Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information (ESI)

Dual Defect System of Tellurium Antisites and Silver Interstitials in Off-Stoichiometric $Bi_2(Te,Se)_{3+y}$ Causing Enhanced Thermoelectric Performance

Cham Kim,*[a] David Humberto Lopez,[b] Dong Hwan Kim[a] and Hoyoung Kim[a]

[a] Daegu Gyeongbuk Institute of Science and Technology (DGIST), 333 Techno Jungang-daero, Daegu, 42988, Republic of Korea

[b] Department of Chemical and Environmental Engineering, University of Arizona, 1133 E. James. E. Rogers Way, Tucson, AZ, 85721, USA

ESI 1. Theoretical simulation/calculation of Ag amount in $Bi_2Te_{2.90}Se_{0.15}$

As explained in the Experimental details (2.2. Sample preparation), the amount of Ag in $Bi_2Te_{2.90}Se_{0.15}$ was adjusted by using different amount of $AgNO_3$. 15g of $Bi_2Te_{2.90}Se_{0.15}$ was mixed with 250 ml of 4 mM $NaBH_4$ (aq) and different amount of $AgNO_3$ was added to the mixed solution.

For instance, to prepare the $Bi_2Te_{2.90}Se_{0.15}$ with 0.3 wt% Ag, 0.045 g of Ag (=0.417 mmol Ag) is required; thus, 0.417 mmol of $AgNO_3$ should be used as shown in Eq. A.

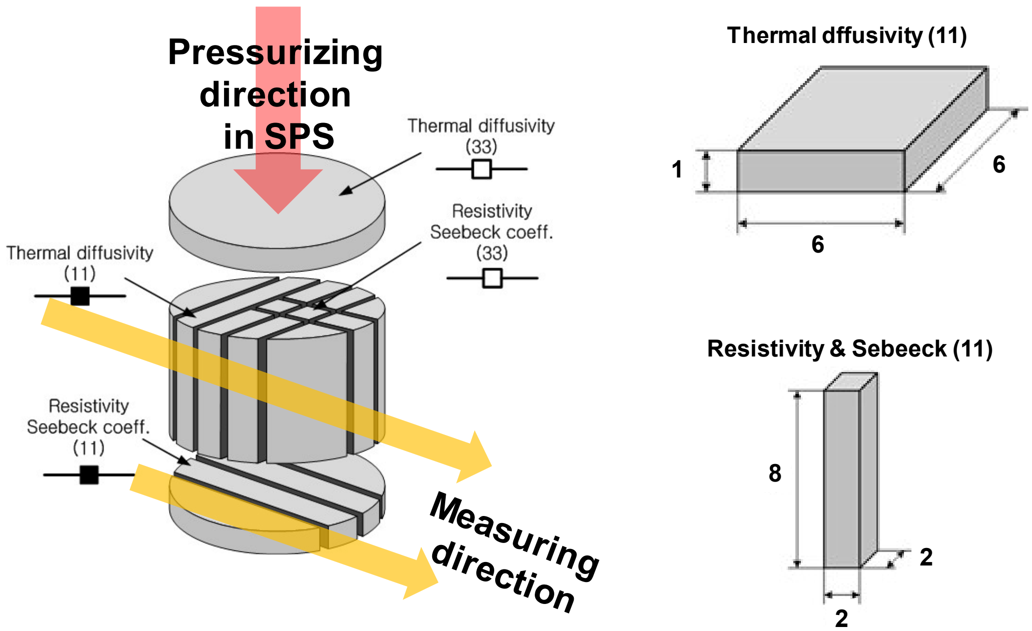
$$AgNO_3\ (aq) \leftrightarrow Ag^+ + NO_3^- \text{ -- (Eq. A)}$$

From the initially prepared 2 mM $AgNO_3$ aqueous solution, we collected approximately 208.5 ml (i.e., 0.417 mmol $AgNO_3$) and added it to the mixed solution of $Bi_2Te_{2.90}Se_{0.15}$ and $NaBH_4$. Theoretically, 1 mol $AgNO_3$ should be reduced by 1 mol $NaBH_4$, thus affording 1 mol Ag (Eq. B);

$$AgNO_3 + NaBH_4 \rightarrow Ag + 1/2H_2 + 1/2B_2H_6 + Na^+ + NO_3^- \text{ --------------------- (Eq. B)}$$

however, the excess of $NaBH_4$ (i.e., 250 ml of 4 mM $NaBH_4$ = 1 mmol $NaBH_4$) was used to guarantee the complete reduction of 0.417 mmol $AgNO_3$ to finally obtain 0.417 mmol Ag (=0.045 g of Ag) deposited onto 15 g of $Bi_2Te_{2.90}Se_{0.15}$ (i.e., 0.3 wt% Ag). The atomic composition of the product was measured by ICP-MS as presented in Table 1. According to the concentration (mg L^{-1}) of the components in the ICP-MS results, the amount of Ag in the product was 0.29 wt%, which is in proximity to the theoretical calculation above. For other Ag compositions, we also confirmed that Ag amount of the theoretical calculation was in accordance with that of the experimental results.

ESI 2. Specimen processing for thermoelectric characterizations



The product specimen obtained from a spark plasma sintering (SPS) process was cut into the two different dimensions (i.e., 11, 33) for the measurement of thermal diffusivity and resistivity (or Seebeck coefficient). 11 and 33 indicate in-plane and out-of-plane direction for the measurement, respectively. Considering the typical anisotropic nature of Bi_2Te_3-based materials, it is required to observe the properties along consistent direction; thus, we measured the thermoelectric properties of only those faces of the specimens that were perpendicular to the pressurizing direction (i.e., we measured the 11 specimens). The standard deviations of the properties were obtained with the processed specimen couples (with 11 direction) of five different raw specimens per each material. The standard deviations were shown as error bars (Figure 1, 6, and 7).