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Structural modifications and non-monotonic carrier concentration in $Bi_2Se_{0.3}Te_{2.7}$ by reversible electrochemical lithium reactions

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Abstract

Reversible electrochemical lithium intercalation/deintercalation reactions have been applied to integrally modify the thermoelectric performance of $Bi_2Se_{0.3}Te_{2.7}$ compounds. The carrier concentration of $Bi_2Se_{0.3}Te_{2.7}$ has been precisely controlled experimentally through the adjustment of the residual lithium content. The variations of electronic transport properties of $Li_xBi_2Se_{0.3}Te_{2.7}$, including electrical conductivity, Seebeck coefficient and carrier concentration, as a function of the intercalated lithium amount (x), show a special non-monotonic P-type to N-type doping trend. This variation is caused by the competition of two mechanisms controlling the carrier concentration: (i) decreasing of the Se/Te ratio through a Li–Se reaction that reduces the amount of the Te_{Bi} or Se_{Bi} antisite defects and therefore the electron concentration; (ii) n-type doping by lithium that provides the electron. Moreover, the nanoparticle exfoliation during lithium intercalation and deintercalation reactions leads to the formation of an internal nanocrystalline composite structure which effectively reduces the lattice thermal conductivity. Through an integral modification of both electrical and thermal transport properties, the maximum ZT value of $Li_xBi_2Se_{0.3}Te_{2.7}$ was improved by nearly 25%.

Keywords: Thermoelectric; Carrier transportation; Nanostructure; Lithium reaction; Bismuth chalcogenides

1. Introduction

Thermoelectric (TE) materials have received considerable attention due to their prospective use as solid state energy conversion devices converting heat into electricity or operating as heat pumps [1–7]. The performance of a thermoelectric material is evaluated by the figure of merit ZT ($ZT = S^2\sigma T/\kappa$, where S, σ and κ represent the Seebeck coefficient, electrical conductivity and thermal conductivity, respectively. To obtain a high ZT value, the thermoelectric material has to be integrally optimized from both the electronic and thermal perspective [1–3]. Regarding the electronic properties, the carrier concentration of a TE material must be adjusted to optimize the power factor $S^2\sigma$. From the thermal transport point of view, one must ensure as small a thermal conductivity as possible. The latter consists of two contributions, the electronic thermal conductivity κ_e tied to the electrical conductivity via the Wiedemann–Franz law and the substantially independent lattice thermal conductivity κ_L.

The past dozen or so years have witnessed a major rejuvenation of interest in the field of thermoelectricity. Apart from significant improvements of the classical TE materials such as Bi_2Te_3/Sb_2Te_3, PbTe and Si–Ge alloys achieved by their structural optimization [1], novel families of TE materials have been identified, among them skutterudites, clathrate compounds, half-Heusler alloys, $Mg_2Si_{1-x}Sn_x$ solids solutions, liquid-like $Cu_{2-x}Se$ and oxide materials [1,3,8–10]. Spurred by promising developments of lower-dimen-

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sional structures such as nanowires [11–13] and superlattices [14,15] that display enhanced TE properties, an interest in bulk nanostructured materials that would have an immediate impact in practical energy conversion applications has grown rapidly and a spectacular progress has been achieved recently. Two basic strategies of forming a nanostructured bulk material have been pursued: (i) compacting nanopowdered materials prepared by extensive ball milling, wet chemical precipitation or melt spinning [16–25]; and (ii) utilizing classical metallurgical approaches such as in situ precipitation and spinodal decomposition [26–30], where the nanostructure is formed inside the bulk matrix material.

Bismuth chalcogenide compounds (such as $Bi_2Se_xTe_{3-x}$ and $Bi_{2-y}Sb_yTe_3$) are the best thermoelectric materials near and below room temperature and, so far, have no serious rival in this temperature range. As a result, further improvements to their thermoelectric performance are very desirable. Bismuth chalcogenide compounds possess the hexagonal layered structure typified by stacking of quintuple layers of mostly covalently bonded Te(1)–Bi–Te(2)–Bi–Te(1) with the neighboring quintuple layers held together by weak van der Waals bonds [31–38]. Based on such a structure, in this paper we use reversible electrochemical lithium intercalation and deintercalation reactions to optimize the thermoelectric performance of the $Bi_2Se_{0.3}Te_{2.7}$ compound, one of the best n-type forms of bismuth chalcogenides. We make systematic investigations of the morphology and correlate its changes with the transport response of the material as various cycles of lithium intercalation and deintercalation are applied. A precise control of lithium intercalation and deintercalation reactions governs the lithium content in the sample which, in turn, determines the carrier density. Moreover, the lithium intercalation and deintercalation process generates nanometer-scale grain structures inside $Bi_2Se_{0.3}Te_{2.7}$ that are effective in scattering mid-frequency phonons and reduce the thermal conductivity. The above two adjustments – the carrier density and the thermal conductivity – achieved by controlling the intercalation/deintercalation processes broaden the possibilities for further optimization of the thermoelectric performance of this canonical thermoelectric material.

2. Experimental

2.1. General description of the fabrication method

In general, two approaches were applied for the preparation of the $Li_xBi_2Se_{0.3}Te_{2.7}$ samples with defined lithium contents. In the first approach, the combinations of electrochemical lithium intercalation and deintercalation processes were applied to obtain the desired lithium content in the sample [38]. This approach consists of the following three steps: (1) electrochemical lithium intercalation of the $Bi_2Se_{0.3}Te_{2.7}$ micropowder to a nominal intercalation amount of 25 mA h g^{-1}; (2) electrochemical lithium deintercalation of the above obtained $Li_xBi_2Se_{0.3}Te_{2.7}$ powder to various nominal deintercalation levels; and (3) rinsing of the final product in acetone and sintering it into a bulk material by spark plasma sintering (SPS). In the second approach, only the electrochemistry lithium intercalation process was applied to obtain desired lithium content in the sample. It has two steps: (1) electrochemical lithium intercalation of the $Bi_2Se_{0.3}Te_{2.7}$ micropowder to defined nominal intercalation amounts of 4, 8 and 25 mA h g^{-1}; and (2) rinsing of the lithium intercalated powder in acetone and sintering it into a bulk material by SPS.

2.2. Preparation of pristine microsized $Bi_2Se_{0.3}Te_{2.7}$ powder

Pristine $Bi_2Se_{0.3}Te_{2.7}$ micropowder for electrochemical lithium intercalation was fabricated by mechanically mashing crystalline rods. The crystalline rods were made by melting and directional solidification of stoichiometric amounts of pure elemental Bi, Se and Te.

2.3. Description of electrochemical lithium reactions

The electrochemical lithium reactions were performed by assembling a self-contained two-electrode Swagelok-type cell in an argon box as described in our previous investigation [36–38]. Briefly, 1 g micropowder of $Bi_2Se_{0.3}Te_{2.7}$ compound was pressed into one electrode of the cell, acting as the positive electrode, while a pure lithium foil was used as the negative electrode of the cell. Glass fiber from Whatman was used as a separator between the positive and negative electrodes. The cell was filled with an electrolyte which consisted of a solution of 1 M $LiPF_6$ solution in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume).

Lithium intercalation and deintercalation reactions were initiated by discharging and recharging the above assembled cell using the LAND 2001 CT battery testing system. The nominal lithium intercalation and deintercalation amount was determined by varying the electrical discharge per mass (Q/m), where Q and m represent the transferred electrical charge and mass of bismuth chalcogenide compounds, respectively. By using constant discharge or recharge current (I), the variation in the electrical charge ($Q = It$) can be controlled through the discharging or recharging time (t). In the first approach, lithium intercalation of $Bi_2Se_{0.3}Te_{2.7}$ was conducted under 0.5 mA discharging current for 50 h to achieve the 25 mA h g^{-1} nominal lithium intercalation amount. After that, various deintercalation cycles were carried out under 0.2 mA recharging current to nominal deintercalation amounts in the range 0–27 mA h g^{-1}. When using the second approach, lithium intercalation of $Bi_2Se_{0.3}Te_{2.7}$ was conducted under 0.5 mA discharging current for 8, 16 and 50 h to achieve the 4, 8 and 25 mA h g^{-1} nominal lithium intercalation amounts, respectively.