学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（理学）　氏名　シーアイ　サティシュ

学 位 論 文 題 名

High Pressure Synthesis and Characterization of Non-Oxide Superconductors
（非酸化物超伝導体の高圧合成と特性評価）

Non-oxide solid materials have attracted considerable attention owing to their unique magnetic and superconducting properties. Non-oxide materials are relatively stable against chemical attack, and the corresponding superconducting critical current is usually very high. These compounds have therefore been used in many practical and scientific applications. However, the synthesis of some of them by employing conventional methods is difficult. We expected that a high-pressure and high-temperature technique would be beneficial in the synthesis of these compounds and in further exploring new-composition non-oxide materials with superior properties.

My focus in this study was on the synthesis of a high-quality superconducting non-oxide compound and in the detailed study of its crystal structure, superconducting nature, and magnetic and thermal properties. To synthesize high-quality materials, I used a high-pressure and high-temperature method that involved quenching the sample to room temperature before releasing an applied pressure of typically 6—17 GPa. To characterize the materials, high-quality samples were analyzed by synchrotron X-ray diffraction and neutron diffraction, and magnetic, electrical, and thermal properties were measured. In this study, I focused on three series of materials, namely, transition-metal carbide, BiS_2 layered chalcogenide, and Fe-based silicide.

The cubic δ-MoC phase in the transition-metal carbide was selected to be studied because the carbon stoichiometric phase has never been synthesized. A theoretical study predicted that in the case of stoichiometric MoC, if it is synthesized, superconductivity will appear at a critical temperature that is considerably higher than the critical temperatures that have thus far been achieved (14.7 K was claimed to be the highest, although it was not experimentally proven). Under the high-pressure and high-temperature conditions, the cubic δ-$MoC_{0.681}$ and δ-$MoC_{0.746}$ phases were finally synthesized by heating at 6 GPa and 17 GPa, respectively. The stoichiometric MoC was unfortunately synthesized under these conditions. The characterization of the material indicated that carbon vacancies were formed in the host cubic structure and that the vacancies were highly robust even when the material was prepared from stoichiometric ratios of C and Mo. However, a thermodynamically stable structure with ordered vacancies did not account for the robust features; rather, the theoretically predicted inherent phonon instability at the stoichiometric composition may be the reason for the robust vacancies. In addition, the superconducting properties were intensively studied using a weak coupling model. The critical temperature of 14.3 K was evidenced to reflect the bulk nature of δ-$MoC_{0.746}$.

A new type of layered-structure material with bismuth and sulfur was claimed to be a superconductor, and it had a great impact on research on new superconducting materials. However, the detailed properties of the material and the cause for the superconductivity were not well established. In this study, the BiS_2 layered $Bi_4O_4S_3$ and $LaOBiS_2$ phases were successfully synthesized by the high-pressure and the high temperature technique, and the crystal structure and the superconductivity were investigated in detail. The results clearly indicated that the superconductivity does not truly reflect the bulk nature of the BiS_2 layered phases, regardless of the manner in which the compounds were synthesized. This conclusion contradicted the results of ongoing studies on these compounds.

Recently, Fe-based superconductors have attracted considerable attention, and many compounds in this series have been extensively studied. All the compounds are highly toxic in nature because the common As-containing unit (Fe_2As_2 layer) is essential for the superconductivity. Therefore, in this study, non-toxic or less-toxic superconductors were studied to enhance superconductivity further. The exploration of highly abundant silicon materials containing Fe was targeted: heavy fermion materials $Ln_2Fe_3Si_5$ (Ln = rare earth element) were prepared by the high-pressure synthesis method, and the chemical substitution effect was investigated. Note that thus far, few studies have focused on these compounds because of difficulties in their synthesis by conventional methods. To my knowledge, systematic chemical substitution has been achieved only little. In this study, successful synthesis of $Yb_2Fe_3Si_5$ and up to 40 at% substitution of Ca for Yb were achieved using the high-pressure synthesis technique, and the resultant systematic changes in the magnetic and electrical properties were analyzed in detail.

In summary, superconductivity and magnetism have been developed toward useful applications; however, many aspects of superconductivity and varieties of magnetism remain unclear, and therefore, there is great scope for future research on them. In the present study, I focused on three series of non-oxide superconducting materials and the potential for further development toward practically useful and scientifically significant superconductors.