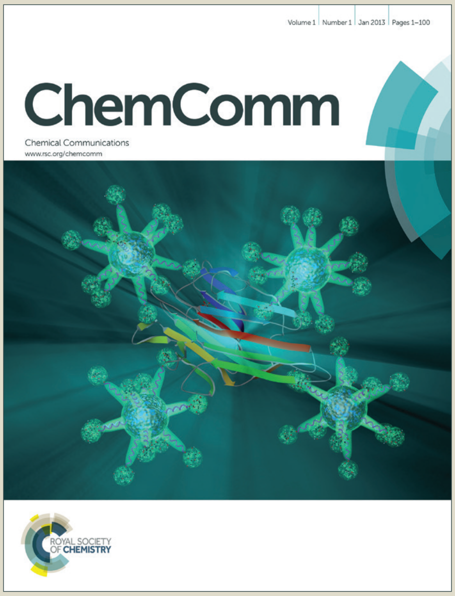

Inhomogenous doping induced nanocrystals imperfect self-assembled to synthesis of porous $AgPb_{10}BiTe_{12}$ nanosheets and their thermoelectric transport properties

Qun Wang,* Yuanyuan Fang, Hang Yin and Jianjun Li*

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For the first time, quaternary single-crystal-like porous $AgPb_{10}BiTe_{12}$ nanosheets in two solid forms (solid solution and Bi-rich region coexist) were achieved. A significant enhancement of thermoelectric performance was realized through nanoscale grain boundaries and macroscale porous structures.

Nanostructuring is a promising strategy to realize factorial increases in thermoelectric (TE) figure of merit *ZT* (defined as $(S^2\sigma/k)T$, where σ, S, T and k are the electrical conductivity, Seebeck coefficient, absolute temperature and total thermal conductivity, respectively), for scavenging electric power from sources of waste heat.[1] Nanoscale confinement not only facilitates a decrease in k by enhancing boundary scattering, but also allows for increases in σ and S through quantum effects.[2] Since the discovery of an enhanced TE performance at elevated temperature (*ZT*=2.2 at 800 K) on materials with compositions lead-antimony-silver-telluride (LAST) alloys (conventionally denoted as $AgPb_mSbTe_{m+2}$) by the Kanatzidis research group in 2004,[3a] considerable investigations related to a series of quaternary PbTe-based alloys $Ag_{1-x}Pb_{18}MTe_{20}$ (M = Bi, Sb, La), etc,[3b] have been carried out due to the increasing consciousness of the adverse impacts of industrialization on our environment. As for these bulk material prepared by solid state reaction, it is revealed that they are inhomogeneous on the nanoscale with widely dispersed nanocrystals embedded in a PbTe matrix. On the other hand, apparently different from correspongding bulk counterparts, ternary and quarternary nanocrystalline $Pb_mSb_{2n}Te_{m+3n}$[4a] and LAST-m[4b] fabricated by solution synthesis route behave as a metastable solid solution at low temperature. In our previous work, PbTe and $AgPb_mMTe_{m+2}$ ((M = Sb, La) nanostructures[5] have been fabricated by a solvothermal method. However, the simple and efficient sloution route to synthesize nanocrystalline $AgPb_mBiTe_{m+2}$ still remains a great challenge.

Nanoporous materials, a representative type of nanostructured materials, possess large specific surface area, exhibiting promising potential for a variety of important applications.[6] Especially, the family of 2D porous materials for TE applications is of primary interest. However, compared with the theoretical calculations, according to our knowledge, experimental studies on porous sheet-like TE materials are still in its infancy so far.[7] Herein, we prepared single-crystal-like porous Ag, Bi-codoped PbTe (defined as $AgPb_{10}BiTe_{12}$) nanosheets with Bi-rich nanoinclusions by a triethanolamine (TEA) assisted solvothermal method for the first time. The $AgPb_{10}BiTe_{12}$ porous nanosheets displayed unusual electrical transport properties and high TE performance.

The morphology and structure of the black $AgPb_{10}BiTe_{12}$ product synthesized at 180 °C for 18h were firstly revealed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1a and Fig. S1, ESI† obviously present that high yield $AgPb_{10}BiTe_{12}$ sample (85 % based on Pb) consists of two-dimensional macro-sized porous morphology. The sample exhibits a high density of clear porous structure with the diameters ranging from 20 to 100 nm in the transmission electron microscopy (TEM) image (Fig 1b). Interestingly, some pores are hexagonal or pseudo hexagonal shaped (see the inset of Fig 1b), and the 120 or 60° inner angles between the adjacent edges of the pores should correspond to the {110} and {101} planes for the fcc crystal structure.

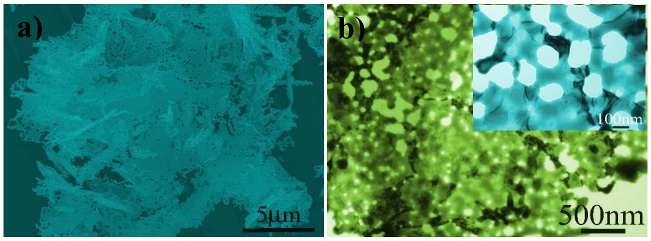

Fig. 1. FESEM a) and TEM images b) of $AgPb_{10}BiTe_{12}$ nanosheets.

The crystal structures and compositional variations of the synthesized $AgPb_{10}BiTe_{12}$ resulting from doping affect the lattice vibrations and the electron phonon interactions were investigated by X-ray diffraction (XRD) and Raman technology (see Fig S2-3, ESI†). These results indicate the surface of $AgPb_{10}BiTe_{12}$ is thin amorphous Pb-rich layer due to the preferential oxidation. Brunauer-Emmett-Teller and Barrett-Joyner-Halenda (BET/BJH) methods were further conducted to demonstrate the porous structure information (see Fig. S3, ESI†).

Department of Chemistry and National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin, 150001, People's Republic of China.
E-mail: wangqun5992@hit.edu.cn;
Fax: +86-451-86413753; Tel: +86-451-86413753

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In order to confirm whether the prepared porous nanosheets are phase-segregated or solid solutions. Fig. 2 shows a high-angle annular dark-field (HAADF) micrograph of a selected dense and intact area of an individule porous nanosheet. From the associated elemental maps of Ag, Pb, Bi, and Te in Fig. 2b-e, one can see that four elements are uniformly distributed, confirming the homogeneous phase behavior of the nanocrystals, which is also consistent with the XRD result. In contrast to the reported nanosegregated bulk quaternary LAST-m systems, no phase separation was observed within the selected $AgPb_{10}BiTe_{12}$ domains.

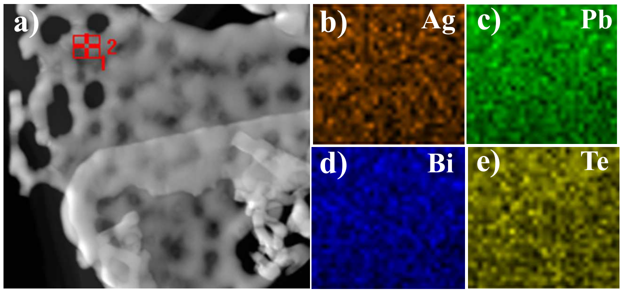

Fig. 2. a) HAADF-STEM image; the corresponding EDS elemental maps of b) Ag, c) Pb, d) Bi, and e) Te.

The ideal substitution generally takes place: $2Pb^{2+} \rightarrow Bi^{3+} + Ag^{+}$, however, the fact is not just like this. Surprisingly, the EDS line profiles recorded from the edge of the pore marked in red retangle (Fig. 3a,b) show that the content of Pb, Sb, Te is higher than that of Ag. It is well known that the preparation of quarternary nanocrystals with multicomponent can be challenging because of the limited availability of suitable and compatible precursors in the reaction medium in order to avoid a tendency toward phase separation.[4b, 8a] The most common way to dope nanomaterials is to include impurities in precursor solutions.[8a] Thus, in the present work, triethenthmine (TEA) was properly designed for complexation of all the metal ions to balance their reaction reactivity, which results in growth of the PbTe host crystal and to deposition of dopant ions to succeed in incorporating dopants during crystal growth. Excess dopants amount breaking reaction reactivity balance is easy to induce the appearance of impurity phases (see Fig. S5, ESI†). The low content of Ag may be attributed to unstable $Ag(TEA)^{+}$, "self-purication" mechanism: the Ag impurity formation energy in nanomaterials is much higher than in bulk materials, as well as high diffusion coeffiicient. Furthermore, the careful HRTEM observation of the area clearly reveals two series of clearly different crystal lattices (Fig. 3c). The distance in the right zone between neighboring fringes is 0.222 nm, closing to the (220) lattice spacing of PbTe-based solid solutions (JCPDS card No.65-9499), while the left hexagonally symmetric fringes zone indicates the domains rotate to a different orientation.[8b] The corresponding hexagonally spot pattern of SAED can be indexed as the [111] zone axis of a face-centered cubic (fcc) structure, indicating a short-range nanocubes disorder distribution and mesoscale grains embedded in porous nanosheets. In addition, EDX spectra of the porous nanosheet collected at different positions shows Bi-rich region appeared (see Fig. S4, ESI†).

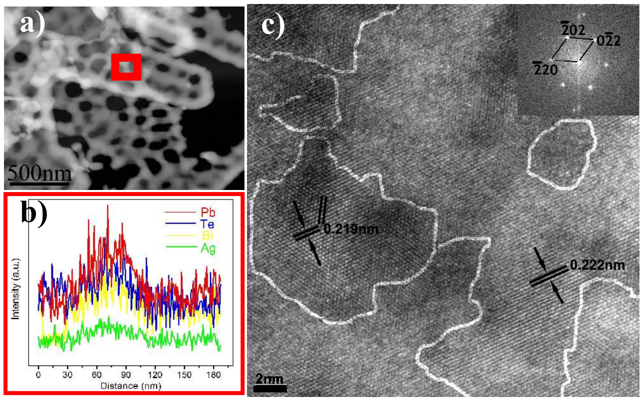

Fig. 3. a) STEM image of samples acquired in the TEM, b) a line scan and c) HRTEM image of sample.

In order to better understand the evolution processes and elucidate the growth mechanism of porous nanosheets from our reaction system, the intermediates were collected and studied at different reaction stages. In the earliest stage, when we reduced the chemical reaction time to 30 minutes, few aggregates consisted of nanocube with the diameter of about 15 nm are clearly observed in Fig. S6a, (ESI†). When the reaction time is increased to 4 h, the obtained products become integrated nanosheets with many pits on the rough surface and the edges of the sheets become broken (see Fig. S6b,c, ESI†), indicating these small nanoparticle aggregates appear to randomly coalesce and fuse into sheet-like structures, which accord with two series of lattice fringes HRTEM result. As we all know, PbX (X=S, Se, Te) 2D nanostructure as a member of non-layered compounds have a highly symmetric cubic crystal structure and can hardly spontaneously integrate into 2D superstructures. It is of great interest to understand the anisotropic growth mechanisms of such materials system with centrosymmetric lattice. Thus, the first question is what is the driving force for the assembly of units collide and then attaching each other into nanosheets? The role of Ag, Bi dopants in determining the morphologies of the nanocrystals was presented in Fig. S7, (ESI†). In our present experiment, in the absence of Ag, Bi dopant, Ag, Bi was substituted by Ag, M=La, Sb under identical experimental condition, flower-like crystal were obtained. In heterovalent doping, impurities in a different valence state than the host cations are intentionally incorporated to provide either extra electrons (n-type) or extra holes (p-type), and simultaneously the spatial redistribution of Ag, Bi atoms in the crystal lattice, which caused the electron charge density of the crystal surface variation.[9a] Thererfore, the interparticle force at the nanoscale is attributed to anisotropic dipolar NP-NP interaction.[9b]

On the basis of the above analysis, the first question can be answered. Interestingly, prolonging the reaction time further to 8 h, it can be seen that the intermediates retain two-dimensional macro-sized morphology with the gradual appearance of meso/macropores throughout the nanosheets. Many crystal interfaces and nanopores are observed in the nanosheet (see Fig. S6d-f, ESI†), which originate from imperfect assemble process. Another possible reason could be the unit cell volume expansion due to extrinsic doping, which generated a large lattice strain and caused the dislocation in nanosheet. Subsequently, the following questions need to be raised. How did the nanosheet with many pits on the surface convert into porous nanosheet? At present, it is commonly accepted that there are two routes to prepare 2D porous sheet/plate structure by bottom-up and top-down fabrication, respectively. First, nanoparticle imperfect self-organization of adjacent nanocrystals to form porous structure. For instance, a ultrathin porous monolayer of PbS 2D network were synthesized through collective coalescence of PbS nano dots due to non-ideal attachment.[10] Second, elimination reaction by removing chemical components from the original parent template, is one important member of the transformation reaction family.[11] That means perfect plate/sheet containing some defects (chemically active sites) or active elements was transformed to porous through etching and extracting some elements in the parent template.[12] Combined with the expriments of variation of temperature and KOH amount (see Fig. S8-9, ESI†), it is reasonable to expect that the second route is responsible for the formation of porous nanosheets. Therefore, imperfect self-assemble driven by dipole interaction (step I) and etching defects reaction process (step II) can be proposed, according to the extensive experimental data (Scheme 1, ESI†).

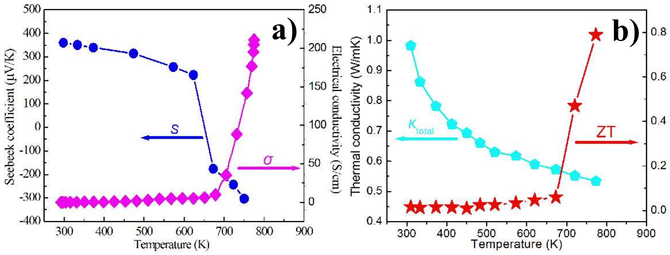

Fig. 4. Temperature dependence of (a) σ, S and (b) k, ZT.

Recently, research on dense materials compacted from solution-based synthesized binary PbTe and PbS nanocrystal has attracted a broad interest.[13,14] Here, we investigated temperature-dependent electrical conductivity (σ), Seebeck coefficient (S) and thermal conductivity (k) between 300 and 750 K. The σ (Fig. 4a) of the porous nanosheets unchanges with increasing temperature from room temperature to about 670 K and then increases from 12.4 $S\cdot m^{-1}$ at 670 K to 42.5 $S\cdot m^{-1}$ at 710 K and sharply goes to 220 $S\cdot m^{-1}$ at 750 K, which is larger compared to that of PbTe (23.7 S/cm at 710K)[13]. This unusual behavior is explained by carrier scattering at interfaces and the activation energy is E_B=118 meV (see Fig. S10, ESI†). Fig. 4a shows a change in sign of the S ($p \rightarrow n$, from 351.7 $\mu V\cdot K^{-1}$ at 300 K to -312.4 $\mu V\cdot K^{-1}$ at 750 K). This phenomenon indicates that holes and electrons are two competitive carriers in quantity, which is attributed to the filter effect of energy barrier between two grains.[13,14] Additionally, the k (Fig. 4b) at 300 K is measured to be 0.98 W/mK and then drops to 0.56 W/mK at 750 K, suggesting a negligible contribution from bipolar thermal conductivity.[14] This reduced k compared with bulk PbTe (0.8 W/mK at 720 K)[15] is associated with the efficient scattering of phonons at high number of grain boundaries and crystal interfaces around pore edges. The calculated power factor ($PF=S^2\sigma$) (see Fig. S10, ESI†) and the ZT (Fig. 4b) is 0.46 at 570 K, which is larger than the reported one for PbTe (about 0.12 at 570 K)[13] and is smaller than reported ZT value for $PbTe/Bi_2Te_3$ (0.72 at 570 K)[15]. The nanomaterials' stability was tested (see Fig. S11). Similar changes of electrical properties were also observed in $(PbTe)_{0.28}(PbS)_{0.72}$ nanocomposites.[13] These findings reveal that the formation of a solid solution coupled with Bi-rich regions in $AgPb_{10}BiTe_{12}$ porous nanosheets allows synergistically much enhanced thermoelectric properties through the significant reduction of thermal conductivity.

In summary, a single-crystal-like porous quaternary $AgPb_{10}BiTe_{12}$ nanosheets in two solid forms (solid solution and Bi-rich region coexisted nanostructure) were achieved for the first time. Imperfect self-assemble driven by dipole interaction (step I) and etching defects reaction process (step II) can explain the formation of $AgPb_{10}BiTe_{12}$ porous nanosheets. We highlight that the formation of solid solution and Bi-rich zone on the edge of macropore synergistically much enhanced the thermoelectric properties. Importantly, this simple synthetic strategy may inspire a new trail of thought toward the syntheses of other ternary and quaternary 2D porous PbTe-based TE nanomaterials.

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