論文 / 著書情報
Article / Book Information

題目(和文)	マイエナイト中に包接された電子と水素化物イオンの定量とマイエナイト電子化物・金属複合体の熱電子放出特性
Title(English)	Quantitative Determination of Electron and Hydride Ion Incorporated in Mayenite and Thermionic Electron Emission Properties of Mayenite Electride-Metal Composites
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	材料物理科学　専攻	申請学位（専攻分野）： Academic Degree Requested	博士（工学） Doctor of
学籍番号： Student ID Number		指導教員（主）： Academic Advisor(main)	林　克郎
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要旨（英文 800 語程度）
Thesis Summary (approx.800 English Words)

This doctoral thesis focuses on studies of mayenite ($12CaO \cdot 7Al_2O_3$, C12A7) incorporating electron and/or hydride (H^-) ion. C12A7 has positively-charged cage structure and can incorporate various anions. Concentration determinations of chemical species incorporated in C12A7 cages are important in discussions of properties of C12A7. In this thesis, an iodometric titration and extended volumetric method have been studied for developments of chemical determination methods for electron and/or hydride ion in C12A7 cages. Although electron-doped C12A7 (C12A7 electride) has reasonable thermionic emission properties due to the low work function comparable to alkali metals, it usually does not form an ohmic contact with metals owing to its intrinsic low work function and surface degradation. To solve these problem, a composite consisting of C12A7 electride and metallic titanium was synthesized and its thermionic electron emission properties were measured.

Chapter 1 introduces mayenite and conventional thermionic cathodes, and describes objects of the studies in this doctoral thesis.

In chapter 2, an iodometric titration method has been applied to determination of electron encaged in C12A7 cages. C12A7 electride samples were prepared by a thermal reduction process, which the single crystalline C12A7 is annealed with titanium pellets in an evacuated silica glass capsule. In this method, powdered C12A7 electride sample is dissolved in an iodine solution containing HCl. The electrochemical potential change was measured during dissolution of C12A7 electride in an iodine solution. The initial potential of this solution was around 0.62 V (vs. NHE). However, the potential dropped to around 0 V (vs. NHE) after dissolution of powdered C12A7 electride in the solution. The electrochemical potential measurement indicates that electrons released from cages reduce preferentially iodine molecules than protons in the iodine solution. Electron concentrations determined by this titration were compared with other determination methods such as thermogravimetric analysis, and optical reflectance. Furthermore, the electron concentration value for the metal-insulator transition was re-evaluated from the result of conductivity measurement and electron concentrations determined by this iodometric method. Compared to other method for concentration determination of

electron in C12A7 cages, this method has advantages of accuracy, simple process and small amount requirement of sample.

Chapter 3 has addressed developing of a volumetric method combined with deuterium-labeling and mass spectrometry for simultaneous determination of H^- ion and electron in C12A7 cages. C12A7 samples incorporating with H^- ion and electron were prepared by a thermal process that C12A7 is annealed with CaH_2 powder in an evacuated silica glass tubes. For deuterium labeling, in the process of the extended volumetric method, sample is dissolved to DCl-D_2O in an Einhorn fermentation tube. Evolved gas is collected and its volume is measured. Then, sample gas is injected to a vacuum chamber equipped with a quadrupole mass spectrometer, and deuterium-labeled species are distinguished by mass-to-charge ratios (m/e). When C12A7 incorporated with both H^- ion and electron was dissolved in DCl-D_2O, most of each chemical species are labeled to HD (m/e=3) and D_2 (m/e=4), respectively. From the result of mass spectrometry, ratios of chemical species in sample gas are obtained. Then, each concentration of H^- ion and electron are calculated from volume of collected gases and ratios of spices. Results from this deuterium-labeled volumetric analysis combined with mass spectrometry provided concentration-change behaviors of incorporated chemical species over the annealing time. Obtained incorporation behaviors are explained by differences of diffusion rates and thermodynamic stabilities of chemical species. This extended volumetric method enables us to distinguish and determine simultaneously H^- ion and electron in C12A7 cages.

A composite consisting of C12A7 electride and metallic titanium was synthesized by spark plasma sintering (SPS) technique in chapter 4. For preparation of C12A7 electride, dense C12A7 pellets were annealed with titanium shots in an evacuated silica glass tube. After the thermal treatment, the reacted surface layers were removed. Obtained pellets of C12A7 electride was ground to powder. Powdered C12A7 electride and metallic titanium were uniformly mixed by using an alumina mortar in air, and then filled in a carbon die. When a mixture of C12A7 electride and titanium was sintered at 800 °C for 5 minutes under 112 MPa, the composite specimen was obtained. However, in composites sintered at above 900 °C, decomposition of C12A7 electride phase was observed by X-ray diffraction. Thermionic electron emission properties of the specimen were measured in a vacuum condition of ~1×10^{-5} Pa. This composite cathode exhibits reasonable emission densities below 700 °C. Although this composite exhibits thermionic electron emission properties comparable to conventional thermionic cathode below 700 °C, heating at 1000 °C suppress emission densities due to decomposition of C12A7 electride. From measurement results, the work function was evaluated. The specimen exhibits ohmic contact with graphite and metallic materials. This ohmic contact is inherited from metallic titanium.

In chapter 5, the studies included in this doctoral thesis are generally summarized.