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RAPID COMMUNICATION

Giant enhancement in thermoelectric performance of copper selenide by incorporation of different nanoscale dimensional defect features

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Abstract
We report a simple experimental strategy for enhancing the figure-of-merit (ZT) of thermoelectric materials by introducing different kinds of defect features, including nano-porosity, in a range of nano to meso-scale dimensions, employing spark plasma assisted (SPS) reaction sintering of mechanically alloyed nanopowders. This strategy has been experimentally demonstrated in a well known thermoelectric compound, Cu_2Se, which is shown to yield a high ZT of 2.1 at 973 K, which is among the highest reported value for this material and shows ~40% increase over its bulk melt-processed counterpart. The main contribution to the enhanced ZT, despite moderate values of power factor, primarily originates from a very small value of thermal conductivity of 0.34 W m^{-1} K^{-1}. This low thermal conductivity owes its origin primarily to the enhanced low-to-high wavelength phonon scattering by different kinds of defects, in a wide spectrum of nano to meso-scale dimensions, involving microstructural defects generated during high-energy ball milling, abundant nanocrystalline grain boundaries due to very low crystallite size, and more importantly the nano-to-meso scale residual porosity created due to SPS at optimized process parameters. The role of SPS in enhancing the ZT has been discussed and this strategy can also be applied to other thermoelectric materials.

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Introduction

Thermoelectric devices permit a direct conversion of heat into electrical energy and *vice-versa*. Owing to its green technology, vigorous efforts are being made to realize thermoelectric based waste heat recovery devices for energy generation. However, currently the main impediment in this direction is their limited conversion efficiency [1]. The efficiency of power conversion of a thermoelectric device depends mainly on the material's thermoelectric figure-of-merit (ZT), and the commercial realization of efficient thermoelectric devices [2] for power generation is currently hampered by the lack of thermoelectric materials with high ZT [3-7].

In the recent past, Cu_2Se and its derivative compounds have been a subject of keen interest for development of thermoelectric materials with high ZT [8–14]. The earliest report on thermoelectric bulk Cu_2Se is by Xing-Xing et al. [8] who reported a peak ZT of 0.38 at 750 °C. Later, Liu et al. [9] reported the thermoelectric behavior of Cu_2Se and they inferred a '*liquid-like*' behavior of Cu ions around the crystalline sub-lattice of Se, resulted in an intrinsically low lattice thermal conductivity culminating in an enhanced ZT of 1.5 at 1000 K in bulk Cu_2Se synthesized employing vacuum melting followed by consolidation using spark plasma sintering (SPS). Recently, ZT of 1.6 at 973 K has been achieved [10] in Cu_2Se synthesized by ball milling followed by hot pressing. After the initial report of Liu et al. [9] on Cu_2Se as a high ZT thermoelectric material, several other Cu_2Se based materials with relatively high ZT have been reported. Ballikaya et al. [12] have reported a ZT ~1 at 900 K in Ag doped Cu_2Se synthesized by melting, annealing followed by SPS. Although, recently a high ZT of 2.3 has been reported for iodine doped Cu_2Se [13], but it is at a much lower temperature (~400 K), where a second order monoclinic to cubic phase transition takes place in this material, which results in favorably altering the thermal and electrical transport parameters, leading to a high ZT.

Cu_2Se based TE devices have been a subject of discussion [15,16] due to several constraints, including Se evaporation at high temperatures and more importantly the electro-migration of Cu. However, the focus of the present study is only to demonstrate a substantial enhancement in ZT by incorporation of different nano to meso-scale dimensional defect features, including residual porosity. Cu_2Se has been selected for experimental proof-of-concept study of our proposed strategy as it is a well established binary thermoelectric compound.

The dimensionless ZT [17] is defined as $ZT = S^2\sigma T/(\kappa_e + \kappa_L)$, where S, σ, and T are the Seebeck coefficient, electrical conductivity, and absolute temperature, respectively and κ_e and κ_L are electronic and lattice contribution to the thermal conductivity. Reducing κ_L has been an important strategy to improve ZT [18] as κ_e is coupled to σ through the Wiedmann-Franz law. Since both σ and κ are intimately related to the microstructure of the material, one way to improve ZT is *via* nanostructuring [19-23], which allows improvement in the power factor ($S^2\sigma$) and a simultaneous reduction in κ_L leading to an enhancement in ZT. This strategy has been earlier successfully demonstrated on several nanostructured thermoelectric alloys and compounds [20,24-30] and the enhancement in ZT in some cases has been reported to be as high as 3.5 [24] to 6 [30] fold, over their bulk counterparts.

Kanatzidis's group has recently proposed a panoscopic approach [28,31,32] for the enhancement of ZT in thermoelectric materials by introduction of different dimensional atomic (point defects), nano (line and interfacial defects) and meso-scale (nano-precipitate grain boundaries) features, which contribute to the scattering in a large spectrum of short-to-long wavelength heat-carrying phonons. It is well known that in thermoelectrics most of the heat is transported by mid-to-long wavelength phonons [3,17,33,34], thus the meso-scale defect features are expected to play a dominant role in controlling the thermal conductivity. Employing this all length-scale hierarchical structuring approach, Kanatzidis et al. [32] have reported a high ZT ~2.3 in PbTe with 4 mol% SrTe nanoprecipitates. On the other hand, there are several theoretical [28,35-38] and experimental [39-41] studies in the literature, reporting a considerable enhancement in ZT due to nanoporosity, owing to the reduction in thermal conductivity. These results show that the degradation of electrical conductivity due to the inclusion of nanopores is more than compensated by a large reduction in the phonon thermal conductivity and an increase in Seebeck coefficient, resulting in a significantly enhanced ZT. In the present study, we have employed a similar panoscopic all length-scale hierarchical structuring approach for enhancing ZT in Cu_2Se, except that we have introduced controlled nanoporosity as the nano to meso-scale defect feature in the nanostructured material matrix, and these nanoscale pores act as additional scattering centers for heat-carrying phonons. This approach for obvious reasons is simple, as the size and distribution of nano to meso-scale porosity in the thermoelectric material matrix can be engineered experimentally by optimizing the process parameters of SPS [40,42] and the volume fraction of process control agent added during high energy ball milling (HEBM) [27,43], to match the wavelength range of the phonons to be scattered. Further, apart from residual porosity, the other nano-scale defect features like, dislocations and nanoscale grain boundaries in Cu_2Se nanostructured matrix are introduced during its powder metallurgy processing [19,43,44] employing high energy ball milling followed by SPS at optimized process parameters. SPS, apart from retaining these nanoscale defect features [27,45] also aids in the creation of a distributed nano to meso-scale residual porosity [40,42] in the Cu_2Se nanostructured matrix. The overall effect of these nano to meso-scale defect features leads to an abundant scattering of low-to-high wavelength phonons resulting in a very small value of thermal conductivity ~0.34 W m^{-1} K^{-1} (at 973 K) thereby in turn enhancing the ZT.

In the present studies, we describe a simple way of nanostructuring Cu_2Se, which allows realization of a ZT ~2.1 at 973 K, which is higher by ~30–40% than the highest reported for this material [9,10]. This value of ZT, which is ~40% higher than its melt-processed bulk counterpart, is among the highest reported for thermoelectric materials and is primarily due to an exceptional reduction in thermal conductivity (~65%) on nanostructuring, which introduces various types of defects, in a wide spectrum of nano to meso-scale dimensions and these can scatter low-to-high wavelength heat-carrying phonons. Our approach involves controlled HEBM to produce Cu_2Se nanopowders followed by their consolidation employing SPS at optimized process parameters. To compare our results with the earlier reports in the literature [9,10], bulk Cu_2Se samples were also synthesized