Ball-Milling Synthesis Investigation of a-MgAgSb to Enhance Thermoelectric Properties and Reproducibility

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Abstract:

Unideal multi-step synthesis and challenges regarding the reproducibility of high-performing α-MgAgSb has set precedent for modifying high energy ball-milling synthesis procedures to improve its thermoelectric properties. Refining efforts to regulate the presence of impurity phases (e.g., Ag_3Sb, AgMg, Sb, and $Mg_{54}Ag_{17}$) by time-effective phase content control has been reported in literature, but synthesis optimization remains relatively unexamined. In this work, we demonstrate that a high ZT of 1.21 at 423 K for $MgAg_{0.97}Sb_{0.99}$ can be obtained by high energy ball-milling of Mg and Ag for ten hours and by later incorporating Sb for five hours, proceeded with six hours of annealing at 573 K. Ongoing investigation of this study revealed a potential maximum ZT of 1.36 at 473 K. The α-MgAgSb:Sb ratio exhibited was 98.52:1.48% with no other impurity phases present. Fine tuning Sb particle size may affect precursor mixing homogeneity, evidenced by gradual thermoelectric property improvement in this study. Achieving this ratio of α-MgAgSb and secondary-phase Sb with this simpler synthesis process makes way for employing MgAgSb as thermoelectric materials.

Introduction and Background:

High performing thermoelectric (TE) materials for power generation at low temperatures remain of interest for mitigating usable heat loss in a wide variety of energy systems. The dimensionless figure of merit, $ZT = S^2\sigma T\kappa^{-1}$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the total thermal conductivity, characterizes the thermoelectric performance of a material or device. According to Zhihang et al., α-MgAgSb (*I*42c) can exhibit a high ZT ranging from 1.2 to 1.4, though at 550 K [1]. A trade-off between the temperature-dependent S, σ, and κ exists to achieve high performance, prompting multifaceted investigation of the effects of synthesis modification on TE properties. For instance, enhancing S2σ, otherwise known as the power factor (PF), while suppressing lattice thermal conductivity κ_L is imperative for maintaining a high ZT.

In this study, we investigate the effects of ball-milling time steps on MgAgSb phase ratios and S, PF, ZT, κ_L, electrical resistivity (ρ), total thermal conductivity (κ), and weighted mobility (μ_W). The MgAgSb alloys were prepared by one-step and two-step high energy ball-milling. Mg and Ag milled first for the two-step process, later introduced with Sb particles on the second step. Spark plasma sintering (SPS) and thermal annealing proceeded, to induce phase transitions at a maximum temperature of 300K. Results provided insight on how phase composition can be tuned through honing the order or duration of ball-milling time steps. Shorter and less involuted ball-milling time steps without the need for defect or band structure engineering can provide a simpler route to synthesizing high-ZT α-MgAgSb.

Results and Summary:

Figure 1 contains XRD patterns of samples A-H, revealing the effects of high energy ball-milling step changes on MgAgSb phase content. The following sample names correspond with the following ball-milling time steps and Sb sizes: i) A = 5 hours, ii) B = 5 hours and 5 hours, iii) C = 10 hours, iv) D = 10 hours and 5 hours, v) E = 5 hour and 5 hours, with crushed Sb, vi) F = 10 hours and 5 hours, with crushed Sb, vii) G = replicate of F, and viii) H = 10 hours, with crushed Sb. Sample F had the highest relative peak intensity with minimal broadening at 23.8° 2Θ, whereas samples A, B, C, and H exhibited slight peak broadening. The impurity phase AgMg was identifiable in all samples, except E and F, with $Mg_{54}Ag_{17}$ being present in only A, B, and H. Peaks attributed to impurity phases were more prominent in samples subjected to the one-step for five hours, two-steps for five hours, and one-step for ten hours procedures, indicating a lack of AgMg precursor phase to α-MgAgSb transitions. Depending on

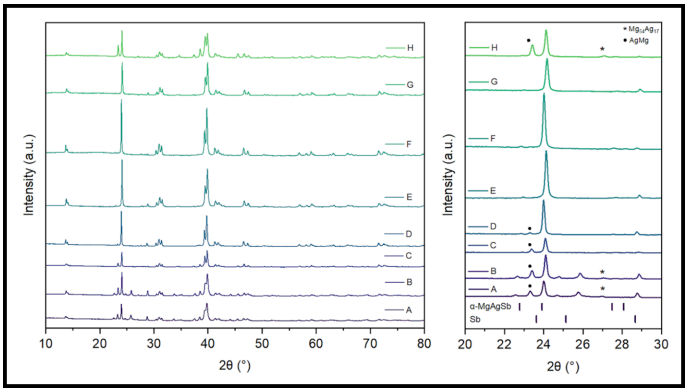

Figure 1: (Left) XRD patterns and (Right) 20°-30° 2Θ range of $MgAg_{0.97}Sb_{0.99}$ samples A-H. Relevant Bragg positions for α-MgAgSb and Sb are shown at the bottom for reference (Right).

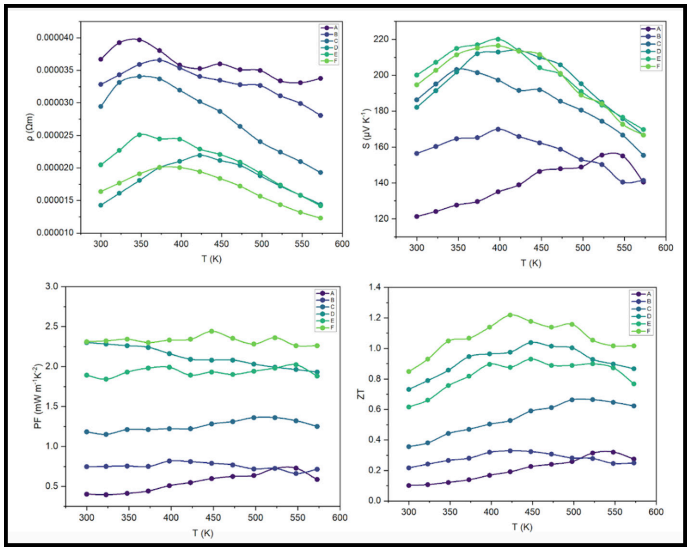

Figure 2: Electrical resistivity (ρ), Seebeck coefficient (μVK^{-1}), power factor ($mW\ m^{-1}K^{-2}$), and ZT vs. temperature.

the initial phases formed during the first milling step and the duration of the second milling step, desirable phases whereby κ_L is minimized and ZT is maximized may form, as evidenced by the XRD patterns and TE properties for samples E and F.

Figure 2 provides insight on the thermoelectric properties against temperature, with samples A-F being investigated. The ρ vs. T plot revealed that sample F exhibited the lowest electrical resistivity, with only a peak resistivity of 2.007E-5 Ωm at 373K. Sample F's peak high Seebeck coefficient of 216.35 μV K^{-1} at 398K and power factor of 2.44 mW $m^{-1}K^{-2}$ at 448 K gives rise to sample F's high ZT value. Electrical resistivity can simply be represented as $\rho = \sigma^{-1}$, in accordance with the Drude-Sommerfeld free electron model.

Therefore, it is possible that sample F exhibited comparably larger σs enabling for the minimization of ρ, thus improving the power factor given that $PF = S^2\sigma$. Sample F's comparably high Seebeck coefficient also contributed to a high PF, though the magnitude of each S and σ contribution is dependent on temperature. Sample F was able to achieve a ZT of 1.04 at 348K, with a peak ZT of 1.22 at 423K. Though an ongoing investigation, replicate sample G demonstrated a maximum ZT of 1.36 at 473K, thus indicating reproducibility of thermoelectric properties despite slight phase impurity ratio changes. In conclusion, ZT values were successfully increased by controlling BM procedures. Compared to other complex and time-consuming procedures, this synthesis is quite simple and effective to obtain high ZT samples.

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References:

[1] Liu, Zihang, et al., "High Thermoelectric Performance of α-Mgagsb for Power Generation." Energy and Environmental Science, The Royal Society of Chemistry, 18 Oct. 2017.