論　文　要　旨

Thesis Abstract

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主論文題名　（Title）

High-Pressure Synthesis and Characterization of High-Entropy Metal Disulfides with Pyrite-type Structure

内容の要旨(Abstract)

High-entropy materials (HEMs) attract great attention and show superior physical properties compared to conventional materials. They are composed of several elements in equimolar composition with high-configurational entropy forming a solid solution, for example, metal mono-oxide, (Mg, Co, Ni, Cu, Zn)O. In this compound, three types of basic metal oxides are incorporated into one major rock salt-type structure under high-temperature conditions, then followed by the quenching process to keep the high-temperature phase at room temperature, the so-called "entropy-stabilized phase." It will be decomposed into a mixture of oxides if annealed at a lower temperature, suggesting a "metastable phase." This concept inspired the author of this thesis to find another HEMs as well as the crystal structure and physical properties. A few high-entropy metal sulfides (HES) were reported as highly promising electrocatalysts in oxygen evolution reactions and as high-performance Li-ion battery electrodes. These materials have low crystallinity and, are partially amorphous and were synthesized under atmospheric conditions at low temperatures. From the study literatures, there is no report on the structural analysis and physical properties of HES.

Pyrites (MS_2) are well known to have the simplest crystal structure among the transition metal disulfides. They belong to a cubic system with space group Pa that shows diverse transport and magnetic properties owing to 3*d* orbital splitting configurations. Multiple elements in the cation sites are expected to show the remarkable physical properties of pyrites. It is also important to comprehend the structural characteristic changes between high-entropy compounds and the parent compounds from the local electronic structure analysis. I studied my project to elucidate the high-entropy effects in high-entropy metal disulfides (HEMD). There are three objectives of this study. The first is to explore a new HEMD with a pyrite structure. The second is to reveal the term "high entropy" by investigating its crystal structure, transport and magnetic properties. The last is to investigate the effect of high entropy in the local electronic structure.

To achieve the goals, the HEMD samples were synthesized using the high-pressure high-temperature (HPHT) method to keep the sulfur's stoichiometry and enable it to obtain a metastable phase at high temperatures. The structural characteristics were analyzed using X-ray diffraction measurement, while magnetic and electric properties were investigated using the Magnetic and Physical Properties Measurement System, respectively. The local electronic structure of HEMD and the simple pyrites were studied using X-ray absorption spectroscopy (XAS) analysis with charge transfer multiplet cluster model calculation.

From the structural analysis, equimolar multi-metal disulfides of (Fe, Co, Ni, Cu)S_2 and (Fe, Co, Ni, Cu, Ru)S_2 crystallized into pyrite structures using HPHT method by high-entropy stabilized effects. The lattice parameters and bond distances obey the averaged ionic size. Both (Fe, Co, Ni, Cu)S_2 and (Fe, Co, Ni, Cu, Ru)S_2 show a metallic character and ferrimagnetic ordering with T_C = 130 K. The fitting of a Curie-Weiss law to the inverse magnetic susceptibility of (Fe, Co, Ni, Cu)S_2 obtained a constant Weiss θ_p = ─124. 20 K with μ_{eff} = 1.50 μB that indicates strong antiparallel

interactions although some of the parent compounds are semiconducting and non-magnetic suggesting the integration of physical properties the so-called cocktail effect. Furthermore, HEMD samples were decomposed into a mixture of NiAs-type and pyrite-type structures under ambient pressure at an annealing temperature of 400 ˚C, confirming the metastable phase.

The Fe, Co, and *L*-edge XAS suggest the divalent metal states in both (Fe, Co, Ni, Cu)S_2 and its parent compounds. Unexpectedly, the Cu *L*-edge XAS of HEMD and CuS_2 suggests the combination of monovalent and trivalent copper states. The hybridization strength ($pd\sigma$) of (Fe, Co, Ni, Cu)S_2 is weaker in Fe 3*d*-S 3*p* and Co 3*d*-S 3*p*and stronger in Ni 3*d*-S 3*p* and Cu 3*d*-S 3*p*corresponding to structural distortion. A negative charge transfer energy (Δ) of pyrite compounds corresponds to a *p*-*p* lowest energy excitation in the extended Zaanen-Sawatsky-Allen phase diagram. An exception for Ni *L*-edge XAS, the transition of $-\Delta$ to $+\Delta$ in Ni *L*-edge XAS of parent and HEMD reflects the transition physical properties of insulating NiS2 and metallic HEMD.

In conclusion, HEMD of (Fe, Co, Ni, Cu)S_2 and (Fe, Co, Ni, Cu, Ru)S_2 with a pyrite structure have been successfully obtained using the high-pressure and high-temperature method by the high-entropy stabilized effect. The crystal structure of (Fe, Co, Ni, Cu)S_2 was refined by the single crystal X-ray diffraction, providing the averaged ionic radius of the parent compounds. It shows metallic character and ferrimagnetic ordering Tc = 130 K, probably due to the cocktail effect. The local structure of the specific metal in HEMD of (Fe, Co, Ni, Cu)S_2 is different from the parent compounds, suggesting the lattice distortion effect in HEMD. These findings contribute to material science and physics in exploring the structural analysis and transport and magnetic properties of HEMD by employing HPHT method. The effects of high entropy in HEMD can be revealed both in the macroscopic phase and structural analysis and microscopic local electronic structure analysis.

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