Paper

Novel Iron Oxides with Square Planar Coordination from Low Temperature Synthesis

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SYNOPSIS

By using new synthetic approaches, one can create new families of materials which could lead to new chemical and physical properties. From this philosophy, we have synthesized novel iron oxides by topochemically extracting oxygen from well known perovskites derivatives SrFeO_3 , layered $\text{Sr}_3\text{Fe}_2\text{O}_7$ and brownmillerite $\text{CaFeO}_{2.5}$. The new materials SrFeO_2 , $\text{Sr}_3\text{Fe}_2\text{O}_5$ and CaFeO_2 possess FeO_4 square planes and derivatives. These novel materials show new structures in which exotic electronic and magnetic properties can be witnessed. They also provide clues to understand oxygen diffusion in solids. In this review, we describe the chemical and physical properties of these novel iron oxides.

KEY WORDS

Perovskites, infinite layer, square planar coordination, iron oxides, hydride reduction, soft-chemistry

1 Introduction

Low temperature reactions such as intercalation and deintercalation allow the rational design of structures by preserving the main framework of a given compound, leading to the modification of coordination. This is in marked contrast with high temperature synthesis which limits the control of coordinations to those within known geometries. Iron is one of the most abundant metals on earth and forms numerous oxides, some of which are used in industry for pigments and ferrite magnets. In almost all of these oxides, iron bonds tetrahedrally, pyramidally or octahedrally with oxygen atoms. By using a low temperature synthesis approach we have been able to synthesize new materials containing iron in an oxygen square planar coordination.

2 SrFeO_2

$\text{SrFeO}_{3-\delta}$ ($0 \leq \delta \leq 0.5$) (Fig. 1a) has been intensively studied because it exhibits, for example, fast oxygen transport combined with high electron conductivity at low temperatures. It is thus a potential candidate for electrodes for solid oxide fuel cells and batteries¹⁾, membranes for oxygen separation²⁾, catalysis³⁾ and gas sensors⁴⁾. The $\delta=0.5$ phase (Fig. 1b) was the reduction limit of this compound despite extensive attempts to control the oxygen content including synthesis at high temperature with

oxygen partial pressure ranging from 10^{-9} to 100 MPa^{5,6)}, electrochemical reactions⁷⁾, fabrication epitaxial thin films under different atmospheres⁸⁾.

Our approach follows recent success in the use of hydrides of electropositive metals as powerful reducing agents (e.g. CaH_2 and NaH). For instance, reaction with NaH of LaSrCoO_4 and $\text{Yb}_2\text{Ti}_2\text{O}_7$ yielded $\text{LaSrCoO}_{3.38}$ ⁹⁾ and $\text{Yb}_2\text{Ti}_2\text{O}_{6.43}$ ¹⁰⁾, respectively. Here, we have been able to overcome the $\delta=0.5$ limit of $\text{SrFeO}_{3-\delta}$ to form SrFeO_2 ¹¹⁾. This structure was synthesized by mixing SrFeO_3 with CaH_2 (1 : 2 molar ratio) and heating the mixture under vacuum at 280 °C for one day. The pseudo-cubic phase ($a \approx 3.86 \text{ \AA}$) transforms to a tetragonal structure ($a = 3.9911$

Fig.1 Schematic structure of the perovskite SrFeO_3 (a), the brownmillerite $\text{SrFeO}_{2.5}$ (b) and the infinite layer SrFeO_2 (c).

Å and $c = 3.4748$ Å). The x-ray pattern (Fig. 2) revealed a $P4/mmm$ space group, which is the same as the infinite layer compound SrCuO_2 . The stoichiometry (1:1) between strontium and iron was checked by EDX, and thermogravimetric measurement showed an oxygen stoichiometry of 2 in agreement with $\delta = 1$. Rietveld analysis from both x-ray and neutron diffraction confirmed that the structure is isostructural with SrCuO_2 (Fig. 1c). Thus, the structure can be described as an infinite layered structure with iron bearing a square planar oxygen coordination. There was only one report on such a coordination, the gillipsite $\text{BaFeSi}_4\text{O}_{10}$ ¹²⁾. $\text{CaFe}_3\text{Ti}_4\text{O}_{12}$ and $\text{CaFeTi}_2\text{O}_6$ were claimed to possess FeO_4 square planes but there are four long Fe-O bonds and two short Fe-O bonds¹³⁾.

Iron in SrFeO_2 is bivalent and in the high spin state ($S=2$). This compound is magnetically ordered at room temperature having a G -type antiferromagnetic structure with the spin lying onto the ab plane. Despite its low dimensional structure, the Néel temperature appears to be fairly high (473 K). This is due to the strong interactions in the ab plane as well as in between vertical $\text{Fe}\cdots\text{Fe}$. The $(d_{xz}, d_{yz})^3(d_{xy})^1(d_{z^2})^1(d_{x^2-y^2})^1$ electronic configuration was first suggested, in reason of small quadrupole splitting values possibly indicating a degenerated ground state. However, Jahn-Teller distortion has not been observed at low temperature. Further investigations using density functional theory, band structure and total energy calculations revealed that the d_{z^2} level has the lowest energy level and is doubly occupied due to lower Coulomb repulsion and a possible intra-atomic mechanism associated with the hybridization of d_{z^2} with the $4s$ energy level. The resulting electronic configuration $(d_{z^2})^2(d_{xz}, d_{yz})^2(d_{xy})^1(d_{x^2-y^2})^1$ explains the absence of structural transitions at low temperatures

distortions as well as the observed magnetic structure^{14,15)}.

The high pressure investigation of SrFeO_2 led to the discovery of a spin transition to the intermediate state $S=1$ accompanied by a transition from an antiferromagnetic insulating state to a ferromagnetic half metal¹⁶⁾. The intermediate spin state is rare for d^6 elements and occurs mostly in five-fold coordinated compounds (e.g. $\text{TbBaCo}_2\text{O}_5$ with a pyramidal coordination), moreover spin transition has never been observed in tetra-coordinated metal. At the critical pressure of 33 GPa, SrFeO_2 decreases its volume by 3 % and the electronic configuration of iron changes from $(d_{z^2})^2(d_{xz}, d_{yz})^1(d_{xy})^1(d_{x^2-y^2})^1 (=d^6)$ to an exotic $(d_{z^2})^2(d_{xz}, d_{yz})^3(d_{xy})^1(d_{x^2-y^2})^{0.5} (=d^{6.5})$ state due to the strong in-layer hybridization between $\text{Fe}-d_{x^2-y^2}$ and $\text{O}-p_\sigma$ bonding states, leading to an electronic instability towards depopulation of $\text{Fe}-d_{x^2-y^2}$ and $\text{O}-p_\sigma$ bonding states. The transition to a half-metallic state is of high interests and provides a hope that higher pressure could lead to superconductivity. Much effort to reduce the pressure transition has to be done and the study of other structures containing square planes could lead to this result.

Hydride reduction was later on applied for the first time to thin film of SrFeO_3 by Inoue and coworkers¹⁷⁾ who synthesized epitaxial films of SrFeO_2 . Such reaction applied to thin film opens new doors towards possible applications. Recently, Ju et al. predicted a strong optical anisotropy in SrFeO_2 and suggested applications in optoelectronics¹⁸⁾.

3 $\text{Sr}_3\text{Fe}_2\text{O}_5$

Following the synthesis of the infinite layer structure, $\text{Sr}_3\text{Fe}_2\text{O}_5$ was synthesized from the slightly oxygen deficient layered perovskite compound $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ (Fig. 3)¹⁹⁾. The structure of $\text{Sr}_3\text{Fe}_2\text{O}_7$ consists of double sheets of SrFeO_3 perovskite separated by SrO rocksalt layers. In this phase, it is known that oxygen vacancies are located only at the apical O(1) site and the structure is kept tetragonal ($I4/mmm$) for $0 \leq \delta \leq 1$. Using a similar method to SrFeO_2 , we were able to yield $\text{Sr}_3\text{Fe}_2\text{O}_5$ (Fig. 3c). The new lattice is orthorhombic $Immm$ ($a = 3.51485(2)$ Å, $b = 3.95271(2)$ Å, and $c = 20.91251(10)$ Å) (Fig. 4). Rietveld analysis of SXRD and neutron scattering showed that the original double perovskite layers become decoupled into ladders running along the b axis. It was revealed that the reaction proceeds from $\text{Sr}_3\text{Fe}_2\text{O}_7$ to $\text{Sr}_3\text{Fe}_2\text{O}_6$ by the removal of the O(1) sites resulting in pyramidal planes and further reduction of the $\delta = 1$ phase gives the removal of one oxygen of the O(2) site and the transfer of one oxygen to the O(1) site leading to $\text{Sr}_3\text{Fe}_2\text{O}_5$.

Fig.2 XRD patterns of SrFeO_3 (up) and SrFeO_2 (down).

Fig.3 Structure of the layered perovskite $\text{Sr}_3\text{Fe}_2\text{O}_7$ (a), $\text{Sr}_3\text{Fe}_2\text{O}_6$ (b) and $\text{Sr}_3\text{Fe}_2\text{O}_5$ (c).

Fig.4 X-ray diffraction patterns of $\text{Sr}_3\text{Fe}_2\text{O}_7$ (up) and $\text{Sr}_3\text{Fe}_2\text{O}_5$ (down).

This new structure can be considered as a two-leg spin ladder system ($n=2$). Spin ladder system has been widely studied as theories predict that the ground state of an $S=1/2$ ladder is a gapped singlet spin liquid state when the n number is even but is a gapless singlet spin liquid state when n is odd. Therefore, it is interesting to compare the copper(II) and iron(II) ladder systems $\text{Sr}_{n-1}\text{Cu}_n\text{O}_{2n-1}$ and $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{2n+1}$. In the former, the ladders share their O-O edges to form dense $\text{Cu}_n\text{O}_{2n-1}$ sheets. The iron(II) ladders, on the other hand, are dispersed in the I -centered orthorhombic lattice with their legs and rungs oriented along the b and c axes, respectively.

Mössbauer spectroscopy as well as neutron diffraction showed no magnetic order at room temperature and that at 4 K iron is in the same state as in SrFeO_2 . Magnetic moments are aligned parallel to the c axis and the magnetic structure is a G -type antiferromagnetic structure, the same spin

Fig.5 Schematic view of CaFeO_2 (a) and the oxygen coordination of calcium (b).

transition as found in $\text{Sr}_3\text{Mn}_2\text{O}_7^{20}$.

It is highly desirable to extend this family of compounds with respect to n to get a better understanding of the magnetic properties of these materials.

4 CaFeO_2

The stability of SrFeO_2 against cation substitution was shown by the synthesis of the solid solution $\text{Sr}_{1-x}\text{Ca}_x\text{FeO}_2$ ($0 \leq x \leq 1$). Powder XRD pattern showed that the structure was very similar to SrFeO_2 . However, the replacement of the interlayer cation resulted in longer reduction time for Ca rich phases. The lattice parameters exhibited a linear evolution from SrFeO_2 to $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$ and a structural phase transition around $x=0.8^{21}$. For the end member CaFeO_2 , we were able to observe additional diffraction peaks showing the formation of a $\sqrt{2}a_p \times \sqrt{2}a_p \times c_p$ superlattice²². In this structure, the infinite FeO_2 layers contain FeO_4 units which distort heavily from square-planar toward tetrahedra and rotate along the c -axis. It is well known that perovskite structure ABO_3 are governed solely by the size of the A site. When the so-called Goldschmidt factor t is close to 1 as in SrFeO_3 , one obtains an ideal structure with the cubic space group, and the A site is 12-fold coordinated by oxygen atoms (Fig. 1a). When t deviates from 1, tilting or rotating BO_6 octahedra of various types occur, leading to lowered coordination numbers, lowered symmetries, and superstructures. In such cases, the BO_6 octahedra are considered to be rigid and preserve their shape upon rotations. In SrFeO_2 , strontium occupies an 8-fold site within the iron square planar framework. In CaFeO_2 , calcium has a 6-fold coordination in reason of the FeO_4 units which experience both tilting and distorting (Fig. 5b).

Such lattice distortions usually strongly affect the magnetic interactions via the rupture of the perfect $\angle M\text{-O-M} = 180^\circ$ angle. The simple substitution of strontium by calcium in SrFeO_2 should increase the Néel Temperature (T_N) in reason of shorter Fe-Fe distances. In this case, the

$\angle \text{Fe-O-Fe}$ change from 180° to 160° (-11%) and the T_N drops from 470 K to 420 K (-11%). This slight change is remarkable; for instance the Néel temperature of the well-studied perovskite system AMnO_3 ($A = \text{La}$ and rare earth elements) is drastically modified (140 K for La and 25 K for Gd) by small angle changes (155.1° for La and 146.2° for Gd). This contrasting behavior of CaFeO_2 is explained by the strong hybridization of the $\text{Fe-}d_{x^2-y^2}$ and the $\text{O-}p_\sigma$ orbital are barely influenced by the bridging angle. The CaFeO_2 structure shows how FeO_4 can be flexible to accommodate its environment and further investigation against temperature and substitutions are ongoing in order to observe the limits of this coordination.

5 Conclusion

Unlike the case of cuprates, the coordination geometries in iron oxides were almost exclusively restricted to 3D polyhedra. The use of CaH_2 has allowed us to overcome these restrictions and to open new doors toward novel iron oxides with square planar coordination and therefore new chemical and physical properties. These new materials are remarkable in reason of their flexibility and capability of oxygen uptake and release. It would be interesting to test hydride reduction on other iron oxides to create new members of spin ladders (Fig. 6) and also on other transition metal oxides to possibly create novel coordinations and overcome oxygen content limits.

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Fig.6 Schematic representation of n -legged spin ladders in structures containing square planes. $n = 1$ i.e. one dimensional chain (a), $n = 2$ corresponding to $\text{Sr}_3\text{Fe}_2\text{O}_5$ (b), $n = 3$ corresponding to the hypothetical $\text{Sr}_4\text{Fe}_3\text{O}_7$ (c), $n = \infty$ corresponding to SrFeO_2 (d).

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