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論文題目	Low Temperature Synthesis and Properties of Ferromagnetic–Metal Nanomaterials and Square-Planar Coordinate Iron Oxides (強磁性金属ナノ粒子および平面四配位鉄酸化物の低温合成と物性)		
<p>Conventional high temperature synthesis methods carried out above 500 °C are widely used to obtain new materials in solid state chemistry. However, the main difficulties of such methods are to control materials physical and chemical properties, which are strongly related to its morphology and their crystal structure. In the present thesis the author demonstrates low temperature synthesis of ferromagnetic-metal nanomaterials and of square planar coordination iron oxides, focusing on their structural stability and magnetic properties.</p> <p>In Chapter 1, we implemented successfully a facile, one-pot solventless synthesis procedure, starting from acetylacetonate salts and CaH₂ to obtain ferromagnetic metallic NPs at low temperatures. The use of CaH₂ as a reductant drastically reduces reaction temperature down to 140 °C when nickel(II) acetylacetonate is used as the starting material. Powder X-ray diffraction and transmission electron microscope studies reveal the formation of metallic Ni NPs with face-centered cubic as well as hexagonally close-packed structure, depending on the reaction temperature. Also carbon-coated metallic Fe NPs are successfully produced, demonstrating the versatility of this method. Such carbon-coated ferromagnetic metallic nanoparticles have a wide range of applications from magnetic sensors to biomedical devices.</p> <p>In Chapter 2, synthesis for carboxylated SiO₂-coated α-Fe NPs (α-Fe@SiO₂@COOH NPs) was successfully carried out via CaH₂-mediated reduction of SiO₂-coated Fe₃O₄ NPs followed by surface carboxylation. The use of CaH₂ is essential to form the α-Fe core while keeping the well defined morphologies of the pristine NPs intact. These particles showed very</p>			

high magnetic properties with the M_s of 154 emu/g-Fe, which is about 1.5 times higher than that commercially available contrast agent Resovist. The introduction of COOH-group has been found to lead to excellent aqueous dispersibility and facilitate greatly the subsequent modification with a variety of functional molecules. Enhanced corrosion resistivity, facile aqueous dispersibility, and low cytotoxicity can give this α -Fe nanoparticles the potential to be a versatile platform in biomedical and medical applications such as magnetic separation, magnetically guided drug delivery, hyperthermia and MRI.

In Chapter 3, we report low temperature synthesis of multi-wall carbon nanotube (MWCNT) loaded with ferromagnetic (Ni or Fe) NP by pyrolyzing metal organic salts with CaH_2 . Chemical vapour deposition (CVD), arc discharge and pyrolysis of metal organic salts, has been the widely used way of producing MWCNTs having an advantage for mass production, but usually need high reaction temperatures more than 700 °C. This sets limitation for choice of starting materials and control of MWCNT architectures. The use of CaH_2 , enabled formation of MWCNTs at temperatures as low as 400 °C. Such drastic decrease in reaction temperature will give more freedom in design and synthesis of MWCNT-based materials and also suppress formation of carbon black as a by-product. We thus believe that the current study significantly contributes to MWCNT-based materials science and technology since MWCNT-based materials has a wide variety of applications such as electrodes for electrocatalysis and biosensing.

In Chapter 4, we investigated the Fe-site substitution effect on the structural and magnetic properties of the infinite layer iron oxide $\text{Sr}(\text{Fe}_{1-x}\text{M}_x)\text{O}_2$ ($\text{M} = \text{Co}, \text{Mn}$) using synchrotron X-ray diffraction, neutron diffraction, and ^{57}Fe Mössbauer spectroscopy. Both

systems have a similar solubility limit of $x \approx 0.3$, retaining the ideal infinite layer structure. The magnetic properties are little influenced by Co substitution. On the contrary, Mn substitution drastically destabilizes the *G*-type magnetic order, featured by a significant reduction and a large distribution of the hyperfine field in the Mössbauer spectra. Although chemical substitution changing SrFeO₂ insulator to metallic was unachieved, study with external influence such as high pressure might give expected results.

In Chapter 5, we demonstrated the synthesis of Sr₂FeO₃ through metal hydride reduction of the Ruddlesden-Popper layered perovskite Sr₂FeO₄. The Rietveld refinement synchrotron and neutron powder diffraction data revealed that the structure Sr₂FeO₃ contains corner-shared FeO₄ square-planar chains running along the [010] axis is isostructural with Sr₂CuO₃. The new framework is the $n = 1$ member of the serial lattice system Sr _{$n+1$} Fe _{n} O _{$2n+1$} connecting between 2D and 3D. Compared to other existing compounds, *i.e.* SrFeO₂ ($n = \infty$) and Sr₃Fe₂O₅ ($n = 2$), Sr₂FeO₃ has the lowest magnetic ordering due to the unidirectional loss of the *J*// superexchange interaction.

The current thesis brings to a focus a low temperature synthesis study with exceptionally strong reductant CaH₂ that enables synthesis of new materials both at nano and atomic scale, by changing materials morphology or their structure. Current low temperatures synthesis can be extend to other transition metal or their oxides both in bulk and nano scale provides access to better control over their structure and magnetic properties, that have remained challenging with the conventional methods.

(論文審査の結果の要旨)

本論文は、非溶液型の低温反応により得られる強磁性ナノ粒子と鉄酸化物の合成と磁性についてまとめたものである。論文は二部五章から構成され、成果の概要は以下の通りである。

第一部では、CaH₂を用いた還元反応によって強磁性ナノ粒子の合成を行なった。その結果、アセチルアセトン塩とCaH₂との反応により、ニッケル、あるいは鉄からなる強磁性ナノ粒子を得ることに成功した。低温(140°C)での合成は粒子凝集の抑制を、炭素皮膜形成はナノ粒子の酸化抑制を可能にした。また、SiO₂皮膜されたFe₃O₄ナノ粒子を α -Feナノ粒子に変換することに成功した。このSiO₂皮膜 α -Feナノ粒子は、154 emu/g-Feもの高い飽和磁化をもち、カルボキシル基などの修飾も容易であり、耐食性にも優れるという特色をもつ。さらには、ニッケル、あるいは鉄のナノ粒子を含有する多層カーボンナノチューブを、CaH₂存在下、400°Cで有機酸塩の熱分解反応によって得た。

第二部では、平面四配位をもつ鉄酸化物の合成と物性を調べた。CaH₂を用いた低温還元反応によって、一層型Ruddlesden-Popper相Sr₂FeO₄の基本骨格を維持したまま酸素を規則的に取除き、平面四配位が一次元状に並んだ新物質Sr₂FeO₃を得ることに成功した。この物質は、ホモロガスシリーズSr_{n+1}Fe_nO_{2n+1}のn=1に相当し、既に報告されているSrFeO₂(n=∞)、Sr₃Fe₂O₅(n=2)とあわせ次元性と磁性の関係を明らかにした。さらに、SrFeO₂の鉄サイト置換を試みたところ、Mn、Coがそれぞれ30%固溶することを見出した。Mn置換系に現れる磁気転移温度の大きな低下から、面間相互作用のフラストレーション効果を議論した。

以上の結果は、非溶液型の低温反応によって得られた新規鉄酸化物の興味深い構造や物性を明らかにしたものであり、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25年2月27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。