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Charge and spin order in the perovskite CaFe0.5Mn0.5O3: Charge disproportionation behavior of randomly arranged Fe4+

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Abstract

B-site-disordered perovskite CaFe0.5Mn0.5O3 with unusually high valence Fe4+ was synthesized using a high-pressure technique. Fe4+ randomly distributed at half of the B sites shows charge disproportionation to Fe3+ and Fe5+. The spins of Fe3+,Fe5+, and Mn4+ order below 90 K. Analysis of low-temperature neutron powder-diffraction data revealed a G-type antiferromagnetic structure—where all the nearest-neighboring spins of Fe3+,Fe5+, and Mn4+ couple antiparallel—and the small ordered moment of 0.58μB reveals local charge ordering that gives rise to predominant Fe3+-O-Fe5+ antiferromagnetic arrangements. Despite the identical chemical compositions of CaFe0.5Mn0.5O3 and Ca2FeMnO6, the magnetic structure of the present CaFe0.5Mn0.5O3 is very different from the noncollinear one of layered B-site-ordered Ca2FeMnO6.

Introduction

At low temperature some perovskite structure oxides with the unusually high valence Fe^{4+} show characteristic charge behaviors relieving the instability of the high valence state. The simple perovskite $CaFeO_3$ and the *A*-site-ordered perovskite $CaCu_3Fe_4O_{12}$ are examples of such oxides, and they show a charge disproportionation (CD) transition in which Fe^{4+} changes to Fe^{3+} and Fe^{5+} ($2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$). This CD in the three-dimensional Fe^{4+} sublattice occurs below the magnetic transition temperature and produces rock-salt-type ordering of Fe^{3+} and Fe^{5+}.

We recently found that a similar CD occurred in the two-dimensional Fe^{4+} sublattice of the layered double perovskite Ca_2FeMnO_6, which consists of alternately stacked $Fe^{4+}O_6$ and MnO_6 octahedral layers. In that material the Fe^{4+} in the two-dimensional layers shows CD below about 200 K, and the resultant Fe^{3+} and Fe^{5+} are ordered in a checkerboard manner. Further cooling results in a magnetic transition at 95 K, and the competing magnetic interactions among Fe^{3+}, Fe^{5+}, and Mn^{4+} stabilizes an unusual noncollinear ferrimagnetic spin structure. The neighboring spins in each Fe and Mn layer couple antiferromagnetically, and the charge disproportionated Fe^{3+} and Fe^{5+} spins thus result in ferrimagnetism. This noncollinear magnetic structure is different from the helical magnetic structure of Fe^{3+} and Fe^{5+} spins along the <111> direction in the pseudo-cubic $CaFeO_3$ and is also different from the ferrimagnetic structure in $CaCu_3Fe_4O_{12}$, where both Fe^{3+} and Fe^{5+} spins are coupled antiferromagnetically with the *A*-site Cu^{2+} spins, forming a ferromagnetic sublattice at the Fe site.

In the work reported here we have synthesized $CaFe_{0.5}Mn_{0.5}O_3$, which has a chemical composition identical to that of the layered double perovskite Ca_2FeMnO_6 but a disordered arrangement of *B*-site Fe and Mn. We found, surprisingly, that this *B*-site-disordered $CaFe_{0.5}Mn_{0.5}O_3$ also shows a CD of Fe^{4+} at a low temperature. We have used powder neutron diffraction (PND) analysis to investigate the magnetic structure of this newly synthesized compound, and here we compare the crystal and magnetic structures of the *B*-site-disordered $CaFe_{0.5}Mn_{0.5}O_3$ with those of the layered *B*-site-ordered Ca_2FeMnO_6. We also discuss the CD and magnetic transition behaviors of this new phase.

Experiments

A polycrystalline sample of $CaFe_{0.5}Mn_{0.5}O_3$ was synthesized in a solid-state reaction under a high-pressure and high-temperature condition. A mixture of stoichiometric amounts of $CaCO_3$, Fe_2O_3, and $MnCO_3$ was calcined at 1250°C in air. The calcined powder was then sealed in a Pt capsule with the oxidizing agent $KClO_4$ and held at 5.3 GPa and 1100°C for 30 minutes before quenching to room temperature. The pressure was then reduced slowly to ambient and the reacted sample was removed from the capsule, washed several times with distilled water to remove residual KCl and $KClO_4$, and was then dried.

The crystal and magnetic structures were analyzed by measuring PND patterns. Time-of-flight PND experiments were performed at the WISH beamline of ISIS at RAL. The data were analyzed with the FullProf Rietveld program. The valence state of Fe was estimated with Mössbauer spectroscopy measurements. The spectra were measured in transmission geometry with a constant-acceleration spectrometer using a $^{57}Co/Rh$ radiation source and were fitted with Lorentzian functions. Magnetic properties were measured with a commercial Quantum Design MPMS SQUID magnetometer.

Results and Discussions

Figure 1(a) shows the PND pattern at room temperature and the results of crystal structure refinements for the obtained $CaFe_{0.5}Mn_{0.5}O_3$. The corresponding pattern and results for the layered double perovskite are shown in Fig. 1(c). In the pattern for $CaFe_{0.5}Mn_{0.5}O_3$ neither superstructure peaks related to the Fe/Mn ordering at the *B*-site (e.g. those at d =3.5 and 7.5 Å seen in the pattern for layered Ca_2FeMnO_6) nor diffuse intensities due to the short range orderings of the *B*-site cations are evident. The observed diffraction pattern of $CaFe_{0.5}Mn_{0.5}O_3$ is well reproduced with a $GdFeO_3$-type perovskite structure model with a space group *Pnma* and a $\sqrt{2}a\times2a\times\sqrt{2}a$ unit cell (a represents the lattice constant of the simple perovskite structure, ~3.8 Å), and the refinement results are listed in Table 1. The Fe and Mn ions occupy the 4*b* site, and the refined occupancies are 51.2(2)/48.8 % for Fe/Mn. Note also that each refined lattice parameter is, in keeping with Vegard's law, between the parameters corresponding to the two end-composition compounds of $CaFeO_3$ and $CaMnO_3$. The above results confirm the random distribution of the Fe and Mn ions at the *B* site in $CaFe_{0.5}Mn_{0.5}O_3$.

The valence state of Fe in $CaFe_{0.5}Mn_{0.5}O_3$ was verified from the ^{57}Fe Mössbauer spectra. As shown in Fig. 2 (a), the observed spectrum at room temperature is well fitted with a single paramagnetic component with the isomer shift (IS) of 0.04 mms^{-1}. This small value is typical for unusual Fe^{4+} and is also very close to that observed in the layered $Ca_2Fe^{4+}MnO_6$ (0.02 mms^{-1}). The absence of any trace of Fe^{3+} in the spectrum confirms that all the Fe ions in the $CaFe_{0.5}Mn_{0.5}O_3$ were Fe^{4+}. Therefore, two samples having an identical chemical composition with the unusually high valence Fe^{4+} at room temperature can be made: one is the present *B*-site-disordered $CaFe_{0.5}Mn_{0.5}O_3$ and the other is the layered *B*-site-ordered Ca_2FeMnO_6 reported in ref. [*]. Comparing the Mössbauer spectra, one sees that the local environments of Fe^{4+} in the two samples appear to be quite similar to each other in spite of the difference in the degree of long range order.

Importantly, as shown in the Mössbauer spectra at 3 K (Fig. 2(b)), Fe^{4+} in the *B*-site-disordered $CaFe_{0.5}Mn_{0.5}O_3$ shows CD at low temperatures. The observed spectrum is reproduced with two magnetically ordered sextets with almost equal intensities. Their ISs are −0.01 and 0.35 mms^{-1} and the corresponding hyperfine fields (HF) are 28.8 and 44.3 T, which are close to the values for charge-disproportionated Fe^{5+} (IS = −0.01 mms^{-1} and HF = 27.4 T) and Fe^{3+} (IS = 0.35 mms^{-1} and HF = 43.4 T) in the layered *B*-site-ordered Ca_2FeMnO_6. (Would it be more appropriate to compare to IS and HF of CaFeO3, in view of following discussion?) $CaFe_{0.5}Mn_{0.5}O_3$ may be described as a diluted variant of charge-ordered $CaFeO_3$ where half of the Fe sites at random are replaced by charge-inactive Mn^{4+}. The resulting coverage of Fe-O-Fe linkages is 25% which is close to the estimates of 24.7 to 25.6% for the bond percolation threshold for a simple cubic lattice. Although no long range order is observed by PND, the Mössbauer results and percolation theory suggest that Fe3+/Fe5+ charge order will occur over local domains. This is in keeping with the ferrimagnetism of $CaFe_{0.5}Mn_{0.5}O_3$ as described later. [It is surprising that all the Fe^{4+} ions randomly distributed the half of the *B* sites also show CD. CD of Fe^{4+} has been reported to occur in the three-dimensional cubic ($CaFeO_3$ and $CaCu_3Fe_4O_{12}$) and two-dimensional square (Ca_2FeMnO_6) sublattices of Fe^{4+}, producing respectively the rock-salt-type and checkerboard-type orderings of Fe^{3+} and Fe^{5+}. The present results, however, show that a complete cubic or square network of the unusually high valence Fe^{4+} ions is not necessary for the CD transition. perhaps delete this?]

It is difficult to determine the distribution of Fe^{3+} and Fe^{5+} in the CD state from the diffraction data. In the PND pattern at 2K shown in Fig. 1(b), neither apparent superstructure nor distortion from the room temperature crystal structure is detected, and the nuclear diffraction intensities are essentially the same as those at 300 K. Although the CD transition is often accompanied by a crystal structure transition, this appears to be suppressed by dilution with Mn^{4+} in the present *B*-site-disordered $CaFe_{0.5}Mn_{0.5}O_3$.

The magnetic properties and structure of charge-disproportionated $CaFe_{0.5}Mn_{0.5}O_3$ are of particular interest in relation to the diluted charge order. As shown by the temperature dependence of magnetic susceptibility (Fig. 3(a)), $CaFe_{0.5}Mn_{0.5}O_3$ shows a magnetic transition around 90 K, which is very close to the magnetic transition temperature of the layered double perovskite Ca_2FeMnO_6. Field dependence of the magnetization revealed that the compound has a small spontaneous magnetization of about 0.2 μ_B per $CaFe_{0.5}Mn_{0.5}O_3$, which is also very close to that of the layered and ordered Ca_2FeMnO_6 (Fig. 3(b)). Local magnetic environments of the charge-disproportionated Fe^{3+} and Fe^{5+} evaluated from the HF values in the Mössbauer spectrum (Fig. 2(b)) are also not so different from those in the layered *B*-site-ordered compound. It is thus notable that the two compounds with different *B*-site cation ordered structures show similar magnetic behaviors.

In contrast, magnetic reflections of $CaFe_{0.5}Mn_{0.5}O_3$ in the PND pattern obtained at 2 K are very different from those of the layered *B*-site-ordered Ca_2FeMnO_6, indicating that the magnetic structures of the two compounds are not identical. The present $CaFe_{0.5}Mn_{0.5}O_3$ shows an apparent magnetic superstructure peak at $d \approx 4.3$ Å, while the layered *B*-site-ordered Ca_2FeMnO_6 shows three strong magnetic superstructure peaks indexed as 010/001, 110/011, and 210/201 (Figs. 1(b) and 1(d)). The peak at $d \approx 4.3$ Å corresponds to 110 or 011 reflections of a $\sqrt{2}a\times2a\times\sqrt{2}a$ unit cell, indicating the presence of a G-type antiferromagnetic (AFM) spin structure, where all the nearest neighboring spins couple antiparallel to each other. The fit of a G-type magnetic structure to the PND data at 2 K gives an average refined moment of 0.58(x) μ_B per cation. This ordered moment is very small compared to the ideal 3.5 μ_B average magnetic moment for 25% Fe^{3+} ($S = 5/2$), 25% Fe^{5+} ($S = 3/2$), and 50%-Mn^{4+} ($S = 3/2$) ions randomly distributed at the *B* sites, and demonstrates that that there is large disordered component to the magnetic order.

Although PND reveals a simple G-type AFM spin structure, a spontaneous magnetization of 0.2 μ_B is observed in the magnetization-field measurements. . There are two plausible explanations for this. The first is that weak ferromagnetism is symmetry-allowed in Pnma perovskites with G-type AFM order, and is observed in many RFeO3 and RCrO3 materials for various rare earth elements R. A second explanation is that ferrimagnetism arise from the formation of local charge ordered regions as noted above. This is the more likely origin given the similarity of the magnetic properties to those of the cation and charge ordered Ca_2FeMnO_6. Local charge ordering at the 90 K magnetic transition favors Fe^{3+}-O-Fe^{5+} arrangements over the Fe^{3+}-O-Fe^{3+} and Fe^{5+}-O-Fe^{5+} alternatives, so inthe G-type AFM spin structure, the Fe^{3+} magnetic moments are aligned in the opposite direction to the Fe^{5+} moments (Fig. 4). The Mn^{4+} cations are equally substituted for Fe^{3+} and Fe^{5+} in the diluted charge ordered domains, and so their ordered magnetic moments-cancel each other, and so do not give net magnetization. This model predicts an ideal magnetization of 0.25 μ_B (?? shouldn't this be 0.25(5-3) = 0.5 $\mu_{B\,?}$)for $CaFe_{0.5}Mn_{0.5}O_3$, which is consistent with the observed magnetization of 0.2 μ_B given further reductions due to disorder. Although this model assumes dominant AFM Fe^{3+}-O-Fe^{5+} interactions, the observed helimagnetism of $CaFeO_3$ shows that these connections can lead to competing AFM and FM interactions. Competition between AFM and FM Fe^{3+}-O-Fe^{5+} and also Mn^{4+}-O-Fe^{5+} interactions, plus the structural disorder present in $CaFe_{0.5}Mn_{0.5}O_3$ results in a large proportion of the spins being disordered or remaining dynamic below the magnetic ordering transition. This is consistent with the 5-K paramagnetic susceptibility of $CaFe_{0.5}Mn_{0.5}O_3$ being greater than that of cation-ordered Ca_2FeMnO_6 , as shown by the high field M-H slopes in Fig. 3b.

It is worth noting again that the Fe^{3+} and Fe^{5+} Mössbauer spectra and the magnetic behaviors of the present $CaFe_{0.5}Mn_{0.5}O_3$ are quite similar to those of the layered *B*-site-ordered Ca_2FeMnO_6 with the same chemical composition but a different magnetic structure. Although the local aliovalent Fe^{3+}-O-Fe^{5+} arrangements in the CD states play an important role in determining the magnetic structures in both compounds, the *B*-site ordering makes the magnetic structures different.

Conclusions

The *B*-site-disordered perovskite-structure oxide $CaFe_{0.5}Mn_{0.5}O_3$ was obtained using high-pressure synthesis. The PND structure analysis and the Mössbauer spectroscopy results revealed that the compound contains Mn^{4+} and unusually high valent Fe^{4+} ions randomly distributed over the *B* sites, and that the chemical composition of this oxide is identical to that of the layered B-site-ordered Ca_2FeMnO_6. Like Ca_2FeMnO_6, $CaFe_{0.5}Mn_{0.5}O_3$ shows CD of Fe^{4+} at low temperatures and has a magnetic transition at 90 K. Magnetic structure analysis with the PND data revealed that $CaFe_{0.5}Mn_{0.5}O_3$ has a G-type AFM spin structure although a small spontaneous magnetization is observed in magnetization-field loops. This is consistent with local charge ordering that gives rise to Fe^{3+}-O-Fe^{5+} antiferromagnetic interactions so inexact cancellation of opposing Fe^{3+} and Fe^{5+} spins produces ferromagnetism. The magnetic structure of $CaFe_{0.5}Mn_{0.5}O_3$ is thus very different from the noncollinear magnetic structure of Ca_2FeMnO_6.

Table 1. Refined crystal structure parameters of $CaFe_{0.5}Mn_{0.5}O_3$ at room temperature (obtained in Rietveld analysis of the PND data.) Space group, *Pnma*, *a* = 5.3177(3) Å, *b* = 7.5035(4) Å, and *c* = 5.3041(3) Å. Rwp = 4.59%.

Atom	*x*	*Y*	*Z*	*B* (Å^2)	occupancy
Ca	0.0282(6)	0.25	0.993(1)	0.94(6)	1.0
Fe	0.0	0.0	0.5	0.11(7)	0.510(2)
Mn	0.0	0.0	0.5	0.11(7)	0.490(2)
O1	0.2892(5)	0.0350(4)	0.7153(6)	1.26(6)	1.0
O2	0.4879(6)	0.25	0.0617(7)	0.70(7)	1.0

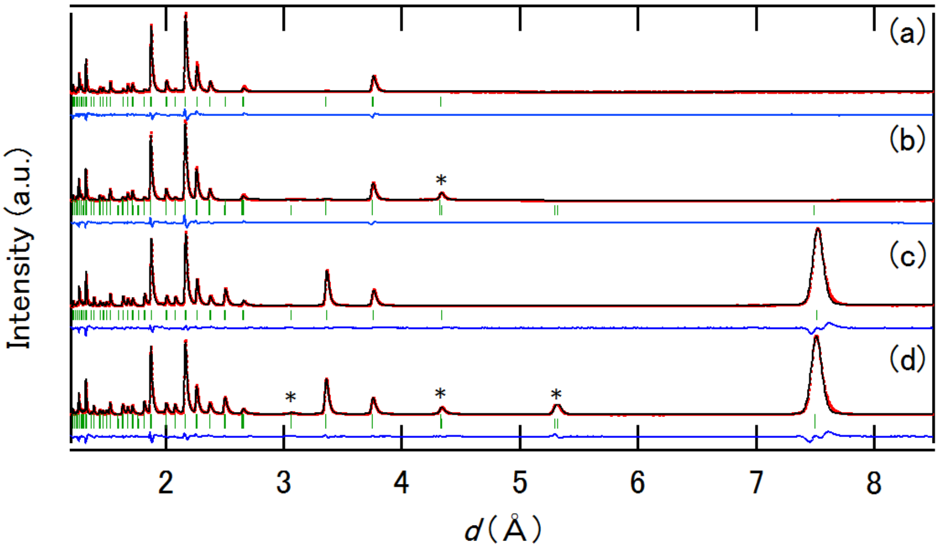

Figure 1. Neutron diffraction patterns and refinement results for *B*-site-disordered perovskite $CaFe_{0.5}Mn_{0.5}O_3$ (a) at 300 and (b) 2 K. Corresponding patterns and results for the layered double perovskite Ca_2FeMnO_6 at 300 (c) and (d) 2 K are reproduced from [*]. The dots, black lines, blue lines, and vertical marks represent observed patterns, calculated patterns, differences between observed and calculated intensities, and Bragg refraction points, respectively. Marked peaks are typical magnetic reflections.

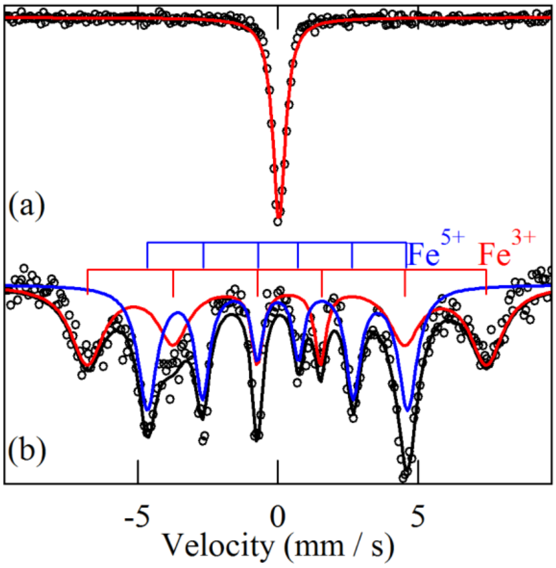

Figure 2. Mössbauer spectra of *B*-site-disordered $CaFe_{0.5}Mn_{0.5}O_3$ measured (a) at room temperature and (b) 3 K. The circles are observed data, and the spectra are fitted with (a) a singlet component and (b) two sextets corresponding to Fe^{3+} and Fe^{5+} components.

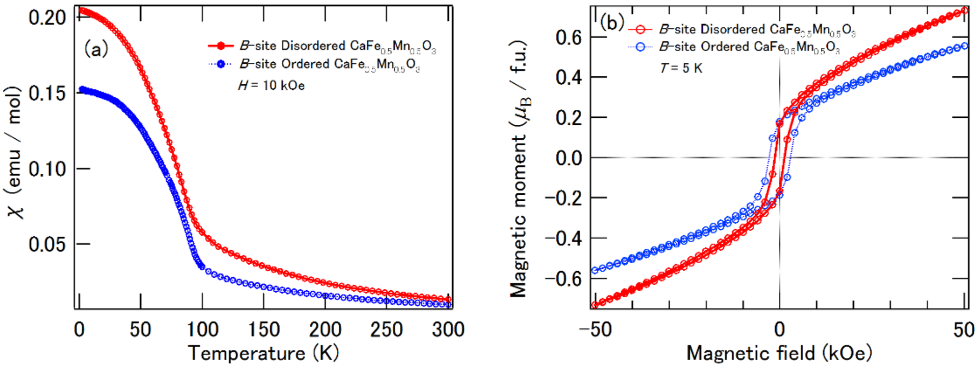

Figure 3. Magnetic properties of *B*-site-disordered $CaFe_{0.5}Mn_{0.5}O_3$ (red) together with those of the layered *B*-site-ordered double perovskite Ca_2FeMnO_6 (blue). (a) Temperature dependence of magnetic susceptibility χ. (b) Magnetic field dependence of magnetic moment.

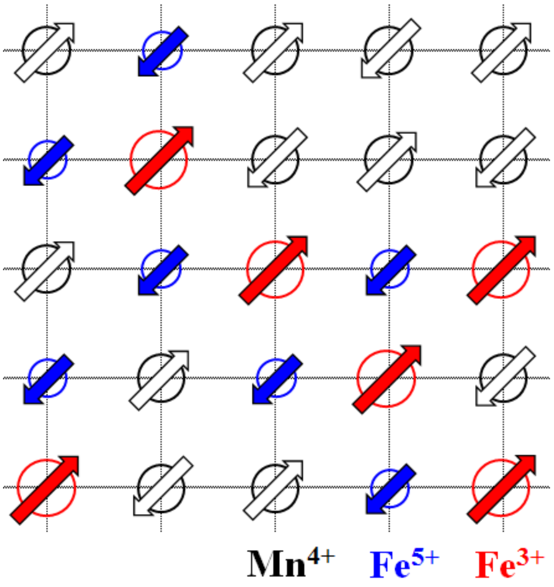

Figure 4. Idealised model for the local spin and charge ordering in *B*-site-disordered $CaFe_{0.5}Mn_{0.5}O_3$. Red, blue, and white arrows represent magnetic spins of Fe^{3+}, Fe^{5+}, and Mn^{4+}, respectively. G-type antiferromagnetism over local Fe^{3+}-O-Fe^{5+} arrangements give rise to the observed ferrimagnetism. In reality spin directions are disordered around the ideal directions resulting in a small net ordered moment.