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A Study of Microdomain Formation and Structural Intergrowth in the Oxygen-Deficient Perovskite $Ca_2Fe_{2-x}Cr_xO_{5+y}$ by Mössbauer Spectroscopy

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The oxygen-deficient perovskite system $Ca_2Fe_{2-x}Cr_xO_{5+y}$ ($x = 0.5, 0.67, 1.0$) has been studied by Mössbauer spectroscopy and X-ray powder diffraction techniques. The nature of the material obtained depends strongly upon the conditions of preparation, although the iron is always present as Fe^{3+}. Complete reduction ($y = 0$) can be achieved *in vacuo* for $x < 0.56$ to give a single-phase brownmillerite containing Cr^{3+} fully ordered onto the octahedral sites. At higher chromium content a three-phase product is obtained. Preparations in air are 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 Cr is incorporated into a perovskite-related lattice as Cr^{4+}. There is evidence for microdomain formation with Cr^{4+} concentrating in the domain walls, and for structural intergrowth of the $A_2B_2O_5$ brownmillerite and $A_3B_3O_8$ lattices.

Introduction

The perovskite structure, ABO_3, has the ability to stabilize cations in unusually high oxidation states, and the anion sublattice can accommodate a high concentration of vacant sites. The recent discovery (*1*) of superconductivity in the so-called 1:2:3 compound $YBa_2Cu_3O_{7-y}$, which is an oxygen-deficient perovskite, has magnified interest in these materials. The compound $Ca_2Fe_2O_5$ is one of a series of compounds with the general formula $A_2B_2O_5$ which are derived from the perovskite structure by the introduction of an ordered array of oxygen vacancies. In $Ca_2Fe_2O_5$, $Sr_2Fe_2O_5$, and $Sr_2Co_2O_5$ the vacancies order so as to create a structure with alternate layers of octahedrally and tetrahedrally coordinated transition metal cations; this is known as the brownmillerite structure after the mineral Ca_2FeAlO_5, although individual compounds usually show subtle crystallographic differences. The structure of $Ca_2Fe_2O_5$ itself is well known (*2–4*): the orthorhombic cell in the conventional space group setting of *Pnma* has the parameters $a = 5.4253(5)$, $b = 14.7687(17)$, and $c = 5.5980(5)$ Å.

The partial substitution of Fe by Cr to give $Ca_2Fe_{2-x}Cr_xO_5$ has been reported by Grenier *et al.* (*5*). In material prepared in air at 1150°C, the maximum chromium content achieved was $x = 0.5$ (25%), and the relative octahedral : tetrahedral site occupation was found to be 38 : 12, i.e., corresponding to the formula $Ca_2[Fe_{0.62}Cr_{0.38}](Fe_{0.88}Cr_{0.12})O_5$ where [] and () enclose the octahedral and tetrahedral site cations, respectively. The

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Néel temperature was reported to be 600 K. In our recent work on Sr_2FeCoO_5 it was shown that the stoichiometric brownmillerite could be obtained by careful choice of conditions (*6*, *7*), and that the relative site occupancy could be varied. More interestingly, partial oxidation of Sr_2FeCoO_5 was found to give small microdomains of the brownmillerite lattice with excess oxygen accommodated in the domain walls. The degree of oxidation depends on the annealing conditions and the rate of quenching.

A logical extension of this work was to reexamine the substitution of chromium in $Ca_2Fe_2O_5$ under a wide range of experimental conditions. It is now evident from the new results reported here that the system is far more complex and unusual than the early work had suggested.

Experimental

Accurately weighed amounts of spectroscopic grade Fe_2O_3, Cr_2O_3, and $CaCO_3$, with stoichiometric ratios appropriate for $Ca_2Fe_{2-x}Cr_xO_5$ ($x = 0.50, 0.67$, and 1.00), were ground together in a ball mill, pressed into a pellet, and initially fired in a platinum crucible at 1200°C for 8–11 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*Kα* 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 $78 < T < 600$ 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

Although the earlier work (*5*) had only achieved a 25% substitution of Cr^{3+} into $Ca_2Fe_2O_5$ in air, it seemed feasible that this limit would be increased under a low partial pressure of oxygen to prevent oxidation of the chromium. The compositions of $Ca_2Fe_{2-x}Cr_xO_{5+y}$ with $x = 0.50, 0.67$, and 1.00 were chosen because the integer–cation ratios of 3 : 1, 2 : 1, and 1 : 1 might facilitate the production of ordered structures. Thus the known preference of Cr^{3+} for octahedral coordination suggested that Ca_2FeCrO_5 might exist under appropriate conditions as a fully ordered brownmillerite.

The initial ceramic preparation in all cases was carried out at 1200°C in air. Aliquots of this material were then annealed for several days in air or argon, or under vacuum, at a number of different temperatures. The chemical analyses and phase analysis by X-ray powder diffraction are summarized in Table I.

Annealing in air and slowly cooling to room temperature resulted in the production of a substantial quantity of $CaCrO_4$ (in the Cr^{6+} oxidation state) which was easily identifiable in the X-ray pattern. Other phases included a brownmillerite (presumably ion rich, but containing some chromium). As these samples were multiphase, they were not investigated in detail.

Preparations in vacuo

A sample with $x = 0.50$ was annealed *in vacuo* ($<10^{-4}$ torr) at 1200°C and then rapidly cooled. Chemical analysis showed $y = 0.005 \pm 0.005$. The sample was a deep maroon color, compared with the more usual black of the oxidized samples. The X-ray characterization showed it to be a crys-

TABLE I

THE CHEMICAL ANALYSES AND X-RAY PHASE ANALYSIS FOR SAMPLES OF NOMINAL COMPOSITION $Ca_2Fe_{2-x}Cr_xO_{5+y}$ UNDER A RANGE OF EXPERIMENTAL CONDITIONS

Conditions	$x = 0.50$ y	phases	$x = 0.67$ y	phases	$x = 1.00$ y	phases
1200°C slow cool	0.343	CC + BM			0.705	CC + BM + CR
1350°C quench	0.230	BM + P	0.326	IG	0.469	OP + (?)
1300°C quench	0.213	BM + P	0.344	IG	0.464	OP + (CR) + (?)
1200°C quench	0.181	BM + P	0.304	IG	0.513	OP + CR + (?)
1100°C quench	0.235	BM + CR + [?]	0.411	BM + CR + [?]	0.540	BM + CR + (CF)
1000°C quench	0.288	BM + CR + [?]	0.454	BM + CR + [?]	0.669	BM + CR + (CF)
1200°C argon	0.027	BM	0.012	BM + (CF) + (CaO)	0.048	BM + CF + CaO
1200°C vacuo	0.005	BM	0.012	BM + (CF) + (CaO)	0.030	BM + CF + CaO

Note. The annealing was carried out in air unless otherwise stated, and quenching was carried out in liquid nitrogen.

Phases shown in parentheses were minor components. BM, brownmillerite, $Ca_2(Fe,Cr)_2O_5$; CF, $Ca(Fe,Cr)_2O_4$; P, cubic perovskite; CR, $Ca_3Cr_2O_8$; CaO, calcium oxide; CC, $CaCrO_4$; OP, orthorhombic perovskite $\sqrt{2}a_p \times 3a_p \times \sqrt{2}a_p$; IG, intergrowth of BM/OP; [?], another phase must be present but not detected by X-rays; (?), traces of unidentified phases.

talline brownmillerite which could be indexed on a cell with $a = 5.408$, $b = 14.666$, $c = 5.591$ Å. The cell volume is 1.1% smaller than for $Ca_2Fe_2O_5$, consistent with the replacement of Fe^{3+} by the smaller Cr^{3+} ion. The ^{57}Fe Mössbauer spectrum at 78 K (Fig. 1) is also typical of a brownmillerite, comprising two overlapping six-line magnetic hyperfine patterns from the octahedral and tetrahedral sites. Both sites show a large quadrupole perturbation ε but of opposite sign, different chemical shifts δ, and flux densities B, and with the spins aligned perpendicular to the b-axis in the G-type magnetic structure the two hyperfine patterns are well resolved. The hyperfine parameters are given in Table II. In $Ca_2Fe_2O_5$ these two components have the same intensity because of the equal numbers of sites, but in the present case the lines from the octahedral sites are weaker because of preferential substitution by chromium. Computer analysis of the line areas (assuming that both sites have the same recoilless fraction) produced the result that 97 ± 3% of the Cr^{3+} cations are on octahedral sites. Thus within experimental error the $x = 0.50$ sample is completely ordered. This is consistent with the known site preference of Cr^{3+}, but is substantially different from the previous work (5). A possible reason for the discrepancy, which will become clear below, is that their samples were partially oxidized and not in fact a stoichiometric brownmillerite.

The temperature dependence of the Mössbauer spectrum is shown in Fig. 2. At 460 K the spectrum comprises a paramagnetic doublet which appears to be symmetrical despite the presence of two sites in different proportions. Detailed analysis reveals that this is a result of having two overlapping doublets with different chemical shifts, but an almost identical quadrupole splitting of 1.40 mm sec^{-1} and broadened lines. The Néel temperature was determined to be 455 ± 5 K (compared to 725 K for $Ca_2Fe_2O_5$). This decrease in Néel temperature is surprisingly large for substitution by another magnetic cation in a G-type magnetic structure with antiferromag-

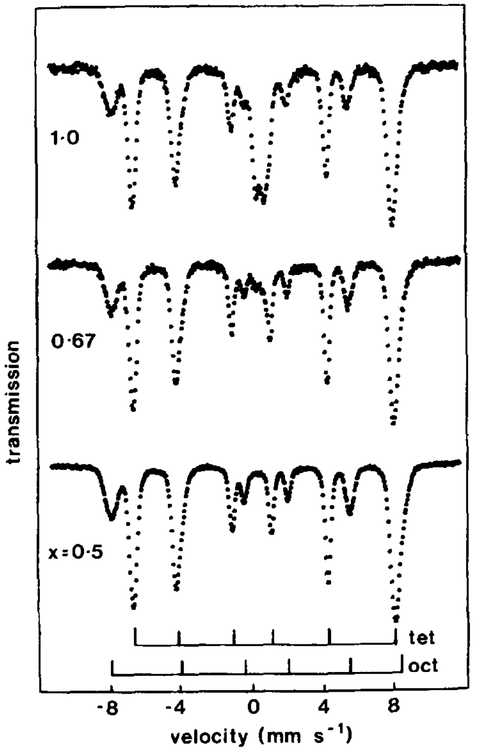

FIG. 1. The Mössbauer spectra at 78 K for samples of $Ca_2Fe_{2-x}Cr_xO_5$ (x = 0.5, 0.67, 1.0) prepared *in vacuo* at 1200°C.

netic coupling to nearest neighbour cations. Although one might have looked for an explanation in terms of magnetic exchange within the brownmillerite lattice, it is important to note that the simpler orthorhombic perovskites $EuFe_{1-x}Cr_xO_3$ show a similar anomaly (*8*) which is presumably a more general feature of the Cr–Fe superexchange interactions.

The hyperfine patterns broaden considerably with rise in temperature so that a detailed analysis is not possible, but the main reasons for this behavior are well understood (*8–10*). However, it is important to note that there is no evidence for significant relaxational collapse in the spectrum until a reduced temperature of $T/T_N > 0.9$.

The equivalent preparation *in vacuo* for $x = 1.00$ was not single phase. Evaluation of the X-ray data showed that the brownmillerite $Ca_2(Fe,Cr)_2O_5$ was accompanied by $Ca(Fe,Cr)_2O_4$ and CaO. The structure of the ferrite $CaFe_2O_4$ is well known (*11–13*); the compound is antiferromagnetic below 200 K (*14*) and is isostructural with β-$CaCr_2O_4$. The observed *d*-spacings are intermediate between these two end members, consistent with the presence of a solid–solution. Since the phase is calcium deficient, the excess calcium is seen as the oxide. The Mössbauer spectrum at 78 K of this sample (Fig. 1) is similar to that for $x = 0.50$ but now shows a strong paramagnetic central feature. The magnetic behavior of the solid–solution $Ca(Fe_{1-z}Cr_z)_2O_4$ is complex (*15*), but the Néel temperature falls with increasing z to circa 130 K at $z = 0.5$; thereafter with further increase in z it is described as showing no long-range order at 4.2 K until near the β-$CaCr_2O_4$ end member. The paramagnetic feature in the spectrum at 78 K is thus consistent with a Cr-rich composition in this solid–solution. Assuming that all iron sites have the same recoilless fractions, and that all the Cr in the brownmillerite phase is on octahedral sites, the area ratios at 78 K correspond to an approximate composition of 0.56 $Ca_2(Fe_{1.43}Cr_{0.57})O_5$ + 0.44 $Ca(Fe_{0.45}Cr_{1.55})O_4$ + 0.44 CaO, which is fully consistent with this observation. The nominal composition of the brownmillerite component suggests that the limit of solubility of Cr^{3+} in $Ca_2Fe_2O_5$ is circa 28%. The equivalent preparation *in vacuo* with $x = 0.67$ was composed mainly of a brownmillerite, but the X-ray pattern also showed weak lines from the other two phases, consistent with this estimate, and the Mössbauer spectrum in Fig. 1 also shows that a second iron-bearing phase is present in small quantities.

Samples annealed in flowing argon at 1200°C were basically similar to the above. However, the color was now black, suggesting a slight degree of residual oxidation which was confirmed by chemical analysis.

TABLE II

MÖSSBAUER PARAMETERS FOR VARIOUS BROWNMILLTERITE-RELATED PHASES

Nominal composition	T_N(K)	T(K)	B(T)	δ (mm sec^{-1})	ε (mm sec^{-1})	Site
$Ca_2Fe_2O_5$	725	295	51.4	0.34	−0.27	O
			43.8	0.17	0.35	T
$Ca_2LaFe_3O_8$	735	290	52.1	0.36	−0.20	O
			43.1	0.19	0.29	T
$Ca_2Fe_{1.5}Cr_{0.5}O_5$	455	78	50.4	0.45	−0.28	O
(1200°C—vacuo)			45.4	0.28	0.34	T
		290	43.7	0.32	−0.28	O
			37.0	0.17	0.32	T
$Ca_2Fe_{1.5}Cr_{0.5}O_{5.288}$	640	78	52.8	0.45	−0.28	O
(1000°C—air)			46.7	0.28	0.36	T
		290	48.5	0.34	−0.29	O
			41.4	0.18	0.36	T
$Ca_2Fe_{1.5}Cr_{0.5}O_{5.187}$	570	78	51.8	0.44	−0.27	O
(1200°C—air)			46.4	0.27	0.33	T
		290	47.4	0.35	−0.36	O
			40.3	0.17	0.34	T
$Ca_2Fe_{1.5}Cr_{0.5}O_{5.230}$	580	78	51.8	0.43	−0.27	O
(1350°C—air)			46.2	0.26	0.33	T
		290	46.0	0.33	−0.31	O
			39.5	0.16	0.27	T

Preparations in Air ($x = 0.50$)

Samples with $x = 0.50$ were annealed in air at 1000, 1100, 1200, 1300, and 1350°C for several days and then quenched, either by removal from the furnace or much more rapidly by dropping into liquid nitrogen. The chemical analyses which are obtained from the redox behavior of the metals showed that all these materials were substantially oxidized. The value of y for an assumed formulation of $Ca_2Fe_{2-x}Cr_xO_{5+y}$ was systematically slightly higher for the slower air-quench, but the actual difference was very small. The rate of oxidation during cooling in air is very much slower than was found earlier (*6*) in Sr_2FeCoO_5, and we are confident that quenching into liquid nitrogen effectively preserves the composition pertaining to the annealing temperature: a more detailed spectroscopic characterization was carried out on these samples, although we found no significant differences between equivalent pairs of samples.

The Mössbauer spectra of all the oxidized samples showed no evidence for any significant fraction of the iron in an oxidation state higher than +3. It is therefore legitimate to regard the chromium as partially oxidized to the +4 (or higher) state. From previous studies, the brownmillerite lattice as such does not readily take up extra oxygen without transformation to a different phase, although the way in which this occurs may be quite subtle.

The quenches from five different temperatures could be divided into two distinct categories. The 1000 and 1100°C quenches gave X-ray patterns which showed the presence of a brownmillerite, the *d*-spacings suggesting an iron-rich composition, and a second phase which was positively identified as the Cr^{5+} oxide $Ca_3Cr_2O_8$. The structure of the latter is known to be related to that of various phosphates (*16*) and therefore contains the CrO_4^{3-} ion, but the X-ray pattern is characteristic (*17*); the pure compound melts at

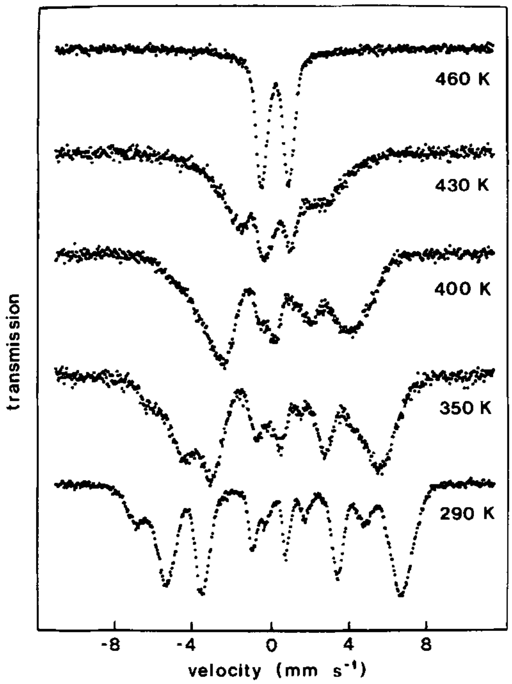

FIG. 2. The temperature dependence of the Mössbauer spectrum of $Ca_2Fe_{1.5}Cr_{0.5}O_5$ prepared *in vacuo* at 1200°C.

1228°C (*18*), and is unlikely to contain any iron. This is a calcium-rich phase, and implies the simultaneous presence of a calcium-deficient phase such as $Ca(Fe,Cr)_2O_4$. However, there is no conclusive evidence for a third phase in the X-ray pattern, and it may be effectively amorphous to X-rays. The Mössbauer spectra at 78 K (Fig. 3) and 290 K (Fig. 4) show a brownmillerite pattern with an additional weak paramagnetic feature which becomes magnetic in the vicinity of 78 K. The occupancy by iron of the octahedral sites in the brownmillerite is much higher at 43% of the total iron than was found in the vacuo preparation. If it is assumed in an analogous way that all the Cr^{3+} is on octahedral sites, then the estimated composition of the phase is $Ca_2Fe_{1.75}Cr_{0.25}O_5$, i.e., with only half the intended chromium content (the possibility of a small degree of oxidation cannot be excluded). This is totally consistent with the formation of a substantial quantity of $Ca_3Cr_2O_8$, and the observed oxygen content also implies that about half of the chromium is in this compound. The temperature dependence of the Mössbauer spectrum for the 1000°C quench (not shown) reveals some measure of relaxational collapse at 500 K, but the magnetic interactions do not finally disappear until 640 ± 5 K, again consistent with a high iron content. The identity of the third phase present remains elusive.

The samples with $x = 0.50$ annealed at 1200, 1300, and 1350°C in air were distinctly different. The oxygen content was just below that required ($y = 0.25$) for 100% oxida-

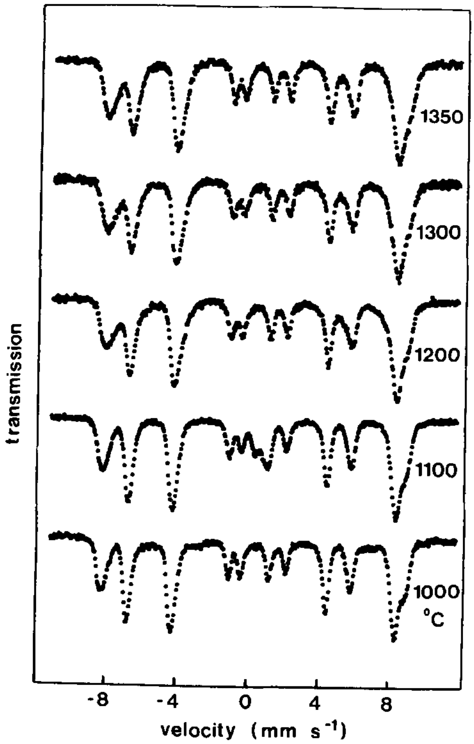

FIG. 3. The Mössbauer spectra at 78 K of $Ca_2Fe_{1.5}Cr_{0.5}O_{5+y}$ (nominal composition) annealed in air at various temperatures and quenched into liquid nitrogen.

tion to Cr^{4+}. The X-ray patterns comprised a brownmillerite pattern with slightly broader lines, but with the superposition of a broadened cubic perovskite pattern which is more intense at the higher temperature. There were no lines from $Ca_3Cr_2O_8$. Although this result could be produced in principle by a two-phase mixture, such a behavior is also shown by brownmillerites containing microdomains, where domains smaller than 200 Å in diameter result in a broadened cubic X-ray pattern. This was convincingly demonstrated for Sr_2CoFeO_5 in our earlier work (6), where it was concluded that the excess oxygen is accommodated in the domain walls. In the present instance the Mössbauer spectra at 78 K show a typical brownmillerite pattern (Fig. 3), although the outer lines are somewhat broader than normal. The area ratios at 78 K for the 1200°C quench reveal that some 48% of the total iron content is on octahedral sites, implying either that the brownmillerite lattice is extremely iron rich, or that there is considerable site disorder. The evidence suggests that all the iron-containing phases contain layers of octahedral and tetrahedral sites with a *G*-type magnetic structure.

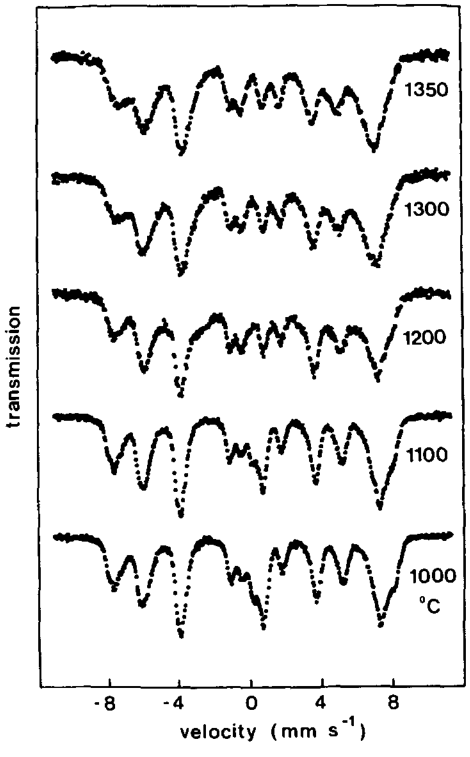

FIG. 4. The Mössbauer spectra at 290 K of $Ca_2Fe_{1.5}Cr_{0.5}O_{5+y}$ (nominal composition) annealed in air at various temperatures and quenched into liquid nitrogen.

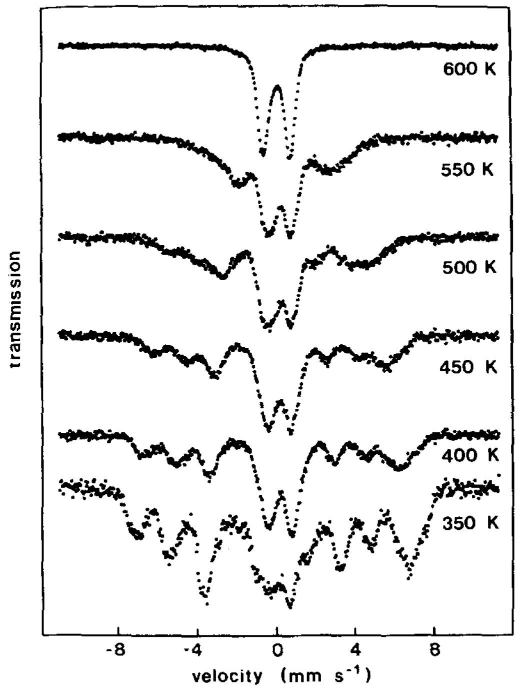

FIG. 5. The temperature dependence of the Mössbauer spectrum of $Ca_2Fe_{1.5}Cr_{0.5}O_{5.181}$ (nominal composition) annealed in air at 1200°C and quenched into liquid nitrogen.

A more significant difference is seen in the spectra of 290 K. For 1000 and 1100°C the spectrum (Fig. 4) comprises two superimposed magnetic patterns with a weak additional paramagnetic phase. For 1200°C and above (Fig. 4), the spectrum shows a very substantial and broad absorption across the whole spectrum which resembles a curved baseline (the data were rigorously corrected for baseline curvature) which was not evident at 78 K, nor is it found in the nonoxidized brownmillerite with 25% Cr. Although all three samples show similar magnetic flux densities at 78 K, there is a noticeable decrease in the values at 290 K and an increase in the broadening of the outer lines as the annealing temperature increases.

The temperature dependence for the 1200°C quench is shown in Fig. 5. Magnetic interactions finally disappear at about 570 ± 5 K, again implying the presence of an iron-rich brownmillerite phase. However, substantial relaxational collapse is clearly evident at 350 K in continuation of a process which appears to begin as low as 200 K (not all the spectra are shown). Such relaxation is not found in the $x = 0.50$ vacuo brownmillerite; furthermore, it is unlikely that cation disorder at this composition would have such an effect. We believe that this is good evidence for a textured intergrowth or microdomain behavior. The observation of broad cubic perovskite reflections in the X-ray pattern implies the existence of some very small domains which give an averaged X-ray pattern; it is evident however that there must be a considerable range in domain size in this sample.

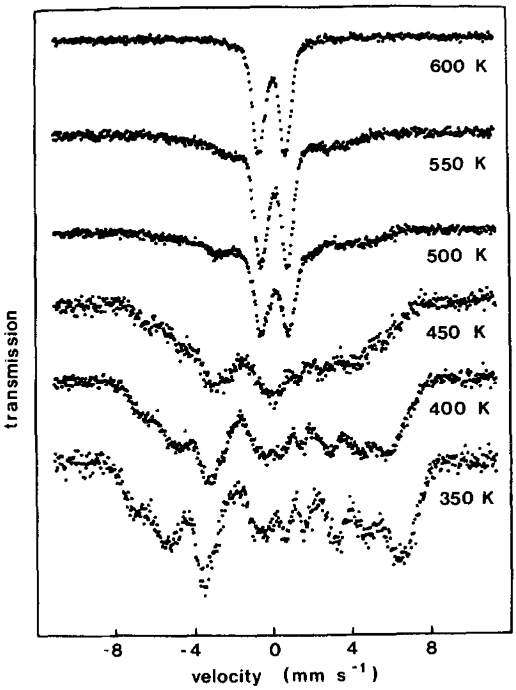

FIG. 6. The temperature dependence of the Mössbauer spectrum of $Ca_2Fe_{1.5}Cr_{0.5}O_{5.230}$ (nominal composition) annealed in air at 1350°C and quenched into liquid nitrogen.

The temperature dependence for the 1350°C quench is shown in Fig. 6. Magnetic interactions disappear at about 580 ± 5 K, essentially analogous to the 1200°C quench. However, the emergence of a strong central feature in the spectrum is delayed until a much higher temperature is reached. A possible explanation for this is that the microdomains are much more uniform in size at 1350°C. Selective growth of some microdomains at the expense of others is likely to occur at 1200°C as a prerequisite for the nucleation of the multiphase system at lower temperatures. The question of the identity of the intergrown structures will be returned to later.

Preparations in air ($x = 0.67$ and 1.00)

Similar samples with $x = 0.67$ were prepared by annealing in air at various temperatures and quenching into liquid nitrogen. The results correlated very closely with those for $x = 0.50$. Mössbauer spectra at 78 K (Fig. 7) and 290 K (Fig. 8) showed the same clear distinction between material annealed at 1000 and 1100°C on the one hand, and at 1200, 1300, and 1350°C on the other. The X-ray patterns of the former samples still showed the brownmillerite and $Ca_3Cr_2O_8$ patterns, but the paramagnetic iron-bearing phase which is now more intense at 290 K (Fig. 8) has not been positively identified. The oxygen content is consistent with the formation of a substantial amount of Cr^{5+}.

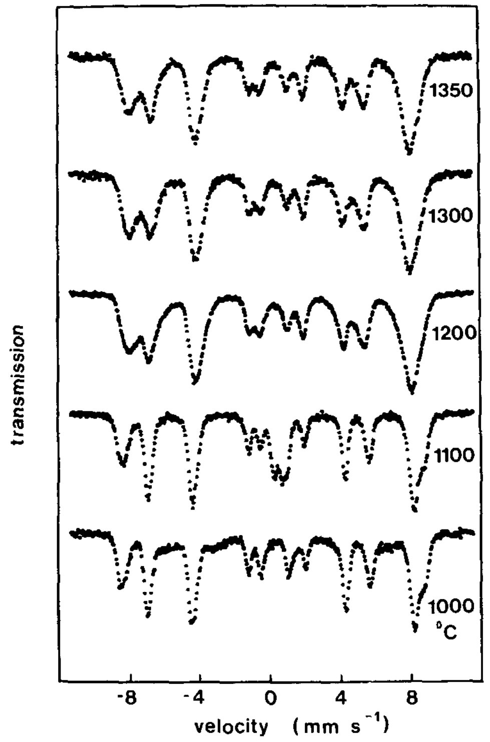

FIG. 7. The Mössbauer spectra at 78 K of $Ca_2Fe_{1.33}Cr_{0.67}O_{5+y}$ (nominal composition) annealed in air at various temperatures and quenched into liquid nitrogen.

For the other three samples the oxygen content is close to the ideal figure (y = 0.333) for complete oxidation to Cr^{4+}. The X-ray pattern of the quench from 1200°C closely resembles a brownmillerite, but the lines are less sharp. The pattern continues to change with increase in the annealing temperature until it begins to resemble the pattern described below for the OP phase at x = 1.00, but the characteristic 020 reflection at d = 7.28 Å is retained although broadened substantially. There is no evidence for a cubic perovskite pattern, but the Mössbauer spectra (Figs. 7 and 8) are clearly similar to those for x = 0.50 and suggest a brownmillerite-related lattice. It is argued below that the results are consistent with an intergrowth of the BM and OP lattices. The relative areas of the two hyperfine fields at 78 K show a significant increase in the occupation of octahedral sites to an estimated 55% of the total iron.

The temperature dependence of the Mössbauer spectrum for the 1350°C quench with x = 0.67 (not shown) shows that magnetic hyperfine splitting disappears at 445 ± 5 K, to leave a broad paramagnetic doublet in which, once again, the two types of coordination are not resolved. The lower ordering temperature is consistent with a higher chromium content in the iron-bearing phase. The symmetry and isomer shifts of the spectrum confirm that all the iron is in the +3 oxidation state. This result can be compared with that for the 1200°C quench where most of the magnetic splitting has collapsed at 400

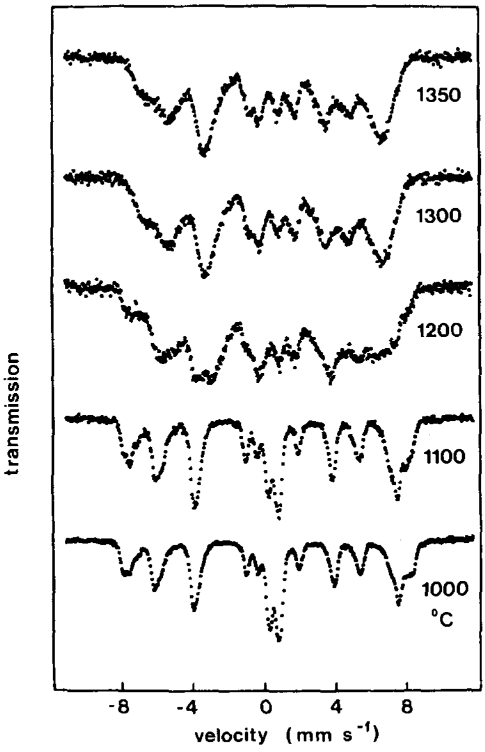

FIG. 8. The Mössbauer spectra at 290 K of $Ca_2Fe_{1.33}Cr_{0.67}O_{5+y}$ (nominal composition) annealed in air at various temperatures and quenched into liquid nitrogen.

K, but a weak residual contribution is seen up to circa 570 K. This sample is clearly more inhomogeneous than the 1350°C quench, apparently containing regions which are iron-rich as a prelude to phase separation.

The same series of preparations with $x = 1.00$ throw additional light on the system. The Mössbauer spectra at 78 K (Fig. 9) and 290 K (Fig. 10) dramatically confirm the change in behavior at circa 1200°C with the high-temperature quenches being paramagnetic at 290 K. The X-ray patterns for the 1000 and 1100°C quenches finally confirm the existence of the $Ca(Fe,Cr)_2O_4$ phase which had been postulated for smaller values of x. The $Ca_3Cr_2O_8$ phase was also identified in the 1200 and 1300°C quenches, although in the latter case it is faint and is believed to be the product of fast oxidation during the transfer from the furnace. More importantly, the dominant phase at 1350°C has been identified as an orthorhombic perovskite supercell ($\sqrt{2}a_p \times 3a_p \times \sqrt{2}a_p$), and the *d*-spacings are given in Table III. The crystallinity of the sample is poor, but the low-angle 010 reflection is characteristic, and suggests that the phase is a brownmillerite relative with the same OOTOOT. . . layer sequence as found, for example, in $Ca_2LaFe_3O_8$ (*19*). The similarity of the X-ray pattern to that of the 1350°C $x = 0.67$ quench (which has a nominal composition of $Ca_3Fe_2CrO_{7.988}$) suggests that this stacking sequence can indeed occur, although probably intergrown with other stacking sequences.

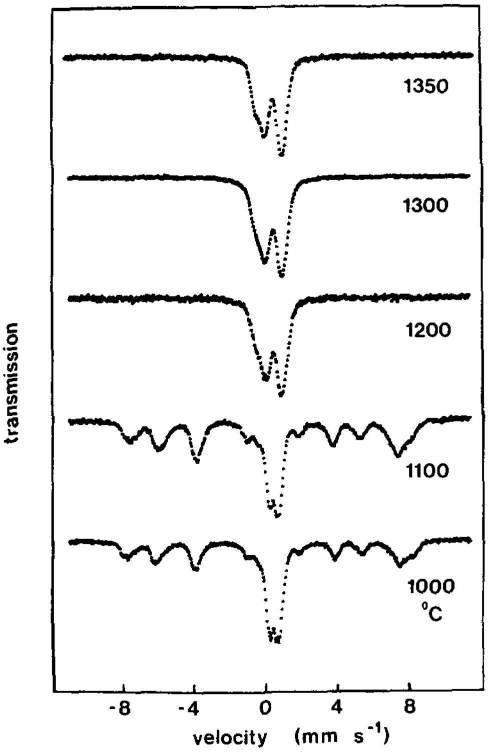

FIG. 10. The Mössbauer spectra at 290 K of Ca_2FeCrO_{5+y} (nominal composition) annealed in air at various temperatures and quenched into liquid nitrogen.

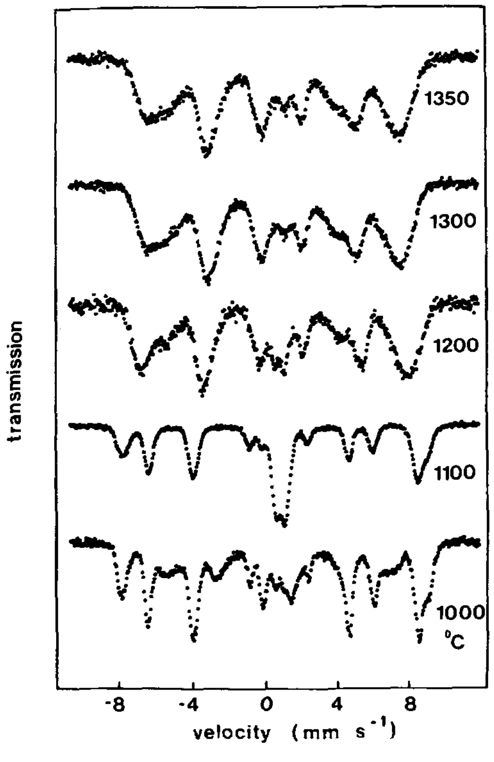

FIG. 9. The Mössbauer spectra at 78 K of Ca_2FeCrO_{5+y} (nominal composition) annealed in air at various temperatures and quenched into liquid nitrogen.

The Mössbauer spectrum of the 1350°C quench with $x = 1.0$ as a function of temperature is shown in Fig. 11. The ordering temperature is 235 ± 5 K, consistent with a high chromium content. The 1200 and 1300°C quenched samples are very similar. The paramagnetic spectrum at 290 K is asymmetric because of the different proportions of the two site coordinations. Once again all the iron is present as Fe^{3+}. A spectrum (not shown) collected with a lower velocity range was analyzed in detail. A simple two doublet model was not altogether convincing, and it appears that there is some degree of variation in the octahedral and tetrahedral site environments. The observed octahedral : tetrahedral ratio is 62 : 38. The Mössbauer spectrum at 4.2 K (Fig. 11) comprises two overlapping and broadened magnetic hyperfine sextets with flux densities of circa 48.6 and 42.7 T, which can be assigned to octahedral and tetrahedral coordinations, respectively. The quadrupole parameters, ε, are of opposite sign as expected for a brownmillerite-related structure. The area ratio of 66 : 34 agrees well with that obtained in the paramagnetic state. If the lattice is indeed based on an OOTOOT . . . layer sequence then the observed site population would suggest that the Fe and Cr are highly disordered. The oxygen content is too high for the ideal

TABLE III

THE X-RAY DIFFRACTION PATTERN FOR $Ca_2FeCrO_{5.469}$ QUENCHED IN AIR FROM 1350°C (ORTHORHOMBIC: $a = 5.432$, $b = 11.20$, $c = 5.467$ Å)

d_{obsd}	d_{calcd}	h	k	l	I_{obsd}
11.191	11.197	0	1	0	vw
5.623	5.599	0	2	0	vw
4.909[a]	4.913	0	1	1	vw
3.900	3.899	1	2	0	w
3.854	3.854	1	0	1	mw
3.728	3.732	0	3	0	mw
3.084	3.083	0	3	1	vw
3.071[a]	3.076	1	3	0	vw
2.797	2.799	0	4	0	vw
2.734	2.734	0	0	2	s
2.713	2.716	2	0	0	s
2.681	2.681	1	3	1	vs
2.493	2.492	0	4	1	w
2.259[a]	2.265	1	4	1	w
2.205[a]	2.205	0	3	2	w
2.195[a]	2.196	2	3	0	w
1.927	1.927	2	0	2	s
1.865	1.866	0	6	0	s
1.733[a]	1.733	0	2	3	w
	1.732	0	5	2	
1.713[a]	1.712	2	3	2	w
1.679	1.680	1	6	1	w
1.638	1.638	0	3	3	w
1.568	1.568	1	3	3	m
1.561	1.561	3	3	1	m
1.541[a]	1.541	0	6	2	mw
1.540	1.538	2	6	0	mw

[a] Not used in cell refinement because of low resolution.

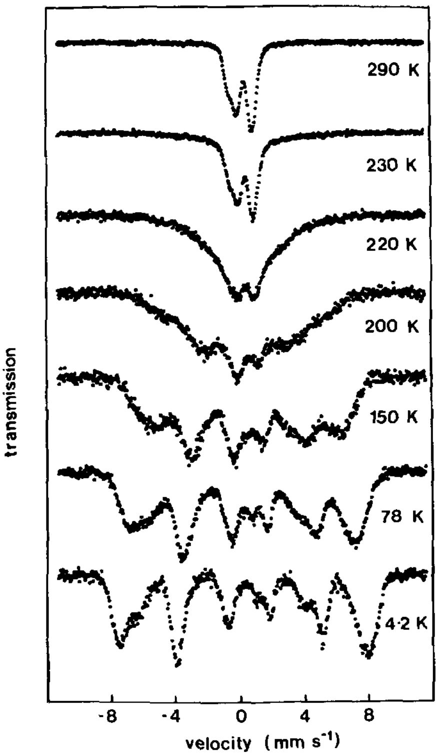

FIG. 11. The temperature dependence of the Mössbauer spectrum of $Ca_2FeCrO_{5.469}$ (nominal composition) annealed in air at 1350°C and quenched into liquid nitrogen.

stoichiometry, implying that there may be some degree of intergrowth.

The Nature of the High-temperature Phases

Let us now consider a model for the oxidized intergrowth phases which exist at 1200°C and above. The model which we propose is that the structure is based upon a macroscopic perovskite lattice in which there is a substantial segregation of Cr and Fe cations and of oxygen vacancies. This can be achieved in more than one possible way. In the first instance, regions of an Fe-rich brownmillerite (domains) could be separated by Cr^{4+}-rich domain walls, the latter containing few oxygen vacancies and locally approximating to a $CaCrO_3$ perovskite. The brownmillerite regions or domains would be likely to orient in three orthogonal directions by the local ordering of oxygen vacancies along the (110) axes of the cubic perovskite. Magnetic coherence would be lost at the domain boundaries such that the smallest domains of brownmillerite behave similarly to superparamagnetic particles and show relaxation behavior with rise in temperature. Such effects were reported earlier in Sr_2CoFeO_{5+y} (*6*) and $Ca_2LaFe_3O_{8+y}$ (*19*).

However, it is interesting to note that the Cr^{4+} perovskite, $CaCrO_3$, has only been prepared under high pressure from CaO + CrO_2 (*20, 21*), and the volume of the orthorhombic unit cell is substantially smaller per formula unit than that of the brownmillerite described here. We have found that preparations made by heating $CaCO_3$ + Cr_2O_3 at 1200°C in air and quenching into liquid nitrogen yielded mixtures of $Ca_3Cr_2O_8$, $CaCr_2O_4$, and a trace of $CaCrO_4$, but no evidence for any perovskite phase. Thus although Cr^{4+} might aggregate into the domain walls and so produce a microdomain texture which could be "cubic" to X-rays, the intergrowth of large regions of $CaCrO_3$ with the brownmillerite is most unlikely. The nucleation of $Ca_3Cr_2O_8$ (which melts at 1228°C) as a second phase below 1200°C provides a mechanism for the ex-solution of the Cr which would be already conveniently concentrated in the domain boundaries. Magnetic coherence between different regions of brownmillerite is unlikely, so that substantial relaxation effects can be expected in the Mössbauer spectra.

Some support for this model is provided by the related $Ca_2Fe_{2-x}Mn_xO_{5+y}$ system, which differs in that there is no evidence for the existence of Mn compounds with an oxidation state greater than +4. Electron diffraction data have provided clear evidence for the intergrowth of brownmillerite and perovskite-related microdomains (*22, 23*).

An alternative model is to propose the existence of intergrowths between $Ca_2Fe_2O_5$ (stacking sequence OTOT′. . .) and $Ca_3(Fe,Cr)_3O_8$ (stacking sequence OOT . . .). There is clear evidence for the macroscopic existence of the latter in the x = 1.00 quenched samples. The electron configuration (d^2) and ligand-field stabilization of Cr^{4+} is consistent with some degree of preference for occupation of the octahedral sites, but the Mössbauer data suggest that the cation distribution is highly disordered. Intergrowths of the OTOT′ and OOT sequences have also been observed by electron diffraction in the $Ca_2Fe_{2-x}Mn_xO_{5+y}$ system (*24*), and under appropriate conditions intergrowth of $Ca_2Fe_2O_5$, $Ca_3(Fe_{1-x}Mn_x)_3O_8$, and also $CaMnO_3$ have been seen (*25*); the intergrowths can occur with both large and small domain sizes depending on conditions of preparation so that X-ray diffraction may show the existence of separate phases or only an averaged "cubic" phase. Thus there are grounds to suggest that there are strong structural similarities between the Cr and Mn systems, the primary difference being the tendency for Cr to oxidize to Cr^{5+} with the exsolution of $Ca_3Cr_2O_8$ at temperatures below 1200°C. The effective domain sizes appear to be larger for the Cr system as all the X-ray patterns show considerable evidence for perovskite supercells.

Acknowledgments

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