	にわ　えいき
氏　　名	丹羽　栄貴
授与学位	博士（工学）
学位授与年月日	平成２２年９月８日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科(博士課程)機械システムデザイン工学専攻
学位論文題目	High Temperature Function Design of Electron Conductive Oxide by Composition Control (電子導電性酸化物の組成制御による高温機能設計)
指導教員	東北大学教授　水崎　純一郎
論文審査委員	主査　東北大学教授　水崎　純一郎　東北大学教授　湯上 浩雄 東北大学教授　川田 達也　東北大学准教授　佐多 教子 (環境科学研究科)

論文内容要旨

The objective of this thesis is to define the design guide of polycrystalline electron conductive materials by the composition control. $SrTiO_3$ was selected as the model material of electron conductive oxide because the crystal structure is simple (cubic perovskite-type structure) and has rather high chemical stability. Moreover, $SrTiO_3$ related oxides are used at various fields. For example, these oxides are used as ceramic capacitor and barista because dielectric constant of these oxides has rather high at room temperature and is paraelectrics. These oxides are also used as photocatalyst, semiconductor and gas sensor and so on. Moreover these oxides are used as membrane substrate material because it is easy to prepare this oxide into the plate of the single crystal. The single crystal of $SrTiO_3$ is also used as the artificial diamond to have the refractive index close to that of diamond. Recently, Mitsubishi Heavy Industries, Ltd. reports that $SrTiO_3$ related oxides are used as interconnector material of SOFCs. These oxides are expected as oxide interconnector material for the future and are paid attention for the development. The conductivity of $SrTiO_3$ related oxides was measured and was tried with defect chemistry. The report of defect chemistry on $SrTiO_3$ is limited, especially on poly crystal. This thesis consists of the following chapters.

The purpose of this thesis is establishing the functional design guide of electron conductive oxide with $SrTiO_3$ related materials as the model material. In chapter 2, the formation reaction of $SrTiO_3$ from $SrCO_3$ and TiO_2 discussed thermodynamically and kinetically and reaction mechanism is evaluated. Based on revealed reaction mechanism, the trend of the formation of the single phase of $SrTiO_3$ is determined. The defect equilibrium of Nb-doped and Y-doped $SrTiO_3$ were discussed with the conductivity data and fitting model in chapter 4 and 5, respectively.

In chapter 2, the reaction rate of the formation of $SrTiO_3$ form $SrCO_3/TiO_2$ was measured and the reaction model of the formation of $SrTiO_3$ was prepared to discuss how to prevent the formation of the second phase such as Ruddlesden-Popper phases, Sr_2TiO_4 and $Sr_3Ti_2O_7$. As the problem of the preparation of $SrTiO_3$, Ruddlesden-Popper phase is formed when there are locally nonuniform in the mixure of $SrCO_3$ and TiO_2. In this study, we selected a conventional method to prepare $SrTiO_3$,

namely the solid state reaction method of $SrCO_3$ and TiO_2, to clarify the reaction mechanism thermodynamically and kinetically. The reaction rate can be measured rather easily because the weight reduction is caused by the release of CO_2 gas as the progress of the formation of $SrTiO_3$. The reaction rate constant was estimated with the measured reaction rate and the reaction model. The activation energy for the formation of $SrTiO_3$ was estimated from the relationship between the reaction temperature and reaction rate constant. From the result of thermal analysis, anatase-type TiO_2 has higher reactivity than rutile-type TiO_2 because $SrCO_3/TiO_2$(anatase) is much formation of $SrTiO_3$ at lower temperature. It is revealed that $SrCO_3/TiO_2$(anatase) is not only the formation energy is lower but also the temperature of thermodynamic reaction is lower from the result of TG-DTA and DSC. Moreover it is revealed that $SrCO_3$ and TiO_2 react without the decomposition of CO_2 (from $SrCO_3$ to SrO) because the temperature of the decomposition of CO_2 is lower than that of the formation of $SrTiO_3$ from the mixture of $SrCO_3$ and TiO_2.

From the result of the reaction rate measurement, it is revealed that the reaction rate between $TiO_2/SrCO_3$ is parabolic rate law and fit Jander model. The reaction rate and the activation energy for the formation of $SrTiO_3$ were estimated from the result of thermogravimetry with Jander reaction rate equation. The reaction rate of TiO_2(anatase)/$SrCO_3$ and those of TiO_2(rutile)/$SrCO_3$ is almost same. The activation energy for cation diffusion of TiO_2(anatase)/$SrCO_3$ is also almost same.

In chapter 3, based on the result of the previous chapter, the optimization of the preparation condition of $SrTiO_3$ single phase was tried and discussed. The atmosphere of the formation of the poly crystal of the single phase of $SrTiO_3$ is researched with the atmosphere dependent of reaction rate measurement. The optimization of preparation conditions of $SrTiO_3$ single phase was performed by changing the atmospheres. Moreover the difference of the reaction rate was also examined at the various atmospheres. In the performed atmosphere, the reaction rate under static air and pure CO_2 was fit to the Jander model. Form these results, $P(CO_2)$ is important factor to prepare the $SrTiO_3$ single phase. The activity of SrO can be controlled by the change of CO_2 partial pressure, $P(CO_2)$. Under pure CO_2 and static air, the activity of SrO is reduced and the single phase of $SrTiO_3$ is formed because $P(CO_2)$ is rather high.

From the result of previous chapter, it is revealed that the reaction from $SrCO_3/TiO_2$ to $SrTiO_3$ is limited by the A-site cation diffusion. Then, in this chapter, the reaction rate of $BaCO_3/TiO_2$ and that of $CaCO_3/TiO_2$ are to be measured. These reactions are going to be described Jander reaction model as well as the case for $SrCO_3/TiO_2$ and the reaction rate of three kinds of powder mixtures was almost the same because these reactions are formations of perovskite-type oxides from the carbonate of alkaline-earth metal and TiO_2 and are limited by A-site cation diffusion. The activation energies of three kinds of mixtures were also almost same. It is revealed that the energy barrier for the cation diffusion into prerovskite-type structure is independent on the radius of the cation.

In chapter 4, the conductivity of the poly crystal of Nb-doped $SrTiO_3$ was measured and analyzed with defect chemical model. The relationship among the carrier concentration, temperature and oxygen partial pressure are discussed. Important thermodynamic parameters, the enthalpy of the oxygen vacancy formation and the electronic mobility are estimated from the experimental data and defect model. The electron conductivity of Nb-doped $SrTiO_3$ is thermally activated like metals at all measurement regions in this study because the temperature dependence of conductivity decreases with the increase of the temperature. The electron mobility of Nb-doped $SrTiO_3$ does not depend on the concentration of the extrinsic donor. The trend of these results fit between the data of Nb-doped and reported La-doped $SrTiO_3$. Moreover, it is revealed from the electron mobility of temperature dependence that the electron conduction is controlled by the acoustic phonon scattering because the electron mobility of the temperature dependence shows almost -1.5 powers.

In chapter 5, the conductivity of the poly crystal of Y-doped $SrTiO_3$ was measured. The defect equilibrium of Y-doped $SrTiO_3$ was discussed. It is revealed that the electron mobility of Nb-doped $SrTiO_3$ does not depend on the concentration of extrinsic donor in previous chapter. On the other hand, the conductivity data of Y-doped $SrTiO_3$ cannot be fit to the defect equilibrium model of general donor-doped $SrTiO_3$. It is assumed that a portion of Y^{3+} moves to Ti-site and operates as accepter. This phenomenon is special trend on only Y-doped $SrTiO_3$ because the radius of Y^{3+} is the median value of the radius of Sr^{2+} and Ti^{4+}. The defect equilibrium model for the conductivity of Y-doped $SrTiO_3$ was set and the concentration of extrinsic accepter on Ti-site was estimated.

The temperature dependence of the electron mobility shows almost -1.5 powers and the electron conduction is controlled by the acoustic phonon scattering as well as Nb-doped $SrTiO_3$. It is assumed that electron mobility is same between Nb-doped and Y-doped $SrTiO_3$ and the concentration of extrinsic accepter of Y ion were calculated. It can be regarded that above assumption is realized because the temperature dependence of the concentration of calculated extrinsic accepter is almost constant. It can be considered that assumption of extrinsic accepter of Y ion on Sr-site is acceptable because the concentration of extrinsic accepter is rather low. Form these result, the Kröger-Vink diagram of Y-dope $SrTiO_3$ was proposed.

It is revealed that the equilibrium constant for the formation of oxygen vacancy does not depend on the doped site and dopant species and the equilibrium constant increases with increase of the concentration of extrinsic donor. It is revealed that the enthalpy of oxygen vacancy formation decrease with the increase the concentration of extrinsic donor. Therefore, it is revealed that oxygen vacancy is easier to form with the increase of concentration of extrinsic donor.

The guideline of the function design of the electron conductive ceramics by the composition control was proposed with donor-doped $SrTiO_3$ from above result.

論文審査結果の要旨

チタン酸ストロンチウム系などに代表される酸化物半導体は，高い誘電率，大きなバンドギャップ，高い耐熱性などを示すことから，次世代電子材料として高い関心を集めている。酸化物半導体では，キャリアの濃度が固溶した異価不純物イオンの濃度と，酸素量が化学量論数から僅かに変動する酸素不定比組成によって大きく変化する。然るに，チタン酸ストロンチウムの場合は，不純物相として酸化ストロンチウムを多く含む層状化合物が共存してしまうことが多く，単相を得るための条件や，異価不純物添加効果を記述する欠陥平衡関係などが未だに明確にされておらず，材料機能設計のための基礎が確立していない。

本論文は，チタン酸ストロンチウム系を主な題材として取り上げ，固相反応による合成機構とその速度論的解明，単一相形成のための合成条件決定，異価イオン固溶による電子機能制御のモデルと実験的検証などを通じ，酸化物半導体素子設計のための基盤構築を目指したものであり，全編６章からなる。

第１章は序論であり，本研究の背景，目的および構成を述べている。

第２章では，空気中で炭酸ストロンチウムと酸化チタンの固相反応によりチタン酸ストロンチウムが生成する過程を，熱重量分析，示差熱分析，走査型電子顕微鏡観察，粉末Ｘ線回折法などの標準的な実験手法を駆使することで速度論的に解明し，反応が，チタン酸ストロンチウム相の中をストロンチウムが拡散する過程で律速されることを明らかにしている。重要な成果である。

第３章では，上述固相反応を，酸素と窒素の混合ガス中，炭酸ガス中，水素－窒素混合ガス中などで行わせた場合の熱重量測定についての結果と考察を述べている。炭酸ガスが入っていない雰囲気では，チタン酸ストロンチウムと併せてストロンチウムを多く含んだ不純物相が生成してしまうことを明らかにし，その原因を熱力学的に明らかにしている。製造プロセスにおける単一相の安定な生成に関わる重要な成果である。

第４章では，ニオブを添加したチタン酸ストロンチウム焼結体の還元雰囲気での高温電子導電率の酸素分圧依存についての計測結果と考察について述べている。欠陥平衡論から予測される導電率の雰囲気依存と実測値との対比から，ニオブがチタンを置換して固溶すること，添加量に関わらず移動度が一定であること，などを明らかにしている。ニオブ添加チタン酸ストロンチウム焼結体の還元雰囲気で欠陥平衡関係を明らかにした新しい成果である。

第５章では，イットリウムを添加したチタン酸ストロンチウム焼結体についての，還元雰囲気での高温導電率の測定結果と欠陥平衡論による考察を述べている。そのなかで，イットリウムはチタン位置とストロンチウム位置の双方に置換固溶することなどが明らかされている。これは新しい知見である。

第６章は結論である。

以上要するに本論文は，高温無機材料の基礎測定手法と欠陥平衡論を駆使して，酸化物半導体機能設計の指針を展開したもので，機械システムデザイン工学とセラミックス基礎科学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。