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Doping Strategies with Selenium to Increase Electrical Conductivity and Thermoelectric Performance of Copper Iodide

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Description

Copper Iodide (CuI) emerges as a material in the realm of thermoelectric technology, particularly for applications requiring ambient to low-temperature energy. This semiconductor exhibits a wide bandgap and is categorized as a p-type material, making it suitable for thermoelectric generators designed to convert heat into electricity using the Seebeck effect. Its unique properties include high optical transparency and effective hole transport, which are advantageous for applications in transparent electronics and energy harvesting devices. CuI exists in three main allotropes depending on temperature: Zincblende γ-CuI (below 350℃), wurtzite β-CuI (350°C - 380℃), and rocksalt α-CuI (above 380℃). These phases exhibit distinct crystal structures affecting their thermoelectric properties, especially in terms of electrical conductivity and thermal stability. The valence band of CuI primarily consists of Cu 3d and I 5p orbitals, while the conduction band is dominated by Cu 4s states. Vacancies such as copper vacancies and other defects like iodine vacancies, antisite copper and copper interstitial play critical roles in modulating its electronic properties, particularly the carrier density and mobility required for efficient thermoelectric conversion.

Electrical conductivity

Despite its characteristics, CuI faces challenges in achieving high electrical conductivity compared to other transparent conductive materials like Indium Tin Oxide (ITO). This limitation restricts its widespread commercial use in transparent electronics and thermoelectric devices. To overcome this hurdle, researchers are exploring both intrinsic and extrinsic doping strategies to enhance its electrical properties. Intrinsic doping involves varying the stoichiometry of CuI through growth conditions or post-fabrication treatments. These methods aim to optimize the formation of defects such as VCu and VI, which act as charge carriers in the material. However, intrinsic doping alone may not sufficiently increase σ to competitive levels for practical applications. Extrinsic doping introduces foreign elements into the CuI lattice to enhance its electrical conductivity. Various dopants, including alkali metals (e.g., Cs), metal ions (e.g., Al, Ga, Sn, Ag), rare-earth elements and chalcogens (e.g., S, Se, Te), have been investigated for their ability to improve σ. Among these, chalcogens are particularly due to their low formation energy and compatibility with the CuI structure. Selenium doping in CuI has garnered attention for its potential to significantly increase Hole density (H) and thereby improve σ. Experimental studies, such as those conducted by and theoretical predictions by have highlighted Se as an effective dopant capable of modifying the defect chemistry within CuI. Reported a substantial increase in H due to Se doping, indicating its potential to enhance the material's electrical properties for practical applications [1-5].

Thermoelectric performance

Despite the progress in understanding the electrical and optical effects of Se doping, its impact on the thermoelectric properties of CuI remains underexplored. Thermoelectric performance relies on optimizing the dimensionless figure-of-merit (ZT), which depends on α (Seebeck coefficient), σ (electrical conductivity), and κ (thermal conductivity). Enhancing σ through Se doping could potentially boost the power factor (α^2σ), crucial for improving ZT and overall thermoelectric efficiency. Future research should focus on systematically investigating the thermoelectric properties of Se-doped CuI, including comprehensive studies on α, σ and κ under varying doping levels and crystal phases. Understanding the mechanisms governing charge transport and thermal properties in Se-doped CuI will facilitate the design of optimized thermoelectric materials for ambient to low-temperature applications. Moreover, integrating Se-doped CuI into practical thermoelectric devices could pave the way for sustainable energy harvesting solutions that capitalize on ambient heat sources [6-10]. While CuI shows promise as a transparent and efficient thermoelectric material, ongoing research into doping strategies, particularly with chalcogens like Se, holds significant potential for enhancing its electrical conductivity and expanding its applications in renewable energy technologies. Efforts in this direction are crucial for realizing CuI's role in sustainable energy generation and addressing global energy challenges.

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