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A Study of the Oxygen-Deficient Perovskite System $Sr_2Fe_{2-x}Cr_xO_{5+y}$ by Mössbauer Spectroscopy

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The oxygen-deficient perovskite system $Sr_2Fe_{2-x}Cr_xO_{5+y}$ (x = 0.5, 0.67, 1.0) has been studied by Mössbauer spectroscopy and X-ray powder diffraction techniques. The material obtained is strongly dependent upon the conditions of preparation, although the iron is usually present as Fe^{3+}. The system as a whole is more strongly oxidized than the calcium analogue, from which it differs considerably, and significant amounts of $Sr_3Cr_2O_8$ and $SrCrO_4$ may be formed in air. Several single-phase perovskite-related compounds have been observed. Most significant of these is a rhombohedral 15R-phase with a large unit cell, the nature of which is uncertain. Evidence was also found for an orthorhombic perovskite which is probably the $n = \frac{5}{2}$ member of the $A_nB_nO_{3n-1}$ series. A number of cubic phases have been prepared. Mössbauer spectroscopy has been used to characterize the iron site environments and magnetic behavior of these materials. © 1990 Academic Press, Inc.

Introduction

In an earlier paper (*1*) we have reported a detailed investigation of the perovskite system $Ca_2Fe_{2-x}Cr_xO_{5+y}$ (x = 0.5, 0.67, 1.0) by Mössbauer spectroscopy and X-ray powder diffraction. The nature of the material obtained depends strongly upon the conditions of preparation. Complete reduction ($y = 0$) was achieved *in vacuo* for $x < 0.56$ to produce a single-phase brownmillerite, analagous to $Ca_2Fe_2O_5$, containing Cr^{3+} fully ordered onto the octahedral sites. For $x > 0.56$ *in vacuo*, a three-phase mixture of $Ca_2(Fe,Cr)_2O_5$, $Ca(Fe,Cr)_2O_4$, and CaO was obtained. Preparations in air were found to be strongly oxidized with the exsolution of Cr^{5+} in $Ca_3Cr_2O_8$ (or Cr^{6+} in $CaCrO_4$) below 1200°C. Above this temperature the chromium was incorporated into the perovskite-related lattice as Cr^{4+}. Structural intergrowth of the ABO_3 perovskite, $A_2B_2O_5$ brownmillerite, and $A_3B_3O_8$ lattices was observed. There was also evidence for microdomain formation with concentration of Cr^{4+} in the domain walls.

The corresponding strontium system, $Sr_2Fe_{2-x}Cr_xO_{5+y}$, has been examined some considerable time ago (*2*), but in insufficient detail to allow a realistic comparison with the calcium system. This paper reports the results of our work on $Sr_2Fe_{2-x}Cr_xO_{5+y}$ and demonstrates the very considerable differences between the Ca and Sr systems under equivalent experimental conditions.

Experimental

Accurately weighed amounts of spectroscopic grade Fe_2O_3, Cr_2O_3, and $SrCO_3$, with stoichiometric ratios appropriate for $Sr_2Fe_{2-x}Cr_xO_5$ (x = 0.5, 0.67, and 1.0) were

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ground together in a ball mill, pressed into a pellet, and initially fired in a platinum crucible at 1200°C for 11–18 days with intermediate grindings before quenching onto a metal plate in air. Aliquots of this material were then annealed for several days under a variety of conditions as detailed in the text.

Initial characterization in each case was by X-ray powder diffraction recorded with a Philips diffractometer using nickel-filtered Cu$K\alpha$ radiation. Chemical analyses for nominal Cr^{4+}/Fe^{4+} content were carried out by digestion in a standardized solution of ammonium iron(II) sulfate in the presence of HCl and titration with cerium(IV) sulfate using ferroin as indicator. The results obtained were reproducible and self-consistent and correlated well with weight-loss measurements where these were also available. Mössbauer data were collected in the temperature range $4.2 < T < 600$ K using a ^{57}Co/Rh source matrix held at room temperature; isomer shifts were determined relative to the spectrum of metallic iron.

Results and Discussion

The compositions of $Sr_2Fe_{2-x}Cr_xO_{5+y}$ with $x = 0.5$, 0.67, and 1.0 were chosen to enable direct comparison with the equivalent calcium results (*1*) and to facilitate the production of any ordered structures which might exist with the integer cation ratios of 3 : 1, 2 : 1, and 1 : 1. The initial ceramic preparation was usually carried out at 1200°C in air with several intermediate grindings before a final anneal for several days in air (or argon or *vacuo*) at a controlled temperature before quenching into liquid nitrogen (from air) or cooling quickly. The chemical analyses and phase analysis by X-ray powder diffraction and Mössbauer spectroscopy are summarized in Table I. The product can be either a perovskite-related single phase or a mixture of phases depending upon conditions.

The strontium system differs most markedly from the calcium system in that the degree of oxidation under given conditions of preparation as shown by the value of y is always substantially greater in the former. Samples with $x = 0.67$ and 1.0 which were annealed in air below 1200°C showed substantial oxidation to Cr^{6+} in the form of $SrCrO_4$, which is easily identified from the X-ray pattern (*3*). This agrees with the earlier report (*2*). At 1200°C and above, the phase $Sr_3Cr_2O_8$ containing Cr^{5+} was identified (*4*). These observations are comparable with the observed exsolution of $CaCrO_4$ and $Ca_3Cr_2O_8$ in our earlier work. However, the low melting point of $Ca_3Cr_2O_8$ (1228°C) leads to the formation of perovskite-related intergrowths above ~1200°C with the exsolution of $Ca_3Cr_2O_8$ upon annealing below this temperature. In the present instance $Sr_3Cr_2O_8$ was observed for a sample with $x = 0.67$ annealed at 1400°C. The corresponding perovskite-related intergrowth was not found. All the samples with $x = 0.67$ and 1.0 annealed in air were multiphase. It is worth noting that oxidation to Cr^{5+} takes place even more readily in the barium analogues: attempted preparations of $Ba_2Fe_{2-x}Cr_xO_{5+y}$ formed a simple equimolar mixture of $Ba_3Cr_2O_8$ and γ-$BaFe_2O_4$ under a wide variety of final annealing conditions including 1200°C under flowing argon. Nevertheless, in the strontium case, by reducing the partial pressure of oxygen it became possible to produce a number of interesting apparently single-phase materials. In discussing these it is convenient to refer initially to the preparations for $x = 1.0$ and then to draw comparisons with the remaining compositions.

Rhombohedral Perovskite Phase (15R)

Samples of Sr_2FeCrO_{5+y} annealed under argon at 500, 800, and 1200°C were found to give a sharp X-ray pattern which was clearly derived from a large supercell of the cubic perovskite lattice. The d-spacings are given in Table II and can be indexed on the

TABLE I

CHEMICAL ANALYSES AND X-RAY PHASE ANALYSIS FOR SAMPLES OF $Sr_2Fe_{2-x}Cr_xO_{5+y}$ UNDER A RANGE OF EXPERIMENTAL CONDITIONS

	$x = 0.50$		$x = 0.67$		$x = 1.00$	
Conditions	y	Phases	y	Phases	y	Phases
1200°C, slow cool	—	—	—	—	1.101	15R + SS
1400°C, quench	0.392	P	0.495	P + (SR)	—	—
1300°C, quench	0.450	P	0.507	P + (SR)	0.959	P + SR
1200°C, quench	0.496	P + 15R	0.656	15R + (SR)	0.938	15R + (SR)
1100°C, quench	0.571	15R + (P)	0.753	15R + (SS)	1.359	15R + SS + (SR)
1000°C, quench	0.637	15R + (P)	0.750	15R + (SS)	1.398	15R + SS + (SR)
900°C, quench	0.657	15R + (P)	0.750	15R + (SS)	—	—
800°C, quench	0.640	15R + (P)	0.751	15R	—	—
1200°C, air/argon	0.285	OP + BM	0.326	OP	0.492	15R
800°C, air/argon	—	—	—	—	0.544	15R
500°C, air/argon	—	—	—	—	0.560	15R
1200°C, argon only	0.283	OP + BM	0.312	OP	0.260	OP
1200/800°C, argon only	0.530	P	0.649	P + (15R)	0.446	3R
1350/800°C, argon only	—	—	—	—	0.510	P
1200°C, *vacuo*	0.107	P	0.161	P + (?)	0.318	P + (SR)

Note. The final annealing was carried out in air with a quench into liquid nitrogen, under flowing argon or *in vacuo*. The initial reaction was in air except where indicated. Phases shown in parentheses were minor components. P, cubic perovskite; BM, brownmillerite $\sqrt{2}a_p \times 6a_p \times \sqrt{2}a_p$; OP, orthorhombic perovskite $\sqrt{2}a_p \times 10a_p \times \sqrt{2}a_p$; 15R, rhombohedral perovskite (15R); 3R, rhombohedral perovskite (3R); SR, $Sr_3Cr_2O_8$; SS, $SrCrO_4$.

basis of a rhombohedral cell, space group probably $R\bar{3}m$, with $a = 11.97$ Å, $\alpha = 26.86°$. The equivalent hexagonal cell has $a = 5.560$, $c = 34.60$ Å, which implies a trigonal distortion along the [111] axis of the ABO_3 cubic perovskite, the stacking sequence of the AO_3 layers repeating every 15 layers. For this reason we shall refer to the phase as the 15R-phase.

The identification of the unit cell was confirmed by examining high-resolution X-ray powder diffraction data collected on the powder diffractometer 8.3 at the Synchrotron Radiation Source at Daresbury and neutron powder diffraction data collected on powder diffractometer D1a at ILL Grenoble. However, a full structural refinement has not yet been achieved, due to the large size of the unit cell and the lack of a reliable structural model. We intend to perform EXAFS measurements in the near future in an attempt to obtain new information on the local environments of the iron and chromium cations. Meanwhile a number of remarks can be made concerning the structural possibilities, and these will be discussed in the light of the spectroscopic data which is presently available.

The large cell of the 15R-phase suggests a well-ordered arrangement of the atoms, although this is not easy to identify. Several possibilities must be considered. First, the AO_3 layers may be stacked so as to generate a mixture of corner and face-sharing BO_6 octahedra. There are two possible 15R sequences: *hhhhc*, or (2)1(1)1 in the Zhdanov notation, generates columns of five face-sharing octahedra which are joined at the ends by corner sharing; in *hcchc*, or (3)(2), there are six pairs of face-sharing octahedra

TABLE II

X-RAY DIFFRACTION PATTERN FOR $Sr_2FeCrO_{5.544}$ ANNEALED IN ARGON AT 800°C

d_{obs}	d_{calc}	h	k	l	I_{obs}
11.523	11.529	1	1	1	mw
3.949	3.951	2	2	1	w
3.834	3.843	3	3	3	vvw
3.449	3.448	2	2	3	mw
3.215	3.216	3	3	2	vw
2.809	2.809	3	3	4	vs
2.781	2.779	1	−1	0	vs
2.633	2.632	4	4	3	vw
2.396	2.400	1	1	−1	vvw
2.380	2.383	0	0	2	vvw
2.328	2.328	4	4	5	m
2.305	2.306	5	5	5	mw
2.271	2.273	1	1	3	m
2.198	2.198	5	5	4	vw
2.104	2.103	2	2	4	vw
2.000	2.000	5	4	3	w
1.975	1.975	4	4	2	s
1.874	1.874	6	6	5	w
1.784	1.785	5	5	3	w
1.627	1.627	7	7	6	mw
1.609	1.608	6	6	4	ms
1.604	1.604	1	1	−2	ms

Note. 15R, rhombohedral: $a = 11.97$ Å, $\alpha = 26.86°$; hexagonal cell: $a = 5.560$, $c = 34.60$ Å.

and three octahedra with corner-sharing only. Second, there could be an ordered arrangement of the Fe and Cr cations to generate the supercell. Third, the substantial number of oxygen vacancies could lead to a large supercell as in the orthorhombic perovskite-related structures. Fourth, the ligand-field effects from the transition-metal ions could be relevant. More than one of these considerations could be involved simultaneously. We have used Mössbauer spectroscopy to obtain characterization of the Fe sites in this structure as part of a wider structural characterization which is still in progress.

The Mössbauer spectrum of the 15R-phase annealed at 800°C under argon ($Sr_2FeCrO_{5.544}$) is shown in Fig. 1 as a function of temperature. The spectra are typically those of an Fe^{3+} compound, there being no evidence for any higher oxidation state. The phase thus approximates a composition of $Sr_2Fe^{3+}Cr^{4+}O_{5.5}$, the dominant oxidation state for chromium being nominally +4. The magnetic hyperfine sextet seen at 4.2 K has a flux density of $B = 50.7$ T, an isomer shift of $\delta = +0.51$ mm sec^{-1}, and a quadrupole perturbation parameter of $\varepsilon = 0.07$ mm sec^{-1}. However, the linewidths are extremely broad (~1 mm sec^{-1}). This is often found in disordered solid-solutions where the combination of small differences in flux density and quadrupole interaction

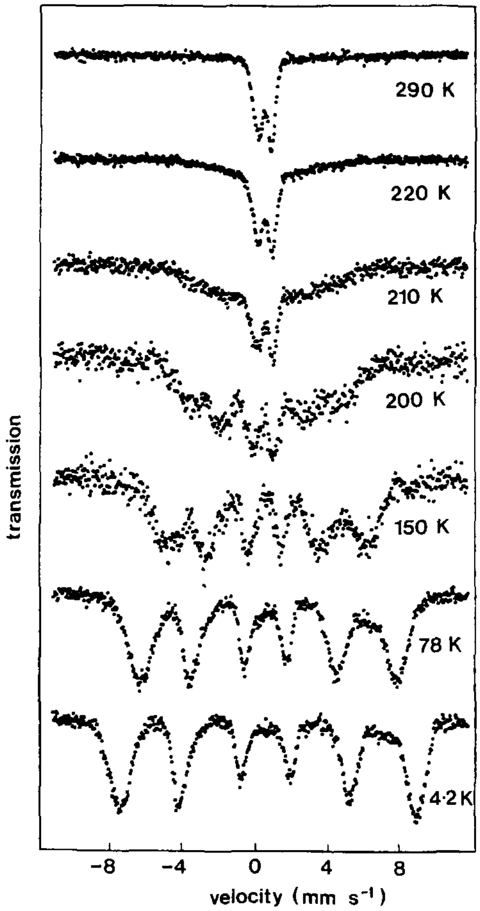

FIG. 1. Temperature dependence of the Mössbauer spectrum of $Sr_2FeCrO_{5.544}$ prepared in air and finally annealed under argon at 800°C (the 15R-phase).

at each individual site result in overall broad lines, which can disguise the fact that there are several site symmetries. The broadening and collapse of the spectrum as the temperature approaches the magnetic ordering temperature of ~230 K are also consistent with this view. Above 230 K the spectrum becomes a simple paramagnetic pattern with quadrupole splitting. The spectrum at 290 K recorded with a smaller velocity scan is shown in Fig. 2a. The marked asymmetry in the spectrum suggests that the Fe sites do not all have the same isomer shift, although all are present in the +3 oxidation state. While an apparently acceptable data analysis can be obtained with three superimposed but symmetrical quadrupole doublets, it is far from clear that a small number of unique sites actually exist. However, the isomer shift must decrease from circa 0.38 to 0.27 mm sec^{-1} as the quadrupole splitting increases from circa 0.57 to 1.29 mm sec^{-1} in order to generate the observed asymmetry. An isomer shift of +0.38 mm sec^{-1} is reasonable for Fe^{3+} ions in 6-coordination to oxygen. In $Sr_2Fe_2O_5$ and $Sr_2LaFe_3O_8$ the Fe^{3+} ions in 4-coordination have an isomer shift of only +0.17 mm sec^{-1} at 290 K (*4*) and flux densities of only 46.4 and 44.3 T at 4.2 K, respectively. There is thus evidence to suggest that the 15R-phase does *not* contain Fe^{3+} ions in 4-coordination to oxygen, although the observed range of isomer shifts suggests that some sites may be 5-coordinate with a larger quadrupole splitting from the lower symmetry environment.

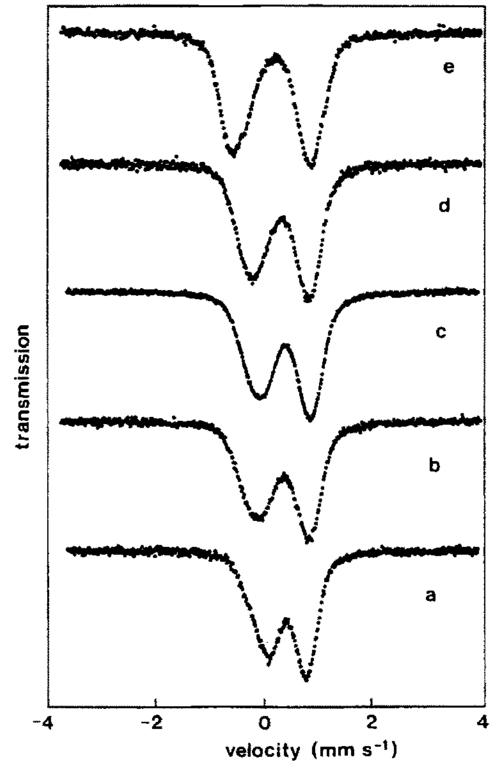

FIG. 2. Mössbauer spectra of (a) $Sr_2FeCrO_{5.544}$ (the 15R-phase) at 290 K, (b) $Sr_2FeCrO_{5.446}$ (the 3R-phase) at 323 K, (c) $Sr_2FeCrO_{5.510}$ ("cubic" phase) at 290 K, (d) $Sr_2FeCrO_{5.260}$ (orthorhombic $n = \frac{5}{2}$ phase) at 323 K, (e) $Sr_2Fe_{1.5}Cr_{0.5}O_{5.107}$ (cubic) at 500 K.

The possibility that the oxidation state of Cr is +4 may be significant. The electron configuration in octahedral symmetry is d^2 ($^3T_{1g}$), which is threefold degenerate and is unstable according to the Jahn-Teller theorem. A trigonal distortion to D_{3d} symmetry would split the triplet level, the maximum ligand field stabilization being obtained for a ^3E_g ground state; i.e., for an elongation along the trigonal axis as indeed occurs in the present instance. The trigonal symmetry may therefore derive from the presence of the Cr^{4+}, although the 15R-structure would indicate additional cation or oxygen-vacancy ordering. Some support for this was obtained by the observation of a simple 3R-perovskite. Further information concerning the 15R-phase was obtained from the $x = 0.5$ preparations in air, and these results are described below in connection with the high-temperature cubic perovskite phase.

Rhombohedral Perovskite (*3R*)

In an attempt to reduce the oxidation of the system, samples were also prepared by carrying out the entire reaction under flowing argon. This was only partially successful because the samples with $x = 1.0$ in particular proved to be exceptionally good at scavenging traces of oxygen from the gas stream. A preparation of $Sr_2FeCrO_{5.446}$ carried out at 1200°C with the final anneal at 800°C, the whole reaction sequence being carried out under argon, gave a much simpler X-ray pattern which could be indexed on the basis of a simple rhombohedrally distorted perovskite (3R-phase) with $a = 3.933$ Å, $\alpha = 89.4°$ (hexagonal cell $a = 5.533$, $c = 6.883$ Å). The *d*-spacings are given in Table III. The elongation along the trigonal axis is very close to that observed in the 15R-phase, although the cell volume is smaller by 1.5%. The high-angle reflections are broadened, and we believe that this sample represents a disordered version of essentially the same structure. The Mössbauer characterization is also very similar (Figs. 2a and 3), although a weak magnetic effect persists up to about 295 K.

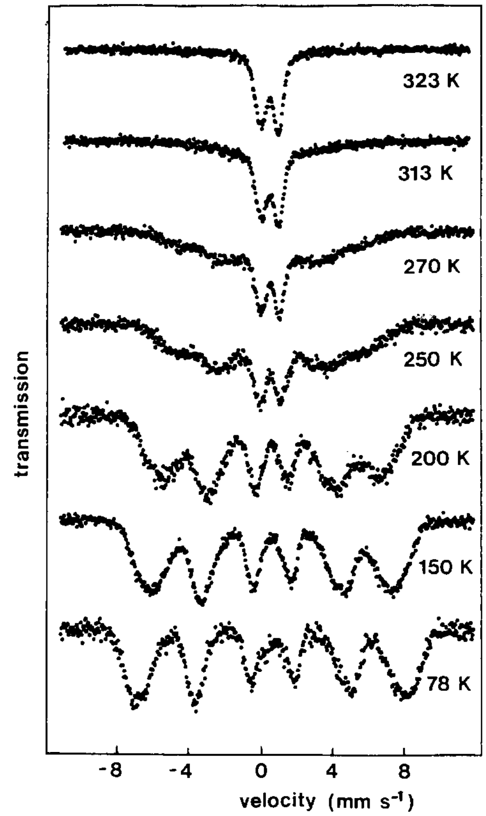

FIG. 3. Temperature dependence of the Mössbauer spectrum of $Sr_2FeCrO_{5.446}$ prepared under argon at 1200°C and finally annealed at 800°C (the 3R-phase).

TABLE III

X-RAY DIFFRACTION PATTERN FOR $Sr_2FeCrO_{5.446}$ PREPARED UNDER ARGON AND FINALLY ANNEALED AT 800°C

d_{obs}	d_{calc}	h	k	l	I_{obs}
3.938	3.932	0	0	1	w
2.792	2.794	1	1	0	vs
2.767	2.767	1	−1	0	vs
2.294	2.293	1	1	1	w
2.261	2.263	1	1	−1	mw
1.967	1.966	0	0	2	m
1.619	1.619	1	1	2	w
1.602	1.603	2	1	−1	m
1.397	1.397	2	2	0	w
1.384	1.383	2	−2	0	w

Note. 3R, rhombohedral: $a = 3.933$ Å, $\alpha = 89.4°$; hexagonal cell: $a = 5.533$, $c = 6.833$ Å.

A further sample similarly prepared at 1350°C with the final anneal at 800°C, $Sr_2FeCrO_{5.510}$, gave an X-ray pattern which was a broadened cubic perovskite pattern with $a = 3.931$ Å. Once again the Mössbauer characterization (Fig. 4) was similar, but with magnetic interactions disappearing at circa 275 K. The Mössbauer spectrum at 290 K (Fig. 2c) can be interpreted as a number of quadrupole doublets with the isomer shift decreasing from circa 0.37 to 0.29 mm sec^{-1} as the quadrupole splitting increases from circa 0.68 to 1.42 mm sec^{-1}. The isomer shifts are thus comparable with those for the 15R phase, implying no changes in coordination number, whereas the quadrupole splittings are notably larger.

We believe that both these samples may be either poorly crystalline or disordered forms of the 15R structure.

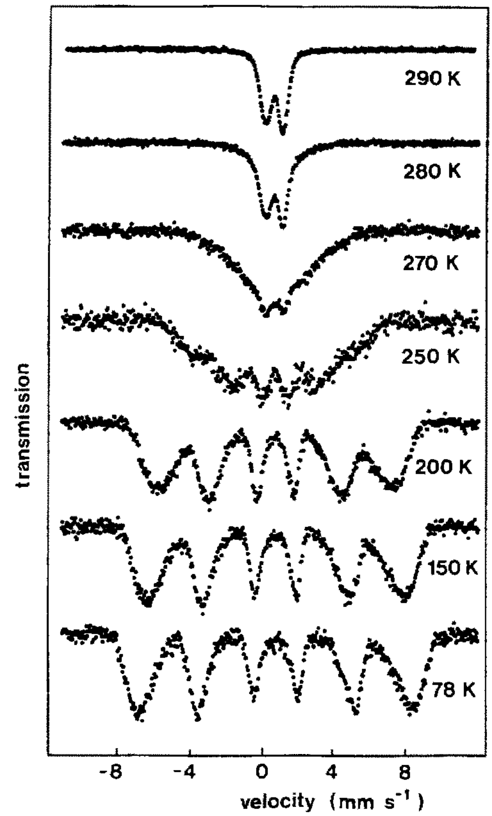

FIG. 4. Temperature dependence of the Mössbauer spectrum of $Sr_2FeCrO_{5.510}$ prepared under argon at 1350°C and finally annealed at 800°C (the "cubic" phase).

Orthorhombic Perovskite ($n = \frac{5}{2}$)

A preparation carried out completely under argon at 1200°C and cooled quickly to reduce further oxygen scavenging produced a sample of composition $Sr_2FeCrO_{5.260}$, which showed yet another large perovskite supercell. This has been tentatively identified as the $n = \frac{5}{2}$ member of the $A_nB_nO_{3n-1}$ series of orthorhombic perovskites, the 040 reflection at a *d*-spacing of 10.0 being characteristic. This structure was first reported in $Ca_5Fe_4TiO_{13}$ (*5*) and subsequently in $Ca_4YFe_5O_{13}$ (*6*). Ordered layers of octahedral (O) and tetrahedral (T) *B*-sites are arranged normal to the *b*-axis to generate the layer sequence OOTOT . . . , compared to OTOT′ . . . in $A_2B_2O_5$, and OOT . . . in $A_3B_3O_8$. In the present instance the high-angle reflections were broad, indicating poor crystallinity and perhaps some degree of intergrowth with other stacking sequences, presumably due to the excess of oxygen over the ideal of $y = 0.2$. Consequently, a complete indexing of the pattern for such a large cell was not viable, although the estimated lattice parameters of $a = 5.53$, $b = 39.48$, $c = 5.62$ Å are consistent with a strontium analogue of the calcium compounds.

The Mössbauer spectra (Fig. 5) show an ordering temperature of circa 295 K. The

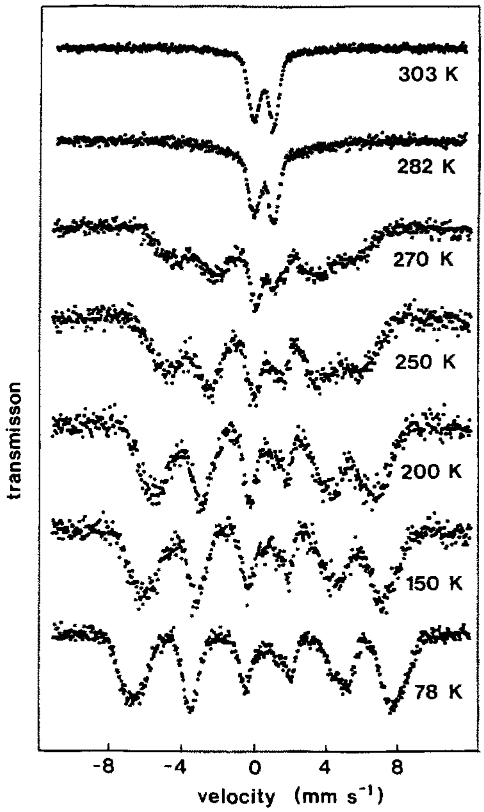

FIG. 5. Temperature dependence of the Mössbauer spectrum of $Sr_2FeCrO_{5.260}$ prepared under argon at 1200°C and quickly cooled (orthorhombic perovskite $n = \frac{5}{2}$).

spectrum above this temperature (Fig. 2d) is still an asymmetric quadrupole pattern from Fe^{3+}, but the center of gravity is significantly more negative. This is consistent with an overall decrease in the average coordination number, although the possibility of a difference in second-order Doppler shift has not been excluded. The magnetic hyperfine pattern at 78 K clearly contains more than one hyperfine field. The $n = \frac{5}{2}$ structure embodies two different octahedral sites in addition to the tetrahedral site but the broad resonance lines and expected cation disorder prevent a detailed analysis. Trial fits of a two-field model produced flux densities of 46.9 and 42.2 T and corresponding isomer shifts and quadrupole perturbations that were not unreasonable for octahedral and tetrahedral sites, respectively. Thus the Mössbauer data provide some support for the OOTOT . . . stacking sequence of the $n = \frac{5}{2}$ orthorhombic structure as the basis for this phase. The areas for the octahedral and tetrahedral sites are approximately equal, implying considerable Fe and Cr disorder.

There are also indications of the OOTOT . . . stacking sequence in samples with x = 0.5 and 0.67 prepared under argon. The oxygen content is similar in all cases (y = 0.26–0.33), but at x = 0.5 the X-ray powder diffraction data also shows lines characteristic of the OTOT′ . . . brownmillerite stacking sequence. Thus there is a strong possibility that disordered intergrowths may be occurring. The magnetic exchange interactions increase as the Fe^{3+} content increases so that all these samples order magnetically well above room temperature.

High-Temperature Cubic Perovskite

The samples with x = 0.5 annealed in air at 1300 and 1400°C and quenched into liquid nitrogen gave very sharp X-ray lines easily indexed as a cubic perovskite with a = 3.935 Å. The Mössbauer spectra at 78 and 290 K (Figs. 6 and 7) show magnetic hyperfine patterns with a pronounced inward broadening which is slightly asymmetric at 78 K, implying the presence of more than one distinct site despite the cubic lattice. The magnetic splitting of the 1300°C quench (y = 0.540) decreases with rise in temperature until disappearing at 578 K to give a broad quadrupole pattern. A simple two-field fit of the 78 K data gives flux densities of about 53 and 48 T, and these decrease to about 47 and 41 T at 290 K. We believe that this phase contains largely disordered vacancies and cations, although there may be some degree of local order which is not de-

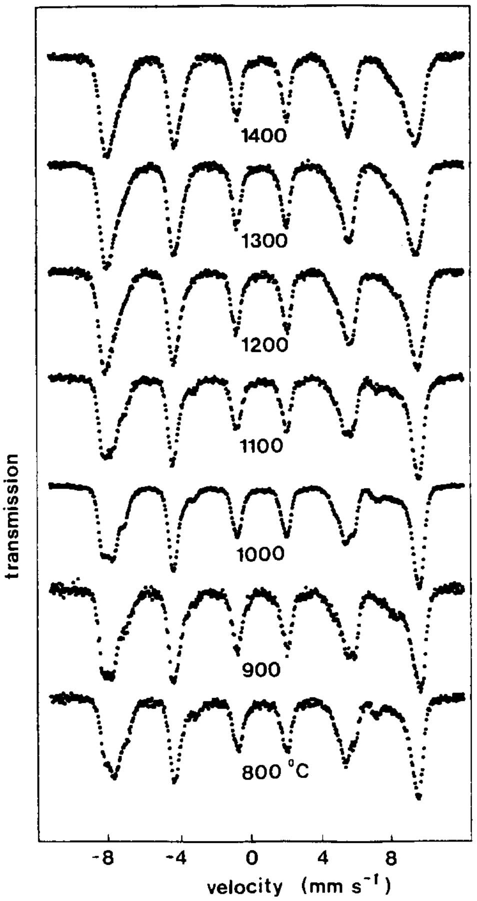

FIG. 6. Mössbauer spectra at 78 K of $Sr_2Fe_{1.5}Cr_{0.5}O_{5+y}$ annealed in air at various temperatures and quenched into liquid nitrogen.

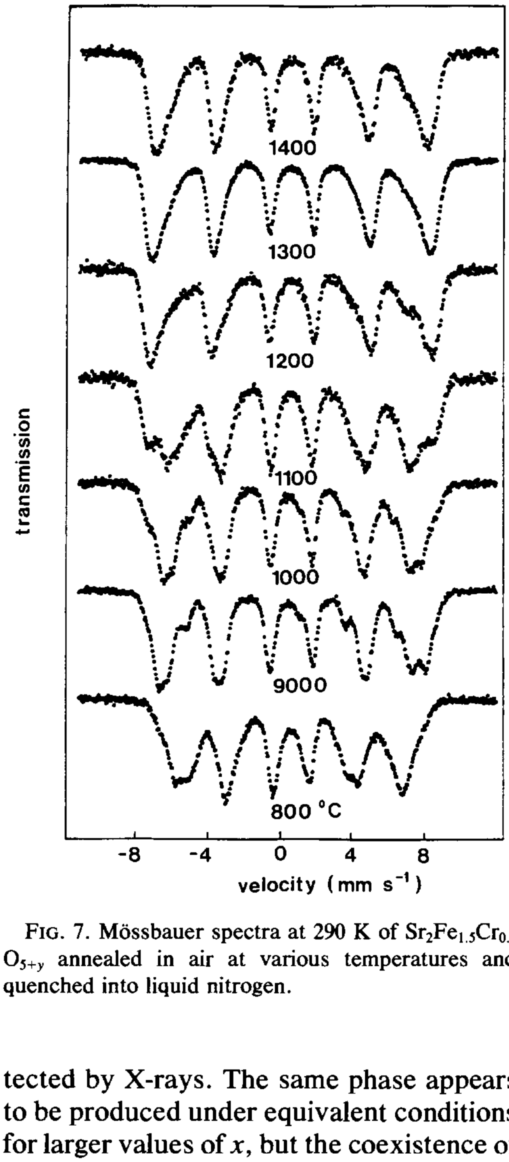

FIG. 7. Mössbauer spectra at 290 K of $Sr_2Fe_{1.5}Cr_{0.5}O_{5+y}$ annealed in air at various temperatures and quenched into liquid nitrogen.

tected by X-rays. The same phase appears to be produced under equivalent conditions for larger values of x, but the coexistence of $Sr_3Cr_2O_8$ makes the characterization less certain.

The oxygen content and lattice size are similar to those for the "cubic phase" ($x = 1.0$, $y = 0.510$) made under argon. However, the Cr content of $x = 0.5$ would stipulate an oxygen parameter of $y = 0.25$ for an ideal Cr^{4+}/Fe^{3+} composition. We have found no evidence to suggest that the chemical analysis is incorrect. Thus it would seem that either the chromium is oxidized further to produce localized Cr^{5+} ions, or perhaps more likely the electrons are contributed to an itinerant band system. The Sr FeO_{3-y} system is well known to show itinerant electron behavior (*7–10*). Recent work in our laboratory (*11, 12*) on charge disproportionation in Fe^{4+} oxides has shown that high nominal charges originating from a charge density wave can become attached to individual sites in a perovskite lattice without any associated shortening of the metal–oxygen bonds. The failure to detect high charge states in the Mössbauer resonance would imply that most of the charge can be associated with the Cr sites. We hope to investigate the role of small concentrations of chromium in $SrFeO_{3-y}$ in the near future.

Samples with $x = 0.5$ annealed in air in the range 800–1200°C and quenched into liquid nitrogen contain both the cubic perovskite and the 15R phases, with the proportion of the latter increasing and the value of y increasing toward the lower temperatures. The presence of the cubic perovskite is not very obvious in the X-ray pattern because the small number of lines tend to overlap with strong lines in the 15R pattern. The temperature dependence of the Mössbauer spectrum of the 1000°C quench is clearly consistent with the coexistence of two magnetic phases with ordering temperatures of circa 505 (15R) and 580 K (P). Although we have been unable to produce a pure sample of the 15R phase with $x = 0.5$, the ordering temperature of 505 K, when compared to that of 295 K for $x = 1.0$, confirms that there is a considerable increase in the amount of Fe^{3+} in this phase, and that both the high-temperature perovskite and 15R phases contain the same cation ratio. The X-ray pattern was indexed on a cell with $a = 12.05$ Å, $\alpha = 26.81°$; the interfacial angle has not changed significantly, but the cell edge is notably larger (cf. 11.97 Å at $x = 1.0$). The same unusual supercell has been formed despite a reduction in the chromium content of some 50%, but the oxygen vacancy concentration is approximately the same. This implies that ordering of the Fe/Cr cations is much less important than oxygen-vacancy ordering or layer-stacking. Further work on this 15R phase now in progress may clarify the situation.

The 15R phase with $x = 0.5$ in the quenches from 1000 and 900°C clearly shows considerable structure in the Mössbauer magnetic hyperfine patterns, particularly at 290 K where at least three fields with flux densities of circa 45, 41, and 36 T are present in addition to the residual cubic components. We believe that there is no significant proportion of oxidation states higher than +3. However, there are subtle differences within the spectra as a whole which are difficult to explain in the absence of a model structure, and a more detailed analysis is not considered to be feasible at the present time.

Preparations in Vacuo

In an attempt to reduce the oxygen content further and to obtain compounds containing only Cr^{3+} and Fe^{3+}, samples of material prepared initially in air were finally annealed for several days at 1200°C *in vacuo* ($<10^{-4}$ Torr). As can be seen in Table 1, the values of y were considerably reduced, but remained significantly above zero.

The sample with $x = 0.5$ gave the sharp X-ray pattern of a cubic perovskite with $a = 3.917$ Å. The cell volume is significantly smaller than that for the high-temperature preparation in air ($a = 3.935$ Å). The Mössbauer spectra (Fig. 8) show the phase to contain Fe^{3+} and to be magnetically ordered below 463 ± 2 K. Above this temperature the spectrum (Fig. 2e) comprises a quadrupole doublet with a large splitting of circa 1.40 mm sec^{-1}, although once again the lines are broadened because all sites are not identical. The site symmetries about the Fe^{3+} cations are apparently more irregular in this phase than in the others. The magnetic spectra in Fig. 8 show substantial broadening due to variations in the relative orientations of the spin axis and the electric field gradient tensor, but the comparative sharpness of the inner lines proves that there is also some variation in the magnitude of the flux density. These results show no evidence for the formation of a brownmillerite lattice as found in the comparable calcium preparation.

The sample with $x = 0.67$ proved to be very similar but with a lower ordering temperature. The X-ray pattern showed some evidence for the presence of an unidentified second phase.

The sample with $x = 1.0$ retained extra

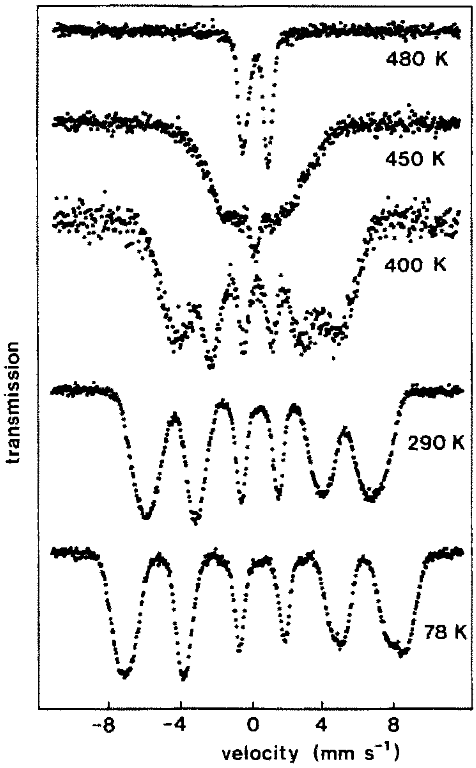

FIG. 8. Temperature dependence of the Mössbauer spectrum of $Sr_2Fe_{1.5}Cr_{0.5}O_{5.107}$ annealed *in vacuo* at 1200°C.

oxygen ($y = 0.318$) partly due to the presence of $Sr_3Cr_2O_8$. In an attempt to prepare samples fully reduced to Cr^{3+}, a reaction mixture with $x = 1.0$ was heated under vacuum from the beginning to 1200°C and then cooled quickly. The product was a three-phase mixture comprising a cubic perovskite, an unidentified minor component, and a fugitive phase which appeared to have a hexagonal cell and was rapidly transformed upon exposure to air to a phase with a very broad perovskite pattern. These materials have not been characterized in detail.

Conclusions

We have now shown that the $Sr_2Fe_{2-x}Cr_xO_{5+y}$ system ($x = 0.5, 0.67, 1.0$) is distinctly different from the calcium analogue. Oxidation is always greater under equivalent conditions of preparation. No evidence has been found for the formation of a brownmillerite lattice, although this may be due to the presence of a significant oxygen excess in all samples prepared. There is no evidence to suggest that the strontium system can produce the structural intergrowths which were such an important feature of the calcium system above 1200°C.

Nevertheless, a number of interesting perovskite-related compounds have been observed by careful control of the experimental conditions. Most significant of these is the 15R-phase; work to determine the nature of the large unit cell is continuing. Evidence was also found for an orthorhombic perovskite which is probably the $n = \frac{5}{2}$ member of the $A_nB_nO_{3n-1}$ series. A number of cubic phases have also been characterized, and Mössbauer spectroscopy has revealed major differences in the iron site environments which are not otherwise apparent.

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