Elucidating the Local Structure and the Mechanism for Hole Conductivity in Cu-As-Te Thermoelectric Glasses by XANES spectroscopy and Quantum Simulations

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Abstract

Thermoelectricity (TE), efficiently converting wasted heat into electricity, can be considered a viable route to solid-state cooling and power generation. The main paradigm in the present researches on TE is focused on the "phonon glass electron crystal" model [1], which proposes an offbeat combination of glass-like low-thermal conductivity (k) and crystal-like high-electrical conductivity (σ). More recently, semi-conducting chalcogenide glasses, which are known to inherently possess high Seebeck coefficient (S) and low k, are looked upon as potential TE materials [2]. The main limiting factor in these glasses is their mediocre σ. Recently it was found that doping glasses with Cu leads to a huge enhancement in σ [3]. 20% Cu-doping in arsenic telluride shows an increase in σ by almost 5 orders of magnitude (_˜ 6 S/m) compared to the pristine arsenic telluride glass (_˜ 10-4 S/m), without dismantling its amorphous structure and its characteristic high S and low k. These Cu-As-Te glasses have been analyzed by X-ray Absorption Spectroscopy, both near-edge (XANES) and in the extended region (EXAFS), in order to shed light on the mechanism for the huge increase of conductivity that was found with Cu doping. Experimental data have been modeled by means of multiple-scattering calculations. Our model suggests that the experimental results can be interpreted in terms of a small charge-transfer from Te to Cu, leading to an unexpected positive valence for Te. On the basis of these findings, a global picture explaining

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the enhancement of electrical conductivity with Cu doping has been proposed: electrical conductivity is determined by the holes created in non-bonding Te 5p orbitals (lone pair) by Cu acceptors [4]. The critical parameter to increase σ is the number of Cu-Te bonds that are formed and not simply the number of Cu atoms.
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