

論文内容要旨

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学位論文の 題 目	A study of crystal-site structure and solid-solution region of langasite-type oxide crystal with four elements (4 元系ランガサイト型酸化物結晶の結晶サイト構造と固溶領域に関する研究)		

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論 文 內 容 要 旨

A langasite-type piezoelectric crystal with $A_3BC_3D_2O_{14}$ structure, especially a langasite-type crystal with four elements, has been found to be a suitable substrate for a high temperature pressure sensor in the automobile combustion chamber. The electrical resistivity of bulk crystal used as the high-temperature pressure sensor is required to be at least $10^{10} \Omega \cdot \text{cm}$ at temperatures up to 400 °C.

The crystal-site structure describes possible locations for constituent elements and metal vacancies. The presence of metal vacancies is closely related to the carrier concentration of the crystal and dominates the electrical conductivity. Hence the survey of the location of the vacancy is important. Following the Hume-Rothery rule [1] for solid solution, eight crystal-site structures were proposed for CTGS. Through the analysis of the degrees of freedom for each site in CTGS, which takes mass conservation, charge balance and chemical potential equilibrium into consideration [2], three crystal-site structures out of eight were possible to exist. The possible crystal-site structures were labeled as the V_A , V_B , and V_C model, which has metal vacancy locates at A, B and C site, respectively.

The study of the solid-solution region of the compound is important in both views of science and technology of crystal growth: 1. The solid solution range characterizes the composition shift from the stoichiometric composition of a crystal, which reveals the occupancy of a vacancy and anti-site defects. 2. A narrow solid solution range usually accompanies a highly ordered structure, as atoms are restricted to specific sites and thus a

highly homogeneous bulk crystal is expected. However, no study on solid solution range in langasite-type crystal with four elements has ever been reported.

This thesis focuses on a langasite-type crystal with four elements with composition of $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ (CTGS), including the crystal-site structure of CTGS and its solid solution range.

In langasite-type crystal with $\text{A}_3\text{BC}_3\text{D}_2\text{O}_{14}$ structure, site A is always fully occupied. Three compositional series of CTGS, Series I, II and III, were synthesized. In Series I, CaO and Ta_2O_5 are constant, while Ga_2O_3 and SiO_2 are variable, in Series II, CaO and SiO_2 are constant, while Ga_2O_3 and Ta_2O_5 are variable, in Series III, CaO and Ga_2O_3 are constant, while SiO_2 and Ta_2O_5 are variable. The conventional XRD analysis was insufficient to determine the solid solution range for CTGS as the intensities of the secondary phase reflection peaks were not strong enough to allow quantitative analysis. We therefore applied a lever rule to examine the proportions of secondary phases [3], analyzed by backscattered electron image (BEI) observations combined with EPMA analysis.

The BEI observation results in Series I to III showed that one or two phases among four secondary phases were possible to coexist with CTGS phase: $\text{Ca}_3\text{Ta}_2\text{Ga}_4\text{O}_{14}$ (CTG), CaTa_2O_6 (CT2), CaSi_2O_5 (CS2) and $\text{Ca}_3\text{Ga}_4\text{Si}_2\text{O}_{14}$ (CGS). The variation of proportions of the secondary phases associated with the bulk compositions in each serial were determined by BEI observation. We subsequently calculated the boundary compositions of the CTGS solid solution range by applying a lever rule to the proportions of the secondary phases and the CTGS by combining with the composition of the secondary phase. When the initial bulk composition yields an equilibrium assembly of a single secondary phase and the CTGS matrix, one degree of freedom is available for varying the composition of coexisting CTGS. The calculated CTGS compositions corresponding to these initial compositions were varied and form a portion of the boundary of the CTGS solid solution. In contrast, when the initial compositions produce two secondary phases and CTGS matrix, the corresponding compositions of CTGS converge due to the absence of any degrees of freedom. This analysis takes the Gibbs phase rule into consideration. Using the results from Series I to III, the CTGS solid-solution region was eventually determined to be, $\text{CaO-Ta}_2\text{O}_5$: 15.9-16.6 mol%; $\text{CaO-Ga}_2\text{O}_3$: 49.6-49.9 mol%; and CaO-2SiO_2 : 33.4-34.3 mol%. The solid solution range of CTGS occupies a Ta_2O_5 -poor, slightly Ga_2O_3 -poor and slightly SiO_2 -rich region, which supports the V_B model of crystal-site structure: Si enters site C to compensate the charge imbalance caused by vacancy in site B. CTGS has a narrow solid solution range when compared with langasite-type crystal with three elements, which suggested CTGS to be more promising in the application of high temperature pressure sensors. The procedure used in this study is novel

and should be applicable to the assessment of the solid solution ranges for other complex oxide materials.

References:

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[2] Satoshi Uda, “*Chapter 4: Stoichiometry of Oxide Crystals*”, *Handbook of Crystal Growth*, Vol. IA, Fundamentals: Thermodynamics and Kinetics, and Transport and Stability, edited by T. Nishinaga,. Elsevier B.V., 175-214 (2014)

[3] Hengyu Zhao, Satoshi Uda, Kensaku Maeda, Jun Nozawa, Haruhiko Koizumi, Kozo Fujiwara, The Solid-Solution Region for the Langasite-type $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ Crystal as Determined by a Lever Rule, *J. Cryst. Growth*. **415**, 111 (2015).

論文審査の結果の要旨

本学位論文は、“A study of crystal-site structure and solid-solution range of langasite-type oxide crystal with four elements”「4 元系ランガサイト型酸化物結晶の結晶サイト構造と固溶領域に関する研究」と題し、全 5 章から構成されている。

第 1 章では、船舶や自動車のエンジン内に装着する燃焼圧センサーの基板材料として相転移のないランガサイト型の結晶が有望であることを述べた。特に、高温で高抵抗を示すには正孔を放出する金属空孔の少ない 4 元系のランガサイト型結晶が有利であることを示した。

第 2 章では、4 元系のランガサイト型結晶として $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ (CTGS) を研究対象に選び、 $\text{A}_3\text{BC}_3\text{D}_2\text{O}_{14}$ のランガサイト構造を持つ同結晶のサイト構造を決定した。まず、古典的な Hume-Rothery 則を利用して 8 つのサイト構造の候補を導いた。次に、各サイトに対して構成要素の数とこれらに課せられる束縛条件から自由度を検討するという新しい手法により、候補をさらに 2 つまで絞った。

第 3 章では、CTGS の固溶領域を「てこの法則」を利用して求めた。「てこの法則」を利用した新しい方法では境界組成から十分に離れた組成を出発組成として使用することができるので異相の出現が明確になり正確な境界組成を求めることができる。また、母相と共存する異相の数は、Gibbs の相律から見事に説明され、自由度が 1 ある出発組成領域を選ぶことにより固溶領域が十分に描けることを示した。画期的な方法である。求めた固溶領域から、第 2 章で求めた 2 つの候補の中から 1 つを CTGS のサイト構造として決定した。

第 4 章では、CTGS が調和融解物質であることを高温示差熱分析から明らかにし、CTGS 単結晶育成時に出現する異相が液体の不混和現象に起因することを異相の形状・組成および結晶分化過程から説明した。

第 5 章では、本研究のまとめを行い、第 3 章で示した「てこの法則」による固溶体領域組成の決定法が一般に多成分物質に適用されることを述べた。

以上の研究成果は、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、趙 衡煜提出の博士論文は、博士（理学）の学位論文として合格と認める。