

氏 名 Nur Ika Puji Ayu

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学位論文題目 Synthesis and Structural Studies on  $(\text{Ba,Sr})_3\text{Ga}(\text{H,D})\text{O}_4$  and  
 $\text{Ba}_2\text{LiD}_3\text{O}$  Oxyhydrides

論文審査委員 主 査 大友 季哉  
物質構造科学専攻 教授  
齊藤 高志  
物質構造科学専攻 准教授  
伊藤 晋一  
物質構造科学専攻 教授  
小林 玄器  
物理科学研究科 構造分子科学専攻 准教授  
神山 崇  
Spallation neutron science center, Institute of  
High Energy Physics, Chinese Academy of Science,  
Senior Adviser  
萩原 雅人  
日本原子力研究開発機構 原子力科学研究部門  
物質科学研究センター 研究員

本学位論文は高エネルギー加速器科学研究科物質構造科学専攻と物理科学研究科構造分子科学専攻による学内共同研究指導<sup>1</sup>によるもの。

<sup>1</sup> 学内共同研究指導

本学の学生が、自身の所属する専攻と、所属する研究科の他の専攻又は所属する研究科以外の研究科による共同の研究指導を受けるプログラム。

(Form 3)

## Summary of Doctoral Thesis

Name in full Nur Ika Puji Ayu

Title Synthesis and Structural Studies on  $(\text{Ba,Sr})_3\text{Ga}(\text{H,D})\text{O}_4$  and  $\text{Ba}_2\text{LiD}_3\text{O}$  Oxyhydrides

Oxyhydrides, or partial substitution of oxide by hydrides, recently gains popularity due to several exciting characteristics such as superconductivity, metal to insulator transition, catalytic activity, and superionic conduction<sup>1</sup>. Unique characteristics of hydride, including its polarizability, strong reduction ability, and high mobility in the material, make it a good candidate as an ion carrier. On the other hand, the preparation of oxyhydrides with poor elemental selectivity becomes challenging for material exploration. Regarding this background, the research topics of hydride material exploration and ionic conduction study of hydrides in the superionic oxyhydride were investigated in the present study from the viewpoint of crystal structure.

The material exploration of oxyhydrides was first initiated by the topotactic reduction reaction of transition metal oxides  $\text{LaSrCoO}_4$ <sup>2</sup>. Several oxyhydrides were then reported containing a transition metal, alkali metal, or alkaline-earth metal atoms. There is less report on p-metal element oxyhydrides despite the important role of p-metal cations in some functional compounds due to their duality of ionicity and metallicity. Refer to the study of p-element metal oxyhydrides on  $\text{Ba}_3\text{AlO}_4\text{H}$  and  $\text{Sr}_3\text{AlO}_4\text{H}$ <sup>3,4</sup>, a new oxyhydrides containing p-metal cation, gallium, have been synthesized in this study. A polycrystalline sample of  $A_3\text{GaHO}_4$  ( $A = \text{Ba}, \text{Sr}$ ) was prepared by solid-state reaction under high pressure. The stoichiometric mixture of raw materials,  $\text{AH}_2$  (99.5%, Mitsuwa Chemical Co.),  $\text{AO}$  (99.99%, Aldrich), and  $\text{Ga}_2\text{O}_3$  (99.99%, Aldrich), was heated up to 800°C under 2 GPa for 0.5 hours. The obtained gray-colored powder sample was then characterized by the synchrotron X-Ray Diffraction (SXR) at BL02B2, SPring-8, and neutron diffraction (ND) at BL09 SPICA, MLF, J-PARC.

The SXR and ND refinement results indicated non-stoichiometric compositions of  $(\text{Ba,Sr})_{3-y}\text{GaO}_4\text{H}_x$  ( $x=0.22-0.30, y=0.10-0.15$ ) which adopted an anti-perovskite structure of tetragonal  $I4/mcm$ . The structure is an anti-perovskite structure with  $\text{GaO}_4$  tetrahedra ordered in the  $\text{HBa}_6$  octahedra framework, where hydride is located in the center of the octahedra. The hydrides are ordered in the structure with partial occupancy confirmed from

the neutron diffraction pattern refinement of the deuterated sample. As reported in other isostructural compounds, the Bond Valence Sum (BVS) calculation results in an under-bonding state of apical Ba sites in  $\text{HBa}_6$  octahedra, indicating local ordering as reported in  $\text{LaSr}_2\text{AlO}_5$ <sup>5</sup>. Regarding stability,  $\text{Ba}_{2.85}\text{GaO}_4\text{H}_{0.70}$  is unstable in the air. The thermogravimetry (TG) measurement using Rigaku Thermo Plus 8121 up to 500°C revealed hydride to oxide replacement is possible in  $\text{Ba}_{2.85}\text{GaO}_4\text{D}_{0.70}$  upon heating under dry oxygen flow. Because the ionic size of hydride is flexible, in conclusion, the anti-perovskite oxyhydrides containing  $\text{GaO}_4$  and  $\text{AlO}_4$  unit were summarized to obtain the degree of flexibility of hydride and provide crystal chemistry knowledge of an anti-perovskite oxyhydrides stability range for future material exploration.

In the point of view of oxyhydrides properties, the ionic conduction study of hydrides in the superionic oxyhydride was performed. As hydride has large mobility and other distinct characters as charge carriers, the recent study on  $\text{K}_2\text{NiF}_4$ -type structure oxyhydrides reported pure hydride conduction with a practical conductivity at an intermediate temperature<sup>6</sup>. The current report by Takeiri et al.; on superionic hydrides revealed high conductivity of  $\text{Ba}_{1.75}\text{LiH}_{2.7}\text{H}_{0.9}$  (BLHO) with conductivity  $\sim 10^{-2}\text{S/cm}$  at 350°C<sup>7</sup>. The Arrhenius plot of its conductivity shows a jump conductivity which corresponds to order-disorder phase transitions. A nearly temperature-independent conductivity or a flat curve of the Arrhenius plot was observed at high temperatures, indicating a superionic phase. The structure BLHO was tentatively clarified only by the hydrogen phase. The detail of the superionic structure concerning the conduction mechanism was not clear. In order to gain new insight into hydride conduction in BLHO, a deuterated sample was prepared. The deuterated sample, BLDO, was successfully synthesized by a solid-state reaction of the stoichiometric raw materials of  $\text{BaD}_2$  (93%, Kojundo),  $\text{LiD}$  (98%, Aldrich), and  $\text{BaO}$  (99.99%, Aldrich) sintered under a deuterium atmosphere. The temperature-dependent SXRD was performed to confirm that the structure and phase transition behavior of BLDO is similar to the hydrogen sample. In addition, the Electrochemical Impedance Spectroscopy (EIS) measurement was performed to confirm the similarity in conductivity behavior. Then finally, a temperature-dependent neutron diffraction experiment was performed at BL09 SPICA, MLF, J-PARC to investigate the detailed structure supported by MEM analysis.

The structural study of the superionic hydride conductor BLDO with  $\text{K}_2\text{NiF}_4$ -type structure revealed that both hydrogen and deuterium samples have a similar phase transition and conductivity. There are two-phase transitions that occurred from room temperature to 400°C. These transitions

involve  $\beta$ -phase,  $\gamma$ -phase, and  $\delta$ -phase. Although the intermediate phase,  $\gamma$ -phase, of BLDO is slightly different from BLHO, both samples have a similar disordering structure of the superionic phase,  $\delta$ -phase.

The MEM analysis results on the superionic phase indicated that interstitial hydride exists near apical hydride sites. As already reported in other superionic materials that interstitial sites provide an ionic conduction pathway, the interstitial hydride site discovered in BLDO in this study is likely to contribute to its conduction. The interstitial hydride site could facilitate ionic migration between apical sites through an interstitialcy mechanism. The main contribution to the conductivity likely comes from the equatorial hydrides, in which the MEM density map visualized the significant ionic vibration of equatorial hydrides and the lithium vibration forming a circle-like ionic conduction pathway. The contribution of apical hydrogen site to the conduction mechanism and the presence of interstitial hydride at high-temperature phase have never been reported before.

Keywords: *oxyhydrides, p-metal cation, hydride ion conduction, MEM, superionic,*

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## 博士論文審査結果

Name in Full  
氏名 NUR IKA PUJI AYU

Title  
論文題目 Synthesis and Structural Studies on  $(\text{Ba,Sr})_3\text{Ga}(\text{H,D})\text{O}_4$  and  $\text{Ba}_2\text{LiD}_3\text{O}$   
Oxyhydrides

Nur Ika Puji Ayu 氏は、酸水素化物  $(\text{Ba,Sr})_3\text{Ga}(\text{H,D})\text{O}_4$  の合成と結晶化学、および、 $\text{Ba}_2\text{Li}(\text{H,D})_3\text{O}$  のイオン伝導と結晶構造の関係の研究を行った。

p-block を持つ酸水素化物に注目し、Ga を持つ物質群に対して、さまざまな合成法を試みた結果、逆ペロブスカイト型構造を持つ新規な酸水素化物  $\text{Sr}_3\text{GaHO}_4$ 、 $\text{Ba}_3\text{GaHO}_4$ 、 $\text{Ba}_3\text{GaDO}_4$  の超高压合成にはじめて成功した。これらの物質の中性子回折データを解析することにより酸素や水素の欠損について明らかにするとともに、逆ペロブスカイト型構造の安定領域をはじめて提示し、今後の物質開発に向けて貴重な結晶化学知見を得た。

また、 $\text{K}_2\text{NiF}_4$  型構造を持つ酸水素化物超イオン伝導体  $\text{Ba}_2\text{Li}(\text{H,D})_3\text{O}$  の超イオン伝導体相 ( $\delta$ ) への相転移挙動、構造相転移などについて研究をおこなった。重水素置換した  $\text{Ba}_{1.75}\text{LiD}_{2.7}\text{O}_{0.9}$  を合成し H 体と比較した結果、構造相転移やイオン伝導性など全体的特徴は似ているものの、イオン伝導特性に違いが見られることや、中間温度相 ( $\gamma$ ) では D 体と H 体の構造の有意な違いに気づき D 体では超格子を形成していることをはじめて示した。一方、 $400^\circ\text{C}$  の超イオン伝導体相 ( $\delta$ ) の D 体において、マキシマムエントロピー法による散乱長密度解析から見いだした格子間水素をリートベルト解析で確認した。さらに、Li の原子変位が c 軸方向に非常に大きく特徴的であることを踏まえ、伝導メカニズムとして、従来から提案されていた equatorial のみの hopping 伝導以外に、格子間水素や大きな Li イオンの振動が介在している可能性があることを論じた。関連してイオン伝導性の違いが単純な同位体効果では説明できないことも論じた。

本審査では、予備審査での指摘事項に適切に対応したことが示され、これらを反映した発表が行われた。

酸水素化物は、イオン半径が近い二つのアニオン、水素化物イオンと酸化物イオン、が共存しており、多彩な配位がとれるため、さまざまな機能発現が期待されている物質群である。Ayu 氏の研究は、酸水素化物の新規物質合成を成功させるとともに、既知の酸水素化物のイオン伝導特性や相転移挙動、結晶構造との関係について知見を深めたものであり、酸水素化物における物質科学研究に貢献したと判断される。

以上の理由により、審査委員会は、本論文が学位の授与に値すると判断した。