論文 / 著書情報
Article / Book Information

題目(和文)	H[－]/O^{2－}混合アニオンを持つ層状ペロブスカイト遷移金属酸水素化物の合成と評価
Title(English)	Synthesis and Characterization of Layered Perovskite Transition-Metal Oxyhydrides with H[－]/O^{2－} Mixed Anion
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	材料物理科学　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（工学）
学生氏名： Student's Name	方　俊皓	指導教員（主）： Academic Advisor(main)	細野　秀雄
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

The design of functional materials can be achieved based on understanding of the relationship between the material's properties and its electronic structure. In transition-metal oxides, the bonding interaction between the metal cation and surrounding anions determines the electronic structure of metal *d* orbitals. Moreover, the superexchange interaction between transition-metal cations is mediated by an intervening anion. For this reason, "bridging" anion which mediates transition-metal cations plays a key role in emergence of the electronic and magnetic properties of materials. Such importance leads to the study on the mixed-anion transition-metal compounds such as oxyhalides, oxychalcogenides and oxypnictides, but the interaction between metal and ligands is restricted to "*d-p* bonding". The present study was performed to clarify *the role of hydride ion in layered perovskite type vanadium oxide system* by revealing the novel physical and chemical phenomena through the formation of "*d-s* bonding" utilizing partial substitution of oxygen site with hydride ion.

Chapter 1 describes the main concept, background and objective of this study.

In chapter 2, new layered perovskite vanadium oxyhydrides $Sr_2VO_{4-x}H_x$ ($0 < x < 1$) were synthesized and their crystal structures were characterized. By substituting H^- into the O^{2-} site, the hydrogens selectively replace equatorial oxygen sites in V–O planes rather than apical oxygen sites, even before any structural transition occurs. It was found that the structural transition from a tetragonal (space group: *I*4/*mmm*) to an orthorhombic (*Immm*) phase occurs by high degree of order of the hydride ions within metal-oxide planes. The hydride ion ordering and the subsequent crystallographic transition can be explained by switching of the HOMO level from the $(d\pi–p\pi)^*$ antibonding molecular orbital to a lower energy $d\sigma–s\sigma$ bonding molecular orbital.

In chapter 3, the low dimensionalization of magnetic ordering was found in a transition-metal oxide Sr_2VO_4 by substitution of O^{2-} with H^-. Upon increasing x in $Sr_2VO_{4-x}H_x$, the hydride ions were ordered linearly and simultaneously the magnetic susceptibility was suppressed at above the Néel temperature (160 K). It is found that the magnetic suppression was attributed to the formation of one-dimensional antiferromagnetic spin-chain keeping that each of the vanadium is two-dimensionally bridged by hydride and oxide ions.

In chapter 4, theoretical calculations were performed to investigate the origin of the one-dimensional magnetic behavior in a transition-metal oxyhydrides $Sr_2VO_{4-x}H_x$. The calculation results demonstrate that the substitution of hydride ion for the oxide ion breaks the π-exchange interaction between the transition-metal ion and the oxide ion, and causes the anisotropic exchange interaction ($J/J' \sim 6$) originating from the absence of π-bonding between H 1*s* and V 3*d* orbitals.

Chapter 5 summarizes the results and gives the conclusions of the thesis.

In the present study, *the effects of anion orbital symmetry* on the structural and physical properties of transition-metal compounds were clarified using Sr_2VO_4. The perovskite-type 3*d* transition-metal oxides can be categorized by two groups: the transition-metal oxides in which only d_{xy}, d_{yz}, and d_{xz} orbitals are occupied (early transition-metal oxides) and the transition-metal oxides with electrons occupying the $d_{x^2-y^2}$ and d_{z^2} orbitals. When the oxide ions in the former group are substituted by the hydride ions, the absence of an exchange pathway through metal-H-metal can introduce the magnetic low-dimensionalization if the substituted hydride ions are ordered low-dimensionally. For the latter group, the σ-exchange interaction through metal-H-metal works effectively, therefore, low-dimensionalization effect is negligible. For this reason, magnetic low-dimensionalization in the early transition-metal oxyhydride Sr_2VO_3H was realized, while the Co-based oxyhydride $LaSrCoO_3H_{0.7}$ shows the strong antiferromagnetic ordering ($T_N > 350$ K) by the effective superexchange interaction through the Co-H-Co pathway in addition to the Co-O-Co pathway. This study suggests the different standpoint to realize the novel chemical and physical phenomena for transition-metal compounds by utilizing heteromorphic mixed anions.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。
Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).