Development of stable Cu-based argyrodites for highly efficient energy conversion

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Cu-based materials with an argyrodite structure have recently attracted widespread attention due to their promising thermoelectric (TE) performance and ultralow lattice thermal conductivity [1,2]. However, there is very little information on the doping strategies in argyrodites that can effectively control the carrier concentration for optimized electronic transport. In addition, their practical application is frequently impeded by significant stability challenges, predominantly linked to undesirable phase transitions occurring at typical operating temperatures. This underlines again the importance of the development of new doping strategies that may effectively control the position of the chemical potential toward high thermoelectric performance.

Our recent DFT investigation of the density of electronic states in Cu-based argyrodites shows that cations have a dominant role in determining the electronic structure. Consequently, in this research, we focused on the stability of the material by the investigation of the Zn substitution of Cu atoms exploring doping mechanisms. Particularly, we prepared series of Zn-substituted copper-based argyrodites with the chemical compositions $Cu_{8-2x}Zn_xSiS_3Se_3$ also to check the repeatability of transport properties.

First, the careful analysis of phase content and the crystal structure of the nominal sample $Cu_8SiS_3Se_3$ was investigated using TXRD data in temperature range of 298-873 K. TXRD indicated that the undoped material exhibits structural decomposition at high temperatures. To address this limitation, Zn doping was employed with the objective of stabilizing the phase at elevated temperatures and improving the repeatability of the thermoelectric properties The chemical and microstructural analysis of the sintered samples was performed using the SEM/EDS analyses which indicates that the components in the main phase are distributed homogenously, with a trace amount of binary copper-based secondary phase [2]. The scanning thermoelectric microprobe (SThM) technique was additionally used to measure the spatial distribution of the Seebeck coefficient on the sample surface and how the precipitates impact the characteristics of the argyrodites. It was found that Zn doping in the $Cu_{8-2x}Zn_xSiS_3Se_3$ samples lowers electrical conductivity but increases the Seebeck coefficient and most importantly leads to the more repeatable TE properties. This study shows that Zn can be a promising dopant to stabilize argyrodite materials for TE energy conversion.

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