High Pressure Synthesis of SrFe$_{1-x}$Ni$_x$O$_3$

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ABSTRACT

The cubic perovskite structure was stabilized in solid solution of SrFeO$_3$ and SrNiO$_3$. The compounds were obtained by high pressure synthesis and contained high valence state of Fe$^{4+}$ and Ni$^{4+}$ ions in the corner-sharing oxygen octahedra. SrFe$_{1-x}$Ni$_x$O$_3$ with $x = 0.4$ and $0.5$ showed ferromagnetic-like behaviors at room temperature, in contrast to the end member perovskite SrFeO$_3$ ($x = 0$) with helical antiferromagnetism ($T_N = 134$ K). Ni substitution for Fe in the cubic antiferromagnetic SrFeO$_3$ induced the ferromagnetism.

KEY WORDS

high-pressure synthesis, unusual high-valence states, solid solution, crystal structure

1 Introduction

Unusual high oxidation states of some 3d transition-metal cations can be stabilized in oxides. In addition to unusual oxidation states of 2+ and 3+ for Fe typically seen in FeO and Fe$_2$O$_3$, respectively, an unusual high state like 4+ can be stabilized in oxides.$^{1-6}$ The simple cubic perovskite SrFeO$_3$ (see the crystal structure in Fig. 1a) with Fe$^{4+}$, for instance, is prepared by synthesis under a high-pressure and high-temperature condition. Fe$^{4+}$ in SrFeO$_3$ is pretty stable at low temperatures because the linear Fe$^{4+}$-O-Fe$^{4+}$ bonds stabilize broad conduction bands. The nominal d$^4$ electron configuration of Fe$^{4+}$ gives an $S = 2$ high-spin magnetic moment, and the compound shows the antiferromagnetism with the helical magnetic structure below the magnetic transition temperature at 134 K.$^{7,8}$ BaFe$^{4+}$O$_3$ also crystallizes with the perovskite structure. Interestingly, a weak external field induces ferromagnetism in BaFeO$_3$.$^9$

On the other hand, a typical oxidation state for Ni is 2+ as seen in NiO, but a very high oxidation state like Ni$^{4+}$ is stabilized in a few oxides obtained by means of high-pressure synthesis. SrNiO$_3$ and BaNiO$_3$ with Ni$^{4+}$ crystallize hexagonal perovskite structures, which consist of face-sharing NiO$_6$ octahedra (see the crystal structure in Fig. 1b)$^{9,10}$. Ni$^{4+}$ with the nominal d$^6$ electron configuration in the crystal field by six coordinated oxygen ions is considered to have an $S = 0$ low-spin state. Actually, BaNiO$_3$ is reported to show diamagnetism, suggesting the nonmagnetic Ni$^{4+}$.$^{11,12}$

Our primary concern in this study is which crystal structure is stabilized in a solid solution of simple perovskite SrFeO$_3$ with Fe$^{4+}$ and hexagonal perovskite SrNiO$_3$ with Ni$^{4+}$. Magnetic properties of SrFe$_{1-x}$Ni$_x$O$_3$ (SFNO) are also investigated.

2 Experiments

The solid solution samples were prepared by means of high pressure synthesis. Stoichiometric amounts of Fe$_2$O$_3$ and NiO were first mixed, ground in a ball mill, and calcined at 1273 K for 24 hours in air. The obtained powders were then mixed with an appropriate amounts of SrO and 25 wt% KClO$_4$ oxidizing agent, sealed in platinum capsules, and treated at high-temperature and high-pressure conditions. For the synthesis below 10 GPa a DIA-type cubic anvil press, where six tungsten-carbide (WC) superhard alloy anvils synchronously compress the sample through a pyrophyllite medium, was used. For the synthesis from 10 up to 15 GPa a 6-8 Kawai-type multi-anvil high-pressure apparatus was used. The octahedral sample cell assembly is compressed by second-stage eight truncated WC anvils (Fig. 2) loaded on the six first-stage anvils. After the reaction, the sample was taken out and the residual KClO$_4$ and KCl in the sample were removed by washing with distilled water and acetone in turn.

Phase identification was made by X-ray diffraction (XRD) with a Bruker D8 ADVANCE diffractometer using a Cu-Kα radiation.

![Fig. 1 Crystal structures of (a) cubic perovskite and (b) hexagonal perovskite.](image-url)
source. The detailed crystal structure of the identified phase was analyzed with synchrotron XRD data. The room temperature pattern produced at a wavelength of 0.77425 Å was collected with a large Debye-Scherrer camera with an image plate at beamline BL02B2 in SPring-8. The obtained XRD data were analyzed by the Rietveld method using the program RIETAN-FP. Oxidation state of Fe in the sample was estimated by the isomer shift (IS) value in $^{57}$Fe Mössbauer spectrum by using a $^{57}$Co/Rh radiation source. The velocity scale and the IS were determined by using pure iron metal.

Magnetic properties of the samples were measured using a SQUID magnetometer (MPMS, Quantum Design). Temperature dependence of magnetic susceptibility was measured in a 10 kOe magnetic field at temperatures from 5 to 300 K. Field dependence of the magnetization was measured at several temperatures under fields ranging from −24 to 24 kOe.

### 3Results and discussion

Fig. 3 shows XRD patterns of SFNO with $x = 0$, 0.5, 0.75 and 1.0 recorded using Cu-Kα as the radiation source. The observed pattern for the sample with $x = 0.5$ is well reproduced with the cubic $Pm\bar{3}m$ perovskite structure, which is the same as that for SrFeO$_3$ ($x = 0$), although a very small amount of NiO is seen. As shown in Fig. 4, the lattice parameters for the cubic perovskites ($0.0 \leq x \leq 0.5$) decrease linearly with increasing the amount of Ni, also confirming the successful substitution of Ni for Fe in SrFeO$_3$. Note that even with the exceptional peak shape resolution of the SXRD patterns there was no obvious splitting of the stronger Bragg reflections indicative of cubic symmetry. On the other hand, the XRD pattern for the sample with $x = 0.75$ consists of mixed phases. Although the sample includes some mounts of cubic perovskite phase, the obtained lattice parameter for the cubic phase is the same as that for SrFe$_{0.5}$Ni$_{0.5}$O$_3$ (Fig. 4). Attempts to prepare a single phase sample for $x = 1.0$ were unsuccessful. Although SrNiO$_3$ was reported to crystalize with the hexagonal perovskite, the observed XRD pattern did not show that the sample include such a phase. We thus conclude that the solid solubility limit of $x$ in the cubic perovskite SFNO is about 0.5 by the synthesis under present high pressure conditions.

A typical Rietveld refinement result for the cubic $Pm\bar{3}m$ perovskite SFNO ($x = 0.4$) is shown in Fig. 5 and Table 1. The refined occupancy for the oxygen site, 1.005(7), confirms that the oxygen sites are fully occupied. From the refinement result, the Fe(Ni)-O bond distance, 1.91772(1) Å are obtained, and the valence states of Fe and Ni are estimated to 3.92 and 4.06, respectively, from the bond distance...
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The valence state of Fe is also examined by the Mössbauer spectroscopy. Fig. 6 shows the Fe Mössbauer spectroscopy result for SrFe$_{0.5}$Ni$_{0.5}$O$_3$ obtained at 5 K. The spectrum consists of a single component with $IS$ of 0.09 mm/s relative to $\alpha$-Fe and a hyperfine field ($HF$) of 293 kOe. These values are very close to those for SrFeO$_3$. The results, especially the small $IS$ value, lead to a conclusion that the oxidation state of Fe in the cubic perovskite SFNO is kept at 4+ in the range of $0 \leq x \leq 0.5$. Importantly, the results also give the unusually high oxidation state of 4+ for the substituting Ni in the compounds.

The temperature dependence of the magnetic susceptibility of SFNO ($0 \leq x \leq 0.5$) is shown in Fig. 7. As reported previously, SrFeO$_3$ ($x = 0$) shows an antiferromagnetic-like transition at 134 K. The behaviors of the samples with $x = 0.1$ and 0.2 are similar to that of the sample with $x = 0$. On the other hand, large increases in magnetization with decreasing temperature are observed for the samples with $x = 0.4$ and 0.5. Field dependence of magnetic moment at 5 K confirmed the ferromagnetic-like behaviors for the $x = 0.4$ and 0.5 samples with saturation magnetizations 2.38 and 1.80 $\mu_B$/f.u., respectively, as shown in Fig. 8. Even at room temperature the large saturation magnetizations of 1.16 $\mu_B$/f.u. ($x = 0.4$) and 0.98 $\mu_B$/f.u. ($x = 0.5$) are observed. Thus, the results show that the Ni$^{4+}$ substitution in the antiferromagnetic SrFeO$_3$ induces ferromagnetism with a transition temperature higher than room temperature.

Ni$^{4+}$ is believed to have intrinsically an $S = 0$ low-spin state like that of the Ni$^{2+}$ in BaNiO$_3$. Considering that Fe$^{4+}$ spins in SrFeO$_3$ shows helical magnetic structure, the obtained results appear to indicate that the ferromagnetism is induced by introducing nonmagnetic Ni$^{4+}$ ions into the helical antiferromagnetic Fe$^{4+}$ spin sublattice. However, it is interesting to see a recent result by Chen, et al.\cite{14}, where they computed a hypothetical cubic perovskite SrNiO$_3$ by a first-principles method and found that the ground state of SrNiO$_3$ is
ferromagnetic. They also claimed that the Ni$^{4+}$ in SrNiO$_3$ has the
magnetic moment of 0.855–1.689 $\mu_B$ depending on the on-site
Coulomb interaction ($U = 3.0–11.0$ eV). Although the cubic SrNiO$_3$
perovskite could not be synthesized in our present experiments,
the calculation result suggest that the Ni$^{4+}$ magnetic moment of
1.17 $\mu_B$. Very recently, we have performed magnetic circular
dichroism experiment and obtained the spin moments of 3.70 $\mu_B$ for Fe and 1.26 $\mu_B$ for Ni by using magneto-optical sum rules, and the values are quite consistent with the
present values. Therefore, the Ni$^{4+}$ ions in SFNO have substantial
magnetic moments, contrary to expectation of nonmagnetic low
spin state ($t_{2g}, S = 0$) in an octahedral crystal field.

Note, as shown in Fig. 6, the unusual high oxidation state of Fe$^{4+}$
remains down to low temperature and anomalies due to charge
disproportionation of Fe are not observed. This also suggests that
unusual high oxidation state of Ni$^{4+}$ is kept intact and that the
charge disproportionation of Ni and charge transfer between Fe
and Ni do not occur. Because the crystal structures keep the cubic
symmetry for the samples with $x \leq 0.5$, linear Fe(Ni)-O-Fe(Ni)
bonds hold the broad bands in the electronic structure and make
the metallic state stable.

4 Summary

Solid solution samples of SrFe$_{1-x}$Ni$_x$O$_3$ with unusual high valence
Fe$^{4+}$ and Ni$^{4+}$ were prepared by high-pressure and high-temperature
synthesis. The cubic perovskite structures were obtained up to
$x = 0.5$, and single phase samples could not be obtained for $0.5 < x \leq 1.0$. Ni substitution for Fe ($x = 0.4$ and 0.5) in SrFeO$_3$ induced
the ferromagnetism, and the large saturation magnetizations were
observed. The ferromagnetic transition temperatures are higher
than room temperature. The SPring-8 experiments were approved
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