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論文題目	Low Temperature Synthesis and Properties of Novel Iron Oxides with Square Planar Coordination （平面四配位をもつ新規鉄酸化物の低温合成と物性）		
（論文内容の要旨） The high temperature synthesis of iron oxides usually leads to three dimensionally coordinated irons (tetrahedra, octahedra or pyramids). Topochemical reactions performed at low temperature allow preserving the main framework of a material while partially changing the coordination of its components. In this thesis, we present a study of novel iron oxides with square planar coordination obtained through the topochemical reduction of the perovskite SrFeO_3 using CaH_2 as a powerful reducing agent. In chapter 1, we show the reaction of a perovskite SrFeO_3 with CaH_2 yielding SrFeO_2, a new compound bearing an oxygen square-planar coordination around Fe^{2+}. SrFeO_2 is isostructural with the ‘infinite layer’ (IL) structure, and exhibits a magnetic order far above room temperature in spite of the two-dimensional structure, indicating strong in-layer magnetic interactions due to strong Fe d to O p hybridization. The reduction and the oxidation between SrFeO_2 and SrFeO_3 proceed via the brownmillerite-type intermediate $\text{SrFeO}_{2.5}$, and start at the relatively low temperature of 400 K, making the material appealing for a variety of applications, including oxygen ion conduction, oxygen gas absorption and catalysis. In chapter 2, the IL structure is shown to have significant solubility to yield $\text{Sr}_{1-x}\text{Ca}_x\text{FeO}_2$ ($0 \leq x \leq 1$) and is thermally stable (at least as high as 1000 K for SrFeO_2). These results demonstrate that the IL structure, once it is formed at low temperatures, is surprisingly robust owing to the extremely covalent nature of the FeO bond, thereby opening a door to chemical tuning of properties and to possible high-temperature applications. In chapter 3, we study CaFeO_2, with a distorted layered structure. The new phase has been characterized through powder neutron diffraction, synchrotron X-ray diffraction, Mössbauer spectroscopy, XAS experiments as well as first-principles DFT calculations. The XAS spectra near the Fe-K edge for the whole solid solution $(\text{Sr}_{1-x}\text{Ca}_x)\text{FeO}_2$ supports that iron is in a square-planar coordination for $0 \leq x \leq 0.8$ but clearly suggests a change of coordination for $x = 1$. The new structure contains infinite FeO_2 layers in which the FeO_4 units unprecedentedly distort from square-planar toward tetrahedra and rotate along the c-axis, in marked contrast to the well-studied and accepted concept that octahedral rotation in perovskite oxides occurs but the			

octahedral shape is kept almost regular.

In chapter 4, the formation pathway leading to the square planar coordination in SrFeO_2 and in the laddered $\text{Sr}_3\text{Fe}_2\text{O}_5$ is investigated. By using in situ synchrotron x-ray diffraction, we studied the reaction process of $\text{SrFeO}_{2.5}$ as well as $\text{Sr}_3\text{Fe}_2\text{O}_7$ with CaH_2 . The comparison of both of these phases provide clues on how the oxygen anisotropic migration processes and how atoms rearranges to adapt lower oxidation/coordination levels.

The high pressure properties of SrFeO_2 are investigated in chapter 5. Spin transitions have attracted the interest of researchers in various fields since the early 1930s, with thousands of examples now recognized, including those in minerals and biomolecules. However, so far the metal centres in which it has been found to occur are almost always octahedral six-coordinate $3d^4$ to $3d^7$ metals, such as Fe(II) . Under pressure SrFeO_2 exhibits a transition from high spin ($S = 2$) to intermediate spin ($S = 1$). This is accompanied by a transition from an antiferromagnetic insulating state to a ferromagnetic so-called half-metallic state: only half of the spin-down (d_{xz}, d_{yz}) states are filled. These results highlight the square-planar coordinated iron oxides as a new class of magnetic and electric materials.

There are thousands of iron oxides which are readily available. The possibility to access new coordination with lower oxidation is highly interesting towards new physical properties in iron oxides. The infinite layer structure has been shown to be surprisingly stable against chemical substitution. Up to now only pure Fe^{2+} state was observed in this novel category of materials, it would be interesting to substitute the strontium site or the iron site by other elements to dope the infinite layers. These novel phases which would contain square planes and their investigations at high pressure could be of great interest and could lead to new physical properties.

(論文審査の結果の要旨)

本論文では、低温合成反応による平面四配位をもつ鉄酸化物の合成と、その構造、機能性に関する結果をまとめたものであり、主な成果の概要は下記の通りである。

(1) ペロブスカイト構造をとる SrFeO_3 に対し、水素化カルシウムを低温で反応させることによって、全体の $1/3$ の酸素を規則的に取除き、 FeO_4 平面四配位をもつ無限層構造 SrFeO_2 を得ることに成功した。 SrFeO_2 はその二次元的構造にも関わらず非常に高い温度で磁気秩序を起こすことを明らかにした。

(2) 無限層構造の固溶系 $(\text{Sr,Ca})\text{FeO}_2$ の合成に成功した。また、 SrFeO_2 は 1000°C 近くの高温まで安定に存在することを示した。これらの結果より、 SrFeO_2 は化学置換に対しても温度に対しても極めて安定であることを明らかにした。

(3) CaFeO_2 の構造を放射光 X 線回折、中性子回折によって再検討したところ、 SrFeO_2 における平面四配位から四面体方向へと大きく歪むことを見出した。すなわち、 FeO_4 平面四配位は強い結合性と柔軟性を兼ね備えていることを明らかにした。。

(4) 水素化カルシウムによる、 SrFeO_3 から SrFeO_2 への反応過程、 $\text{Sr}_3\text{Fe}_2\text{O}_7$ から $\text{Sr}_3\text{Fe}_2\text{O}_5$ への反応過程を、in situ 放射光 X 線回折測定により明らかにした。特に前者では、前駆体の等方的な構造にも関わらず、極めて異方的に酸素の脱理がおこることを明らかにした。

(5) SrFeO_2 は常圧では高スピン状態であるが、圧力を加えることによって中間スピン状態へのスピン転移を観測した。これは四配位の金属としては初めて認められる現象である。また、このスピン転移と同時に、反強磁性絶縁体が、高い磁気転移温度を保ったまま強磁性金属にかわることを明らかにした。さらに、強磁性状態では伝導電子が 100% スピン偏極したハーフメタル状態であることを明らかにした。

以上の結果は、鉄を舞台とする新しい化学を切り拓いただけでなく、水素化カルシウムを用いた低温無機反応の有用性と発展性を示したものである。よって本論文は博士(工学)の学位論文として価値あるものと認める。また、平成22年7月22日、論文内容とそれに関連した事項について試問を行った結果、合格と認めた。