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| Title        | Theoretical Investigations of La <sub>2</sub> GeO <sub>5</sub> -based Electrolyte for Solid Oxide Fuel Cell Application                               |
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## Abstract of Thesis

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| Title                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Theoretical Investigations of $\text{La}_2\text{GeO}_5$ -based Electrolyte for Solid Oxide Fuel Cell Application<br>(固体酸化物形燃料電池の応用に向けた $\text{La}_2\text{GeO}_5$ をベースとした電解質材料に関する理論的研究) |
| <p>Abstract of Thesis</p> <p>Together with the demand on energy, the depletion of natural resources triggers the necessity of alternative environment-friendly energy. In terms of clean energy conversion to decrease the level of carbon emissions, there is considerable interest in solid oxide fuel cell (SOFC) devices as their high efficiency and wide applications. Although SOFCs are recently gaining interests, the requirement of high operating temperatures (above <math>850^\circ\text{C}</math>) for conventional SOFCs leads to difficulties in thermal cycling accounting for chemical and microstructure degradation and requirement of expensive constituents in interconnects and heat exchangers. The limitation of operating temperatures is mainly due to reduction of oxygen ion conductivity of electrolyte membranes in low temperatures. Therefore it is a crucial subject to find out new solid electrolyte materials made of good oxygen ion conductors that retain their high ionic conductivities at reduced temperatures.</p> <p>In 2001, monoclinic <math>\text{La}_2\text{GeO}_5</math> was experimentally found by Ishihara et al. to have a higher ionic conductivity than usually used electrolyte made of yttria-stabilised zirconia. They reported that the geometry of <math>\text{La}_2\text{GeO}_5</math> consists of two kinds of planar layers, <math>\text{LaGeO}_3</math> and <math>\text{LaO}_2</math> ones. In the <math>\text{LaGeO}_3</math> layers, germanium and three surrounding oxygen atoms form distorted <math>\text{GeO}_4</math> tetrahedral substructures with an <math>\text{sp}^2</math> hybridization configuration. On the other hand, in 2002, Berastegui et al. reported that the configurations of the <math>\text{GeO}_4</math> substructures are <math>\text{sp}^3</math>-like. However, there is no theoretical study about this material. In this paper, by first principles calculations based on the density functional theory, the electronic and oxygen migration properties of pure monoclinic lanthanum germanate were investigated. The monoclinic crystal structure of <math>P2_1/c</math> space group where the configurations of the <math>\text{GeO}_4</math> substructures were <math>\text{sp}^3</math>-like was confirmed by fully optimizing the unit cell. By electronic properties analysis, both <math>\text{La}_2\text{GeO}_5</math> and oxygen-deficient <math>\text{La}_2\text{GeO}_{5-\delta}</math> exhibited insulating properties that had a great significance in electrolyte application. Since the conduction mechanism in this system is oxygen vacancy, it is important to investigate the migration process of oxygen ion through this material. The factors that may influence the magnitude of the ionic conductivity are the concentration of mobile ions, the activation barrier for oxygen conduction and its dependence on structural parameters such as the bottlenecks that connects adjacent sites in the oxygen conduction pathway. Among these factors, the activation barrier is of utmost importance since the dependence is exponential for conductivity. Therefore, activation barrier for oxygen hopping to the oxygen vacancy was taken into account. By using climbing image nudged elastic band (CI-NEB) method, I obtained the activation barriers for oxygen hopping between nearest-neighbor sites and these values were excellently comparable with experimental ones.</p> <p>Experiment alkaline-earth (AE) doping, the monoclinic crystal structure does not change and increases ionic conductivity. Therefore, by using first principles calculation, I investigated the doping effects of AE metals (Ba, Sr and Ca) in monoclinic lanthanum germanate <math>\text{La}_2\text{GeO}_5</math> on its oxygen ion conduction. Although the lattice parameters of the doped systems changed due to the ionic radii mismatch, the crystal structures remained monoclinic. The contribution of each atomic orbital to electronic densities of states was evaluated from the partial densities of states and partial charge densities. It was confirmed that the materials behaved as ionic crystals comprising</p> |                                                                                                                                                                                         |

cations of La and dopants and anions of oxygen and covalently formed  $\text{GeO}_4$ . The doping effect on the activation barrier for oxygen hopping to the most stable oxygen vacancy site was investigated. By tracing the charge density change during the hopping, it was confirmed that the oxygen motion is governed by covalent interactions. The obtained activation barriers showed excellent quantitative agreements with an experiment for the Ca- and Sr-doped systems in low temperatures as well as the qualitative trend including the Ba-doped system.

Recently, there are some experimental studies implying that the ionic conductivity of AE oxides co-doped such as CaO- and SrO-doped ceria is much higher than that of undoped ceria. However, there is neither theoretical nor experimental data about co-doped  $\text{La}_2\text{GeO}_5$ . With an objective of designing the new alternative electrolyte materials, I attempted to co-dope lanthanum germanate by AE substances. In order to investigate the effect of mono-doping and co-doping, one migration path was taken into account and AE metals (Sr and Ca) were substituted to the vicinity La cation sites, and thus first nearest neighbor, second nearest neighbor and third nearest neighbor (1NN, 2NN and 3NN, respectively) configurations of dopant cations were considered. Mono-doped or co-doped systems remained the monoclinic structure of the origin system. The obtained activation barriers of the three configurations of the co-doped system were in between Ca-doped and Sr-doped systems. The comparison of electronic properties of 1NN, 2NN and 3NN in both mono-doped and co-doped systems indicated strong Coulombic interactions between dopant and migrating oxygen ion in the saddle point in 1NN configurations. This resulted in the high activation barrier of this configuration. The activation barriers were found to have the lowest values and smallest differences between mono-doped and co-doped systems for 3NN configurations where the energy difference was only 0.01 eV for Sr- and Ca-doped systems. Hence, co-doping did not reduce the activation barrier. Thus it was concluded that the similarity in ionic radii between dopant (Ca, followed by Sr) and host La cation played the essential role in selecting the suitable dopant for  $\text{La}_2\text{GeO}_5$  system.

Lastly, for the effect of dopant ions on the migration throughout the cell, I provided some Sr mono-doped configurations and possible migration paths in a La-O single layer. The 1NN, 2NN and 3NN of dopant ions were also considered. Two Sr dopant ions being placed in the first, second and third nearest neighbors did not change significantly the super-cell crystal structure. The most energetically favorable site for oxygen vacancy formation was obtained at the site locating near both two Sr dopants in 1NN configurations. The activation energy of the migration path where oxygen vacancy initially locates near both dopant ions was highest. The preferred migration paths were found for oxygen vacancy initially locating far from both of the dopants, i.e. avoiding the dopant, due to the strong trapping at the stable sites.

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

世界的にエネルギーの需要が急増しており、石油をはじめとする天然資源の枯渇の問題が表面化しつつある。この問題を解決するため、再生可能エネルギーの活用技術の開発が急務である。また、環境への配慮から、温暖化ガスである二酸化炭素の排出量の減少も重要である。この 2 つの要請を満たすものとして、高効率性と応用範囲の広さから、固体酸化物形燃料電池 (SOFC) が注目されている。しかしながら、SOFC の極めて高い動作温度 (850℃以上) は、電池材料の熱劣化をはじめとする種々の材料に関する問題をもたらしている。高い動作温度が必要であるのは、低温において、電解質膜の酸素イオン伝導性が急速に低下するためである。この問題を解決すると期待されている物質の一つが、ゲルマン酸ランタン ( $\text{La}_2\text{GeO}_5$ ) である。 $\text{La}_2\text{GeO}_5$  は、従来の固体電解質に用いられてきたイットリア安定化ジルコニアよりも高いイオン伝導性を示すことが実験で確認されているが、その動作原理については明らかになっておらず、物性物理学的基礎研究と応用材料開発研究の両方の観点から、 $\text{La}_2\text{GeO}_5$  物性解析が必要不可欠であった。

本論文では、 $\text{La}_2\text{GeO}_5$  における酸素の伝導特性の解析を目的として、密度汎関数理論に基づく第一原理計算を援用して  $\text{La}_2\text{GeO}_5$  物性解析を行っている。特にイオン伝導性を改善するためのアルカリ土類金属 (Ca, Sr, Ba) 添加の効果の調査を行いその良否を評価し、イオン伝導性を改善する電解質材料デザインへの指針を示した。本論文の主要な成果を以下に要約する。

- 1) これまで議論のあった  $\text{La}_2\text{GeO}_5$  の結晶の電子構造を、第一原理計算を援用して明らかにした。 $\text{La}_2\text{GeO}_5$  は、単斜晶構造をとり、その中の  $\text{GeO}_4$  の四面体サブ構造は、 $\text{sp}^3$ -like な混成軌道による共有結合で形成され、他の部分はイオン性結合からなることを明らかにした。また、この  $\text{La}_2\text{GeO}_5$  および、酸素イオン伝導で重要となる酸素欠陥が導入された  $\text{La}_2\text{GeO}_{5-\delta}$  では、フェルミレベル近傍でギャップが開き絶縁体になっていることを明らかにした。絶縁体であることは、SOFC の電解質材料として必須の要件である。
- 2)  $\text{La}_2\text{GeO}_5$  において、まず最安定酸素欠損位置を探索し、そこに酸素欠陥を導入して、その最隣接酸素の欠損位置へのホッピングにおける活性化エネルギーを climbing image nudged elastic band 法により評価した。得られた結果は、実験と定量的に一致した。ホッピング中の電荷密度の変化を調査することにより、上述の共有結合性相互作用が酸素の運動を支配していることを明らかにした。
- 3) アルカリ土類金属 Ca, Sr, Ba をそれぞれ添加した場合の  $\text{La}_2\text{GeO}_5$  において電子特性を解析し、最安定酸素欠損への酸素のホッピング活性化エネルギーを評価した。添加イオンのイオン半径の相違はあるが、結晶は単斜晶構造を維持し、La と添加アルカリ土類金属の陽イオンと酸素の負イオンのイオン結合性と  $\text{GeO}_4$  の共有結合性からなることを明らかにした。アルカリ土類金属を添加した場合にも酸素のホッピングは主に共有結合性相互作用が酸素の運動を支配していることを明らかにした。Ca, Sr を添加した系では、酸素ホッピングにかかる活性化障壁は、低温における実験と定量的によく一致していることを示した。Ba においては添加効果の傾向のみ一致した。

- 4) セリア系では、Ca と Sr の同時添加が酸素イオン伝導性を飛躍的に改善したという実験報告が当時あったため、 $\text{La}_2\text{GeO}_5$  においても同時添加の効果を評価した。その結果、同時添加においても結晶は単斜晶構造を維持することを示した。様々な添加イオンの配置構造を考慮したが、同時添加による活性化エネルギーは、最良構造で、単体添加の場合とほぼ変わらず ( $\sim 0.01\text{eV}$ )、セリア系とは異なり劇的な効果は無かった。解析の結果、添加イオンとホスト陽イオンのイオン半径の類似性が、最適な添加物質を選択する上で重要な役割を果たすことを明らかにした。

これらの研究成果は、SOFC の電解質材料を開発する上で、重要な知見を提供している。本研究における理論解析は、特性評価だけに留まらず、その特性の起源解明にまで及んでおり、SOFC の高効率化を可能にする電解質の設計に貢献する優れた研究であると評価できる。本論文は、次世代科学技術・材料開発に重要な指針を与えるものであり、応用物理学、特に物性物理学への寄与が大きい。よって、本論文は博士論文として価値あるものと認める。