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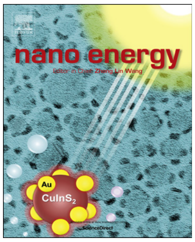

RAPID COMMUNICATION

Controlled growth of bismuth antimony telluride $Bi_xSb_{2-x}Te_3$ nanoplatelets and their bulk thermoelectric nanocomposites

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Abstract

Solution synthesis as a scalable bottom-up growth method shows considerable advantages for designing novel nanostructured bulk composites with augmented thermoelectric performance. Tuning the composition of synthesized materials in the solution process is important for adjusting the carrier type and concentration. Here, we report a modified solvothermal synthesis method for the controlled growth of $Bi_xSb_{2-x}Te_3$ nanoplatelets, which can be sintered into nanostructured bulk pellets by using the spark plasma sintering process. We further demonstrate the tuning of the stoichiometric composition in ternary $Bi_xSb_{2-x}Te_3$ nanoplatelets with high crystallinity and homogenous phase purity, which is proved by X-ray diffraction and Raman spectroscopy. The composition dependence of the thermoelectric performance of *p*-type $Bi_xSb_{2-x}Te_3$ pellets is also systemically studied. The optimized nanostructured bulk $Bi_{0.5}Sb_{1.5}Te_3$ sample is found to have ZT ~0.51 at 375 K, which shows great potential for further improving the thermoelectric performance by this solution synthesis method. Considering the progress in *n*-type Bi-Te-Se composites, our results advocate the promise of bismuth/antimony chalcogenide nanocomposites towards practical thermoelectric applications.

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Introduction

Thermoelectric materials are widely used to harvest waste heat to produce useful electricity based on the Seebeck effect, or to produce heating or cooling when a current runs through two complementary junctions—the so-called Peltier effect. To make the practical applications of thermoelectric materials viable, it is crucial to improve the efficiency of thermoelectric materials by enhancing the materials' dimensionless figure of merit (ZT) [1], where $ZT=(S^2\sigma/\kappa)T=(PF/\kappa)T$, and S, σ, κ, T, PF is the thermoelectric power (Seebeck coefficient), electrical conductivity, thermal conductivity, absolute temperature, power factor, respectively. Thus, an ideal thermoelectric material should have large power factor and low thermal conductivity. There have been consecutive efforts in achieving high-ZT thermoelectric materials since 1940s, but the highest ZT in thermoelectric materials had been remained around 1 lasting to the end of last century [2]. The challenge in improving the ZT value is that the parameters S, σ, κ in a material are mutually constrained, for example, increasing S usually leads to a simultaneous decreasing of σ, and increasing the σ leads to the increase of κ at the same time because of the Wiedemann–Franz law [3]. In 1993, Hicks and Dresselhaus predicted that the ZT value could be greatly enhanced in the quantum-well [4] and quantum-wire [5] structures due to enhanced thermoelectric power and the reduced lattice thermal conductivity, which inspires the nanostructuring approach for high-ZT thermoelectric materials. Nanostructuring engineering in bulk alloys has been proven to be an effective strategy to enhance the thermoelectric performance by reducing the lattice thermal conductivity [6-9]. Moreover, band structure engineering strategies have also been proposed to increase the power factor for high thermoelectric performance [10,11].

Along with the emergence of various new approaches and new materials in the past decade, the ZT values of the bulk materials for high-temperature applications have been greatly improved, such as multiple-filled skutterudites $CoSb_3$ [12], lead antimony silver telluride and its alloy [13], PbTe-based alloys and nanocomposites, [14,15] and the highest ZT peak has been recorded to be ~2.6 at 923 K for the SnSe crystal [16]. However, for the low-temperature (about 200–500 K) cooling and power generation applications, Bi_2Te_3-based bulk materials (*n*-type $Bi_2Te_{3-x}Se_x$ and p-type $Bi_xSb_{2-x}Te_3$) still dominate. Compared with commercial Bi_2Te_3-based alloy ingots, enhanced thermoelectric performances were also observed in nanostructured bulk Bi_2Te_3-based alloys because of the reduced thermal lattice conductivity, which were carried out by various nanostructure engineering approaches such as ball-milling hot-pressing process [17,18], melt-spinning spark-plasma-sintering process [19], hot forging process [20], and solution-synthesis sintering process [21,22].

Solution synthesis is a typical bottom-up assembly approach, which is a facile and scalable method to achieve various nanostructures such as nanowires [23], nanobelts [24], nanoplatelets [25-27], nanonetworks [28], and even heterostructures [29]. Using these nanostructures as building blocks one can harness great possibilities to achieve various novel nanostructured bulk materials for enhancing the thermoelectric performance. However, the solution derived nanostructured bulk materials usually show a low ZT value comparing with the ones made by ball-milling hot-pressing approaches because of the low power factor [30-32], although the lattice thermal conductivity is greatly reduced. For example, a nanostructured bulk Bi_2Te_3 material made from solution synthesized nanoparticles only shows a ZT of 0.04 at room temperature because of the poor electrical conductivity even though the thermal conductivity is as low as $0.51\ W\,m^{-1}\,K^{-1}$ [30]. Thus, to make full advantage of the solution approaches, further systematic controlling on the morphology, structure and composition of nanostructures is greatly needed to optimize the three thermoelectric parameters S, σ, κ for high-ZT bulk nanocomposites. Composition tuning in thermoelectric materials is especially important to adjust the band structure and doping level of the materials for improving the power factor [10]. Up to date, various solution approaches have been widely proposed to synthesize binary Bi_2Te_3 [25,32,33] and Sb_2Te_3 [26,31,34] nanoplatelets, but the research on the solution synthesis of ternary $Bi_2Te_{3-x}Se_x$ and $Bi_xSb_{2-x}Te_3$ with tunable composition is still limited. Previously we reported the solution synthesis of *n*-type $Bi_2Te_{3-x}Se_x$ nanoplatelets and characterizations of the thermoelectric performance of their bulk pellets [22]. In a complete Bi_2Te_3-based thermoelectric device, both *n*-type $Bi_2Te_{3-x}Se_x$ and p-type $Bi_xSb_{2-x}Te_3$ materials are required. Although some solution approaches have also been reported recently for the synthesis of stoichiometric ternary *p*-type $Bi_xSb_{2-x}Te_3$ [35,36], it is still a challenge to improve the power factor of these bulk nanocomposites.

Here, we report a modified solvothermal synthesis method for the controlled growth of $Bi_xSb_{2-x}Te_3$ nanoplatelets, in which the L-cysteine is used as reducing agent to obtain homogenous stoichiometric composition. Using this solution method, the tuning of the stoichiometric composition in ternary $Bi_xSb_{2-x}Te_3$ is successfully realized. Phase segregation problem is overcome by this modified approach. By spark plasma sintering (SPS) of the $Bi_xSb_{2-x}Te_3$ nanoplatelets, the corresponding nanostructured bulk pellets are prepared for thermoelectric characterizations. The optimized nanostructured bulk $Bi_{0.5}Sb_{1.5}Te_3$ sample is found to have ZT ~0.51 at 375 K, which shows great potential for further improving the thermoelectric performance by the solution synthesis method.

Experimental details

Sample preparation

In a typical synthesis of $Bi_{0.5}Sb_{1.5}Te_3$ nanoplatelets, 3.26 g potassium telluride monohydrate ($K_2TeO_3\cdot H_2O$), 0.77 g bismuth acetate ($Bi(OOCCH_3)_3$), 1.79 g antimony acetate ($Sb(OOCCH_3)_3$), 2.24 g KOH and 0.4 g Polyvinylpyrrolidone (PVP) as stabilizing agent were dissolved in the 160 ml diethylene glycol (DEG) solvent with the aid of sonication. To tune the composition x in the $Bi_xSb_{2-x}Te_3$, the amount of Bi and Sb precursors also changes following the stoichiometric ratio. The mixed solution were transferred to a 250- mL round