論文 / 著書情報
Article / Book Information

題目(和文)	高圧技術を利用したPb含有ペロブスカイト型酸化物の機能性探索
Title(English)	Exploring Functional Properties of Pb-Containing Perovskite Oxides Utilizing High-Pressure Techniques
著者(和文)	劉 丘民
Author(English)	Liu qiumin
出典(和文)	学位:博士(工学), 学位授与機関:東京科学大学, 報告番号:甲第302号, 授与年月日:2025年3月26日, 学位の種別:課程博士, 審査員:東 正樹,舟窪 浩,川路 均,笹川 崇男,片瀬 貴義,山本 隆文
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Institute of Science Tokyo, Report number:甲第302号, Conferred date:2025/3/26, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

（博士課程）
Doctoral Program

論 文 要 約

THESIS OUTLINE

系・コース：Department of, Graduate major in	材料 材料	系 コース	申請学位（専攻分野）：Academic Degree Requested	博士 Doctor of	（ 工学 ）
学生氏名：Student's Name	劉　丘民		審査員主査：Chief Examiner	東　正樹	

The charge degrees of freedom exhibited by transition metal ions in the perovskite oxides have attracted great interest due to the various fascinating properties such as magnetoresistance, metal-insulator transition and superconductivity. Bi and Pb are the main group elements but also have electronic configuration freedoms of $6s^2$ (Pb^{2+}, Bi^{3+}) and $6s^0$ (Pb^{4+}, Bi^{5+}). Because the $6s^1$ configurations (Bi^{4+}, Pb^{3+}) are prohibited, these are called valence skipping ions or negative-U ions. In our previous studies, the charge distribution of $PbMO_3$ and $BiMO_3$ (M: 3d transition metal ions) systematically changes depending on the position in the periodic table. As the atomic number of the 3d transition metal increases, the d-level becomes deeper and the valence decreases. Accordingly, Bi and Pb gradually change from $6s^2$ (Pb^{2+}, Bi^{3+}) to $6s^0$ (Pb^{4+}, Bi^{5+}). The systematic change in the valence distribution arises because the 6s level is close to the d levels of the transition metal and the 2p level of oxygen. Moreover, the charge states of Pb and Bi are highly sensitive to the changes in temperature or pressure conditions.

Among these, $BiNiO_3$, which has a valence distribution of $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$, undergoes an intermetallic charge transfer under pressure, where Bi^{5+} is reduced while Ni^{2+} is oxidized to Ni^{3+}, resulting in a 2.9% volume contraction and a transition to the high-pressure phase $Bi^{3+}Ni^{3+}O_3$. In $BiNi_{1-x}Fe_xO_3$, where Ni is partially substituted with Fe^{3+}, the charge transfer occurs upon heating, leading to a 2.6% negative thermal expansion. This phenomenon exemplifies the functionalization of pressure-induced charge transfer transitions via elemental substitution. This dissertation focuses on the pressure-induced structural phase transitions and charge transfer in Pb-containing perovskite oxides $PbMO_3$ (M = Cr, Fe), both of which have the charge distribution $Pb^{2+}_{0.5}Pb^{4+}_{0.5}M^{3+}O_3$. Utilizing various high-pressure measurement techniques, the study aims to explore the functionalization of these materials. The dissertation is structured into four chapters, which are summarized as follows.

Chapter 1. General Introduction

This chapter provides an overview of perovskite-type oxide materials containing Pb and 3d transition metals, as well as negative thermal expansion materials. It also discusses the research progress on $PbCrO_3$ and $PbFeO_3$, which are the focus of this study. Finally, the objectives of this dissertation are presented.

Chapter 2. Colossal Thermal Expansion in Ca Substituted $PbCrO_3$

$PbCrO_3$ exhibits charge disproportionation between Pb^{2+} and Pb^{4+}, resulting in a charge distribution of $Pb^{2+}_{0.5}Pb^{4+}_{0.5}Cr^{3+}O_3$. At 2.5 GPa, a pressure-induced intermetallic charge transfer occurs, transitioning from the ambient-pressure phase $Pb^{2+}_{0.5}Pb^{4+}_{0.5}Cr^{3+}O_3$ to the high-pressure phase $Pb^{2+}Cr^{4+}O_3$, accompanied by a colossal 9.8% volume contraction, exceeding that observed in $BiNiO_3$.

To functionalize this pressure-induced charge transfer transition, the pressure-temperature phase diagram of $PbCrO_3$ was investigated using synchrotron X-ray diffraction under high-pressure conditions. The results revealed that, in contrast to $BiNiO_3$, the high-pressure phase reverts to the ambient-pressure phase upon heating under pressure. Based on this finding, the stabilization of the high-pressure phase containing Cr^{4+} was successfully achieved by substituting Ca^{2+} for Pb, leading to the realization of colossal thermal expansion in $Pb_{0.7}Ca_{0.3}CrO_3$.

Chapter 3. Pressure Induced Amorphization of Pb^{2+} and Pb^{4+} in Perovskite $PbFeO_3$

$PbFeO_3$ possesses a superstructure with a space group of *Cmcm*, forming a $2a_p \times 6a_p \times 2a_p$ unit cell with a charge distribution of $Pb^{2+}_{0.5}Pb^{4+}_{0.5}Fe^{3+}O_3$. Due to its unique Pb ordering, two Fe^{3+} sites exist in different local environments. To investigate the possibility of a pressure-induced intermetallic charge transfer, synchrotron X-ray diffraction and Mössbauer spectroscopy were conducted under high-pressure conditions, and first-principles calculations were used to estimate the pressure required for charge transfer.

Under high pressure, the disappearance of superstructure-derived XRD peaks was observed, confirming a transition to the high-pressure phase *Pnma* with a $\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$ unit cell, where both Pb and Fe occupy a single crystallographic site. Mössbauer spectroscopy revealed that Fe remains in the 3+ state, while Pb exists in a charge glass state, where Pb^{2+} and Pb^{4+} are randomly distributed in a 1:1 ratio. First-principles calculations corroborated these findings, confirming that charge transfer to $Pb^{2+}Fe^{4+}O_3$ does not occur at least up to 70 GPa.

Chapter 4. General Conclusions

This chapter summarizes the findings of this dissertation. This study focused on the pressure-induced structural phase transitions and charge transfer possibilities in $PbMO_3$ and utilized high-pressure measurement techniques and high-temperature high-pressure synthesis methods to explore their functionalization. The study identified phase transitions to charge glass states induced by temperature ($Pb_{0.7}Ca_{0.3}CrO_3$) and pressure ($PbFeO_3$). These phase transitions resulted in the emergence of colossal thermal expansion, a novel property.

Furthermore, this research proposes new directions for the functionalization of other $PbMO_3$ compounds (M = Mn, Co…) and $(Pb_{1-x}Bi_x)MO_3$. Beyond perovskite oxides, these findings provide crucial insights into the design and characterization of materials with charge disproportionation and charge glass states, contributing to the broader field of functional materials.