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An Investigation of Microdomains in $Ca_2LaFe_3O_{8+y}$ by Mössbauer Spectroscopy

T. C. GIBB

Department of Inorganic and Structural Chemistry, The University of Leeds, Leeds LS2 9JT, England

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The formation of microdomains in the high-temperature oxidized form of $Ca_2LaFe_3O_{8+y}$ has been investigated by Mössbauer spectroscopy. The degree of oxidation is dependent upon the rate of quenching, and it is clear that the mobility of oxygen is very high at 1400°C. The nature of the "equilibrium solid" at this temperature remains uncertain, and it is possible that the microdomains are a product of the quench itself, rather than an inherent part of the structure at high temperature.

Introduction

It has long been recognized that a variable composition in a metal oxide can be achieved in several ways. Point defects, defect complexes, and crystallographic shear planes are all well known. The intergrowth of two or more structural motifs in variable amounts can also occur, and the compound $Ca_2LaFe_3O_8$ in which there is an ordered intergrowth of the perovskite ($CaFeO_3$) and brownmillerite ($Ca_2Fe_2O_5$) lattices has been known for some time (*1, 2*). More recently it has been elegantly demonstrated by electron diffraction techniques (*3–6*) that the high-temperature oxidized form of $Ca_2LaFe_3O_{8+y}$ contains a three-dimensional microdomain intergrowth, with excess oxygen incorporated in the domain walls.

Recent work in this laboratory (*7*) has found evidence from Mössbauer spectroscopy for similar microdomain formation in partially oxidized Sr_2CoFeO_5 quenched from 1200°C in air. However, in this instance it was clearly demonstrated that the oxidation takes place with great rapidity during the quench. Quenching in liquid nitrogen from 1200°C produces stoichiometric Sr_2CoFeO_5 with a random distribution of cobalt and iron on the tetrahedral and octahedral sites of a brownmillerite lattice. This has prompted a reinvestigation of $Ca_2LaFe_3O_{8+y}$ for two main reasons: first to confirm the interpretation for Sr_2CoFeO_5 by verifying that both compounds show the same relaxational collapse in their Mössbauer spectra, and second to investigate the effects of the quench during the preparation in order to establish more clearly the nature of the "equilibrium solid" at 1400°C.

Stoichiometric $Ca_2LaFe_3O_8$ can be prepared by standard ceramic techniques from the mixed oxides/carbonates, with a final anneal for several days under flowing argon at 1150°C (*1, 2*). The structure is derived from the cubic perovskite by an ordered arrangement of oxygen vacancies along [101] axes to give an orthorhombic unit cell with layers of iron cations in tetrahedral coordination, each separated by two layers of iron

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in octahedral coordination to oxygen. It is also described as the $n = 3$ term in a general series $A_nB_nO_{3n-1}$ intermediate between ABO_3 ($n = \infty$, perovskite) and $A_2B_2O_5$ ($n = 2$, brownmillerite), in which different structural motifs produce coherent intergrowths in various proportions along one direction. In actual fact $Ca_2LaFe_3O_8$ is just one composition in a solid solution in which the composition appears to change solely by altering the relative numbers of octahedral and tetrahedral cation layers. Some measure of disorder can therefore be expected, and evidence for this has been found in electron diffraction data (*3*, *4*). In particular, a high-resolution micrograph has been published showing a coherent intergrowth of the $Ca_2Fe_2O_5$ and $Ca_2LaFe_3O_8$ lattices. A full crystal structure of $Ca_2LaFe_3O_8$ has not been obtained as yet, but the major structural features are beyond doubt. Antiferromagnetic ordering takes place below circa 770 K. Mössbauer spectroscopy measurements (*5*) show two well-resolved magnetic hyperfine splittings and confirm the existence of tetrahedral and octahedral iron sites in the expected ratio of 1 : 2. The linewidths are somewhat broader than in the very similar pattern for $Ca_2Fe_2O_5$ (brownmillerite, tetrahedral : octahedral = 1 : 1), and this may reflect the Ca^{2+} and La^{3+} cation distribution which is believed to be disordered and can be expected to produce small local distortions.

A long anneal in air for two weeks at 1150°C followed by a quench was found to result in a degree of oxidation to $Ca_2LaFe_3O_{8+y}$ with $y = 0.030$, but retaining the orthorhombic lattice (*2*).

Quenching from 1400°C gave a "cubic perovskite" phase with $y = 0.125$ (nominally 8.3% Fe^{4+}) (*2*). Subsequent electron diffraction work (*3*) was carried out on a sample with $y = 0.235$ (15.6% Fe^{4+}) prepared by annealing at 1400°C in air and "quick-quenching" down to room temperature. X-ray powder diffraction showed a cubic perovskite pattern ($a = 3.848$ Å). However, electron diffraction revealed a microdomain texture with an intergrowth of small microdomains clearly related to the orthorhombic $Ca_2LaFe_3O_8$ structure (although with tetragonal symmetry) but randomly oriented along each of the three cubic directions. These microdomains were of the order of ~60–100 Å across in size. It is believed that the excess oxygen is effectively accommodated within the domain walls, and not inside the domains themselves. On this basis the domains will be smaller with greater oxygen excess. A micrograph has been observed for one crystal of $Ca_2LaFe_3O_{8+y}$ (*6*) showing an intergrowth of the reduced ordered phase with the oxidized disordered microdomain structure and with an extended defect of some kind close to the border between the two regions. Reduction of $Ca_2LaFe_3O_{8+y}$ in the electron microscope has also been observed with a decomposition into phases based on $Ca_2Fe_2O_5$ and $LaFeO_3$ (*6*). The same microdomain features are found at other Ca/La ratios in the solid solution (*4*), except that the microdomain structure is of the brownmillerite-type, and again oxygen excess is thought to be in the domain walls.

The reasons for the existence of these domain phenomena are not known. Surprisingly, Mössbauer data have not been reported for these microdomain phases.

Experimental

Samples of $Ca_2LaFe_3O_{8+y}$ were made under a range of experimental conditions. Those which are referred to in detail in this paper were prepared as follows. Accurately weighed amounts of dry spectroscopic-grade Fe_2O_3, $CaCO_3$, and La_2O_3 in the stoichiometric ratio appropriate for $Ca_2LaFe_3O_8$ were ground together in a ball mill, pressed into pellets, and fired in a platinum crucible. The first batch of material was fired at 1300°C for 1 day in air and at 1400°C for 5 days with a quench in air and reground on each occasion. The compound sinters extremely well. The batch was then split into three portions and all were fired at 1400°C for 7 days in air before the final quench. Sample 1A was fast-quenched in liquid nitrogen; sample 1B was fast-quenched in air onto a metal plate; sample 1C was quenched in air, reannealed at 1150°C for 5 days, and then fast-quenched in air onto a metal plate.

The second batch of material was split into several portions after grinding, pelleted, and fired once at 1400°C for 2 days and quenched. Samples 2A and 2B were fast-quenched into liquid nitrogen; samples 2C and 2D were fast-quenched in air.

A third batch of material which was quenched twice in air from 1300 to 1400°C after 1 day (sample 3A), was annealed under Argon at 1150°C for 6 days, and then slowly cooled to give stoichiometric $Ca_2La Fe_3O_8$ (sample 3B).

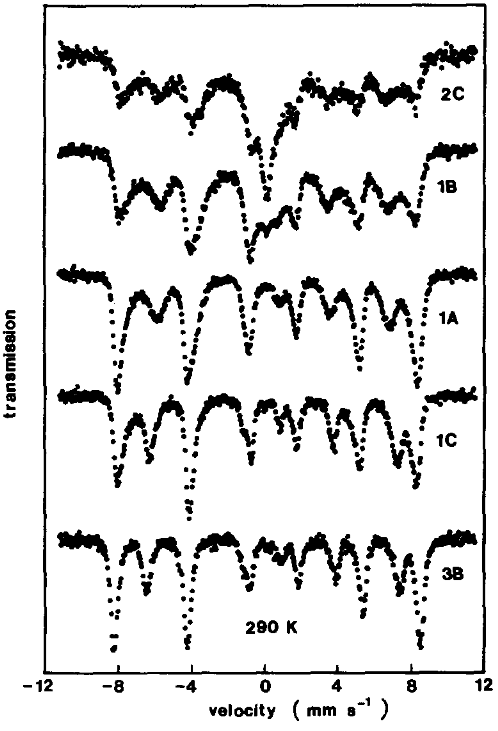

FIG. 1. The Mössbauer spectra at 290 K of five different samples of $Ca_2LaFe_3O_{8+y}$.

Initial characterization in each case was by X-ray powder diffraction recorded with a Philips diffractometer using nickel-filtered Cu$K\alpha$ radiation.

Chemical analysis was carried out to determine the oxygen excess by digestion in a standardized solution of ammonium iron(II) sulfate in the presence of HCl and titrated with cerium(IV) sulfate using ferroin as indicator. The values obtained for y were 0.079 (sample 1A), 0.227 (1B), 0.069 (1C), 0.069 (2A), 0.069 (2B see text), 0.267 (2C), 0.267 (2D), and 0.274(3A).

Mössbauer spectra were recorded in the range 78–300 K with a $^{57}Co/Rh$ source matrix at room temperature; isomer shift values are relative to the spectrum of metallic iron. The main spectrometer was an MS-102 microprocessor by Cryophysics Ltd.

Results and Discussion

(*a*) *Synthesis at 1150°C*

The X-ray pattern for reduced $Ca_2La Fe_3O_8$ (sample 3B) obtained by heating under argon at 1150°C was fully consistent with the published *d*-spacings and the orthorhombic cell (*1*). The Mössbauer spectrum at 290 K (see Fig. 1) and 78 K (see Fig. 2) comprised two overlapping six-line magnetic hyperfine patterns in the ratio 1 : 2 within experimental error, consistent with the tetrahedral : octahedral site ratio and with previously published data (*2*). The lines are noticeably broader than observed for stoichiometric brownmillerites such as $Ca_2Fe_2O_5$ and $Sr_2Fe_2O_5$ (*8*). The presumed disorder of the Ca^{2+} and La^{3+} on the A sites of the perovskite-related lattice will cause local fluctuations in the iron environment and thus lead to this line broadening. The spectrum was also recorded at 180 and 240 K, and the temperature dependence of the

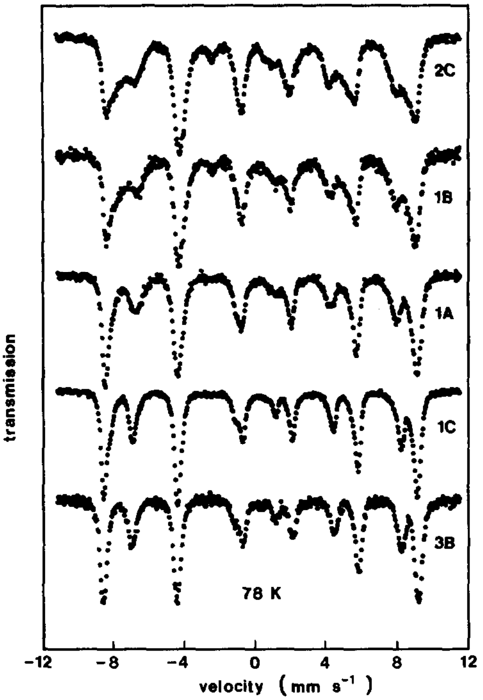

FIG. 2. The Mössbauer spectra at 78 K of five different samples of $Ca_2LaFe_3O_{8+y}$.

flux density of the hyperfine field at both sites is shown in Fig. 3. The Mössbauer spectra of $Ca_2Fe_2O_5$, $Sr_2Fe_2O_5$, and $Ca_2La Fe_3O_8$ are similar in that the second-order quadrupole perturbation parameter ε at both sites is of the same sign and similar magnitude (typical parameters are given in Table I). This confirms that the antiferromagnetic spin ordering must be comparable, with the spins normal to the *b*-axis, i.e., within the cation layers.

Sample 1C which was obtained by annealing at 1150°C in air gave a similar X-ray pattern but with significant line broadening. The chemical analysis gave a composition of $Ca_2LaFe_3O_{8.069}$ ($y = 0.069$), corresponding to 4.6% Fe^{4+}. This composition indicates a higher degree of oxidation than previously reported—a sample annealed at 1150°C for 2 weeks gave $y = 0.030$ (*2*). The Mössbauer spectrum at 78 K shown in Fig. 2 is generally similar to that of the reduced material. In particular, there is no real evidence for the presence of an Fe^{4+} component in the spectrum. The flux density of the hyperfine field at both sites is systematically lower (Fig. 3) than for the reduced materials, and possible reasons for this will be discussed later.

TABLE I

OBSERVED MÖSSBAUER PARAMETERS

Compound	T (K)	B (T)	δ (mm sec^{-1})	ε (mm sec^{-1})	Site
$Ca_2Fe_2O_5$	295	51.4	0.34	−0.27	O
		43.8	0.17	0.35	T
$Sr_2Fe_2O_5$	295	50.1	0.37	−0.35	O
		42.2	0.17	0.30	T
$Ca_2LaFe_3O_8$	290	52.1	0.36	−0.20	O
		43.0	0.19	0.29	T
$Ca_2LaFe_3O_8$	290	52.1	0.375		O
(Ref. (*2*))		42.6	0.190		T

In the Mössbauer spectrum at 290 K there is a noticeable change in the outer lines so that the tetrahedral components ap-

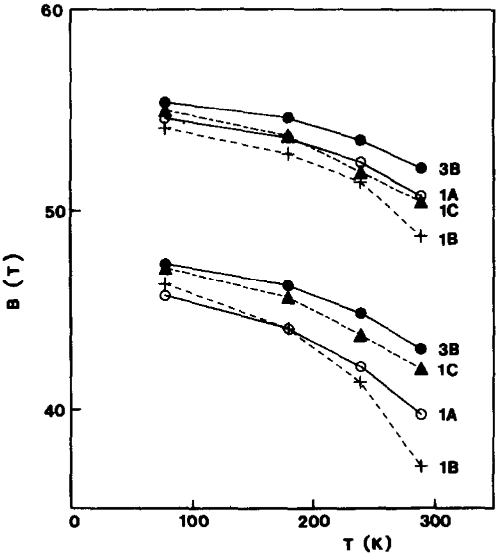

FIG. 3. The temperature dependence of the flux density of the hyperfine field in four different samples of $Ca_2LaFe_3O_{8+y}$.

pear to have increased in relative intensity (see Fig. 1). Upon close inspection, this is probably due to a partial inward broadening of the octahedral-site pattern so that the outermost lines are highly asymmetric, and the tetrahedral lines which remain more symmetrical now overlap with the large tail of the neighboring line. Several possible causes can be enumerated. First, the introduction of extra oxygen into the lattice may produce local variations in the cation-site environments, such that the temperature dependence of the observed field as expressed by molecular field theory may not be the same for all sites (*9*). Second, nonstoichiometry in the lattice could result in frustrated spin-coupling so that the spin relaxation times become shorter and motional collapse of the spectrum commences. Third, the electrons lost upon oxidation may be removed from octahedral cations which are then no longer formally Fe^{3+} or Fe^{4+}, but may have a variable spin-density according to the neighboring oxygen occupation (see Ref. (*10*) for details of several related systems where this seems to occur). A unique interpretation is not possible on present evidence.

(*b*) *Synthesis at 1400°C*

In our earlier work (*7*) on Sr_2CoFeO_5, it was found that quenching in liquid nitrogen from 1200°C produced a stoichiometric product with an orthorhombic brownmillerite lattice. Quenching rapidly in air resulted in significant oxidation of the product which gave an X-ray pattern resembling the superposition of the original brownmillerite pattern with that from a cubic perovskite with broadened lines. The latter was interpreted in terms of the formation of a high proportion of microdomains of brownmillerite less than circa 200 Å in dimension, i.e., less than the resolving power of the X-ray technique, so that an "averaged" structure was observed. The Mössbauer spectra obtained were found to be fully consistent with this hypothesis. Although oxidation clearly leads to the formation of small microdomains, the samples quenched in liquid nitrogen could nevertheless still contain small domains as long as these are somewhat larger than 200 Å. In this respect it may be significant that $Sr_2Fe_2O_5$ heated in a sealed tube above 850°C shows a transition to a cubic perovskite which has been interpreted in terms of microdomain formation (*11*). A similar cubic phase has been found for $Sr_2Co_2O_5$ (*12*), although the situation here is complicated by the existence of a low-temperature "hexagonal" phase which work from our laboratory shows to contain a substantial proportion of face-sharing polyhedra (*13*). However, it seems that neither cubic phase can be preserved by quenching. $Sr_2Fe_2O_5$ quenched in air from 1200°C appears to oxidize to a more conventional two-phase mixture of brownmillerite + perovskite (*7*), although the degree of oxidation can be reduced by quenching in liquid nitrogen. $Sr_2Co_2O_5$ can be quenched in air as a metastable brownmillerite phase. The ordering of vacancies to give a "macrodomain" brownmillerite phase takes place very rapidly during the quenching process, although the existence of microdomains at high temperature cannot be ruled out.

The rate at which Sr_2CoFeO_5 and $Sr_2Fe_2O_5$ oxidize during quenching is quite impressive, and it seems possible that the existence of microdomain boundaries at 1200°C provides ready-made pathways for the invasion by oxygen as the temperature falls. In the published investigations (*3–6*) of $Ca_2LaFe_3O_{8+y}$ it is implied that the quench from 1400°C preserves the equilibrium state at 1400°C. It was therefore decided to investigate the effect of the quenching conditions to ascertain whether or not this is the case.

All samples quenched from 1400°C showed an X-ray pattern which resembled a cubic perovskite, though invariably with some degree of broad basal components to the peaks which suggested incomplete averaging. It did not seem possible to prepare a quenched sample giving an X-ray pattern resembling the orthorhombic phase as was found for Sr_2CoFeO_5. Different quenches were applied to the same batch of starting material in an attempt to minimize other experimental variables. Chemical analysis was carried out as soon as possible after preparation in case the samples were not stable over prolonged periods. Quenching in air from 1400°C onto a metal plate after more than one heating cycle (sample 1B, $y = 0.227$, and 3A, $y = 0.274$) gave consistent results (15–18% Fe^{4+}), and may be compared with a published value ($y = 0.235$) (*2*). Quenching after only one heating cycle (sample 2C, $y = 0.267$, 2D, $y = 0.267$) resulted in a similar degree of oxidation, but the microdomains were clearly smaller on average as seen by a narrowing of the cubic X-ray lines and a greater degree of collapse in the Mössbauer spectra at 290 K (Fig. 1).

Three samples quenched into liquid nitrogen as rapidly as possible (sample 1A, $y = 0.079$, 2A, $y = 0.069$, 2B, $y = 0.069$) showed a reduction in the degree of oxidation by about 70%. Samples 2A and 2B were notionally identical, except that about half the outer regions of the pellet of 2B were abraded away before crushing the remainder for analysis. The similar value of y is consistent with a uniform degree of oxidation throughout the pellet.

Mössbauer spectra for samples 1A (quenched in nitrogen), 1B, and 2C (quenched in air) are shown in Figs. 1 and 2. The spectra for sample 1A are basically consistent with that for $Ca_2LaFe_3O_8$ but do show significant differences. The linewidths are noticeably broader for both sites, although the area ratio of the two patterns remains 1:2 within experimental error. The flux densities of the hyperfine fields are now much smaller than in $Ca_2LaFe_3O_8$ (see Fig. 3), and the discrepancy becomes more marked with increasing temperature. The spectrum of sample 1B at 78 K is similar to that of 1A, although the outer lines have broadened asymmetrically and there is clear evidence for an additional line at ca. -2.4 mm sec^{-1} which may be one component of a magnetic hyperfine splitting produced by Fe^{4+} ions. However, with increasing temperature there is a progressive inward collapse of the spectrum at the expense of the outer resolved hyperfine lines. These features are even more marked in sample 1C, so much so that the baseline of the spectrum appears to be curved. These spectra are generally similar to those recorded for Sr_2CoFeO_{5+y}, and thus strongly support our interpretation of the latter system in terms of microdomain formation.

Many of the features of the spectra can be readily explained in terms of the theory of magnetic hyperfine splitting in microcrystals as detailed by Mørup (*14, 15*). Although microcrystals and microdomains are *not* the same phenomenon, it has been shown that the observed spectra will show similar features in both cases. In the simplest form of the theory, the superparamagnetic relaxation time τ for a microcrystal is given by

$$\tau = \tau_0 \exp(KV/kT),$$

where K is the magnetic anisotropy energy constant, V is the volume of the particle, k is Boltzmann's constant, and T is the temperature. It is customary to define a blocking temperature T_B which is the temperature below which relaxation is negligible and therefore depends on the technique of observation. Even for $kT \ll KV$ the direction of magnetization may fluctuate in directions close to an easy direction of magnetization, with the result that the magnetic hyperfine field observed may be smaller than it would be in the absence of fluctuation by as much as 15%. Thus a reduction in magnetic field can be seen below the blocking temperature where relaxation effects are absent. A solid containing microdomains where the magnetic interactions between domains may not be negligible is equivalent to an assemblage of microcrystals in close contact as considered by Mørup (*14*). He has shown that the inhomogeneities in such a system will produce a range of hyperfine fields and thus broadened lines.

The detailed effects are often obscured in experiments on microcrystals by the wide range of particle sizes present. A more controlled experiment (*16*) has been achieved by preparing magnetic films of Fe_3O_4 of known thickness on a platinum substrate. The two hyperfine fields at room temperature from the A and B sites were seen to decrease from the normal bulk values as the thickness decreased below 300 Å. Simultaneously, there was an increase in the spectral linewidths. The field had decreased by some 12% at a thickness of 33 Å. Superparamagnetic collapse was observed at smaller thicknesses. These effects were interpreted as primarily due to a decrease in particle size.

The observed line broadening and decrease in the average flux density of the hyperfine field upon oxidation of $Ca_2LaFe_3O_8$ (Fig. 3) are thus fully consistent with the formation of small microdomains. The reduction in hyperfine field is not so marked in Sr_2CoFeO_{5+y}, and this may reflect a larger distribution in domain sizes in this instance.

These results confirm that the degree of oxidation in $Ca_2LaFe_3O_{8+y}$ *is* dependent on the quench and that the mobility of oxygen in these compounds is considerable at 1400°C. It is difficult to be certain as to the "equilibrium composition at 1400°C." Measurement of the oxygen content *in situ* cannot be achieved easily at this temperature. It is certainly a possibility that y is effectively zero, but that nevertheless an inherent microdomain structure still exists like that postulated for $Sr_2Fe_2O_5$ (*12*). The high mobility of oxygen observed suggests that the oxygen vacancy distribution in the perovskite lattice may be dynamic, but on the other hand the mobility along microdomain boundaries could well be significantly greater than through the bulk of the microdomains. It is interesting to note that a brief reference to a measurement of the oxygen conductivity in $Sr_2Fe_2O_5$ (*12*) claims that it is not particularly high even above the transition to the cubic phase.

The observation (*6*) of an intergrowth between an ordered orthorhombic lattice and a microdomain texture with an extended defect at the boundary is also open to more than one interpretation. The extended defect may well have created a barrier to the transformation. Is the ordered region a relic of the low-temperature phase which thus escaped conversion to a microdomain texture at 1400°C, or is it a relic of the true high-temperature phase which escaped oxidation during the quench? It is clear that further work is required on these fascinating materials.

It has now been demonstrated that both electron diffraction and Mössbauer measurements have a significant role to play in the characterization of microdomain materials. Electron diffraction can examine a few microscopic regions in a solid sample with considerable elegance, thereby revealing the nature of the microdomains and their relationship with the primary crystal lattice. However, there is always an inherent danger that certain types of particles which are not typical of the sample in general but are particularly amenable to characterization by electron diffraction are given an undue emphasis. On the other hand Mössbauer spectroscopy is able to provide an unweighted average over a much larger volume and is therefore not susceptible to such an effect. It also provides information on the size distribution of the microdomains and on the primary lattice. Furthermore, the Mössbauer measurement is as rapid and convenient to obtain as an X-ray powder pattern and can provide a useful "screening" function as a prelude to more elaborate measurements by electron diffraction to determine the nature of the microdomains.

Acknowledgments

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