recent assertion of such stability is iron molybdenum oxychloride described by Torardi (*1*) which was prepared by the combination of MoO_3, Fe_2O_3, and $FeCl_3$ in a closed ampoule. To further demonstrate the general stability of such iron compounds we have investigated the reactions of iron oxide with a variety of halide fluxes. The novel compounds resulting from these experiments as well as their crystal structures and preliminary magnetic properties are described here.

Experimental

The iron oxyhalides were prepared by mixing an excess of alkaline earth halide, MX_2 (M = Ca, Sr; X = Cl, Br) with iron oxide, Fe_2O_3. The mixtures were placed in Al_2O_3 or Pt crucibles and heated rapidly to high temperatures followed by slow cooling to room temperature. The exact conditions of growth are given in Table I.

It should be noted that the synthesis of these compounds could be done only in a box furnace which utilized a heating element upon which the crucible could sit. Attempts made with vertical tube furnaces or glowbar muffle furnaces invariably produced ferrites. The only observed difference in preparative conditions which could account for this peculiar behavior was the appearance of

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TABLE I

PREPARATIVE CONDITIONS FOR THE ALKALINE EARTH IRON OXYHALIDES

Majority phase	Flux	Weight of flux (g)	Weight of Fe_2O_3 (g)	Soak temp (°C)/time (hr)	Cooling rate (°C/hr)	Crucible material
$CaFeO_2Cl$	$CaCl_2$	30	0.1	800/6	15	Pt
Ca_2FeO_3Cl	$CaCl_2$	30	0.75	850/5	15	Pt
$Ca_3Fe_2O_5Cl_2$	$CaCl_2$	30	1.0	850/8	15	Pt
$Ca_3Fe_2O_5Cl_2$ (large crystals)	$CaCl_2$	500	7.5	900/12	1	Al_2O_3
Ca_2FeO_3Br	$CaBr_2$	35	0.6	850/2	15	Al_2O_3
$Ca_3Fe_2O_5Br_2$	$CaBr_2$	40	0.6	875/2	15	Al_2O_3
Sr_2FeO_3Cl	$SrCl_2$	40	0.5	900/5	10	Pt
$Sr_3Fe_2O_5Cl_2$	$SrCl_2$	50	0.5	925/5	10	Al_2O_3
$Sr_2FeO_3Br_2$	$SrBr_2$	50	0.8	850/1	15	Al_2O_3
$Sr_3Fe_2O_5Br_2$	$SrBr_2$	50	1.0	850/5	15	Pt

convection currents in the molten mixtures leading to oxyhalide growth. Stagnant melts were seen in all other cases. This suggests that movement of some iron species to the flux/atmosphere interface is required for formation of these oxyhalides. The overall reactions which take place are

$$CaCl_2 + \tfrac{1}{2}Fe_2O_3 + \tfrac{1}{4}O_2 \rightarrow CaFeO_2Cl + \tfrac{1}{2}Cl_2$$

$$2CaCl_2 + \tfrac{1}{2}Fe_2O_3 + \tfrac{3}{4}O_2 \rightarrow Ca_2FeO_3Cl + \tfrac{3}{2}Cl_2 \quad (*)$$

$$3CaCl_2 + Fe_2O_3 + O_2 \rightarrow Ca_3Fe_2O_5Cl_2 + 2\,Cl_2. \quad (*)$$

The reactions marked with a star occur for the strontium and bromine analogs.

After the melts were cool, flux was removed by leaching in water. When $CaBr_2$ was the flux there was always a small amount of CaO left on the surface of the product which was removed by rinsing in a 0.5 *M* acetic acid/H_2O solution. The wet products were rinsed with absolute ethanol and then dried and stored *in vacuo*.

TABLE II

LATTICE CONSTANTS OF THE ALKALINE EARTH IRON OXYHALIDES

Material	Crystal class	Dimensions (Å)
$CaFeO_2Cl$	Monoclinic (type 1)	8.712(3) × 3.828(1) × 9.999(4) $\beta = 103.4$
Ca_2FeO_3Cl	Tetragonal (type 2)	3.848(2) × 13.65(1)
$Ca_3Fe_2O_5Cl_2$	Tetragonal (type 3)	3.859(2) × 23.187(5)
Sr_2FeO_3Cl	Tetragonal (type 2)	3.956(5) × 13.98(1)
$Sr_3Fe_2O_5Cl$	Tetragonal (type 3)	3.952(1) × 23.807(3)
Ca_2FeO_3Br	Tetragonal (type 2)	3.862(1) × 14.80(1)
$Ca_3FeO_5Br_2$	Tetragonal (type 3)	3.864(2) × 24.74(2)
$Ca_xFe_yO_zBr$	Tetragonal (undetermined)	3.868(1) × 17.42(1)
Sr_2FeO_3Br	Tetragonal (type 2)	3.971(1) × 15.04(1)
$Sr_3Fe_2O_5Br_2$	Tetragonal (type 3)	3.966(1) × 25.414(5)
$Sr_uFe_yO_wBr$	Tetragonal (undetermined)	3.973(2) × 33.48(3)
Ba_2FeO_3Br	Tetragonal (type 2)	4.011(s) × 15.50(2)

TABLE III

THE STRUCTURAL PARAMETERS OF $CaFeO_2Cl$

Monoclinic, space group *Cm*
$a = 8.712(5)$ Å, $b = 3.828(1)$ Å, $c = 9.999(4)$ Å
$\alpha = \delta = 90°$, $\beta = 103.53°(4)$, $V = 216.1$ Å^3
$Z = 4$, $D_x = 3.33$, $F(0,0,0) = 348.0$, $\mu = 67.4\ \text{cm}^{-1}$
Weight $= (\sigma^2(F) + 0.01F^2)^{-1}$
$R = 0.050$ $R_w = 0.076$
1245 total reflections collected
335 unique reflections having $I > 3\sigma$ used for refinement of 59 parameters yielding 5.6 reflections per parameter

Atom	*X/A*	*Y/B*	*Z/C*	*K*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{equiv}
Fe1	0.00000	0.00000	0.00000	0.5000	0.0255	0.0221	0.0065	0.0000	0.0029	0.0000	0.0181
	0.00000	0.00000	0.00000	0.0000	0.0023	0.0020	0.0022	0.0000	0.0021	0.0000	0.0014
Ca1	0.29679	0.00000	0.74477	0.5000	0.0258	0.0097	0.0155	0.0000	0.0005	0.0000	0.0177
	0.00095	0.00000	0.00067	0.0000	0.0031	0.0020	0.0029	0.0000	0.0034	0.0000	0.0017
Fe2	0.00026	0.00000	0.27433	0.5000	0.0381	0.0118	0.0093	0.0000	0.0101	0.0000	0.0190
	0.00036	0.00000	0.00029	0.0000	0.0031	0.0015	0.0023	0.0000	0.0024	0.0000	0.0015
Cl1	0.37396	0.00000	0.47564	0.5000	0.0414	0.0175	0.0051	0.0000	0.0062	0.0000	0.0212
	0.00137	0.00000	0.00074	0.0000	0.0042	0.0028	0.0048	0.0000	0.0038	0.0000	0.0025
Cl2	0.62299	0.50000	0.30483	0.5000	0.0212	0.0392	0.0233	0.0000	0.0065	0.0000	0.0277
	0.00118	0.00000	0.00090	0.0000	0.0026	0.0037	0.0049	0.0000	0.0036	0.0000	0.0024
Ca2	0.70981	0.00000	0.52901	0.5000	0.0367	0.0245	0.0142	0.0000	0.0143	0.0000	0.0237
	0.00108	0.00000	0.00076	0.0000	0.0042	0.0030	0.0031	0.0000	0.0039	0.0000	0.0022
O1	−0.17010	0.00000	0.11389	0.5000	0.0189	0.0251	0.0098	0.0000	0.0085	0.0000	0.0171
	0.00268	0.00000	0.00195	0.0000	0.0098	0.0097	0.0096	0.0000	0.0079	0.0000	0.0060
O2	0.95579	0.00000	0.45586	0.5000	0.0349	0.0028	0.0153	0.0000	0.0122	0.0000	0.0166
	0.00312	0.00000	0.00283	0.0000	0.0105	0.0061	0.0095	0.0000	0.0083	0.0000	0.0056
O3	0.15653	0.00000	0.16446	0.5000	0.0200	0.0160	0.0096	0.0000	0.0006	0.0000	0.0157
	0.00292	0.00000	0.00247	0.0000	0.0095	0.0097	0.0102	0.0000	0.0084	0.0000	0.0061
O4	0.06354	0.00000	−0.18113	0.5000	0.0228	0.0319	0.0028	0.0000	−0.0014	0.0000	0.0199
	0.00319	0.00000	0.00228	0.0000	0.0099	0.0080	0.0077	0.0000	0.0080	0.0000	0.0053

Lithium intercalation tests were done by adding in *n*-butyllithium in hexane to suspensions of the products in hexane. Pyridine intercalation tests were performed through the addition of freshly distilled pyridine to the solid oxyhalide. All intercalation tests were done at 25°C under a dry nitrogen atmosphere.

X-ray powder diffraction patterns were obtained with a Siemens D-500 θ–θ diffractometer using Cu$K\alpha_1$ radiation and a graphite monochrometer. The diffraction angle was calibrated with pure Si before and after each scan. A scan speed of $\frac{1}{4}°$ 2θ/sec between 10° and 90° was used. Least squares refinement of the interplanar spacings to yield cell constants was done using a local computer program.

Single crystal diffraction intensities were measured on a Nicolet P3F four circle diffractometer with Mo*K* radiation selected with a graphite monochrometer. Full spheres of data with $3° < 2\theta < 50°$ were collected at scan rates of 4–30°/min. Twenty strong reflections were used to determine the cell dimensions and to establish the crystal orientation. Absorption corrections were applied empirically from Psi scans of eight strong reflections. Full matrix structure refinement was done utilizing the program SHELXTL-84 implemented on a Data General Eclipse computer. Mossbauer resonance was measured with an Elscint S-N spectrometer having 20 mCi of Co57 alloyed into a pure Cu source. Velocities were calibrated using pure iron foil.

Results and Discussion

The compounds were synthesized as well-formed red–brown transparent flakes. In all but the case of $CaFeO_2Cl$, the flakes formed with a tetragonal habit having typical dimensions 2 × 2 × 0.005 mm. $CaFeO_2Cl$ grew as

TABLE IV

Bond Lengths (Å) and Bond Angles in $CaFeO_2Cl$

Bond	Length (Å)	Bond	Length (Å)
Fe(1)–O(3)	1.879(22)	Fe(1)–O(1)	2.077(24)
Fe(1)–O(2)	1.982(7)	Fe(1)–O(4)	2.015(26)
Ca(1)–Cl(1)	2.924(12)	Fe(1)–O(2)	1.982(7)
Ca(1)–Cl(1)	2.953(7)	Ca(1)–Cl(1)	2.953(7)
Ca(1)–Cl(2)	2.780(13)	Ca(1)–O(3)	2.315(14)
Ca(1)–O(3)	2.315(14)	Ca(1)–O(4)	2.331(30)
Fe(2)–O(1)	1.919(19)	Fe(2)–O(3)	1.946(28)
Fe(2)–O(2)	1.944(30)	Fe(2)–O(4)	2.013(7)
Fe(2)–O(4)	2.013(7)	Cl(1)–Ca(2)	2.865(15)
Cl(2)–Ca(2)	2.910(8)	Ca(2)–Cl(2)	2.910(8)
Cl(2)–Ca(2)	2.910(8)	Ca(2)–O(1)	2.252(11)
Ca(2)–Cl(2)	3.028(13)	O(1)–Ca(2)	2.522(11)
Ca(2)–O(1)	2.252(11)		
Bond	Angle (deg)	Bond	Angle (deg)
Cl(1)–Ca(1)–Cl(1b)	131.3(3)	Cl(1)–Ca(1)–Cl(1a)	131.3(3)
Cl(1)–Ca(1)–O(3a)	84.2(7)	Cl(1)–Ca(1)–Cl(2b)	75.6(4)
Cl(1)–Ca(1)–O(4a)	134.3(6)	Cl(1)–Ca(1)–O(3b)	84.2(7)
O(3)–Fe(2)–O(2a)	148.1(10)	O(1)–Fe(2)–O(3)	92.3(10)
O(1)–Fe(2)–O(4b)	107.8(6)	O(1)–Fe(2)–O(2a)	119.6(10)
O(3)–Fe(2)–O(4c)	86.1(8)	O(3)–Fe(2)–O(4b)	86.1(8)
Ca(1)–Cl(1)–Ca(1c)	131.3(3)	O(1)–Fe(2)–O(4c)	107.8(6)
Ca(1)–Cl(1)–Ca(1d)	131.3(3)	Ca(1)–Cl(1)–Ca(2)	106.1(3)
Ca(2)–Cl(2)–Ca(1c)	103.7(4)	Ca(2)–Cl(1)–Ca(1c)	100.5(4)
Ca(2)–Cl(2)–Ca(2e)	128.7(3)	Ca(2)–Cl(1)–Ca(1d)	100.5(4)
O(2)–Ca(2)–O(1a)	75.2(7)	Ca(2)–Cl(2)–Ca(2a)	82.3(3)
O(3)–Fe(1)–O(2b)	105.0(7)	Cl(1)–Ca(2)–Cl(2)	77.6(3)
O(1)–Fe(1)–O(2)	89.7(9)	Cl(1)–Ca(2)–Cl(2b)	72.8(3)
O(4)–Fe(1)–O(2b)	33.1(9)	O(2)–Ca(2)–O(1b)	75.2(7)
O(1)–Fe(1)–O(7c)	89.7(9)	O(4)–Fe(1)–O(2c)	83.1(9)

0.005 × 0.5 × 2 mm needles. Under microscopic examination between crossed polarizers, both the flakes and the needles extinguished uniformly, indicating that they were single crystals. Larger crystals could be made when very slow cooling rates and large crucibles were used. As an example, $Ca_3Fe_2O_5Cl_2$ crystals 3 cm × 3 cm × 2 mm were made by cooling at 5°C/hr in a 250-ml crucible. All crystals were micaceous with planes of easy cleavage perpendicular to the shortest dimension for $CaFeO_2Cl$ and perpendicular to the tetragonal axes for the rest.

The crystals were stable for at least 7 years when kept under dry nitrogen at 25°C. Similar stability is seen for most of the materials in air; however, the calcium iron oxybromides decompose slowly in moist air to yield Fe_2O_3 and deliquescent calcium salts. Heating above 350°C also decomposes these materials.

With the exception of $CaFeO_2Cl$ growths, powder X-ray diffraction of the product from one crucible typically indicated the presence of two phases. However, it was possible to measure individual cell constants by grinding large single crystals. All of the compounds but $CaFeO_2Cl$ crystallize with tetragonal cells having the dimensions listed in Table II. $CaFeO_2Cl$ has a monoclinic cell whose dimensions are also given in Table II. From the abundance of available

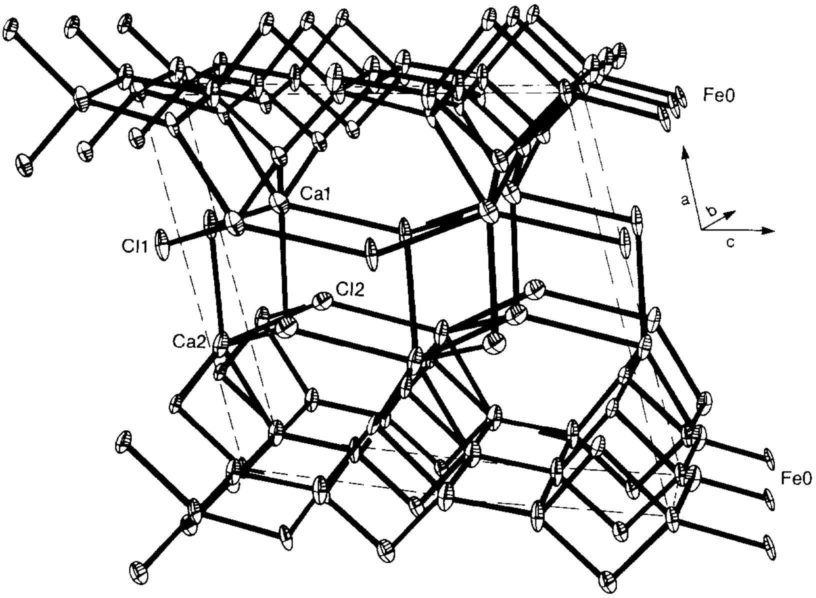

FIG. 1. The structure of $CaFeO_2Cl$.

crystals, several suitable for structure determination were selected.

Type 1, $CaFeO_2Cl$

For 335 unique reflections of a 0.003 × 0.1 × 1.2 mm crystal systematic reflections indicated a *A*-centered cell which limited the possible space groups to *Am*, *A*21, or *A*21/*n*. The final solution of the structure was determined using *Am*, a nonstandard setting of *Cm*. Calcium, iron, and chlorine positions were found using the heavy atom method and the oxygen positions were derived from difference maps. The 59 independent parameters were refined to R and R_w values of 0.0505 and 0.0768, respectively. The atomic positions and thermal parameters are given in Table III. Bond lengths and angles are listed in Table IV. The structure is presented in Fig. 1 and is best described as sheets of iron and oxygen lying parallel to the *ac* plane which are separated from one another by calcium/chlorine regions. The two unique iron atoms are each surrounded by five oxygen atoms having a distorted trigonal biprismatic (tbp) geometry, Fig. 2. The trigonal biprisms interconnect to form the iron/oxygen sheets via

(i) equatorial–equatorial edge sharing of one tbp with an equatorial–equatorial edge of one other tbp,

(ii) equatorial–axial edge sharing of one tbp with an equatorial–axial edge of two other tbps.

This interconnection is shown in detail in Fig. 3.

The nearest neighbors to the Fe–O sheets are calcium atoms which lie at the centers of distorted face-capped octahedra. The capped octahedra are formed from three oxygens from one Fe–O sheet and four adjoining chlorines, Figs. 4 and 5. The calcium polyhedra share edges and thereby link the Fe–O sheet to one another.

Type 2, Ca_2FeO_3Cl

A 1 × 1 × 0.007 mm crystal was selected and shown to have the tetragonal 3.85 × 13.65 Å cell previously identified by powder diffraction. The full sphere of reflection in-

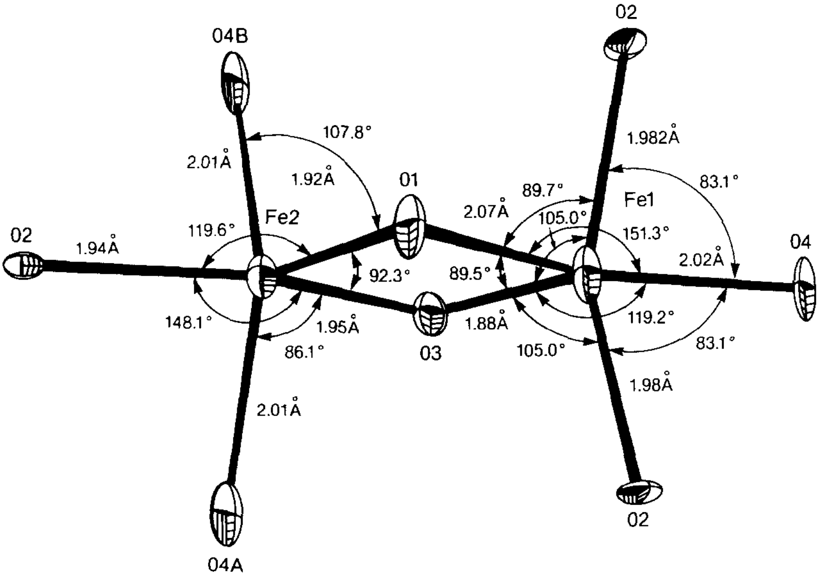

FIG. 2. Iron coordination, bond distances, and bond angles in $CaFeO_2Cl$.

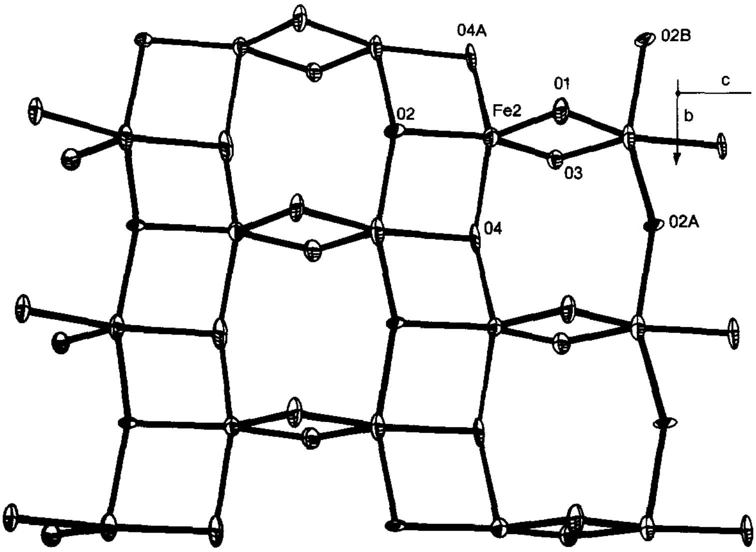

FIG. 3. The Fe–O sheets of $CaFeO_2Cl$; seen projected onto the *bc* plane.

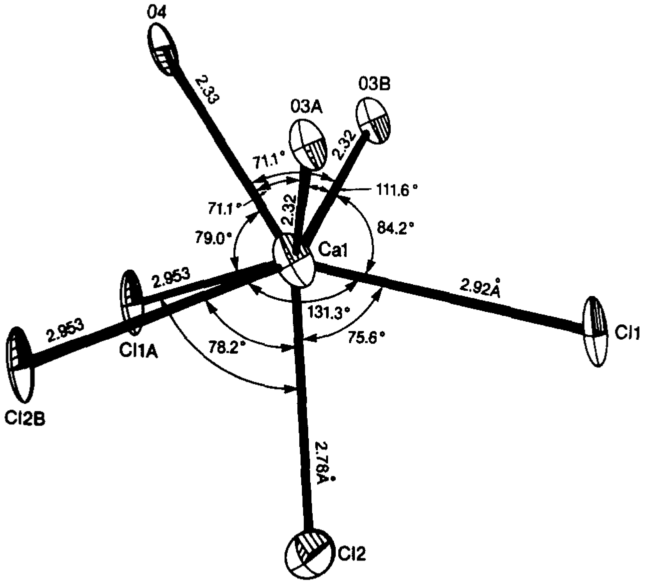

FIG. 4. Calcium 1 coordination, bond distances, and bond angles in $CaFeO_2Cl$.

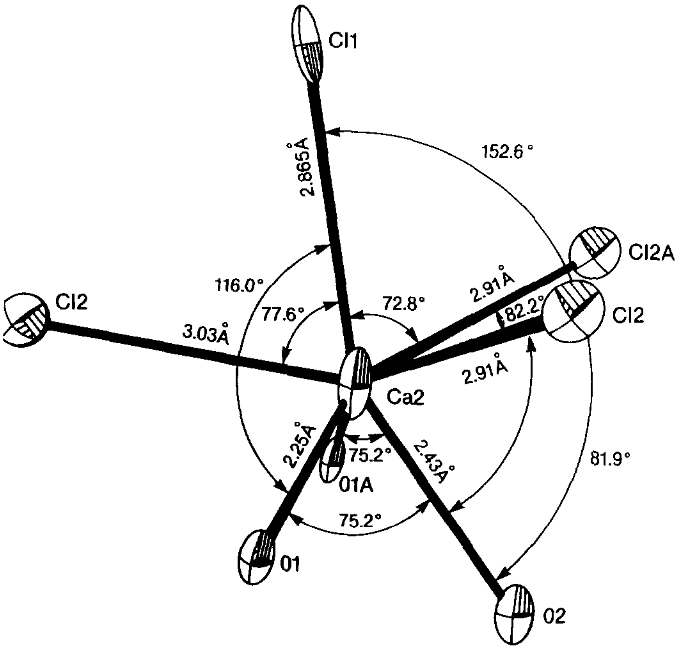

FIG. 5. Calcium 2 coordination, bond distances, and bond angles in $CaFeO_2Cl$.

TABLE V

THE STRUCTURAL PARAMETERS OF $CaFeO_3Cl$

Tetragonal, space group $P4$
$a = 3.848(2)$ Å, $b = 3.848(2)$ Å, $c = 13.65(1)$ Å
$\alpha = \beta = \delta = 90°$, $V = 202.3$ Å^3
$Z = 2$, $D_x = 3.60$, $F(0,0,0) = 213.9$, $\mu = 66.4\ cm^{-1}$
Weight $= (\sigma^2(F) + 0.01F^2)^{-1}$
$R = 0.054$ $R_w = 0.071$
1466 total reflections collected
384 unique reflections having $I > 3\sigma$ used for refinement of 32 parameters yielding 12 reflections per parameter

Atom	X/A	Y/B	Z/C	K	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{equiv}
Fe1	0.00000	0.00000	0.00000	0.2500	0.0003	0.0003	0.0085	0.0000	0.0000	0.0000	0.0030
	0.00000	0.00000	0.00000	0.0000	0.0007	0.0007	0.0017	0.0000	0.0000	0.0000	0.0006
Fe2	0.50000	0.50000	0.41858	0.2500	0.0031	0.0031	0.0285	0.0000	0.0000	0.0000	0.0116
	0.00000	0.00000	0.00027	0.0000	0.0011	0.0011	0.0027	0.0000	0.0000	0.0000	0.0010
Ca1	0.00000	0.00000	0.54999	0.2500	0.0041	0.0041	0.0072	0.0000	0.0000	0.0000	0.0051
	0.00000	0.00000	0.00050	0.0000	0.0012	0.0012	0.0026	0.0000	0.0000	0.0000	0.0010
Ca2	0.00000	0.00000	0.30939	0.2500	0.0177	0.0177	0.0146	0.0000	0.0000	0.0000	0.0166
	0.00000	0.00000	0.00062	0.0000	0.0018	0.0018	0.0037	0.0000	0.0000	0.0000	0.0015
Cl1	0.00000	0.00000	0.77633	0.2500	0.0191	0.0191	0.0402	0.0000	0.0000	0.0000	0.0261
	0.00000	0.00000	0.00091	0.0000	0.0019	0.0019	0.0042	0.0000	0.0000	0.0000	0.0017
Cl2	0.50000	0.50000	0.63152	0.2500	0.0147	0.0147	0.0112	0.0000	0.0000	0.0000	0.0135
	0.00000	0.00000	0.00070	0.0000	0.0019	0.0019	0.0023	0.0000	0.0000	0.0000	0.0012
Ca3	0.50000	0.50000	0.86553	0.2500	0.0220	0.0220	0.0479	0.0000	0.0000	0.0000	0.0306
	0.00000	0.00000	0.00075	0.0000	0.0023	0.0023	0.0057	0.0000	0.0000	0.0000	0.0022
Ca4	0.50000	0.50000	0.12206	0.2500	0.0136	0.0136	0.0104	0.0000	0.0000	0.0000	0.0125
	0.00000	0.00000	0.00057	0.0000	0.0020	0.0020	0.0022	0.0000	0.0000	0.0000	0.0012
O1	0.00000	0.50000	0.97257	0.5000	0.0190	0.0083	0.0393	0.0000	0.0000	0.0004	0.0222
	0.00000	0.00000	0.00141	0.0000	0.0033	0.0027	0.0082	0.0000	0.0000	0.0017	0.0031
O2	0.00000	0.50000	0.44045	0.5000	0.0213	0.0302	0.0361	0.0000	0.0000	0.0004	0.0292
	0.00000	0.00000	0.00113	0.0000	0.0035	0.0042	0.0105	0.0000	0.0080	0.0023	0.0039
O3	0.00000	0.00000	0.12399	0.2500	0.0076	0.0076	0.4001	0.0000	0.0000	0.0000	0.1384
	0.00000	0.00000	0.00302	0.0000	0.0069	0.0069	0.0642	0.0000	0.0000	0.0000	0.0216
O4	0.50000	0.50000	0.27940	0.2500	0.0271	0.0271	0.0001	0.0000	0.0000	0.0000	0.0181
	0.00000	0.00000	0.00114	0.0000	0.0049	0.0049	0.0064	0.0000	0.0000	0.0000	0.0031

tensities was merged to 383 unique reflections. No systematic reflection condition was observed and subsequent resolution of the structure was done using the space group $P4$. The calcium, iron, and chlorine atoms were found from Patterson maps and the oxygen positions resulted from difference maps. Forty independent parameters were refined to R and R_w factors of 0.0537 and 0.0713. The atomic positions and thermal parameters are listed in Table V. The bond lengths and angles are given in Table VI.

Each cell contains two iron, four calcium, two chlorine, and four oxygen atoms. Both irons are surrounded by five oxygens and one chlorine which produce distorted octahedral environments, Fig. 6. Two of the calciums are surrounded by nine oxygens and the other two calciums are bound to four oxygens and five chlorines. All of the local calcium geometries are similar, being that of distorted capped square antiprisms, Figs. 7 and 8. The structure of Ca_2FeO_3Cl is a variation of the $[K_2NiF_4]$ structure; built up of sheets of corner sharing iron–anion octahedra which stack along the c axis, Fig. 9. Nested between the octahedra, near the ideal potassium positions of $[K_2NiF_4]$, are found the calcium atoms.

Type 3, $Sr_3Fe_2O_5Cl_2$

Rotation photos of a 0.9 × 0.9 × 0.035 mm crystal were indexed using a 3.95 × 23.65 Å tetragonal cell. Examination of the diffraction intensities indicated the systematic reflection conditions of a body-cen-

TABLE VI

BOND LENGTHS (Å) AND ANGLES FOR Ca_2FeO_3Cl

Bond	Length (Å)	Bond	Length (Å)
Fe1(1)–Cl(1)	2.985(9)	Fe(1)–O(4)	1.904(22)
Fe(2)–Cl(2)	2.943(16)	Fe(1)–O(1)	1.952(2)
Fe(3)–O(3)	1.856(41)	Fe(3)–O(2)	1.966(4)
Ca(1)–Cl(2)	2.941(6)	Ca(1)–O(2)	2.395(12)
Ca(2)–O(2)	2.751(16)	Ca(2)–O(3)	2.737(5)
CA(2)–O(4)	2.225(25)	Ca(3)–Cl(1)	2.969(5)
Ca(3)–O(1)	2.421(9)	Ca(4)–O(4)	2.744(3)
Ca(4)–O(3)	2.289(41)	Ca(4)–O(1)	2.689(9)
Ca(1)–Cl(1)	3.153(7)	Ca(3)–Cl(2)	3.225(9)
Bond	**Angles (deg)**	**Bond**	**Angles (deg)**
		Cl(1a)–Fe(1)–O(1a)	80.3(3)
O(4)–Fe(1)–Cl(1a)	180.0	Cl(2)–Ca(1)–Cl(2a)	81.7(2)
O(4)–Fe(1)–O(1a)	99.7(3)	Cl(1)–Ca(1)–O(2a)	126.5(4)
O(1)–Fe(1)–O(1a)	88.4(1)	O(3)–Ca(2)–O(4)	83.9(9)
Cl(2)–Fe(2)–O(2)	78.2(6)	O(2)–Ca(2)–O(2e)	59.3(4)
O(2)–Fe(2)–O(3)	101.8(6)	O(3)–Ca(4)–O(4)	82.6(5)
O(2)–Fe(2)–O2(a)	87.6(2)	O(4)–Ca(4)–O(1)	65.7(4)
Cl(1)–Ca(1)–O(2)	126.5(4)	O(1)–Ca(4)–O(1a)	60.8(2)
Cl(1)–Ca(1)–Cl(2a)	67.7(3)	O(4)–Ca(4)–O(4a)	89.0(1)
O(2)–Ca(1)–Cl(2a)	72.5(3)	Cl(1)–Ca(3)–Cl(1a)	80.8(2)
O(2)–Ca(1)–O(2a)	69.2(4)	Cl(1)–Ca(3)–Cl(2)	66.4(5)
O(2)–Ca(2)–O(3)	65.4(7)		
O(3)–Ca(2)–O(3a)	89.4(2)		
Cl(1c)–Ca(3)–O(1c)	74.2(2)		
O(1)–Ca(3)–O(1a)	68.4(3)		

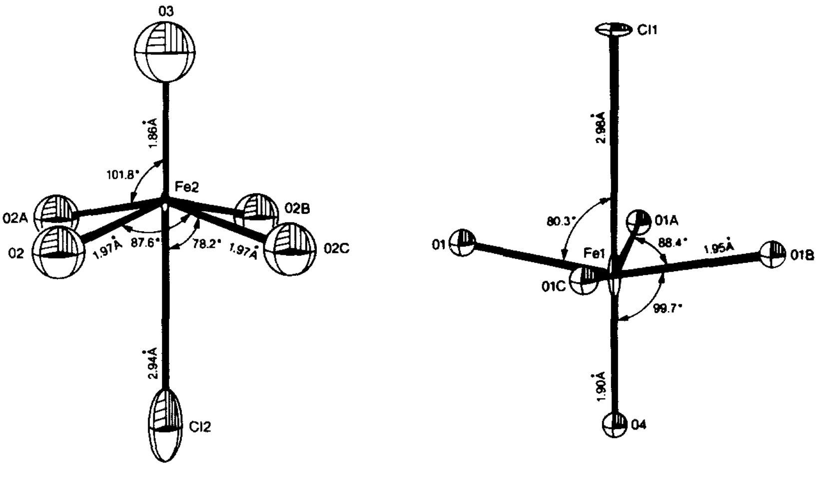

FIG. 6. Iron coordination, bond distances, and bond angles in Ca_2FeO_3Cl.

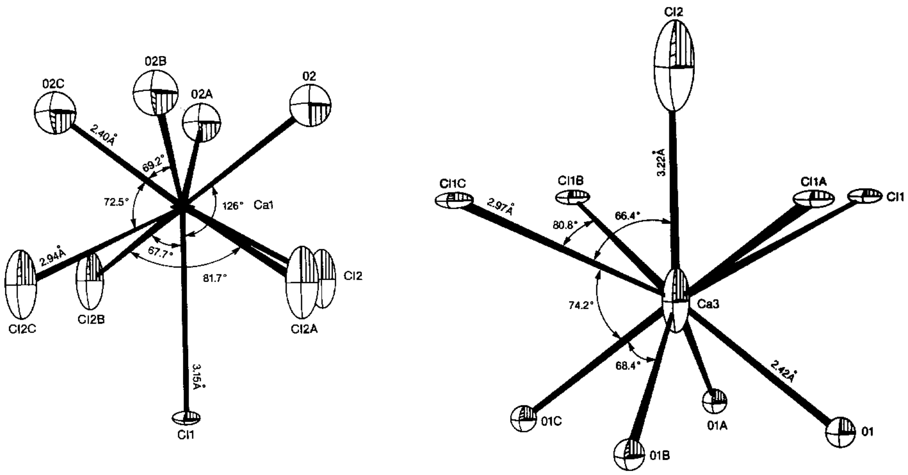

FIG. 7. Calcium 1 and 3 coordination, bond distances, and bond angles in Ca_2FeO_3Cl.

tered cell. Final structure refinement was performed within the symmetry conditions imposed by the space group $I4/mmm$. The set of 205 unique reflections was used to determine the 18 independent atomic parameters yielding the residuals, R and R_w, of 0.0347 and 0.0482. The cell contains six unique atoms whose positions and thermal parameters are given in Table VII. Bond lengths and angles are presented in Table VIII.

The structure of $Sr_3Fe_2O_5Cl_2$ is shown in Fig. 10. It is a distorted version of the $[K_3Ni_2F_7]$ structure composed of stacked sheets of doubled Fe–O–Cl octahedra. The FeO_5Cl octahedra, Fig. 11, share a total of five corners with neighboring octahedra. All of the shared corners are oxygen atoms. The sixth vertex of each octahedron is occupied by chlorine which collectively forms the upper and lower faces of the sheets. The sheets stack along the c axis accompanied by a translation of $1/2a + 1/2b$ so as to allow the chlorines of opposing sheets to achieve the

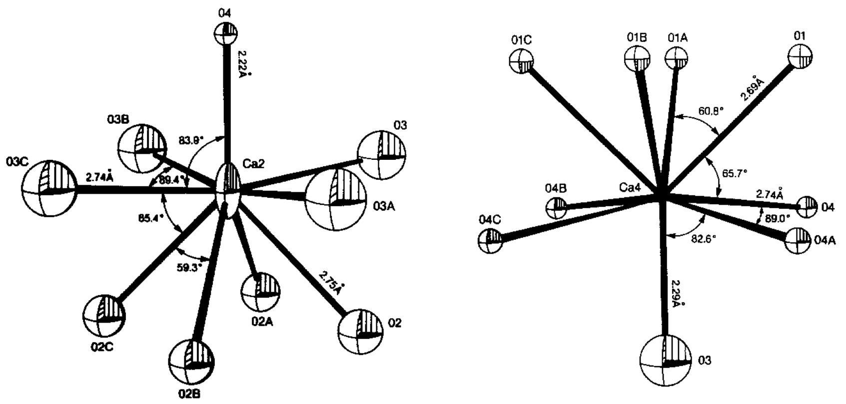

FIG. 8. Calcium 2 and 4 coordination, bond distances, and bond angles in Ca_2FeO_3Cl.

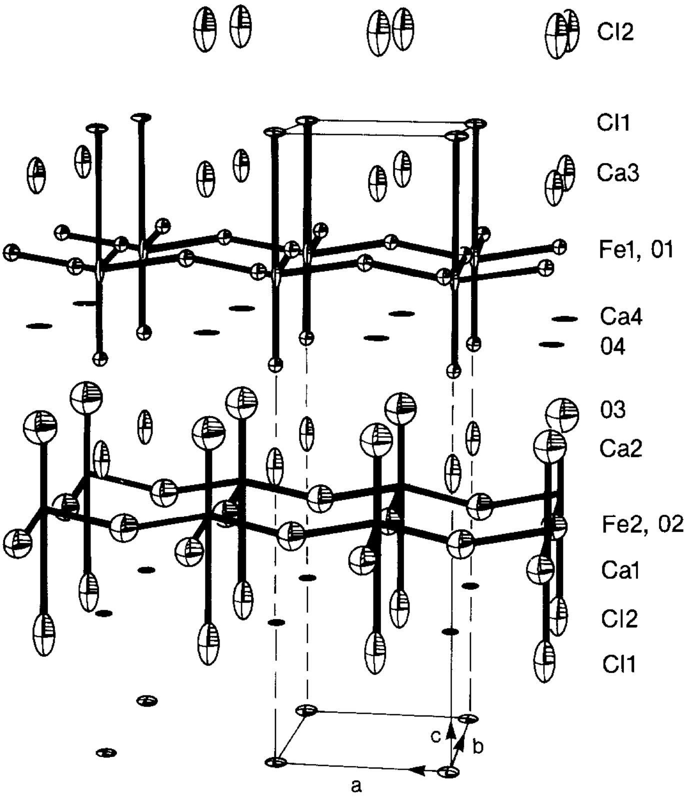

FIG. 9. The structure of Ca_2FeO_3Cl.

densest packing of square nets. The strontium atoms occupy two positions. Sr1 lies in the center of the sheets and is bonded to 12 oxygens in a slightly distorted dodecahedral geometry, Fig. 12. The remaining strontium, Sr2, has four oxygen and five chlorine neighbors distributed in a distorted capped square antiprismatic geometry, Fig. 13.

The structures of two other materials of this type were determined. The pertinent data for $Sr_3Fe_2O_5Br_2$ and $Ca_3Fe_2O_5Cl_2$ are found in Table IX and X.

The dominant structural feature of the alkaline earth oxyhalides is the segregation of the iron/oxygen regions from the halide regions via the creation of layers. The manner in which these layers are formed in Ca_2FeO_3Cl and $Sr_3Fe_2O_5Cl_2$ is not new since it is already found in the [K_2NiF_4]-perovskite structural series (2). The formation of a two-dimensional layer from trigonal bipyramids (tbps) as in $CaFeO_2Cl$ appears unique. A large part of this uniqueness is due to the rarity of tbps in close-packed nonmolecular solids. Indeed, close-packing of the anions must be disturbed to provide tbp sites. In $CaFeO_2Cl$, the presence of two anions of dissimilar radii frustrates normal closest packing, thereby assisting in the tbp site formation.

Between all of the iron/oxygen layers are alkaline earth/halide regions with halogen–halogen contacts. From a simple electrostatic bonding model these regions must contain weaker interatomic bonding than the iron/oxygen regions. The degree of bonding across the halogen–halogen contacts is not readily apparent from the struc-

TABLE VII

THE STRUCTURAL PARAMETERS OF $Sr_3Fe_2O_5Cl_2$

Tetragonal, space group *I4/mmm*
$a = 83.952(1)$ Å, $b = 3.952(1)$ Å, $c = 23.807(3)$ Å
$\alpha = \beta = \delta = 90°$, $V = 371.9$ Å^3
$Z = 2$, $D_x = 4.69$, $F(0,0,0) = 479.8$, $\mu = 268.8\ \text{cm}^{-1}$
Weight $= (\sigma^2(F) + 0.001F^2)^{-1}$
$R = 0.034$ $R_w = 0.048$
2344 total reflections collected
205 unique reflections having $I > 3\sigma$ used for refinement of 18 parameters yielding 11.39 reflections per parameter

Atom	X/A	Y/B	Z/C	K	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{equiv}
Sr1	0.00000	0.00000	0.00000	0.0625	0.0123	0.0123	0.0211	0.0000	0.0000	0.0000	0.0152
	0.00000	0.00000	0.00000	0.0000	0.0005	0.0005	0.0007	0.0000	0.0000	0.0000	0.0003
Sr2	0.00000	0.00000	0.15716	0.1250	0.0099	0.0099	0.0164	0.0000	0.0000	0.0000	0.0121
	0.00000	0.00000	0.00003	0.0000	0.0004	0.0004	0.0005	0.0000	0.0000	0.0000	0.0002
Fe	0.00000	0.00000	0.42127	0.1250	0.0074	0.0074	0.0133	0.0000	0.0000	0.0000	0.0093
	0.00000	0.00000	0.00004	0.0000	0.0005	0.0005	0.0007	0.0000	0.0000	0.0000	0.0003
Cl	0.00000	0.00000	0.29517	0.1250	0.0149	0.0149	0.0183	0.0000	0.0000	0.0000	0.0160
	0.00000	0.00000	0.00008	0.0000	0.0006	0.0006	0.0009	0.0000	0.0000	0.0000	0.0004
O1	0.50000	0.00000	0.09056	0.2500	0.0112	0.0089	0.0179	0.0000	0.0000	0.0000	0.0127
	0.00000	0.00000	0.00015	0.0000	0.0015	0.0015	0.0014	0.0000	0.0000	0.0000	0.0008
O2	0.00000	0.00000	0.50000	0.0625	0.0171	0.0171	0.0051	0.0000	0.0000	0.0000	0.0127
	0.00000	0.00000	0.00000	0.0000	0.0020	0.0020	0.0026	0.0000	0.0000	0.0000	0.0013

ture. In an extreme view there would be no bonding between the sheets and a Van der Waals gap would exist. Such a Van der Waals gap together with the easily reduced Fe^{+3} ions in the sheets would be an ideal lithium or pyridine intercalation host. We found, however, that none of these materials undergo intercalation. This suggests that the halogens do not fully screen the attraction of the alkaline earths for the halogen

TABLE VIII

BOND LENGTH AND ANGLES FOR $Sr_3Fe_2O_5Cl_2$

Bond	Length (Å)	Bond	Angle (deg)
Sr(1)–O(1)	2.921(2)	O(2)–Sr(1)–O(2a)	90.0
Sr(1)–O(2)	2.795	O(2)–Sr(1)–O(2c)	180.0
Sr(2)–O(1)	2.534(2)	O(1)–Sr(1)–O(1a)	57.2(1)
Sr(2)–Cl	3.016(1)	O(1)–Sr(1)–O(2)	61.4(1)
Sr(2)–O(1)	2.534(2)	O(1a)–Sr(2)–Cl	74.0(1)
Fe–O(2)	1.874(1)	Cl(a)–Sr(2)–Cl(b)	81.9(1)
Fe–O(1)	2.001(1)	O(1a)–Sr(2)–O(1b)	66.9(1)
Fe–Cl	3.004(5)	Cl(a)–Sr(2)–Cl(d)	67.8(1)
Sr(2a)–Cl	3.281(2)	O(1)–Fe–O(1a)	88.6(1)
		O(2)–Fe–O(1)	94.8(1)
		O(1)–Fe–Cl	81.1(1)
		O(2a)–Sr(1)–O(2b)	90.0
		O(1)–Sr(2)–Cl(b)	74.0(1)
		Cl(a)–Sr(2)–Cl(c)	81.9
		O(2a)–Sr(1)–O(2c)	90.0
		O(1)–Sr(2)–Cl(a)	138.3

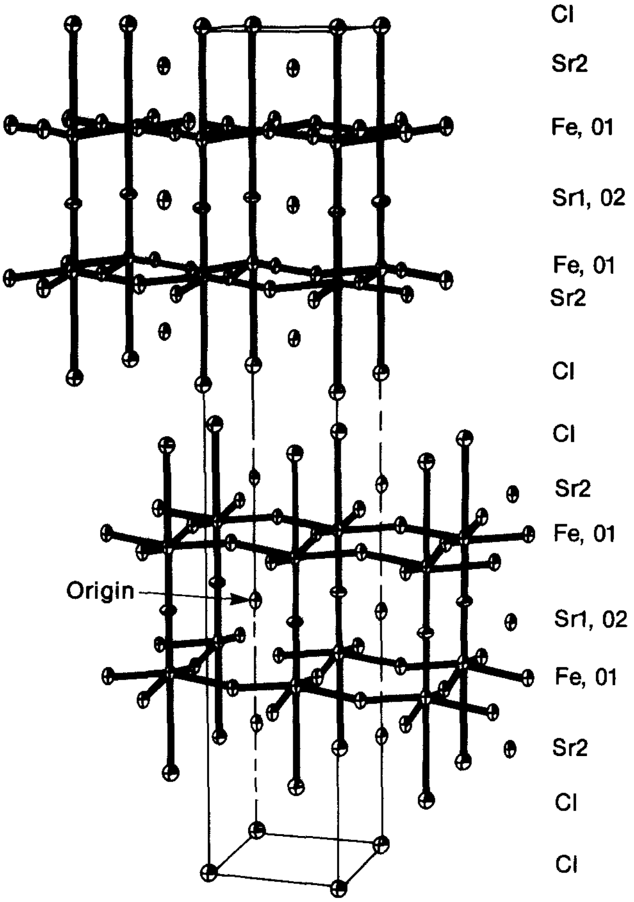

FIG. 10. The structure of $Sr_3Fe_2O_5Cl_2$. The origin is moved to better illustrate the doubled perovskitic layers.

of the opposing sheets. Nevertheless, the long bond between these atoms must be weak and the micaceous cleavage of these materials is consistent with such weak bonding between layers.

Another structural feature is the increase in the cell constants as the cation is changed from Ca to Sr or the halogen is changed from Cl to Br. We find that a cation change results in a relatively equivalent increase in both the *a* and the *c* dimensions whereas an anion change produces an increase predominantly along *c*. Such behavior is a consistent with the position of the halogen on the face of the sheets where a change in size is accomodated by movement of the sheets relative to one another rather than distortions within the sheet.

Examination of the bond lengths shows metal–oxygen distances which are near the ideal predicted from the sum of the ionic radii (*3*). The alkaline earth–halogen distances also lie near the predicted norms. Indeed, the only unusual bond lengths are those of iron to halogen. In both type 2 and type 3 structures the iron–chlorine distances are 2.94–3.00 Å, which is significantly longer than the sum of the ionic radii,

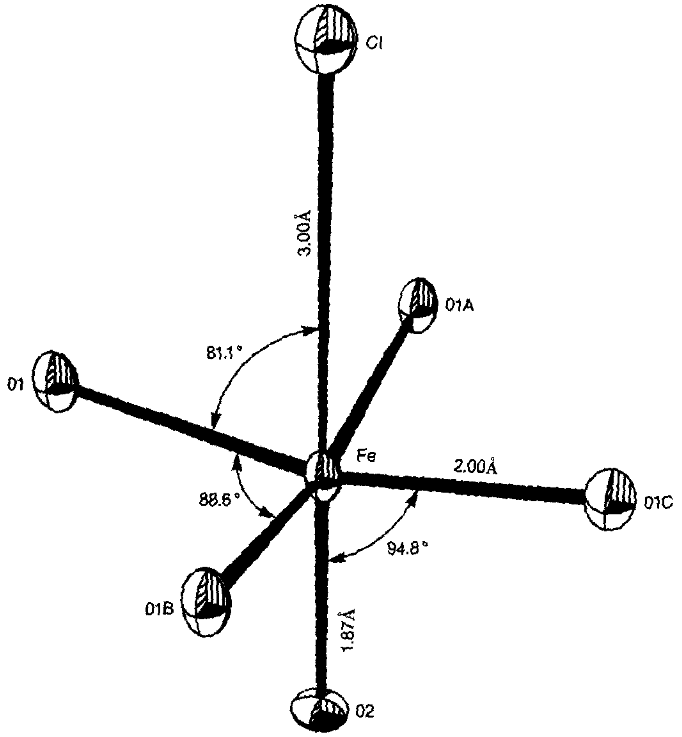

FIG. 11. Iron coordination, bond distances, and bond angles in $Sr_3Fe_2O_5Cl_2$.

2.46 Å. These long bonds are required in order that the alkaline earths occupy their positions between the Fe–O planes and the chlorine planes without exceptional compression of all bonds to the alkaline earths.

Mossbauer Spectra

For Mossbauer effect measurements of $Sr_3Fe_2O_5Cl_2$ and $Sr_3Fe_2O_5Br_2$ single crystals were mounted with their *c* axes parallel to the direction of γ ray propagation. Spectra of the calcium analogs were measured on polycrystalline powders having the same preferred orientation as the single crystals. The resulting spectra exhibit six resonance absorption peaks indicative of magnetic hyperfine splitting and the presence of magnetic order, Fig. 14. Intensity ratios of the six resonance lines are 3 : 4 : 1 : 1 : 4 : 3. These ratios result when the internal magnetic field is perpendicular to the direction of propagation for the γ-ray; so for these materials the magnetic field lies in the *ab* plane. The magnitudes of the internal fields and the isomer shifts are listed in Table XI and are consistent with iron being present in the trivalent, high spin electronic configuration. A Foner magnetometer was used to measure the magnetic moment of the same materials. In both cases the magnetization was less than 1 Bohr magneton, indicating that antiferromagnetic order prevails.

Superexchange between the metal atoms within a single sheet in the type 2 and type 3 structures is a 180° cation–anion–cation interaction. The Goodenough–Kanimori rules (*4*) for this interaction with the metal equal to Fe^{+3} having spin 5/2 qualitatively predicts strong antiferomagnetic exchange, consistent with the experimental observa-

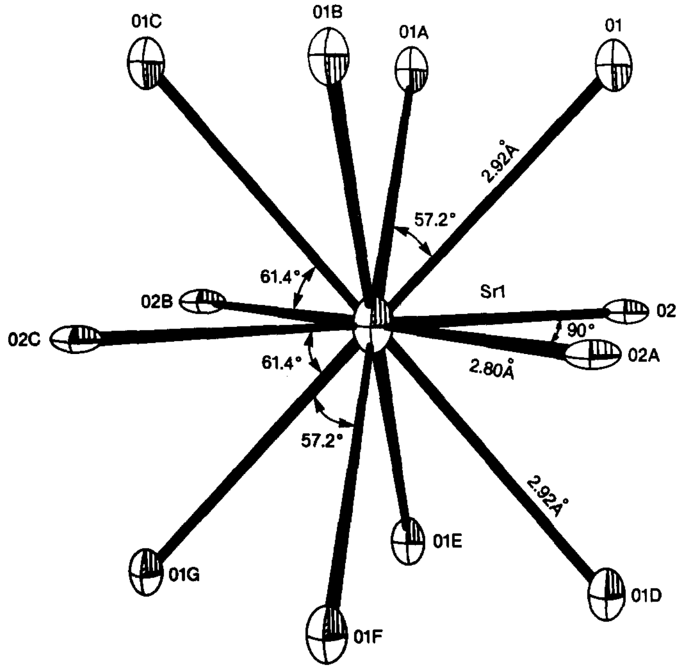

FIG. 12. Strontium 1 coordination, both distances, and bond angles in $Sr_3Fe_2O_5Cl_2$.

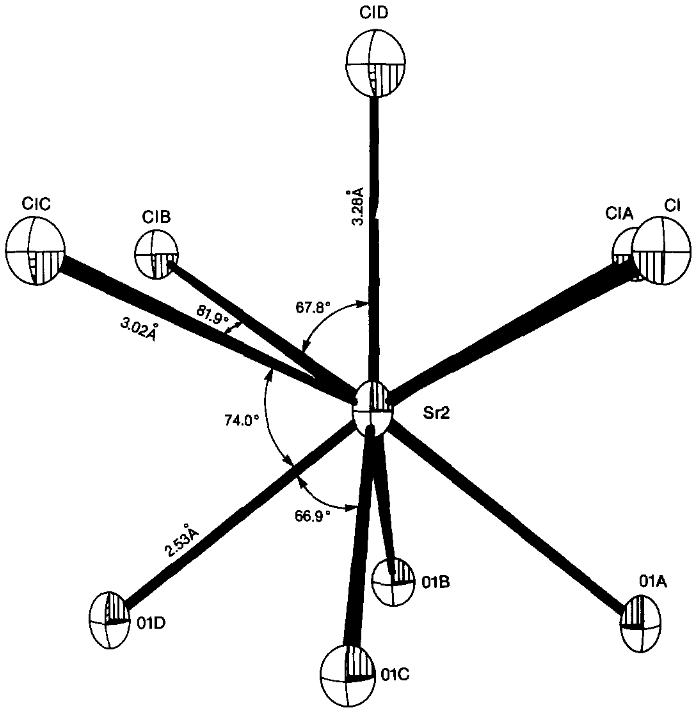

FIG. 13. Strontium 2 coordination, bond distances, and bond angles in $Sr_3Fe_2O_5Cl_2$.

TABLE IX

THE STRUCTURAL PARAMETERS OF $Sr_3Fe_2O_5Br_2$

Tetragonal, space group *I4/mmm*
$a = 3.966(1)$ Å, $b = 3.966(1)$ Å, $c = 25.414(5)$ Å
$\alpha = \beta = \delta = 90°$, $V = 399.8$ Å^3
$Z = 2$, $D_x = 5.10$, $F(0,0,0) = 551.8$, $\mu = 342.4\ \mathrm{cm}^{-1}$
Weight $= (\sigma^2(F) + 0.002F^2)^{-1}$
$R = 0.0374$ $R_w = 0.053$
2819 total reflections collected
146 unique reflections having $I > 3\sigma$ used for refinement of 18 parameters yielding 8.11 reflections per parameter

Atom	X/A	Y/B	Z/C	K	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{equiv}
Sr1	0.00000	0.00000	0.00000	0.0625	0.0074	0.0074	0.0155	0.0000	0.0000	0.0000	0.0101
	0.00000	0.00000	0.00000	0.0000	0.0014	0.0014	0.0021	0.0000	0.0000	0.0000	0.0011
Sr2	0.00000	0.00000	0.14632	0.1250	0.0058	0.0058	0.0140	0.0000	0.0000	0.0000	0.0085
	0.00000	0.00000	0.00000	0.0000	0.0013	0.0013	0.0018	0.0000	0.0000	0.0000	0.0009
Br	0.00000	0.00000	0.30005	0.1250	0.0101	0.0101	0.0176	0.0000	0.0000	0.0000	0.0126
	0.00000	0.00000	0.00000	0.0000	0.0013	0.0013	0.0021	0.0000	0.0000	0.0000	0.0010
Fe	0.50000	0.50000	0.07361	0.1250	0.0033	0.0033	0.0051	0.0000	0.0000	0.0000	0.0039
	0.00000	0.00000	0.00008	0.0000	0.0014	0.0014	0.0023	0.0000	0.0000	0.0000	0.0011
O1	0.50000	0.00000	0.08395	0.2500	0.0046	0.0023	0.0158	0.0000	0.0000	0.0000	0.0076
	0.00000	0.00000	0.00000	0.0000	0.0044	0.0014	0.0102	0.0000	0.0000	0.0000	0.0029
O2	0.50000	0.50000	0.00000	0.0625	0.0141	0.0141	0.0130	0.0000	0.0000	0.0000	0.0138
	0.00000	0.00000	0.00000	0.0000	0.0032	0.0032	0.0044	0.0000	0.0000	0.0000	0.0008

TABLE X

THE STRUCTURAL PARAMETERS OF $Ca_3Fe_2O_5Cl_2$

Tetragonal, space group *I4/mmm*
$a = 3.859(2)$ Å, $b = 3.859(2)$ Å, $c = 23.187(5)$ Å
$\alpha = \beta = \delta = 90°$, $V = 345.3$ Å^3
$Z = 2$, $D_x = 3.68$, $F(0,0,0) = 351.9$, $\mu = 67\ \mathrm{cm}^{-1}$
Weight $= (\sigma^2(F) + 0.001F^2)^{-1}$
$R = 0.0727$ $R_w = 0.1448$
1241 total reflections collected
128 unique reflections having $I > 3\sigma$ used for refinement of 15 parameters yielding 8.53 reflections per parameter

Atom	X/A	Y/B	Z/C	K	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{equiv}
CA1	0.00000	0.00000	0.50000	0.0625	0.0112	0.0112	0.0470	0.0000	0.0000	0.0000	0.0231
	0.00000	0.00000	0.00000	0.0000	0.0030	0.0030	0.0062	0.0000	0.0000	0.0000	0.0025
FE	0.00000	0.00000	0.07990	0.1250	0.0034	0.0034	0.0113	0.0000	0.0000	0.0000	0.0015
	0.00000	0.00000	0.00015	0.0000	0.0021	0.0021	0.0026	0.0000	0.0000	0.0000	0.0013
Ca2	0.00000	0.00000	0.34421	0.1250	0.0002	0.0002	0.0291	0.0000	0.0000	0.0000	0.0099
	0.00000	0.00000	0.00030	0.0000	0.0022	0.0022	0.0034	0.0000	0.0000	0.0000	0.0015
CL	0.00000	0.00000	0.20497	0.1250	0.0196	0.0196	0.0217	0.0000	0.0000	0.0000	0.0203
	0.00000	0.00000	0.00030	0.0000	0.0027	0.0027	0.0040	0.0000	0.0000	0.0000	0.0018
OI	0.50000	0.00000	0.09015	0.2500	0.0237						
	0.00000	0.00000	0.00044	0.0000	0.0033						
	0.00000	0.00000	0.00000	0.0625	0.0650						
	0.00000	0.00000	0.00000	0.0000	0.0100						

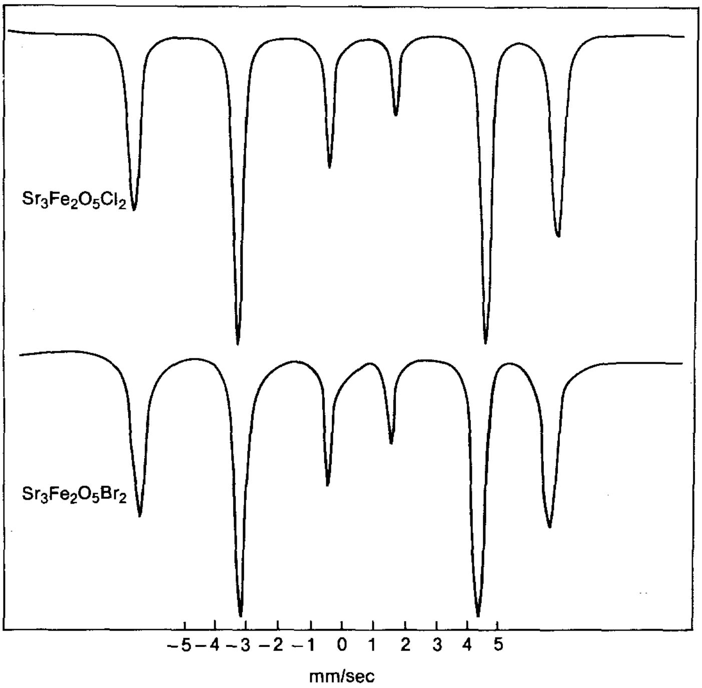

FIG. 14. Mossbauer spectra of $Sr_3Fe_2O_5X_2$ (X = Cl,Br).

tions. However, the superexchange pathway between sheets is not simple and an explanation of the three-dimensional magnetic order is left for future studies.

Conclusions

These new materials reiterate the exceptional stability of iron oxyhalides. Indeed, applying similar synthetic conditions to the other transition metals yields oxyhalides in only one other case; that of the well known alkaline earth copper oxyhalides (*5–9*). The reaction products for the remaining transition metals are oxides, which suggest that higher halogen activities are needed at the temperatures of formation in order for such oxyhalides to be stabilized.

TABLE XI

THE MOSSBAUER ISOMER SHIFTS, QUADRUPLE AND MAGNETIC HYPERFINE SPLITTINGS FOR SELECTED ALKALINE EARTH IRON OXYHALIDES AT 300 K

	ΔFe (mm/sec)	δ (mm/sec)	H (kG)
$Ca_3Fe_2O_5Cl_2$	0.528	0.458	267 (453 at 122 K)
$Ca_3Fe_2O_5Br_2$	0.527	0.358	399
$Sr_3Fe_2O_5Cl_2$	0.657	0.542	422
$Sr_3Fe_2O_5Br_2$	0.657	0.392	407

By analogy to the materials presented here, the synthesis of new complex transition metal oxyhalides would be rewarded with both novel structures and novel magnetic properties.

Acknowledgments

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