

Unraveling Non-polymorphic Phase Evolution in Mg-Ag-Sb for Designing Thermally Recoverable Thermoelectrics

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P-type MgAgSb with excellent room-temperature thermoelectric performance holds great promise for cooling and power generation. However, its practical application has been significantly limited by phase transitions, which are long considered a polymorphic transformation where the compositions remain identical but the crystal structures differ. Here we report the non-polymorphic nature of the complex phase transitions in Mg-Ag-Sb during thermal cycling, yielding four compositionally distinct ternary compounds that crystallize in three different structures. During heating, the tetragonal α -phase MgAgSb decomposes into the tetragonal β -phase $\text{Mg}_5\text{Ag}_{4.32}\text{Sb}_{4.5}$, and subsequently into the cubic γ_{H} -phase $\text{Mg}_5\text{Ag}_{2.11}\text{Sb}_4$, with the progressive precipitation of Ag_3Sb and Sb phases. Upon cooling, the γ_{H} -phase $\text{Mg}_5\text{Ag}_{2.11}\text{Sb}_4$ converts to the cubic γ_{L} -phase $\text{Mg}_5\text{Ag}_{1.18}\text{Sb}_{3.63}$, accompanied by the α phase with substantial Ag_3Sb and Sb phases. The electron localization function and bonding analysis indicate that the Mg-Ag-Sb compound is characterized by ionic interactions, wherein the Ag-Sb bond is notably weaker compared to the Mg-Sb bond. Molecular dynamics simulations reveal that significant Mg and Ag migration within the Sb sublattices underlies the phase evolution. Surprisingly, the rapid atomic diffusion also enables the restoration of the α -phase MgAgSb upon annealing at low temperatures. Successful recovery of the α phase can be realized even after 500 thermal cycles between 423–673 K, demonstrating unprecedented thermal recoverability.

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I. INTRODUCTION

Solid-state thermoelectric devices enable direct conversion between heat and electricity, which allows for applications in power generation and cooling [1–5]. To ensure the stable operation of thermoelectric devices, phase-change materials have often been avoided, or their use has been restricted to temperatures below the critical transition point. In addition, the thermal instability of materials, such as decomposition [6,7] or sublimation, also

poses a major obstacle to their practical application. Hence, it is essential to understand the underlying phase transition mechanism and to design materials with thermal recoverability.

MgAgSb exhibits excellent thermoelectric performance around room temperature [8–15], positioning it as a promising candidate for heat recovery and electronic refrigeration [11–16]. Nevertheless, the application of MgAgSb is limited to temperatures below 573 K, as it undergoes multiple phase transitions at higher temperatures [17,18]. The prevailing understanding is that the phase evolution in MgAgSb occurred via polymorphic transformations [17–19], i.e., the compositions remain identical, but only the crystal structures differ. It involves the low-temperature α -MgAgSb (tetragonal, $I\bar{4}c2$), intermediate β -MgAgSb (tetragonal, $P4/nmm$), and high-temperature γ -MgAgSb (cubic, $F\bar{4}3m$) [17,18].

Experimentally, however, persistent puzzling observations contradict the concept of polymorphic transformations. For example, since the transition from α -MgAgSb to β - and γ -MgAgSb above 600 K frequently leads to the formation of Ag_3Sb and Sb phases [20–22], how can the three phases retain the identical chemical composition? In addition, if the high-temperature melting process can guarantee the formation of γ -MgAgSb, then why are substantial secondary phases of Ag_3Sb and Sb observed when it converts to α -MgAgSb at low temperature [21–23]? Moreover, why does the restoration of the α -MgAgSb coincide with a reduced concentration of these secondary phases after annealing at lower temperatures [21–23]? Thus, elucidating the phase transition and associated evolution of thermoelectric properties in the Mg-Ag-Sb ternary compound is essential.

In contrast to the previously reported polymorphic transformation, here we report that the Mg-Ag-Sb ternary compound undergoes complex phase transitions during heating and cooling, involving four distinct compounds with different compositions, which crystallize in three unique structures. Upon heating, the α -phase MgAgSb (tetragonal, $I\bar{4}c2$) first converts into the β -phase $\text{Mg}_5\text{Ag}_{4.32}\text{Sb}_{4.5}$ (tetragonal, $P4/nmm$), followed by a subsequent transition into the γ_{H} -phase $\text{Mg}_5\text{Ag}_{2.11}\text{Sb}_4$ (cubic, $Fm\bar{3}m$). These transitions are accompanied by the precipitation of Ag_3Sb and Sb phases. During cooling, the γ_{H} phase decomposes into a mixture of the γ_{L} -phase $\text{Mg}_5\text{Ag}_{1.18}\text{Sb}_{3.63}$ (cubic, $Fm\bar{3}m$), the α -phase MgAgSb, and $\text{Ag}_3\text{Sb}/\text{Sb}$ impurities. Molecular dynamics simulations reveal that increasing temperature significantly intensifies the vibration amplitudes of Ag/Mg atoms, inducing atomic migration, while the amplitude of Sb atoms remains stable, corroborating their role as a structural framework. Particularly noteworthy is the thermal recoverability of the α phase through isothermal annealing at low temperatures, enabled by the high mobility of Mg and Ag atoms during these solid-state phase transitions.

II. RESULTS

A. Identification of the non-polymorphic transitions in the Mg-Ag-Sb compound

The temperature-dependent thermoelectric properties of the Mg-Ag-Sb ternary compound during thermal cycling (300–750 K) are illustrated in Figs. 1(a)–1(d). As can be seen, distinct thermoelectric behaviors emerge in different temperature regimes, attributed to phase evolution (α phase, β phase, and γ phase) upon heating. In the α -phase regime, the compound demonstrates optimal thermoelectric properties, achieving a comparatively low electrical resistivity (ρ) of $9.4 \mu\Omega \text{ m}$ at 300 K [Fig. 1(a)], a high Seebeck coefficient (S) peaking at $206.9 \mu\text{V K}^{-1}$ near 423 K [Fig. 1(b)], and low thermal conductivity of $1.1 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K [Fig. 1(c)], collectively yielding a maximum zT of 1.1 at 450 K [Fig. 1(d)]. The β -phase transition triggers significant performance degradation, the Seebeck coefficient plummets from $161.4 \mu\text{V K}^{-1}$ at 564 K to $25.3 \mu\text{V K}^{-1}$ at 633 K, concurrent with a substantial thermal conductivity increase from 1.4 to $11.8 \text{ W m}^{-1} \text{ K}^{-1}$ between 564 and 604 K. The γ phase shows partial performance recovery, with a relatively high Seebeck coefficient and dramatically reduced thermal conductivity. Degradations in the thermoelectric properties of Mg-Ag-Sb ternary compound during the heating process agree well with previous reports [12,17,18,23]. Yet, the evolution of thermoelectric properties during cooling has seldom been discussed. Crucially, phase transitions during cooling are not the exact reverse of those during heating. Instead, the cooling process exhibits marked thermal hysteresis with asymmetric transport behavior. Electrical resistivity first surges to $789.3 \mu\Omega \text{ m}$ at 570 K before abrupt reduction, while the Seebeck coefficient reaches a minimum of $16.3 \mu\text{V K}^{-1}$ at 519 K, followed by partial recovery to $89.5 \mu\text{V K}^{-1}$ at 307 K. The deterioration in electrical transport properties, combined with the gradual increase of thermal conductivity, leads to negligible zT values below 573 K. In other words, the phase transitions observed during heating and cooling cycles of thermoelectric property measurements are irreversible, indicating that they are not polymorphic in nature. Additionally, when the temperature exceeds 733 K, the thermal conductivity exhibits a marked increase, leading to a rapid decrease in zT values within this temperature range.

The phase transitions of the Mg-Ag-Sb during thermal cycling are qualitatively corroborated by differential scanning calorimetry (DSC) analysis [Fig. 1(e) and Supplemental Material Fig. S1] [24]. The heating curve displays three characteristic endothermic events: two consecutive phase transitions at 578 (α phase to β phase) and 643 K (β phase to γ phase), followed by a prominent eutectic reaction peak [18] ($\text{Ag}_3\text{Sb} + \text{Sb} \rightarrow \text{Liquid}$, Supplemental Material Fig. S2) [24] at 735 K, consistent with previous studies [12,17,18]. Notably, the cooling profile exhibits

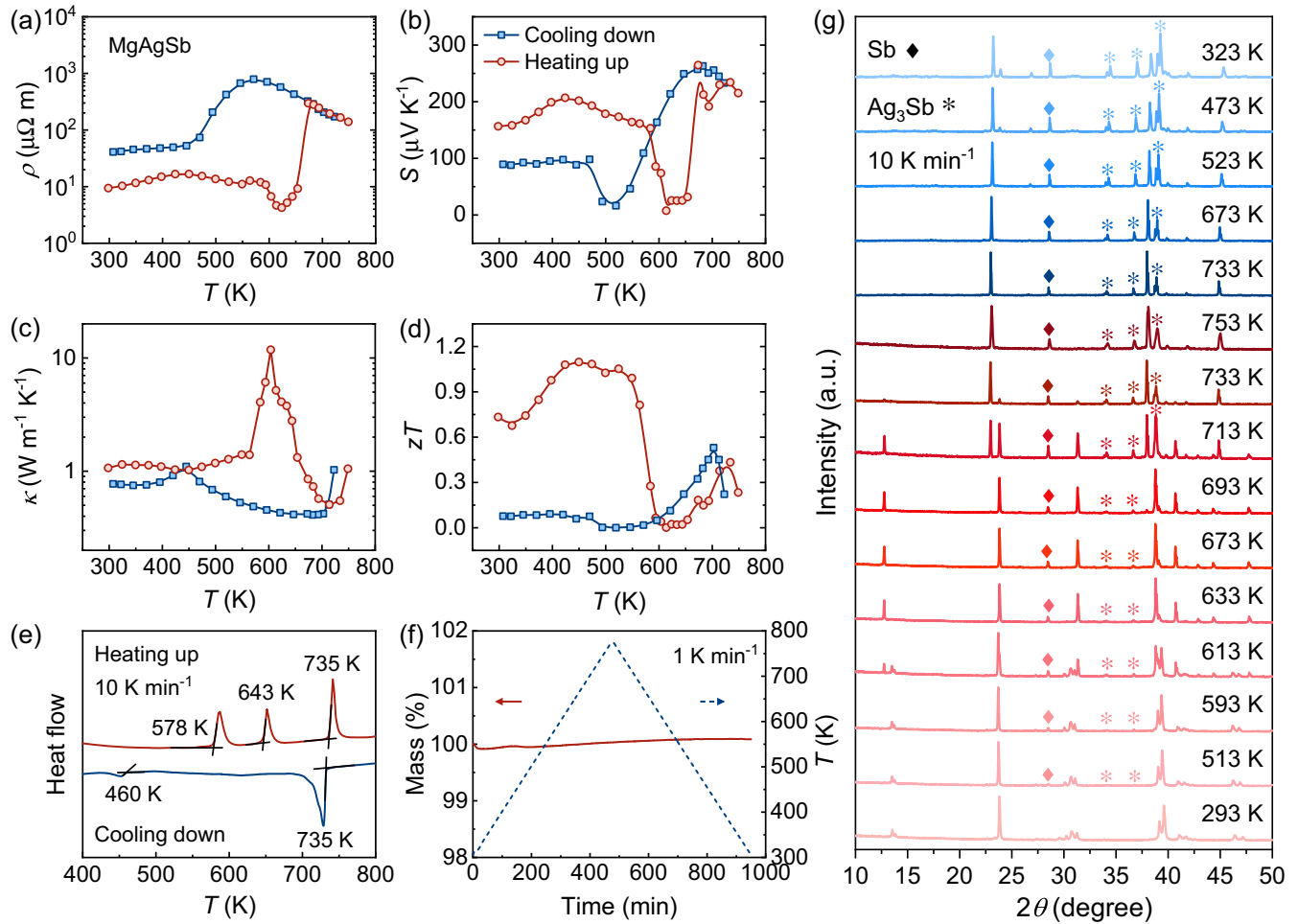


FIG. 1. Temperature-dependent thermoelectric properties and *in situ* powder x-ray diffraction patterns of Mg-Ag-Sb ternary compound. (a) Electrical resistivity, (b) Seebeck coefficient, (c) thermal conductivity, (d) zT during heating up (red circles), and cooling down (blue squares). (e) The DSC curves between 400 and 800 K. (f) The STA curve between 300 and 773 K. (g) *In situ* powder x-ray diffraction patterns over a thermal cycle spanning from 293 to 753 K (heating) and back to 323 K (cooling).

thermal hysteresis with only two exothermic signatures: a sharp eutectic solidification peak at 735 K and a minor peak at 460 K. Again, such phenomena confirm the irreversible phase transitions during thermal cycling. Figure 1(f) and Supplemental Material Fig. S3 [24] show the simultaneous thermal analysis (STA) curve of the Mg-Ag-Sb ternary compound between 300 and 773 K. The negligible mass change ($<0.18\%$) during thermal cycling indicates that phase evolution in Mg-Ag-Sb is independent of the elemental loss. Moreover, it should be noted that different heating and cooling rates used in the thermal analysis (Supplemental Material Fig. S1 and Fig. S3) [24] showed no appreciable impact on the results.

To accurately characterize the temperature-dependent phase evolution in Mg-Ag-Sb, *in situ* powder x-ray diffraction (PXRD) analysis was performed during a thermal cycle spanning from 293 to 753 K (heating) and back to 323 K (cooling), as illustrated in Fig. 1(g) and Supplemental Material Fig. S4 [24]. The α -phase MgAgSb is stable between 293 and 503 K. Upon heating to 513 K, it

undergoes a phase decomposition (Supplemental Material Fig. S5) [24], forming Ag_3Sb and elemental Sb, while the α phase retains its original structure. The β phase emerges at 613 K, marking the onset of a coexisting α - and β -phase region. This coexistence remains unchanged during isothermal holding at 613 K (Supplemental Material Fig. S6) [24]. A complete transition from the α phase to β phase occurs at 633 K, and the β phase remains stable up to 673 K. Subsequent heating to 693 K triggers the emergence of the γ phase, and it becomes the predominant phase at 753 K. The γ phase remains stable during cooling from 733 to 523 K. Minor α -phase nucleation initiates at 473 K, with a slight increase in α -phase content upon further cooling to 323 K. Therefore, the exothermic DSC peak observed at 460 K [Fig. 1(e)] corresponds to the partial phase transition from the γ phase into α phase, accompanied by the precipitation of Ag_3Sb and Sb phases. The observed formation of Ag_3Sb and Sb phases during heating aligns with the prior reports [17,18].

It should be emphasized that polymorphic transformations are phase transitions where chemical compositions remain identical while only the crystal structure changes. However, the continuous precipitation of Ag_3Sb and Sb phases during thermal cycling provides definitive evidence for the non-polymorphic nature of phase evolutions in Mg-Ag-Sb compound. It also implies the off-stoichiometric compositions in both β and γ phases, with $\text{Mg}:\text{Ag}:\text{Sb}$ ratios deviating from the nominal 1:1:1 stoichiometry of the α phase. Such non-equilibrium partitioning requires detailed crystallographic analysis and evaluation of elemental redistribution under thermal cycling.

Crystallographic information of the Mg-Ag-Sb ternary compound is obtained by the Rietveld refinements based on the *in situ* PXRD profiles, and the three crystal structures are shown in Figs. 2(a)–2(c). The α phase crystallizes in the tetragonal space group $I\bar{4}c2$ (No. 120), and the structure features a distorted cubic $[\text{Mg}_4\text{Sb}_4]$ framework formed by

edge-sharing $[\text{MgSb}_6]$ octahedra, with Ag atoms occupying the center positions [Fig. 2(a)]. The β phase maintains tetragonal symmetry (space group $P4/nmm$), edge-shared $[\text{MgSb}_4]$ square pyramids form a layered framework interleaving with Ag atomic layers [Fig. 2(b)]. The high-temperature γ phase was initially reported to crystallize in the space group of $F\bar{4}3m$ (No. 216) [17]. Mi *et al.* [18] proposed a CaF_2 -type structure model ($Fm\bar{3}m$, No. 225) for the polycrystalline XRD profile refinements. However, based on our refinement result, the γ phase crystallized into the antifluorite structure type, consistent with $\text{Mg}_{4.8}\text{Ag}_{1.4}\text{Sb}_4$ single crystal obtained by the flux method [25] (Supplemental Material Fig. S7) [24]. High-resolution single-crystal XRD analysis of γ -phase crystals revealed the Mg and Ag atoms co-occupation at the $8c$ Wyckoff site, bringing an additional fourfold inversion symmetry parallel to the a axis. This symmetry elevation creates a face-centered cubic anionic unit cell formed by Sb atoms and

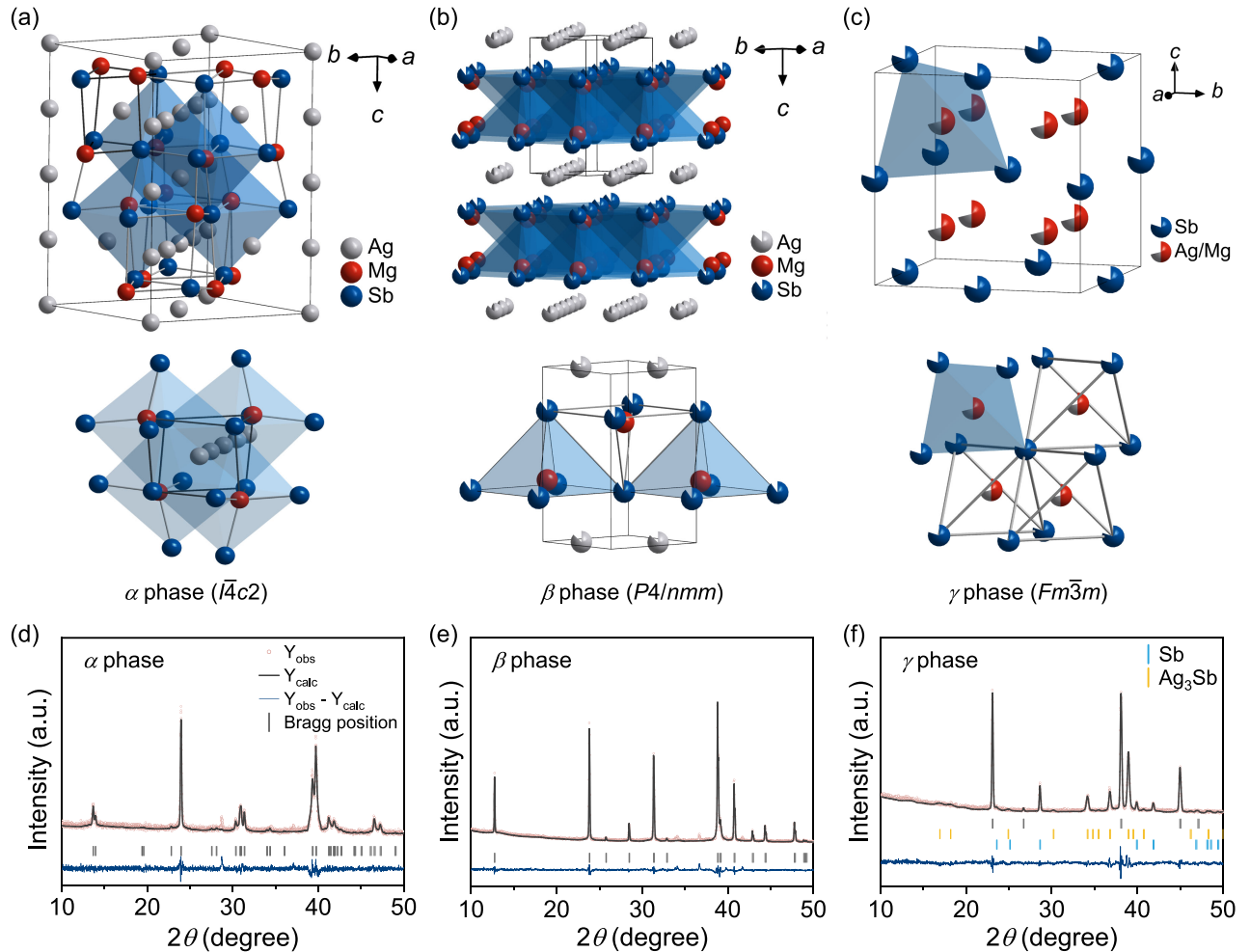


FIG. 2. The crystal structures and Rietveld refinements of the Mg-Ag-Sb ternary compound. Crystal structure of the (a) α phase, (b) β phase, and (c) γ phase, magnesium (Mg), silver (Ag), and antimony (Sb) atoms and vacancies are depicted by red, gray, and blue spheres and transparent segments, respectively. Rietveld refinement results of the (d) α phase, (e) β phase, and (f) γ phase using the *in situ* PXRD data collected at 293, 633, and 753 K, respectively.

encapsulated with a cubic cationic sublattice composed of Mg/Ag atoms.

Figures 2(d)–d(f) show the *in situ* PXRD patterns of the α phase (293 K), β phase (633 K), and γ phase (753 K). The whole profiles are refined by the LeBail methods [26], which demonstrated excellent agreement between the experimental data (red circles) and the calculated ones (black line), with minimal residuals in the difference profiles (blue line). All patterns are annotated with vertical ticks marking the Bragg positions. The LeBail refinement details of unit cell parameters and crystal structure types are presented in Supplemental Material Table S1 [24]. Additionally, the crystal structure of the γ phase at 323 K during the cooling process was refined by the same method (Supplemental Material Fig. S8) [24], revealing isostructural characteristics with the high-temperature γ phase at 753 K. However, progressive precipitation of Ag_3Sb and Sb phases induced a unit cell contraction compared to the high-temperature γ phase. This also results

in a continuously evolving composition of the α and β phases. Rietveld refinement at 633 K gave a β -phase composition of $\text{Mg}_5\text{Ag}_{4.32}\text{Sb}_{4.5}$, consistent with Mi *et al.*'s calculations [18], while the α phase at 293 K retains stoichiometric composition as MgAgSb . Notably, quantification of γ -phase stoichiometries was precluded by multiphase interference in the PXRD patterns, thus necessitating elemental analysis of phases at different temperatures to verify their compositions.

To track the phase evolutions and compositional variations during thermal cycling (from room temperature to 773 and back to 300 K), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were employed on four samples that were quenched during heating (548, 613, 673, and 773 K), and five samples quenched during cooling (673, 573, 473, 423, and 300 K) [Figs. 3(a)–3(f), Supplemental Material Figs. S9–S14, and Tables S2–4] [24]. Quenching from 548 K [Fig. 3(a), Supplemental Material Fig. S10(a), and Table S2] [24] maintained the α

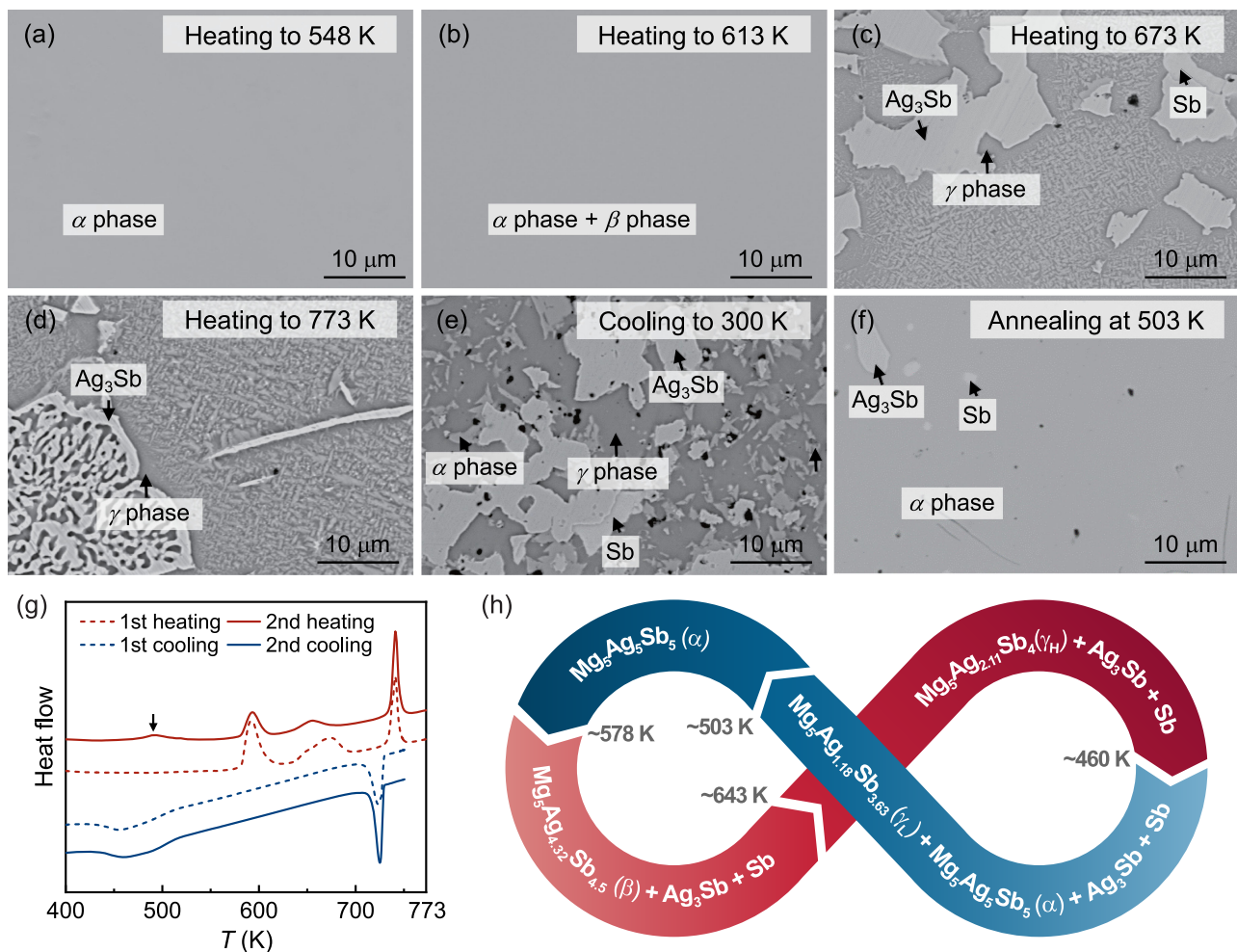


FIG. 3. Temperature-driven phase evolution in Mg-Ag-Sb ternary compound. SEM images show the phase transitions during heating to (a) 548 K, (b) 613 K, (c) 673 K, (d) 773 K, and (e) cooling to 300 K, with (f) annealing at 503 K to restore the α phase. (g) The DSC curves during two consecutive heating-cooling cycles at the maximum temperature of 773 K, and (h) the schematic view of the phase transitions in Mg-Ag-Sb during thermal cycling.

phase, with measured composition of Mg:Ag:Sb = 33.6:33.1:33.3. Subsequent XRD analysis of the 613 K-quenched specimen revealed the coexistence of the α phase and β phase [Supplemental Material Fig. S9(a)] [24]. However, SEM characterization showed insufficient phase contrast to differentiate these two phases [Fig. 3(b) and Supplemental Material Fig. S10(b)] [24]. The γ phase becomes predominant at 773 K [Fig. 3(d), Supplemental Material Fig. S11(b), and Table S2] [24] alongside Ag_3Sb and Sb precipitation, and the composition of the γ phase is determined to be $\text{Mg}_{44.3}\text{Ag}_{20}\text{Sb}_{35.5}$. Furthermore, Ag_3Sb precipitates in the specimens quenched at 773 K exhibit unique morphologies compared to other samples, providing direct evidence of the eutectic melting between the Ag_3Sb and Sb phases.

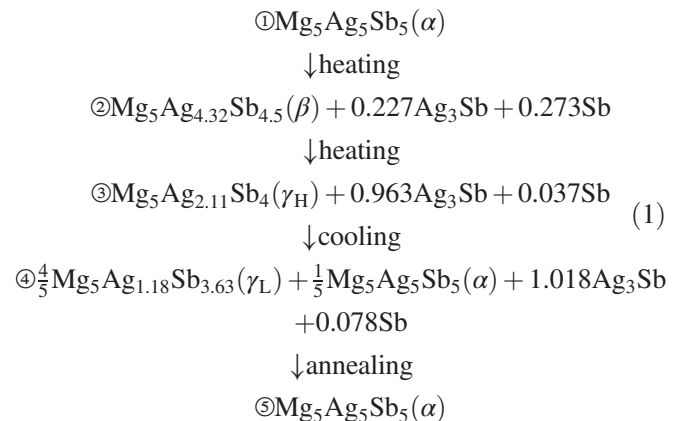
During cooling, complex phase redistribution occurred. At 423 K, the composition of the γ phase becomes $\text{Mg}_{48.5}\text{Ag}_{15.8}\text{Sb}_{35.7}$ [Supplemental Material Fig. S13(b), and Table S4] [24], following the nucleation of the α phase. Ultimately, the room-temperature γ phase exhibited a composition of $\text{Mg}_{50}\text{Ag}_{14}\text{Sb}_{36.6}$ [Fig. 3(e), Supplemental Material Fig. S14(a), and Table S4] [24], accompanied by a further increase in the α -phase content. Notably, the pure β phase was found to be completely absent across all experimental specimens. Differential scanning calorimetry analysis (Supplemental Material Fig. S15) [24] shows that γ phase remains as the dominant phase after heating to 703 K (γ -phase region) and subsequent cooling, while the α phase formed only below 470 K. In contrast, when the maximum temperature is 613 K (β -phase region), the α phase becomes the predominant phase instead of the expected β phase after cooling [27]. These observations demonstrate that the β phase is thermodynamically metastable at ambient conditions, thereby preventing direct experimental verification of its precise composition via *ex situ* characterization techniques.

The γ phase displayed compositional variations during thermal cycling, and its equilibrium phase information was determined (Supplemental Material Figs. S16–S18 and Tables S5–6) [24]. The experimental composition of the specimen with a nominal stoichiometry of Mg:Ag:Sb = 5:1:4 is $\text{Mg}_{51.0}\text{Ag}_{11.8}\text{Sb}_{37.2}$, corresponding to the γ phase observed at room temperature after cooling (γ_L phase). In contrast, Ag-enriched nominal stoichiometries (5:2:4; 5:3:4; 5:4:4) exhibited measured compositions of $\text{Mg}_{45.0}\text{Ag}_{18.5}\text{Sb}_{36.5}$, $\text{Mg}_{45.2}\text{Ag}_{19.9}\text{Sb}_{35.9}$, and $\text{Mg}_{44.8}\text{Ag}_{19.2}\text{Sb}_{36.1}$, demonstrating remarkable consistency with the high-temperature γ phase (γ_H phase). The compositional disparity between the two phases induces a systematic leftward shift in the XRD peaks of the γ_H phase compared with the γ_L phase [Supplemental Material Fig. S16(b)] [24]. Additionally, it is noted that the chemical composition of $\text{Mg}_{4.8}\text{Ag}_{1.4}\text{Sb}_4$ single crystal is consistent with the γ_L phase rather than the γ_H phase (Supplemental Material Table S7) [24]. Although the crystal growth

temperature falls within the stability region of the γ_H phase, it should be emphasized that the crystal growth in the Bi flux [25] is actually governed by the quaternary Mg-Ag-Sb-Bi phase diagram, and preferential crystallization of the γ_L phase is possible.

Despite the observation of the Ag_3Sb /Sb precipitations during the phase transition of Mg-Ag-Sb in early studies, the phase transformation in the Mg-Ag-Sb was regarded as a polymorphic process [17,18]. It can be attributed to the lack of direct evidence in the variation of chemical compositions in the Mg-Ag-Sb compound. In addition, the successful growth of γ -phase single crystals and the preparation of the polycrystalline γ -phase compounds also provide convincing results for the identification of crystal structure and chemical compositions. Herein, by combining refinement and compositional characterization, it is confirmed that the phase transitions in Mg-Ag-Sb is, in fact, non-polymorphic.

Rapid cooling inhibits complete phase transitions due to insufficient atomic diffusion, leading to the retention of metastable phases at room temperature. For instance, a significant amount of γ_L phase is retained when cooling from the γ_H -phase region [Fig. 3(e) and Supplemental Material Fig. S15] [24]. Upon subsequent heating, most of the γ_L phase transforms rapidly into the α phase, manifesting as a small endothermic peak within the temperature range of 470–500 K [Fig. 3(g) and Supplemental Material Fig. S19] [24]. To drive the system to complete equilibrium quickly, annealing at 503 K (Supplemental Material Fig. S20) [24] was employed to facilitate the recovery of the α phase [Fig. 3(f) and Supplemental Material Fig. S14(b)] [24]. Alternatively, controlled slow cooling permits sufficient atomic migration, thereby facilitating spontaneous restoration of the α phase through thermodynamically favored transition pathways. Experimentally, the recovery of the α phase during low-temperature annealing is often mistaken for a polymorphic transformation, hindering elucidation of the true phase transition mechanisms. As evidenced by the preceding analysis and as illustrated in the schematic [Fig. 3(h)], the phase transitions in the Mg-Ag-Sb ternary compound during thermal cycling can be expressed as the following reactions:



B. Microscopic origin of the non-polymorphic transitions

The microstructural evolution induced by thermal cycling is directly observable in the SEM micrographs, with silver migration being particularly prominent [Figs. 3(c)–3(f) and Supplemental Material Figs. S11–S14] [24], and the breaking and reorganization of bonds are inevitable. To elucidate the phase transition mechanism, the electron localization function (ELF) [28–30] analysis with assessments of bond character and strength has been performed. The ELF distributions on the α phase (100), β phase (110), and γ_H phase (110) are shown in Figs. 4(a)–4(c), respectively. Obvious electron localization is observed around Sb atoms (red regions), whereas the degree of electron localization near Mg and Ag atoms is notably lower (blue regions). It differs distinctly from the characteristic electron localization in the C-C covalent bonds of diamond [Supplemental Material Fig. S21(a)] [24]. In contrast, it closely resembles

the scenario where electrons are highly localized around Cl[−] ions in NaCl [Supplemental Material Fig. S21(b)] [24], indicating the Mg-Sb and Ag-Sb bonds are mainly ionic. Quantitative analysis through the integrated crystal orbital bond index (ICOBI) and the integrated crystal orbital Hamilton population (ICOHP) [Fig. 4(d) and Supplemental Material Table S8] [24] provides crucial insights into chemical bonding. The ICOBI [31,32] inversely correlates with bond ionicity, reflecting bond order and character: values approaching 1 signify covalent interactions, whereas values near 0 suggest ionic or delocalized bonding characteristics. The ICOHP quantifies the covalent component strength of chemical bonds [32–35], where the larger the absolute value of its value (usually negative), the stronger the covalent component of the bond.

Figure 4(d) clearly shows the variation in chemical bonding nature and strength for the listed substances: transitioning from typical covalent bonds (e.g., diamond,

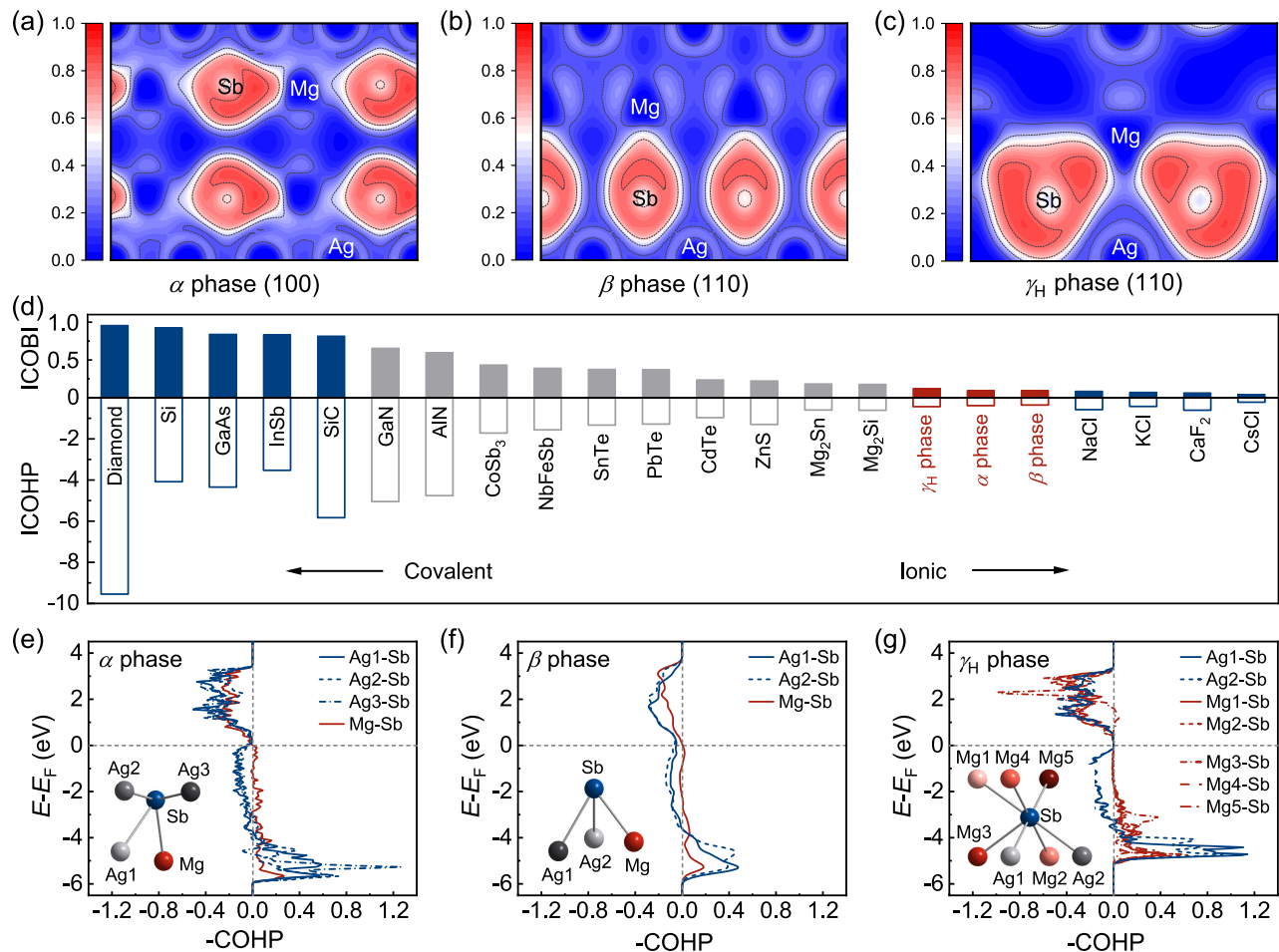


FIG. 4. Electron localization function distributions and bonding characteristics across the Mg-Ag-Sb ternary compound. (a)–(c) the ELF distributions on the α -phase (100), β -phase (110), and γ_H -phase (110) planes, respectively. The ELF values range from 0 to 1, with a color scale representing the degree of electron localization: red indicates highly localized electrons, while blue denotes significant delocalization. (d) Comparison of the ICOBI and ICOHP values among various materials and the Mg-Ag-Sb compound. (e)–(g) Energy-resolved -COHP curves for Ag-Sb and Mg-Sb atomic pairs in different phases, illustrating bonding strength evolution near the Fermi level ($E - E_F = 0$). Inset is the schematic diagram depicting the primary bonding types within the computational crystal structure.

Si, with high ICOBI and strongly negative ICOHP) to typical ionic bonds (e.g., NaCl, KCl, with low ICOBI and weakly negative ICOHP). The calculated ICOBI values across all Mg-Ag-Sb phases consistently range between 0.09 and 0.12, remarkably close to the classic ionic compound NaCl (0.085), indicating that ionic bonding is the predominant bonding type in the Mg-Ag-Sb compound. Concurrently, the ICOHP values for these phases range from -0.35 to -0.43 eV, which closely align with that of NaCl (-0.58 eV). This similarity further supports the predominance of ionic bonding in the Mg-Ag-Sb compound, with negligible contribution from covalent interactions. The Madelung energy per unit volume was compared across several typical ionic compounds (Supplemental Material Table S9) [24] to better evaluate the relative strength of ionic bonding. The absolute value of energy decreases monotonically from α phase through β phase to γ_H phase. The α phase exhibits a value comparable to that of KCl, indicating strong ionic cohesion. In contrast, the lower energies in the β phase and γ_H phase suggest relatively weaker ionic bonding.

Based on the clarified bonding types in the Mg-Ag-Sb compound, crystal orbital Hamilton population (COHP) [33,34] analysis can be employed to further elucidate the bonding characteristics between different atoms and their influence on stability. Notably, the presence of significant antibonding states (i.e., $-\text{COHP} < 0$) in the vicinity of the

valence band maximum (VBM) is indicative of weakened covalent bonding, which correlates with reduced vibrational frequency and enhanced atomic displacement amplitudes. Schematic diagrams of the Ag-Sb and Mg-Sb bonds formed by these atoms in each phase, along with their COHP as a function of energy, are shown in Figs. 4(e)–4(g) and Supplemental Material Fig. S22 [24]. The COHP analysis reveals that, across all three phases, the Ag-Sb interactions exhibit pronounced antibonding character near the VBM, while Mg-Sb bonding states are stabilized at a deeper energy level. This suggests that Mg-Sb bonds are stronger than their Ag-Sb counterparts. Furthermore, given that Ag possesses a heavier atomic mass and fewer valence electrons compared to Mg, Ag atoms are expected to exhibit lower vibrational frequencies and greater vibration amplitudes under thermal excitation, consistent with their weaker bonding environment.

Molecular dynamics (MD) simulations can provide direct validation for this analysis. Figures 5(a)–5(c) show the simulated atomic trajectories for the α phase at 500 K, β phase at 600 K, and γ_H phase at 700 K. In the α phase, Mg, Ag, and Sb atoms exhibit small vibration amplitudes. In the β phase, both Mg and Ag atoms show significantly increased vibration amplitudes relative to Sb atoms, with Ag demonstrating the most pronounced vibrational enhancement, followed by Mg, and the migration of Mg and Ag between different atomic sites becomes possible.

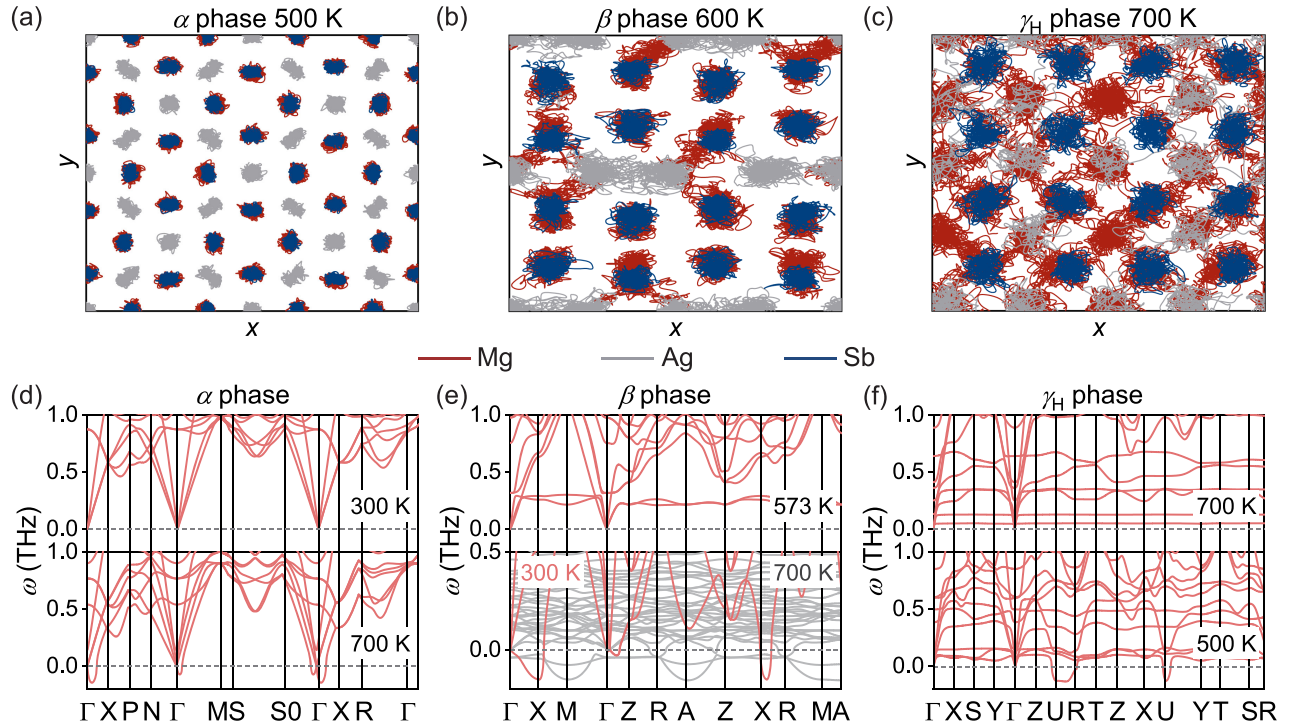


FIG. 5. Molecular dynamic simulations and calculated phonon dispersions of the Mg-Ag-Sb ternary compound. Molecular dynamic simulations of the (a) α phase at 500, (b) β phase at 600, and (c) γ_H phase at 700 K. Calculated phonon dispersions of (d) α phase at 300 and 700 K, (e) β phase at 300, 573, and 700 K, and (f) γ_H phase at 500 and 700 K.

This trend continues in the γ_H phase, where the amplitudes of Mg and Ag atoms strengthen further, while the amplitude of Sb atoms remains relatively small. Molecular dynamics simulations further confirm that the stable Sb atomic framework serves as the structural matrix during phase transitions, enabling the migration of Ag and Mg atoms. The atomic Ag diffusion facilitates the formation of the Ag_3Sb secondary phase [clearly discernible in Figs. 3(c)–3(e)], while concomitant migration of Mg and Ag atoms drives structural reorganization, ultimately establishing the coexistence of multiple phases. This phenomenon shows striking similarities to the liquidlike migration exhibited by Cu^+/Ag^+ ions in typical superionic conductors (e.g., Cu_2Se [36,37], Cu_2S [38,39], and Ag_2Se [40]).

Critically, the increasing mobility of Mg and Ag within the stable Sb framework coincides with the thermal stability windows revealed by the calculated phonon spectra. As shown in the top panel of Figs. 5(d)–5(f) and Supplemental Material Figs. S23–S25 [24], the phonon spectra demonstrate that each distinct phase is thermodynamically stable only within specific temperature intervals. For example, the α phase, β phase, and γ_H phase are stable at 300, 573, and 700 K, respectively. Outside these intervals, the phonon spectra exhibit imaginary frequencies (α phase at 700 K, β phase at 300 and 700 K, and γ_H phase at 500 K), indicating lattice instability and ultimately inducing the phase transitions.

C. Thermal recoverability of Mg-Ag-Sb compound

The phase restoration can be indirectly revealed by the variation in thermoelectric performance [Figs. 6(a)–6(f)]. The thermoelectric properties of Mg-Ag-Sb demonstrate substantial deterioration after heating to 673 K (Fig. 1), and then consecutive characterizations during heating and cooling cycles have been performed. During initial heating, the resistivity plummets from $973.2 \mu\Omega \text{ m}$ at room temperature to $14.7 \mu\Omega \text{ m}$ at 550 K, and the Seebeck coefficient surges from 31.7 to $213.2 \mu\text{V K}^{-1}$ at 475 K. During the cooling process, both electrical resistivity and the Seebeck coefficient exhibited a coordinated variation pattern characterized by a moderate increase followed by a slight reduction, ultimately reaching room-temperature values of $18.4 \mu\Omega \text{ m}$ and $215.8 \mu\text{V K}^{-1}$, respectively. In contrast, thermal conductivity demonstrated an inverse trend, stabilizing at $1.1 \text{ W m}^{-1} \text{ K}^{-1}$ upon cooling to ambient temperature. The thermoelectric properties observed during the second heating process demonstrate exceptional reproducibility. Multiple samples heated to different temperatures all exhibit similar recovery characteristics (Supplemental Material Figs. S26–S30) [24].

To further validate the thermal recoverability of the MgAgSb, the specimen was subjected to 500 thermal cycles between 423 and 673 K, followed by annealing at 503 K. The thermoelectric properties of the as-prepared

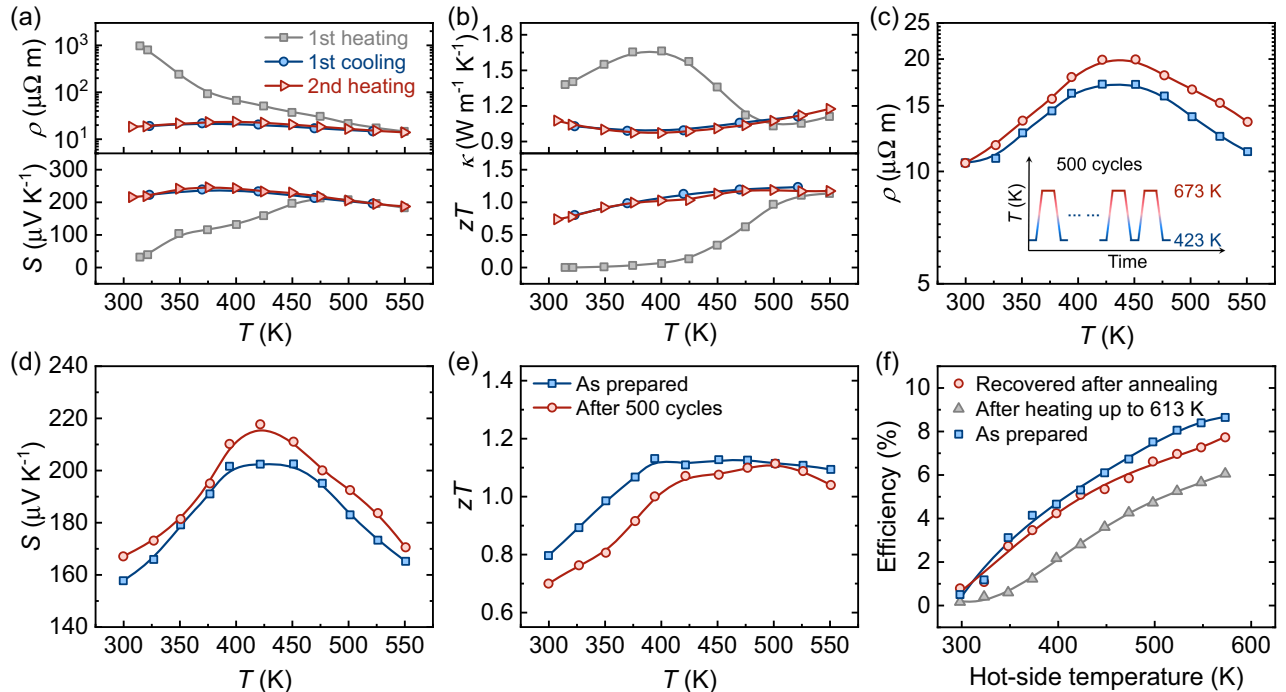


FIG. 6. Cycling stability of the Mg-Ag-Sb ternary compound and performance of the single-leg device. (a) The temperature-dependent resistivity and Seebeck coefficient, (b) thermal conductivity and zT of the Mg-Ag-Sb compound after heating to 673 K in the thermal cycling. (c) The temperature-dependent resistivity, (d) Seebeck coefficient, and (e) zT of the Mg-Ag-Sb compound before and after 500 cycles between 423 and 673 K. (f) The relationship of hot-side temperature and efficiency across the as-prepared state, thermally damaged state, and annealed-recovered state in the MgAgSb single-leg device.

sample and the one after 500 thermal cycles are comparable [Figs. 6(c)–6(e)]. The thermally recoverable characteristics of MgAgSb were further evaluated in a single-leg device. The heat-to-electricity conversion efficiencies of the device were compared among three different states: as-prepared, thermally damaged (heating up to 613 K), and annealing recovered [Fig. 6(f) and Supplemental Material Figs. S31–S33] [24]. Previous studies establish that Ag₃Sb formation through Ag diffusion significantly degrades MgAgSb's thermoelectric performance [11,12,16]. To address this issue, a Mg₂Ni contact layer was implemented along with an Ag metallic layer for welding [41]. The as-prepared single-leg device achieved a conversion efficiency of 8.6% at a temperature difference of 300 K. After thermal degradation at 613 K for 1 h, the device exhibited a conversion efficiency of only 6.1%. It should be emphasized that as testing temperature increases, partial phase restoration occurs. Subsequent annealing further improved the efficiency to 7.7%, demonstrating almost 90% of the initial value.

Collectively, the recovery of the α phase and the restoration of thermoelectric properties after extensive thermal cyclings, along with the recovery of device efficiency following thermal degradation and annealing, unambiguously demonstrate that the Mg-Ag-Sb system exhibits a unique thermal recoverability rarely observed in other materials. Generally, thermal decomposition at elevated temperatures has been observed for most thermoelectric materials. To illustrate this point, the filled skutterudite CeFe₄Sb₁₂ was further investigated. As shown in Supplemental Material Fig. S34(a) [24], CeFe₄Sb₁₂ undergoes a significant non-polymorphic phase decomposition upon heating to 1123 K, with negligible elemental loss (Supplemental Material Fig. S35) [24]. However, subsequent annealing at 773 K does not restore the original phase composition of the decomposed sample. It should be emphasized that the remarkable self-healing capability in the Mg-Ag-Sb compound originates from the rapid atomic diffusion of Ag and Mg. It is reasonable to expect similar atomic diffusion behavior in other materials, such as the Ag-based compounds. For instance, the decomposition of AgSbTe₂ at elevated temperatures leads to the formation of the Ag₂Te secondary phase [Supplemental Material Fig. S34(b)] [24]. Similarly, by employing low-temperature annealing, the recovery of AgSbTe₂ can also be successfully realized. Our results shed some new light on the discovery of thermal recoverable thermoelectric materials.

III. DISCUSSIONS

The results of this study elucidate some key challenges in the synthesis of the α -MgAgSb. Notably, the formation of Ag₃Sb and Sb phases is often unavoidable during the synthesis of polycrystalline α phase, whether via the ball milling method [8,42–45] or the high-temperature melting method [21–23]. It should be noted that the detection

limitations of XRD may preclude the identification of secondary phases, but SEM often reveals their presence. In hot pressing or spark plasma sintering (SPS), precise control of temperature, pressure, and electrical current is crucial. Deviations from optimal processing conditions can easily promote the formation of the β phase or γ phase, consequently inducing the precipitation of Ag₃Sb and Sb phases. Furthermore, potential electrical-field-driven Mg and Ag diffusion necessitates careful verification of the suitability of the SPS process for synthesizing the high-performance α -phase MgAgSb. In the high-temperature melting method, the formation of the γ phase is thermodynamically favored, invariably accompanied by substantial precipitation of Ag₃Sb and Sb phases. because of kinetic limitations during the subsequent low-temperature annealing process, these secondary phases are difficult to eliminate. Similarly, persistent challenges in the growth of the α -phase single crystals also stem directly from these complex phase transitions. The Bridgman and the slow-cooling methods are incapable of synthesizing single-crystalline α phase owing to the preferential formation of γ phase at elevated temperatures. For the flux method, it is crucial to select low-melting-point solvents and conduct crystal growth at low temperatures to avoid the formation of the γ phase. Numerous attempts have been made to grow α -phase single-crystals by the flux method, yet none have succeeded (Supplemental Material Figs. S36–S40) [24].

In addition, the determination of the Mg-Ag-Sb phase diagram provides fundamental guidance for developing high-performance thermoelectric materials. However, the high diffusion rates of Mg and Ag, while promoting rapid equilibration, introduce critical experimental limitations. During high-temperature quenching (e.g., >650 K), excessive atomic mobility impedes the complete suppression of phase transitions, leading to partial retention of the α phase within the target equilibrium phases. Furthermore, the electric fields inherent to SEM and electron probe microanalysis characterizations can induce localized compositional deviations after long-time exposure to electron beam irradiation, complicating accurate phase identification (Supplemental Material Fig. S41) [24]. These interactions between rapid diffusion dynamics and characterization techniques substantially increase the experimental complexity of establishing reliable phase diagrams for the Mg-Ag-Sb ternary system.

IV. CONCLUSIONS

To sum up, our results reveal a sequential decomposition of Mg-Ag-Sb ternary compound during heating: the tetragonal ($I\bar{4}c2$) MgAgSb (α phase) transforms into the tetragonal ($P4/nmm$) Mg₅Ag_{4.32}Sb_{4.5} (β phase), followed by conversion to the cubic ($Fm\bar{3}m$) Mg₅Ag_{2.11}Sb₄ (γ_H phase) with concurrent Ag₃Sb and Sb precipitations. Upon cooling, the Mg₅Ag_{2.11}Sb₄ transforms into the cubic Mg₅Ag_{1.18}Sb_{3.63} (γ_L phase), α phase, and Ag₃Sb/Sb

impurities. Electron localization function and bonding analysis confirm the ionic nature of interactions in the Mg-Ag-Sb compound and further reveal a notable weakness in the Ag-Sb bond compared to the Mg-Sb bond. Molecular dynamics simulations identify Mg and Ag migration in the Sb sublattices as the underlying mechanism driving these transitions. Within their stable ranges, phonon spectra show no imaginary frequencies for the α , β , and γ_H phases. Outside these ranges, imaginary frequencies can be observed, indicating lattice instability that induces phase transitions. Notably, rapid Mg and Ag diffusion facilitates α -phase restoration upon annealing at 503 K and enables 90% device efficiency recovery after thermal shock at 613 K, demonstrating exceptional thermal reversibility. This work provides insights into microstructure evolution and phase transition dynamics in MgAgSb-based thermoelectric materials.

V. METHODS

A. Experiment

1. Materials synthesis

Preparation of the MgAgSb: high-purity Mg pellets (99.8%, ZhongNuo Advanced Material) and Ag pellets (99.9%, ZhongNuo Advanced Material) were precisely weighed in a 1:0.97 molar ratio and loaded into niobium (Nb) tubes. The tubes were sealed using an arc welder under an argon atmosphere. Subsequently, the Nb tubes were encapsulated within quartz ampoules under vacuum. The quartz ampoules were heated to 1173 K in a furnace and held for 12 h, followed by rapid water quenching to obtain homogenized MgAg alloy ingots. Then, the as-prepared MgAg alloy was stoichiometrically weighed (Mg:Ag:Sb = 1:0.97:0.99) and subjected to high-energy ball milling for 10 h. Predetermined Sb shots (99.99%, ZhongNuo Advanced Material) were then added to the milling vial for secondary ball milling (8 h) to achieve homogeneous multiphase mixing. Finally, the powder was consolidated via SPS at 573 K under 80 MPa pressure for 8 min, yielding the MgAgSb disk-shaped samples of $\phi 10 \text{ mm} \times 2 \text{ mm}$. All heat-treated samples were prepared by first encapsulating the specimens in Nb tubes, followed by vacuum sealing within quartz ampoules for subsequent thermal processing.

Preparation of the γ phase: nominal stoichiometries of Mg:Ag:Sb = 5: x :4 ($x = 1-4$) were employed for sample preparation. High-purity elements were precisely weighed and loaded into graphite crucibles, which were then transferred into Nb tubes, and sealed by using an arc welder under an argon atmosphere. Subsequently, the Nb tubes were encapsulated within vacuum-sealed quartz ampoules, and were heated to 1173 K for 12 h, and then cooled (0.5 K min^{-1}) to 753 K for 168 h isothermal annealing, followed by rapid water quenching.

2. Thermoelectric properties characterization

Simultaneous electrical resistivity and Seebeck coefficient measurements were conducted using a commercial CTA system (Cryoall) under a helium atmosphere. For thermal transport analysis, disk-shaped specimens with a diameter of $\phi 10 \text{ mm} \times 1 \text{ mm}$ were prepared to measure thermal diffusivity (D) using laser flash analysis (LFA 457, Netzsch). The specific heat capacity (C_p) of the sample was characterized by a differential scanning calorimeter (DSC, 404 F3 Pegasus, Netzsch). Sample density (d) was determined through the Archimedeian method, enabling thermal conductivity calculation via $\kappa = DC_p d$.

3. Microstructural and phase characterizations

All samples quenched during the thermal cycling process were analyzed using room-temperature powder x-ray diffraction to identify phase compositions. The *in situ* PXRD measurements for Mg-Ag-Sb ternary compound powder were conducted with a heating-cooling rate of 10 K min^{-1} (293-753-323 K). Upon reaching each target temperature, the system was held isothermally for 10 min before data collection, while maintaining a vacuum environment throughout the entire testing process. Both PXRD data were collected via Rigaku SmartLab diffractometer with monochromatic Cu- $K_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$). The microstructure and elemental distribution were systematically characterized through high-resolution scanning electron microscopy (SEM, GeminiSEM 360, Zeiss) coupled with electron probe microanalysis (EPMA, JXA-8100, JEOL). The phase transitions of samples were further characterized by differential scanning calorimeter (DSC, 404 F3 Pegasus, Netzsch). The mass variation of the sample during cycling was characterized via the simultaneous thermal analysis (STA, STA449F5, Netzsch).

4. Single-leg device fabrication and characterization

The Ag/Mg₂Ni/MgAgSb/Mg₂Ni/Ag multilayer architecture was consolidated via SPS at 573 K under the pressure of 85 MPa for 10 minutes. The resulting bulk material was machined into a thermoelectric leg ($4.5 \times 4.5 \times 7.0 \text{ mm}^3$) with Ag foil electrodes bonded to both ends using transient liquid phase bonding, where an Ag-Sn intermetallic compound served as the soldering medium. The output power and energy conversion efficiency (η) of the single-leg thermoelectric device were quantitatively evaluated across varying temperature differentials (ΔT) using a custom-designed characterization system operating under vacuum conditions. This apparatus integrates four-probe electrical measurement modules with precision temperature controllers, enabling the simultaneous acquisition of output power and heat flux.

B. Computation

1. Molecular dynamics simulations and first-principles calculations

Density functional theory (DFT) calculations were carried out using the plane-wave pseudopotential approach as implemented in the Vienna *ab initio* simulation package (VASP) [46,47]. Electron-ion interactions were modeled using the projected augmented-wave (PAW) method [48] with the 3s (Mg), 4d and 5s (Ag), 5s and 5p (Sb) electrons explicitly treated as valence electrons. The exchange-correlation functional was approximated within the generalized gradient approximation formulated by Perdew, Burke, and Ernzerhof [49]. A kinetic energy cutoff of 380 eV was employed for the plane-wave basis set. The electronic Brillouin zone integration was performed using k-point meshes with a grid spacing of $2\pi \times 0.03 \text{ \AA}^{-1}$. To model the disordered solid solutions in β -Mg₄Ag₃Sb₄, γ_H -Mg₅Ag₂Sb₄, and γ_L -Mg₅Ag₁Sb₄ phases, special quasirandom structures (SQSs) based on 11-atom supercell containing a single vacancy for β and γ_H phases and 10-atom supercell containing two single vacancies for γ_L phase were generated using the Integrated Cluster Expansion Toolkit [50,51]. Structural relaxations were conducted via total energy minimization until the residual forces on the atoms fell below $10^{-3} \text{ eV \AA}^{-1}$. Spin-orbit coupling was included in all calculations involving antimony due to its significant atomic mass. For self-consistent electronic structure calculations, Brillouin zone sampling was performed using $6 \times 6 \times 4$, $9 \times 9 \times 7$, $8 \times 8 \times 8$, and $8 \times 8 \times 8$ k-point grids for α -MgAgSb, β -Mg₄Ag₃Sb₄, γ_H -Mg₅Ag₂Sb₄, and γ_L -Mg₅Ag₁Sb₄, respectively. The chemical bonding was extracted from the VASP wave functions by adopting the LOBSTER package [33,52–54].

To investigate finite-temperature structural and vibrational properties, *ab initio* Born-Oppenheimer molecular dynamics (AIMD) simulations were performed using the PAW method under the isothermal-isobaric ensemble. These simulations employed a Langevin [55,56] thermostat and a Parrinello-Rahman barostat [57,58] covering temperatures from 300 to 700 K in increments of 100 K at approximately ambient pressure. Simulations were carried out using a $2 \times 2 \times 1$ supercell (191 atoms) for α -MgAgSb, $2 \times 2 \times 2$ supercells (88 atoms) for both the β -Mg₄Ag₃Sb₄ and γ_H -Mg₅Ag₂Sb₄ alloy, and $2 \times 2 \times 2$ supercells (80 atoms) for the γ_L -Mg₅Ag₁Sb₄ alloy. Each simulation spanned 100 ps with a time step of 1 fs using a plane wave cutoff of 380 eV. An on-the-fly machine learning potential [59–61] was employed to accelerate molecular dynamics simulations, as implemented in the VASP code. Atomic trajectories from the last 50 000 steps after each AIMD simulation were collected after thermal equilibration to compute temperature-averaged structures at each considered temperature and pressure. These thermally corrected structures were subsequently used for phonon

dispersion calculations. Temperature-dependent phonon dispersions for all three phases were obtained using the temperature-dependent effective potential (TDEP) method [62–65], which allows the extraction of both harmonic and anharmonic interatomic force constants. The TDEP calculations were based on *ab initio* Born-Oppenheimer molecular dynamics with a Nose-Hoover thermostat [66], over the same temperature range of 300 to 700 K in 100 K increments. Crystal orbital Hamilton population (COHP) analysis [52] has been performed using the LOBSTER code [67].

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

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