

(続紙 1)

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論文題目	Synthesis and characterization of transition metal oxides and oxyhydrides using epitaxial thin films deposition (エピタキシャル薄膜堆積を使った遷移金属酸化物と酸水素化物の合成と特性評価)		
(論文内容の要旨)			
<p>The use of solid state metal hydrides as reagents for topochemical reductions has allowed the discovery of new oxygen-deficient transition metal oxides and oxyhydrides with unexpected structures and functionalities. Nevertheless, the motivation to investigate physical properties in these compounds is often limited in bulk systems due to extrinsic factors such as low crystallinity or grain boundaries. To overcome these limitations, epitaxial thin films, as an alternative to polycrystalline powder, offer a unique method to probe the intrinsic nature of some mechanisms such as electronic and ionic conductivity. In addition, the variety of single-crystal materials which are now commercially available for substrate applications allows the control of epitaxial thin film orientation and also provides the opportunity to apply a strong bi-axial pressure in different crystallographic directions. This type of “strain engineering” is effective to modify the reactivity and the structure of materials obtained by topochemical reactions with metal hydrides.</p> <p>In this thesis, we focus on the hydride reduction of various materials using bulk powders and epitaxial thin films. In particular, the use of thin films permits the development of structural features and the investigation of physical properties for new compounds which are not accessible in bulk. The metastability of oxyhydrides obtained by topochemical reactions hampered the possibility to sinter pellets at high temperature and therefore, transport measurements with powder samples involve important contribution of grain boundaries. Thin films help us to probe the intrinsic nature of electronic conductivity and the biaxial pressure induced by the substrate is also an invaluable tool for tuning mixed-anion materials.</p>			

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<p>In Chapter 1, the topochemical reduction of the solid solution $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0.5 \leq x \leq 0.8$) with use of CaH_2 has been performed. This reaction, which is not effective with neither $x = 0$ (NdCoO_3) or $x = 1$ (SrCoO_3), yields $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_2$. The structure of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_2$ is unusual for perovskite materials and reveals a three dimensional network of cobalt centers in 4-fold coordination. The magnetic moment in this compound, deduced from Rietveld refinement of neutron powder diffraction, indicates that all cobalt ions are in high-spin configuration, which favors the tetrahedral geometry for CoO_4 polyhedra due to the small crystal field splitting energy in this electronic configuration for $d8 \text{Co}^+$ and $d7 \text{Co}^{2+}$ cations.</p> <p>In Chapter 2, we report the influence of orientation and strain-induced pressure on the topochemical transformation for epitaxial thin films of the $n = 1$ Ruddlesden-Popper perovskite phase LaSrCoO_4. The use of a single crystal substrate of LaSrAlO_4 with 001 and 100 orientations provides the control of anionic distribution in $\text{LaSrCoO}_3\text{H}_{0.7}$ and we present the synthesis of a new tetragonal structure with anion disorder which is inaccessible without epitaxial thin films.</p> <p>In Chapter 3, the preparation and the characterization of the oxyhydrides $\text{ATiO}_{3-x}\text{H}_x$ ($A = \text{Ba}, \text{Sr}, \text{Ca}$) in epitaxial thin film form are obtained with CaH_2 treatment of the oxide precursor films. These films show large concentration of hydride species in the perovskite lattice (up to $4.1 \times 10^{21} \text{ cm}^{-3}$ for $A = \text{Sr}$, i.e. $\text{SrTiO}_{2.75}\text{H}_{0.25}$) accompanied with metallic conductivity, instead of the semiconducting nature observed in bulk. Hall effect measurements show that the carrier concentration is in relatively good agreement with the H^- ions concentration, indicating that most of the carriers are activated, unlike oxygen-deficient $\text{ATiO}_{3-\delta}$.</p> <p>In Chapter 4, a systematic study of the evolution of the electrical properties of BaTiO_3 and SrTiO_3 as a function of hydride ion insertion is proposed. The evolution of the electrical resistivity against temperature as a function of the stoichiometry in $\text{ATiO}_{3-x}\text{H}_x$ ($A = \text{Ba}, \text{Sr}$) (with x varying between 0.14 and 0.58 for $A = \text{Ba}$ and between 0.09 and 0.45 for $A = \text{Sr}$) is correlated, qualitatively and quantitatively, with other type of chemical doping such as Nb-doped or Sb-doped. $\text{SrTiO}_{3-x}\text{H}_x$ exhibits metallic conductivity at much lower carrier concentration ($x = 0.05$) than $\text{BaTiO}_{3-x}\text{H}_x$ ($x = 0.24$) due to the local cation off-centering attributed to the higher radius size of Ba^{2+}, yielding to a universal tendency of carrier injection in ATiO_3 titanates oxide with a</p>			

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<p>perovskite structure.</p> <p>In Chapter 5, the synthesis of a new oxyhydride of EuTiO_3 and the physical properties of the new material are reported. Measurements on both bulk and thin film of $\text{EuTiO}_{3-x}\text{H}_x$ ($x \leq 0.3$) show a ferromagnetic transition around 12 K and a metallic conductivity up to the Curie temperature, where a kink can be observed. The ferromagnetism in $\text{EuTiO}_{3-x}\text{H}_x$ can be explained by the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction between the Eu^{2+} spins mediated by the itinerant Ti $3d$ electrons and the highest measured Curie temperature among doped-EuTiO_3 materials ($\text{Eu}_{1-x}\text{R}_x\text{TiO}_3$ ($R = \text{La}^{3+}, \text{Gd}^{3+}$) or $\text{EuTiO}_{3-\delta}$) is attributed to the ability of hydride ions to induce carrier without diluting the network of magnetic ions nor introducing a large chemical disorder.</p>			