X-ray Characterization of Copper Integration into $Cu_{2x}Hg_{2-x}GeTe_4$ for Thermoelectric Applications

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Abstract

$Cu_2HgGeTe_4$ is a promising thermoelectric material due to its anomalously low lattice thermal conductivity and simultaneously high hole mobility. Phase boundary mapping of the $Cu_2HgGeTe_4$ system revealed that there exists a full solid solution alloy between $Cu_2HgGeTe_4$ and Hg_2GeTe_4. Along this alloy line, the extent of Cu integration (x in $Cu_{2x}Hg_{2-x}GeTe_4$) can be used to control the carrier concentration, which is an important step towards further improving the thermoelectric performance of these materials. In this work, we use variable-temperature X-ray diffraction and resonant X-ray diffraction to resolve the atomic occupancies in the $Cu_{2x}Hg_{2-x}GeTe_4$ structure as we move from Hg_2GeTe_4 ($x = 0$) to $Cu_2HgGeTe_4$ ($x = 1$). We find that Cu exchanges in 2:1 ratio with Hg by simultaneously annihilating a vacancy and substituting for a Hg atom on the $z = ¼$ or $z = ¾$ planes. Furthermore, we demonstrate that the ordering of vacancies, which is present in the ternary material, is maintained as we move along the alloy line from the ternary to the quaternary. An increase in the presence of Cu_{Hg} and Hg_{Cu} anti-site defects is also observed as the extent of Cu integration approaches the quaternary. This work provides an improved understanding of how Cu integrates into the $Cu_{2x}Hg_{2-x}GeTe_4$ structure and how this integration can be used to control the carrier density.