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RAPID COMMUNICATION

Enhanced thermoelectric performance of Bi_2S_3 by synergistical action of bromine substitution and copper nanoparticles

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Abstract
Bi_2S_3 thermoelectric materials have received extensive interests due to the ultrahigh abundance of sulfur element in the Earth's crust. However, the high electrical resistivity of pristine Bi_2S_3 leads to a low ZT value. In this work, incorporating small amounts of $CuBr_2$ into Bi_2S_3 system prepared by melting and spark plasma sintering can remarkably enhance the thermoelectric performance. Cu intercalation and Br substitution at sulfur sites contribute to a sharp decrease of electrical resistivity. Simultaneously, the strong point defects caused by Br alloying and formed Cu nanoparticles noticeably suppress the thermal conductivity. Collectively, the maximum ZT of 0.72 at 773 K is obtained for the 0.5 mol% $CuBr_2$ doped sample parallel to the press direction, which is the highest ZT value ever reported for Bi_2S_3 system, even comparable to the PbS-based thermoelectric materials.

Introduction

In the past decades, thermoelectric materials have drawn worldwide scientific attentions due to the fact that it could be capable to directly and reversibly convert heat energy into electrical power and provide an alternative for power generation and

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refrigeration.[1,2] Generally, the conversion efficiency of thermoelectric materials is dominated by the dimensionless thermoelectric figure of merit $ZT=(S^2\sigma/\kappa)\,T$, where S, σ, κ and T are the Seebeck coefficient, electrical conductivity, the thermal conductivity and the absolute temperature, respectively. Because of the well-known interrelated individual parameters, it is indeed a challenge to separately tune the S, σ and κ for the substantial improvement of the ZT value.[3-5] Several effective strategies, including band engineering, nanostructuring and panoscopic approach,[6-12] or intrinsically low thermal conductivity [13-15] have been successfully introduced and developed to improve the thermoelectric performance.

Despite achieving significant advances in this field, the state-of-the-art thermoelectric materials, including Bi_2Te_3, [10,16-18] PbX (X=S, Se and Te),[12,19,20] Skutterudite, [21] Half-heusler and SiGe,[22-24] contain the rare and expensive elements such as Te and Hf, or toxic elements such as Pb and Sb, which have restricted their applications to niche markets. In order to make further large-scale application, new robust candidates, mainly comprised of non-toxic, inexpensive and earth-abundant elements, are urgent to be discovered and optimized.[25-27]

Most recently, due to the ultrahigh abundance of sulfur (S) element in the Earth's crust, sulfur-based thermoelectric materials have acquired extensive interests,[28-32] particularly for the Bi_2S_3 system.[33-36] As Bi_2S_3 has a wide direct band gap of 1.3 eV, the electrical resistivity of pristine Bi_2S_3 is much higher than that of Bi_2Te_3. Therefore, much efforts have been made to lower the electrical resistivity by Cu doping on Bi site,[33] Cl doping on S site,[34] and solution-based chemistry approaches.[35,36] Among the above methods, the combination of the improved carrier concentration caused by Cl doping on S site and high carrier mobility due to the preferentially oriented structure in the $BiCl_3$ doped Bi_2S_3 leads to the highest ZT value close to 0.6 at 760 K.[34] In addition, Cu intercalation in the layered Bi_2Te_3 system not only increases carrier concentration as electron donor, but also forms Cu nanoparticles to enhance phonon scattering, demonstrating that the intercalation of metal particles in the layered material can be effective to enhance the thermoelectric performance.[37] Therefore, the higher ZT values in the layered Bi_2S_3 system can be expected provided that the combination of Cu intercalation within the van der Waals gaps and halogen ions doping is simultaneously realized. Recently, Luo et al. reported that $CuBr_2$ doping in the $In_4Se_{2.5}$ matrix can significantly increase the ZT value by Cu intercalation and Br doping at Se sites since $CuBr_2$ can be decomposed into Cu and Br at 822.5 K.[38] Herein, our motivation is to enhance the thermoelectric performance of Bi_2S_3 materials via the multiple synergistic roles that $CuBr_2$ doping plays in the matrix. Our investigation shows $CuBr_2$ doping not only lowers the electrical resistivity, but also reduces the thermal conductivity, consequently leading to a high ZT of 0.72 at 773 K for the 0.5 mol% $CuBr_2$ doped Bi_2S_3 sample along the parallel direction to the press direction, which is nearly 800% higher than that of pristine Bi_2S_3.

Experimental section

Starting materials are Bi powder (99.99%, Alfa), S powder (99.999%, Alfa) and $CuBr_2$ powder (99.98%, Alfa). Ingot ($\sim$20 g) with nominal compositions of Bi_2S_3+x mol% $CuBr_2$ (x=0, 0.25%, 0.5% and 1%) were mixed uniformly together by hand in an Ar-filled glove box. Then, the mixtures of these powders were subjected to cold pressing and sealed into quartz tubes. The sealed tubes were heated to 1123 K in 7 h, and then soaked at this temperature for 8 h and subsequently ice-water quenched. The obtained ingots were milled into powder by hand and then densified by spark plasma sintering (SPS) at 823 K for 5 min, resulting in ∅12.7 mm cylinder-shaped samples with a height of about 15 mm. These dimensions ensure that the thermal and electrical properties are measured with the same direction without additional procedures.[39]

X-ray diffraction (XRD) analysis was performed using a PANa-lytical multipurpose diffractometer with an X'celerator detector (PANalyticalX'Pert Pro). The microstructure was observed by field emission SEM (Quanta 200FEG, FEI) and field emission TEM (Tecnai G^2 F30, FEI). Specimens used for TEM were identical with the previous publication.[40]

Room temperature optical diffuse reflectance measurements were performed on finely ground powders to probe optical energy gap of the Bi_2S_3-based materials. The spectra were collected in a Shimadzu Model UV-3101PC double-beam, double-monochromator spectrophotometer (Ultraviolet-Visible absorption Spectra). The SPSed cylinders were cut into bars of $\sim$12 mm $\times$ 2 mm $\times$ 2 mm and coins of $\sim$∅12.7 mm $\times$ 2 mm for the measurement of electrical properties and thermal diffusivity coefficient, respectively. It is well known that the thermoelectric performance of the parallel direction to the press outperforms the perpendicular direction in the anisotropic layered material,[16,41,42], which is further confirmed in the 0.5% $CuBr_2$ doped Bi_2S_3 sample shown in Figure S1. Therefore, the characterization of electrical and thermal transport behavior of our work was done along the parallel direction. The bars were used for simultaneous measurement of the electrical resistivity (ρ) and Seebeck coefficient (S) on a commercial system (ULVAC-ZEM-3). The thermal conductivity was calculated from $\kappa=DC_pd$, where D, C_p and d are the thermal diffusivity, heat capacity, and volume density, respectively. The thermal diffusivity coefficient (D) was measured with the coin sample using the laser flash diffusivity method in a Netzsch LFA457 (NETZSCH, LFA457, Germany), where the specific heat capacity (Cp) was indirectly derived using a representative sample (Pyroceram 9606) in the range 300–773 K. The density (d) was determined by using the Archimedes method, which reached the 99% of the theoretical density (d=6.8 g/cm^3). The Hall Coefficient R_H at room temperature was measured using the PPMS (Physical Properties Measurement System, Quantum Design). The carrier concentration (n_H) was obtained by $n_H=1/eR_H$ and the carrier mobility (μ) was calculated by $\sigma=e\mu n_H$, where e is the electronic charge, and σ the electrical conductivity.

Results and discussion

Figure 1a shows the powder XRD patterns of Bi_2S_3+x mol% $CuBr_2$ (x=0, 0.25%, 0.5% and 1%). All the X-ray diffraction (XRD) peaks show an excellent match to the orthorhombic Bi_2S_3 with space group *Pbnm* without any impurity phase within the detection limits of powder XRD. The lattice parameters calculated from the powder XRD data increase