

## 博士論文審査結果の要旨

博士論文審査委員会

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氏 名	Alicja Klimkowicz
論文題目	Perovskite-based oxygen storage materials
〔論文審査の要旨〕	
<p>本博士論文は、自動車の排気ガス浄化のための三元触媒の助触媒や酸素濃度を高めて燃焼効率を高める酸素燃焼のための酸素源等として使用される酸素吸蔵材料を主にソフトケミカル法(sol-gel法)により作製し、その性能に対して化学組成の最適化を試みたものである。本論文の予備審査は 2015 年 10月 16日(金) 10:00 から豊洲キャンパスの機械機能工学科会議室にて実施した。申請者の1時間ほどの発表の後、審査委員からの質疑を行った。論文全般に対する審査員の意見は概ね好意的であり、論文の構成および内容については、特に、問題なく、博士論文として十分な水準にあることが確認された。ただ、酸素吸蔵・放出のメカニズム、酸素吸蔵材料の形状と活性化エネルギーの関係や作動温度等の科学的・技術的な質問が出されいくつか不備な点が指摘され、修正を要することが明らかとなったが、特に、大幅な修正を必要とするようなものではなかった。その後、申請者により論文の修正がされ、さらに、予備審査後に実験(シンクロトロン放射光実験等)も進められ、博士論文の改定版が、2016年1月に提出されたので、最終審査を実施することとした。最終審査は、2016 年 2 月 15日(月) 13:00から豊洲キャンパスの406教室にて実施した。主査および審査員の他、外国人留学生や本学学生を含む10名の聴講者があった。質問は、酸化還元反応速度等の組成依存性や今後の研究の展望に関する科学的なものがほとんどで、論文の修正等に関するものはなかった。発表および質疑が終了後、審査委員による合否判定の審議を行った。審査委員が記入した学位審査評価シートの評価点は、4つの評価項目「専門性」、「広範な教養」、「業績」、「コミュニケーション能力」のすべてにおいて、地域環境システム専攻が定める採点基準を満たしており、学位審査合格と認められ、最終的な投票の結果、合格と判定された。</p>	

# 論 文 要 旨

## Thesis Abstract

(yyyy/mm/dd) 2016年 01月 12日

※報告番号	第 号	氏 名 (Name)	Alicja Klimkowicz
主論文題名 Perovskite-based oxygen storage materials			
<p>内容の要旨</p> <p>This thesis concerns determination of oxygen storage-related properties, as well as other, basic physicochemical characteristics in a group of candidate oxygen storage materials (OSM), having perovskite-type crystal structure. Series of cation-ordered Mn-based oxides with a general formula of <math>BaLnMn_2O_{5+\delta}</math> (Ln: Pr, Nd, Sm, Gd, Dy, Er and Y), Ln-site substituted <math>BaY_{1-x}Ln_xMn_2O_{5+\delta}</math> (Ln: Pr, Sm, Gd), and doubly doped materials belonging to <math>Ba_{0.9}Sr_{0.1}Y_{1-x}Ln_xMn_2O_{5+\delta}</math> group, and additionally, selected Co- and Fe-containing oxides were characterized in terms of their crystal structure in oxidized and reduced state, structural evolution on temperature and oxygen content. Thorough studies concerning their oxygen storage properties, with oxidation and reduction characteristics recorded as a function of temperature, kinetics of the oxidation/reduction determined from the isothermal studies, as well as reversible oxygen storage capacity (OSC), constitute a main part of the experimental work. Complementary research on microstructure and morphology of the prepared materials, oxidation state of the manganese cations, as well as electrical conductivity and Seebeck coefficient dependence on temperature was also conducted for selected samples. An attempt to elucidate correlation between the chemical composition of the considered oxides and their physicochemical properties influencing oxygen storage performance have been conducted. The performed in this thesis studies allowed to select the best candidate materials, having high and reversible OSC, which surpass the currently commercialized compounds.</p> <p>At the beginning of the thesis, introduction to currently, commercially used oxygen production and storage methods and to oxygen storage materials is given together with a description of the mechanism of incorporation and release of the oxygen into/from the oxides, with following information about four particular OSM systems. Selected applications of the oxygen storage materials (three-way catalytic converters, chemical looping processes, flameless combustion of hydrocarbons) are discussed. Due to the fact that the considered compounds exhibit perovskite-type crystal structure, either with or without cation ordering, a detailed information about structural properties of the parent <math>ABO_3</math>-type, as well as cation-ordered (<math>AA'B_2O_6</math>, <math>A_2BB'O_6</math>) perovskites, and <math>A_2B_2O_5</math>-type brownmillerites are shown. Additional data concerning oxygen nonstoichiometry, transport and magnetic properties of such oxides are also given.</p> <p>Preparation methods of the materials are described together with experimental techniques used for characterization of the synthesized compounds: X-ray diffraction (XRD) and neutron diffraction methods with Rietveld analysis of data, performed at room temperature and at elevated temperatures in various atmospheres, thermogravimetric (TG) analysis conducted as a function of temperature, with isothermal studies executed with a change of atmosphere between synthetic air and 5 vol.% <math>H_2</math> in Ar, microstructural studies using scanning electron microscope (SEM), with additional measurements of the specific surface area by BET technique, X-ray photoelectron spectroscopy (XPS) studies, as well as electrical conductivity and Seebeck coefficient measurements.</p> <p>Research results obtained by author of this thesis are gathered in five following chapters. Detailed information about crystal structure of the oxidized and reduced compounds is shown. Significantly smaller unit cell volume, measured for all the oxidized samples in relation to the respective reduced ones, was explained as originating for a stronger bonding between manganese and oxygen, and smaller average ionic radius of Mn in the oxidized <math>BaLnMn_2O_6</math>, resulting in a decreased Mn-O bond length.</p>			

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<p>Material with the smallest introduced <math>\text{Er}^{3+}</math> lanthanide cations exhibits the least change of volume upon oxidation. For selected materials additional structural measurements as a function of temperature were conducted, which allowed to observe <i>in situ</i> transformations ongoing during the oxidation process. Precise neutron diffraction measurements conducted in Helmholtz Zentrum Berlin in atmosphere of 5 vol.% <math>\text{H}_2</math> in Ar allowed for <i>in-situ</i> observation of the reduction process and determination of the mechanism of the oxygen release. Furthermore, possibility of reduction under low vacuum environment (<math>\sim 100</math> Pa) at elevated temperatures of the oxidized samples was also researched. The performed XPS studies indicated presence of manganese cations having different oxidation states and modification of chemical environment of the elements, between the reduced and oxidized samples. Analysis of the microstructure of the obtained powders was performed, in order to have fully-characterized samples for the TG studies used for comprehensive characterization of all compounds in terms of their oxygen storage-related properties. In all of the cases, close to theoretical value of the OSC was recorded during isothermal experiments performed at <math>500</math> °C with the atmosphere change between synthetic air and 5 vol.% <math>\text{H}_2</math> in Ar gas mixture, corresponding to the change between fully oxidized and fully reduced materials. The recorded reversible capacities correlate well with a molar mass of the compounds, being the highest for <math>\text{Ba}_{0.9}\text{Sr}_{0.1}\text{YMn}_2\text{O}_{5+\delta}</math> (3.73 wt.%). It was documented that for all of the materials the reduction process occurs much slower (on the order of minutes) than the oxidation (seconds), and thus is limiting. Among studied oxides, the best performance was registered for <math>\text{BaY}_{0.75}\text{Pr}_{0.25}\text{Mn}_2\text{O}_{5+\delta}</math> sample, for which the reduction time at <math>500</math> °C improved to 2.6 min on the 50<sup>th</sup> cycle of reduction/oxidation. Further tests proved an excellent stability of this material. The recorded temperature dependence of the reduction time was interpreted on a basis of oxygen diffusion in a bulk, and as such, allowed to calculate the activation energy of the ionic transport. It was also found that materials with larger grains show deteriorated kinetics of the reduction process. For the selected samples electrical conductivity tests shows higher conductivity for oxidized sample than the reduced.</p> <p>Possibility of a major improvement of OSC was explored in studies of properties of Fe- and Co-containing oxides, which were characterized analogously as Mn-containing materials. The highest OSC (exceeding 4 wt.%) was measured for <math>\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}</math>, while the fastest reduction speed at <math>500</math> °C (<math>\sim 2.3</math> min) was found for <math>\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}</math>. The materials were also found to exhibit lower activation energy of the ionic transport. The compounds, however, were shown to suffer from insufficient stability in reducing conditions, especially at higher (<math>\geq 500</math> °C) temperatures, limiting their possible application.</p> <p>Conclusions based on the presented studies and given discussion are listed with recommendations about future research on OSMs also included. It should be emphasized that the recorded oxygen storage performance of majority of the considered materials surpasses that of the commercial materials.</p> <p>In addition, the thesis contains four appendixes. The first one is devoted to a highly-precise structural identification of selected <math>\text{BaLnMn}_2\text{O}_{5+\delta}</math>, which was performed by analysis of synchrotron data gathered at Argonne's Laboratory Advanced Photon Source (USA). Second appendix B contain additional information of neutron diffraction measurement setup and parameters of the structural refinements of the gathered data. Appendix C presents information about submitted patent proposal concerning improvement of OSMs by a high-energy milling process. Selected results of flameless oxidation of <math>\text{CH}_4</math> with <math>\text{BaYMn}_2\text{O}_6</math> used as the catalyst and oxygen carrier are also shown.</p>			