

Real-Space Visualization of the Intrinsic Aging in n -type $\text{Mg}_3(\text{Sb}, \text{Bi})_2$ Thermoelectrics

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Long-term stability in materials is commonly associated with resistance to external perturbations. Yet metastable defect populations may relax spontaneously even in the absence of environmental stimuli, reshaping macroscopic properties over extended timescales. Here, we show the real-space visualization of intrinsic aging of n -type $\text{Mg}_3(\text{Sb}, \text{Bi})_2$ under inert and room-temperature conditions after two-year storage by atomic-scale characterizations. Density-functional-theory calculations and machine-learning molecular dynamics simulations prove that the aging originates from relaxation of a metastable Mg-rich state, in which low vacancy-formation energies and migration barriers enable thermodynamically favorable and kinetically accessible Mg redistribution. Multiscale characterizations further reveal that grain boundaries (GBs) act as fast-diffusion pathways and effective sinks, establishing a hierarchical Mg redistribution process from grain interiors to GBs and surfaces. These results identify intrinsic defect physics as one of the fundamental stability constraints in functional materials and underscore the importance of controlling defect thermodynamics and transport pathways for achieving practically durable materials.

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I. INTRODUCTION

Advanced materials enable next-generation technologies by offering superior performance (strength, efficiency, functionality) through control of composition, defects, and microstructures [1,2]. Yet, high performance, though pivotal, does not fully dictate the practical utility of materials. In addition, long-term reliability ultimately depends on material stability, encompassing mechanical, chemical, and thermal stability over extended operation.

Many high-performance materials are intentionally stabilized in nonequilibrium compositional or defect configurations to achieve superior functional properties. Such metastable states store excess free energy, which can

introduce slow internal relaxation processes mediated by defect redistribution. These gradual atomic rearrangements can drive property drift over extended timescales. Natural aging phenomena in alloys involve the gradual precipitation or clustering of solute atoms from supersaturated solid solutions, leading to an enhancement in mechanical properties [3,4]. In contrast, such an evolution in functional materials often causes performance degradation and is thus distinguished as “intrinsic aging.” Examples include nanostructured metals, which derive exceptional strength from high defect densities but gradually undergo grain-boundary (GB) relaxation and coarsening [5,6]. Hybrid perovskite semiconductors exhibit outstanding optoelectronic performance but suffer from ionic migration and phase segregation under nominally mild conditions [7,8]. These examples illustrate that intrinsic structural evolution can influence material functionality over time, even in the absence of external stimuli.

Thermoelectric (TE) materials could be sensitive for probing defect-driven relaxation, as their performance depends critically on carrier concentration and defect chemistry. Achieving high TE performance requires fine control of carrier density through compositional tuning and defect engineering [2,9,10], often pushing materials into

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metastable regimes. Nevertheless, stability degradation in TE materials has been predominantly attributed to external driving forces [11], including high-temperature volatilization, oxidation, and chemical reactions. Whether intrinsic defect kinetics alone can drive performance evolution under nominally inert conditions remains largely unexplored. Among TE systems, *n*-type $\text{Mg}_3(\text{Sb}, \text{Bi})_2$, one of the most promising materials for near-room-temperature energy conversion owing to its high performance and earth-abundant constituents [12–16], has been limited in its commercialization by its fraught stability [17,18]. Realization of *n*-type conduction relies on Mg-rich compositions that suppress Mg vacancies [19–21], placing the material in a metastable nonequilibrium state with high energy. This raises a fundamental question: Can intrinsic defect relaxation spontaneously drive performance degradation even in the absence of external environmental stimuli such as high temperatures, current, and caustic atmospheres?

Here, we uncover the real-space visualization of the intrinsic aging of polycrystalline *n*-type $\text{Mg}_3(\text{Sb}, \text{Bi})_2$ during the storage of two years in inert environments at room temperature, associated with time-dependent performance degradation. Combining atomic-scale characterizations with density-functional-theory (DFT) calculations and machine-learning molecular dynamics (ML-MD) simulations, we show that this intrinsic aging originates from spontaneous Mg migration from grain interiors toward Mg-deficient GBs and surfaces, accompanied by progressive Mg vacancy accumulation inside grains. High-angle annular-dark-field- (HAADF) STEM characterization reveals fluctuations in the Mg atomic signal within grains. Atom-probe-tomography (APT) analysis reveals an enhanced Mg-deficient tendency at GBs after aging. Time-of-flight–secondary-ion-mass-spectrometry (TOF-SIMS) measurements further confirm the redistribution of Mg content near the sample surface. These findings demonstrate that defect-mediated relaxation can persist over macroscopic timescales even under chemically inert conditions. More broadly, our results establish intrinsic defect kinetics as a hidden stability constraint in non-equilibrium functional materials and highlight the importance of defect and interface engineering for achieving truly durable performance.

II. RESULTS AND DISCUSSION

A. Intrinsic aging under inert storage

To establish a reliable baseline for evaluating stability, we synthesized the polycrystalline samples with the nominal composition of $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ —a classic *n*-type matrix composition with highly reproducible TE properties (see Sec. IV for details). All samples were stored at room temperature in an argon-atmosphere glovebox with rigorous exclusion of moisture and oxygen for up to two

years, thereby eliminating external thermal and chemical driving forces.

The TE performance of the samples gradually degrades with prolonged storage (one month, one-and-a-half months, six months, one year, and two years) under argon atmosphere [Figs. 1(a) and S1 in Supplemental Material [22]], revealing an unexpected intrinsic instability of $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ under inert conditions. After two years, the thermoelectric figure of merit ZT near 300 K decreases from 0.36 to 0.23 (approximately 36%), mainly due to the deteriorated electronic properties. In particular, the Hall carrier concentration (n_H) exhibits a monotonic decreasing trend with the extension of storage time [Fig. 1(b)]. X-ray diffraction and scanning electron microscopy combined with energy-dispersive spectroscopy (see Supplemental Material [22] Figs. S2–S4) show no secondary phases, precipitation, or microstructural coarsening after long-term storage. Given the exclusion of external

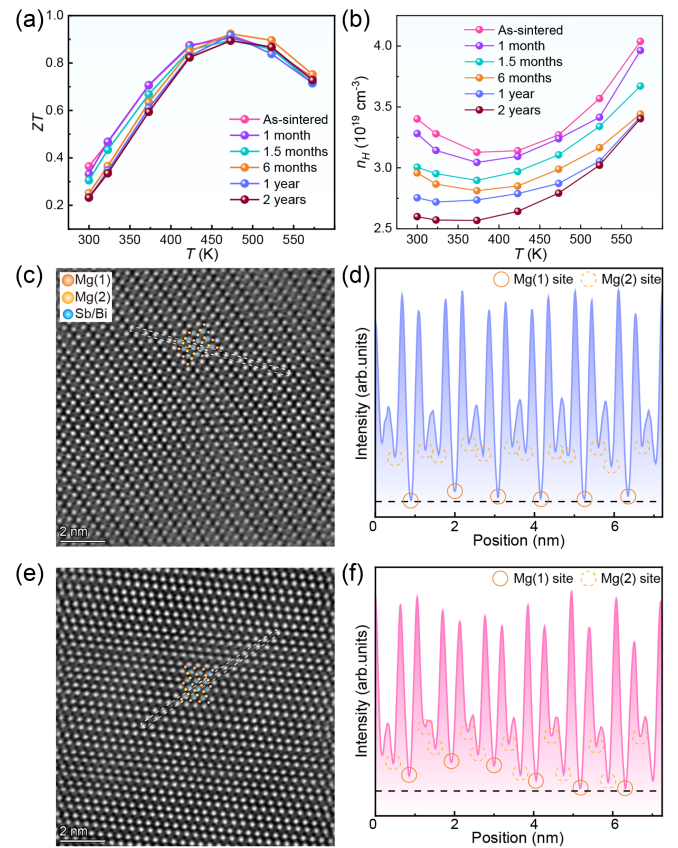


FIG. 1. TE performance and microstructure characterizations on an $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ sample. Temperature-dependent (a) ZT and (b) n_H values for $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ with different storage times in argon atmosphere. (c) HAADF image of as-sintered $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ projected along [100], with atomic sites [Mg(1), Mg(2), Sb] overlaid. (d) Intensity profiles for the dashed rectangular regions in (c). (e) HAADF image of two-year argon-stored $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ projected along [100], with atomic sites [Mg(1), Mg(2), Sb] overlaid. (f) Intensity profiles for the dashed rectangular regions in (e).

stimuli and secondary precipitated phases, this reduction in n_H most plausibly originates from defect redistribution within the bulk.

As the predominant native defects in $\text{Mg}_3(\text{Sb, Bi})_2$ [19], Mg vacancies can capture conduction electrons and shift the Fermi level (E_f) toward the valence-band maximum (see Supplemental Material [22] Figs. S5b and S5c). This downward E_f shift suppresses the ionization of donor dopants, thereby diminishing the number of electrons provided by the donors. Together, these effects collectively lead to a decrease in the net carrier concentration. This inference is supported by x-ray photoelectron spectroscopy (XPS) results (see Supplemental Material [22] Fig. S6), which show systematic shifts of all peaks toward higher binding energies.

Direct atomic-scale evidence for Mg vacancy accumulation is obtained from double Cs-corrected HAADF STEM. $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ grain images acquired in the [100] projection for the as-sintered and two-year argon-stored samples are shown [Figs. 1(c) and 1(e)], respectively. The atomic layers of $\text{Mg}_3(\text{Sb, Bi})_2$ arranged along the [001] direction follow the sequence Mg(1)-(Sb, Bi)-Mg(2)-Mg(2)-(Sb, Bi)-Mg(1), allowing identification of individual atomic columns. The intensity profiles [Figs. 1(d) and 1(f)] are extracted from the marked regions in Figs. 1(c) and 1(e), respectively. The intensity peaks correspond to (Sb, Bi) atomic columns, while the intensity valleys correspond to Mg atomic columns. Owing to their distinct coordination environments, Mg(1) columns exhibit deeper intensity valleys than Mg(2) columns. A striking

contrast emerges upon long-term storage. While the as-sintered sample displays highly uniform intensity among equivalent Mg atomic columns, the two-year argon-stored sample exhibits significant intensity fluctuations at both Mg(1) and Mg(2) sites. Such intensity fluctuations indicate an inhomogeneous distribution of Mg atoms within the lattice, evidencing the accumulation of Mg vacancies at both Mg(1) and Mg(2) sites after long-term storage.

B. Origin of Mg vacancy formation

To elucidate the origin of Mg vacancy accumulation under inert conditions, DFT calculations were performed using Mg_3Sb_2 as a representative host lattice [Fig. 2(a)]. Defect-formation energies of Mg vacancies and Mg interstitials—two predominant native defects in this system [19]—were evaluated as a function of E_f [Figs. 2(b) and 2(c)]. The blue-shaded regions denote the possible ranges of E_f under Mg-poor or Mg-rich conditions determined from our modified-Becke-Johnson band structures result (see Supplemental Material [22] Fig. S5a) following the approach in Ref. [23]. In both Mg-poor and Mg-rich conditions, negatively charged Mg vacancies exhibit the lowest formation energies, indicating a thermodynamically favorable preference for vacancy formation. Given the relatively small difference in vacancy-formation energies between the Mg(1) and Mg(2) sites, even small local perturbations in the environment can destabilize either site and lead to Mg atom detachment. This explains why vacancies at both Mg(1) and Mg(2) sites are simultaneously observed in HAADF-STEM

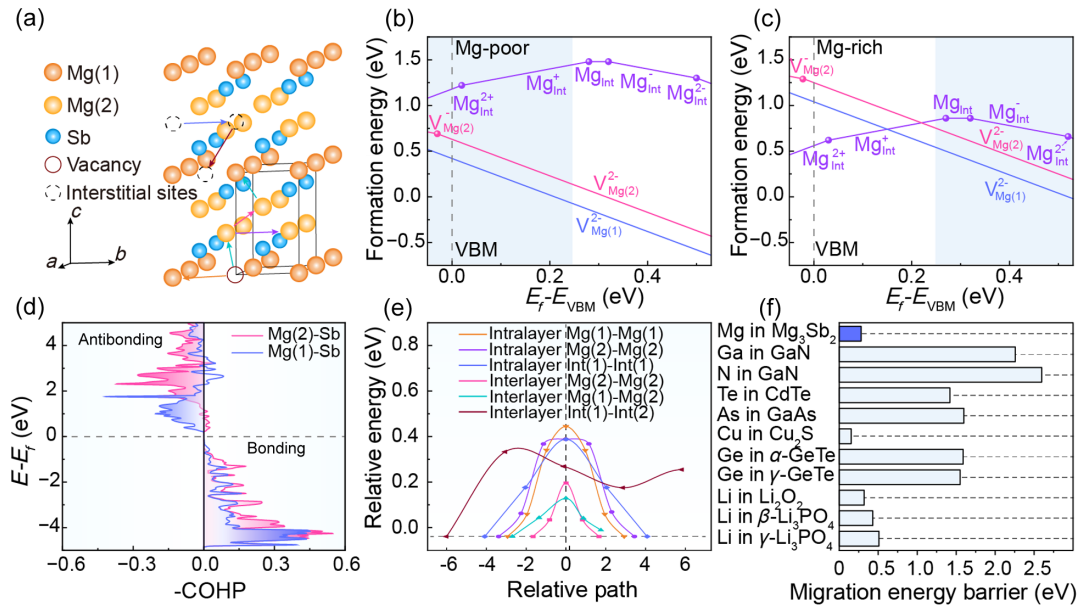


FIG. 2. DFT calculations of defect physics in Mg_3Sb_2 . (a) Crystal structure of Mg_3Sb_2 showing atomic sites, vacancy and interstitial positions, and possible Mg migration paths. Calculated defect-formation energy for (b) Mg-poor and (c) Mg-rich Mg_3Sb_2 . (d) The COHP profiles of Mg(1)–Sb and Mg(2)–Sb bonds in Mg_3Sb_2 . (e) Relative energy barriers for Mg migration along different paths in Mg_3Sb_2 [same color in (a)]. (f) Comparison of matrix atom migration barriers in Mg_3Sb_2 with other common semiconductor materials [24–30].

images [Fig. 1(f)], even though Mg(1) sites exhibit a higher defect-formation propensity than Mg(2) sites.

The chemical bonding mechanisms of the Mg–Sb bond were analyzed by the crystal orbital Hamilton population (COHP) calculations [Fig. 2(d)]. For the Mg(1)–Sb bond, the E_f lies near the boundary between the bonding and antibonding states. As n -type doping shifts E_f upward, the occupation of antibonding states in Mg(1)–Sb bonds increases, weakening the Mg(1)–Sb bonding interaction and reducing the energetic cost of Mg atom removal. In contrast, Mg(2)–Sb bonds remain predominantly bonding states near E_f but undergo similar destabilization once E_f rises further. This electronic-structure-driven bond weakening explains the vacancy-formation tendencies in n -Mg₃(Sb, Bi)₂.

While thermodynamics favors vacancy formation, kinetic accessibility is equally critical for long-term evolution at room temperature. Migration barriers calculated via the climbing-image nudged-elastic-band (CI-NEB) method [31]—each corresponds one to one to the colored trajectories illustrated in Fig. 2(a)—reveal a remarkably low interlayer Mg atom migration barrier of approximately 0.3 eV [Fig. 2(e)]. This value is substantially lower than that of common semiconductors such as GaN [25] and CdTe [26], and approaches those found in superionic conductors as Li₃PO₄ [24] [Fig. 2(f)]. Such low barriers indicate that Mg atoms exhibit high mobility within the Mg₃Sb₂ lattice even near room temperature.

Taken together, the low formation energies and high mobility of Mg establish both thermodynamic and kinetic feasibility for vacancy generation. Mg atoms in Mg₃Sb₂ tend to move away from their lattice sites. However, vacancy formation alone does not guarantee long-term accumulation. Persistent Mg vacancy accumulation requires a continuous removal pathway for mobile Mg atoms. In other words, a sink must exist that absorbs displaced Mg and prevents recombination. This raises the question: What internal sink enables vacancy accumulation in samples that are stored under rigorously inert, room-temperature conditions, without external environmental stimuli?

C. Structural relaxation and hierarchical Mg redistribution

GBs in Mg₃(Sb, Bi)₂ are widely reported to be Mg deficient [32–34]. Displaced Mg atoms are thus expected to migrate toward GB regions under the driving force of chemical potential gradients. To validate this hypothesis, we performed MD simulations using a machine-learning-based interatomic potential (neuroevolution potential), which was trained and validated against first-principles data (see Supplemental Material [22] Fig. S7). Polycrystalline Mg₃Sb₂ supercells with varying grain densities were constructed to assess the influence of GBs on Mg transport behavior [Fig. 3(a)]. Mg diffusivity

was quantified from the mean-squared displacement (MSD) using the Einstein relation [35], and effective diffusion coefficients (D_V) were extracted to account for atomic exchange between bulk and GB regions [36]. Across the simulated temperature range, Mg atom diffusion is faster in polycrystalline supercells than in single-crystal supercells [Fig. 3(b) and Fig. S8 in Supplemental Material [22]]. Moreover, increasing the GB density leads to a systematic enhancement of Mg diffusivity. These results demonstrate that GBs act as fast migration pathways for Mg atoms in Mg₃Sb₂. Once reaching GBs, Mg atoms can rapidly diffuse along these interconnected GB networks and redistribute. In comparison with other compounds, Mg diffusion in Mg₃Sb₂ is substantially higher than in classic TE materials such as PbTe [37] [Fig. 3(b)], highlighting the high atomic mobility of Mg.

Although GBs further enhance Mg mobility in Mg₃Sb₂, enabling faster GB-mediated transport of Mg atoms

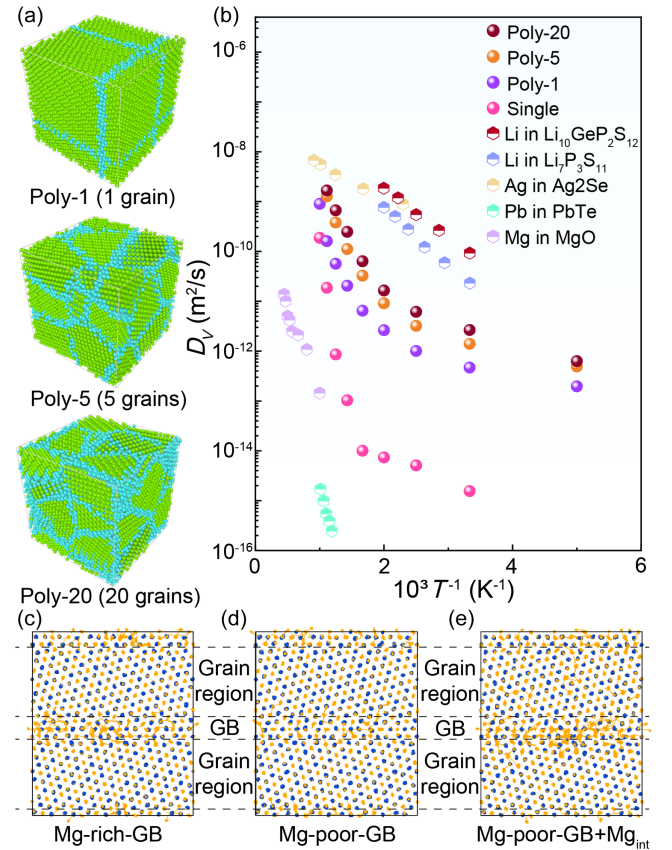


FIG. 3. MD simulations of Mg diffusion in Mg₃Sb₂. (a) Examples of polycrystalline simulation cells with different grain numbers generated and used in this study, where green represents the grains and light blue indicates the GB regions. (b) D_V of an Mg atom as a function of the inverse temperature for different polycrystalline boxes, with comparison to D_V of matrix atoms in other material systems from MD simulations [37–41]. Trajectories of Mg atoms during 2-ns MD simulations in (c) Mg-rich-GB box, (d) Mg-poor-GB box, and (e) Mg-poor-GB box with Mg interstitial at 300 K.

throughout the material, this observation is insufficient to confirm that Mg atoms spontaneously migrate from grain to GBs and segregate there—a critical step needed to explain the accumulation of Mg vacancies within Mg_3Sb_2 grains under long-term storage. Thus, we produce density plots of the accumulated Mg atom trajectories over the simulated timescale [Figs. 3(c)–3(e)], which are a powerful means of visualizing the migration pathways and all the positions in the lattice that are traversed, to confirm our hypothesis. Because of conventional structural analysis methods cannot reliably distinguish grain and GB region in Mg_3Sb_2 at every simulation timestep, we instead employed a symmetric tilt GB model oriented along the [001] axis, which provides a clear geometric distinction between grain and GB regions. Mg atoms exhibit different behaviors in grain and GB regions [Figs. 3(c)–3(e)]. Within grains, Mg atoms predominantly undergo thermal vibration near their lattice sites, resulting in localized trajectories. In contrast, Mg atoms in GB regions exhibit markedly enhanced mobility, with trajectories spanning multiple lattice sites, which confirms the fast-diffusion character of GB regions.

Crucially, Mg diffusion depends sensitively on GB stoichiometry. When the GB is Mg rich [Fig. 3(c)], with all available Mg sites occupied, no migration of Mg atoms from the grain to the GB is observed over the entire simulation. However, under Mg-deficient GB conditions [Fig. 3(d)], Mg atoms adjacent to the GB migrate spontaneously toward the GB within nanoseconds. Furthermore, when the GB is Mg deficient, and the grain region contains Mg interstitial atoms [i.e., Mg atoms displaced from their lattice sites; Fig. 3(e)], the number of Mg atoms migrating from the grain region to the GB increases dramatically. Even trajectories of Mg atoms migrating from the grain center to the GB can be captured. These results demonstrate that Mg-deficient GBs not only act as fast-diffusion pathways but also act as sinks, enabling Mg atoms to migrate spontaneously from the grain interiors toward Mg-deficient GBs, without external stimuli. Such grain-to-GB transport provides the irreversible redistribution pathway required for sustained Mg vacancy accumulation inside Mg_3Sb_2 grains. This process ultimately manifests as the intrinsic performance instability of Mg_3Sb_2 characterized by the time-dependent degradation of TE properties during storage.

However, Mg atoms that migrate to GBs do not necessarily remain trapped there. Once their segregation reduces the chemical potential gradient, further Mg migration toward GBs is suppressed, as shown in the simulations in Fig. 3(a). To clarify the destination of Mg atoms at GBs, we employed APT to investigate the elemental distributions in the vicinity of grain boundaries. To quantify the compositional variation across the GB, 1D concentration profiles were extracted along the direction indicated by the arrows in Figs. 4(a) and 4(b). The black line in Fig. 4(a) serves to indicate the GB location. In the two-year argon-stored sample, the composition profile exhibits a

3% to 4% decrease in Mg concentration across the GB region [Fig. 4(a)], confirming a substantial Mg deficiency at the GBs, which is consistent with previous reports [32–34]. In contrast, such a compositional contrast is significantly less discernible in the as-sintered sample [Fig. 4(b)], since extra Mg has been added in the sample preparation process to compensate for Mg evaporation. Yet, this temporarily Mg-rich condition is thermodynamically metastable, and these compensating Mg atoms will ultimately migrate away under aging. Our APT results imply that GBs are the pathways of Mg migration after storage. The Mg migration causes a chemical potential gradient from the grain interior to the GB area, driving the diffusion of Mg toward GBs, and then departs, repeating the loop. Given this dynamic behavior, the question arises as to where these Mg atoms travel after leaving the GBs.

To further probe long-range Mg transport, we performed TOF-SIMS depth profiling and 3D reconstruction. It should be noted that 3D reconstructions can be generated only from unnormalized raw data. Therefore, these 3D reconstructions merely serve to qualitatively visualize the spatial elemental distribution within individual samples and to identify local compositional variations at comparable depth positions. In contrast, quantitative comparison between the as-sintered and aged samples should be based on the normalized depth profiles, as shown in Fig. 4(c). The normalized depth-profiling curves show that Mg volatilization inevitably occurs during sintering [Fig. 4(c)], leading to a markedly lower Mg content near the surface than in the deeper interior. After two years of argon storage, the sample exhibits an increase in Mg content in the near-surface region and a corresponding decrease in the interior, indicating an Mg redistribution from the interior toward the near-surface region during storage. 3D reconstruction of element spatial distribution [Fig. 4(d)] further confirms this Mg redistribution. While the as-sintered sample exhibits a relatively uniform Mg distribution at the same depth, the two-year argon-stored sample presents pronounced local Mg enrichment within near-surface regions. This is also consistent with our MD simulation results (see Supplemental Material [22] Fig. S9), where Mg atoms can spontaneously migrate toward the surface along GBs—the fast-diffusion pathways—at room temperature. Together, these results establish a redistribution pathway—from grain interiors to GBs and ultimately to surfaces—operating under inert conditions.

A schematic depicting the intrinsic aging mechanism of Mg_3Sb_2 is presented in Fig. 4(e). The degradation of n -type $\text{Mg}_3(\text{Sb}, \text{Bi})_2$ originates from spontaneous Mg redistribution driven by its metastable Mg-rich state. When an Mg concentration gradient or other driving forces exist near GBs, highly mobile Mg atoms spontaneously migrate from the grain interior toward GBs under both thermodynamic and kinetic drives, leaving Mg vacancies inside the grains. Once they have reached the GBs, these Mg atoms diffuse rapidly along these fast-diffusion pathways and migrate

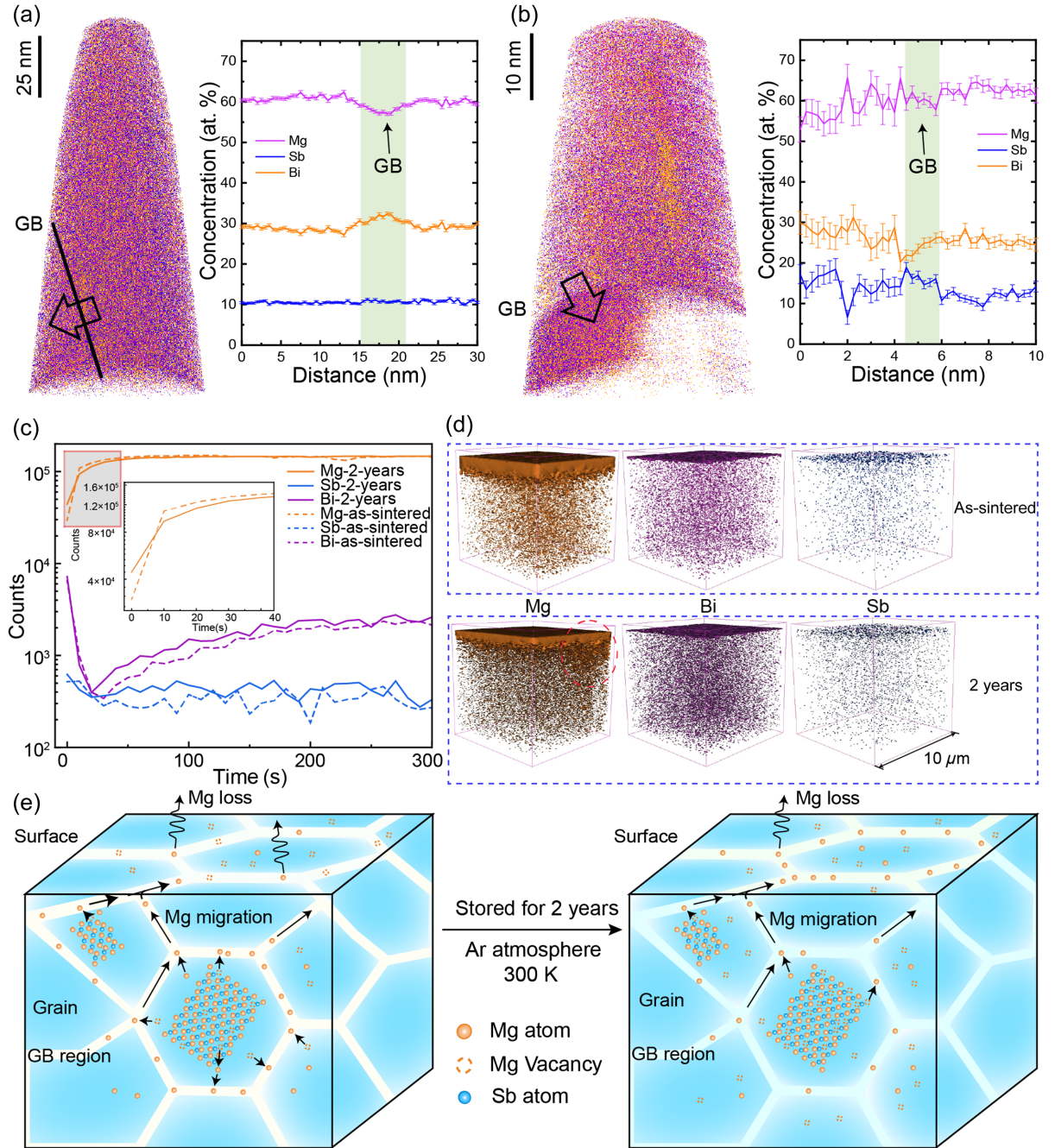


FIG. 4. Characterization of the $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ sample and intrinsic aging schematic of $\text{Mg}_3(\text{Sb,Bi})_2$. APT 3D reconstructions and corresponding 1D composition profile along the arrow of (a) two-year argon-stored and (b) as-sintered $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ samples. (c) Normalized depth profiles and (d) 3D mapping of element distribution of TOF SIMS for as-sintered and two-year argon-stored $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ samples. (e) Schematic of the intrinsic aging mechanism for the Mg migration and loss in $\text{Mg}_3(\text{Sb,Bi})_2$.

toward the surface, resulting in the gradual accumulation of Mg vacancies within grains. If external driving factors (e.g., oxidation, moisture absorption, or Mg volatilization) are present, Mg atoms can continuously migrate toward the near-surface region and be lost therefrom, as commonly recognized [42]. In the absence of such external factors, Mg migration is substantially slowed but ultimately

accumulates at the surface region. These Mg vacancies that accumulate extensively inside the grains—acting as p -type defects—significantly reduce the effective carrier concentration in n -type $\text{Mg}_3(\text{Sb,Bi})_2$, thereby deteriorating its TE performance. These results identify intrinsic defect kinetics as the fundamental origin of long-term instability in $\text{Mg}_3(\text{Sb,Bi})_2$ -based TE materials.

Therefore, in addition to improving thermal stability and chemical stability, intrinsic stability represents an indispensable criterion for realizing long-term reliable $\text{Mg}_3(\text{Sb,Bi})_2$ -based TE materials. More broadly, the present results demonstrate that metastable defect populations can spontaneously evolve over long timescales even under ambient and inert conditions. The resulting property evolution is governed not only by defect thermodynamics, but also by defect transport pathways that determine the kinetics of defect redistribution. In $\text{Mg}_3(\text{Sb,Bi})_2$, GBs play an important role in this process by facilitating Mg redistribution. These findings establish a direct connection between defect thermodynamics, defect transport, and long-timescale property evolution in metastable functional materials.

To directly test the role of grain boundaries, we reduced their density by increasing the sintering temperature. The $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ sample sintered at 1073 K exhibited enlarged grains and markedly reduced grain-boundary density compared to those sintered at 923 K (see Supplemental Material [22] Figs. S3 and S10). After two years of inert storage, performance degradation is substantially mitigated (see Supplemental Material [22] Fig. S11): The power factor at 300 K decreases by only approximately 5%, and ZT by approximately 7%, accompanied by minimal variation in carrier concentration. The weaker aging observed in coarse-grained samples provides independent support for the GB-mediated intrinsic instability and further highlights the important role of GBs in the Mg redistribution process during intrinsic aging.

III. CONCLUSIONS

In summary, we demonstrate that n -type $\text{Mg}_3(\text{Sb,Bi})_2$ exhibits intrinsic time-dependent structural relaxation and performance degradation even under inert storage conditions. This instability originates from spontaneous Mg redistribution driven by the metastable Mg-rich state. DFT calculations reveal thermodynamic preference for Mg vacancy formation and low migration barriers, while ML-MD simulations identify GBs as fast-diffusion pathways that facilitate Mg transport during the redistribution process. Together with atomic-scale and compositional analyses, these results establish an Mg atom spontaneous migration process—from grain interiors to GBs and ultimately to surfaces—that enables sustained Mg vacancy accumulation within grains. More broadly, our findings show the real-space visualization of intrinsic aging of n -type $\text{Mg}_3(\text{Sb,Bi})_2$ and establish a direct connection between defect thermodynamics, defect transport, and long-timescale property evolution in metastable functional materials. This framework may extend beyond $\text{Mg}_3(\text{Sb,Bi})_2$ and offer new perspectives for understanding intrinsic stability in a broad range of metastable material systems.

IV. METHODS

A. Material and synthesis

High-purity Mg(99.95%), Sb(99.999%), Bi(99.999%), and Te(99.999%) were weighed according to the composition of $\text{Mg}_{3.2}\text{Sb}_{0.5}\text{Bi}_{1.495}\text{Te}_{0.005}$ in the glovebox with argon atmosphere. After 5-h mechanical alloying (SPEX 8000M), the ball-milled powders were loaded into graphite dies (diameter: 12.7 mm) for hot pressing under the pressure of 50 MPa and at the temperature of 923 or 1073 K for 20 min. All samples were prepared from the same synthesis batch under identical conditions, and the aged specimens were immediately stored at room temperature in an argon-atmosphere glovebox with rigorous exclusion of moisture and oxygen until characterization.

B. Materials characterization

Phase composition of the samples was characterized by x-ray diffraction (PANalytical diffractometer with a Cu $K\alpha_1$ radiation source). SEM (Merlin Compact) and EDS were used to examine the fracture morphology and element distribution. The XPS (Thermo Scientific K-Alpha) was adopted to examine the chemical state. HADDF-STEM images were performed on a double spherical aberration (Cs)-corrected TEM (Titan Themis G2 60-300, FEI) to investigate the presence of Mg vacancy. The samples for STEM observation were prepared by focused-ion-beam milling (Helios Nanolab G3 UC, FEI) to achieve the appropriate size and geometry. TOF SIMS (ULVAC-PHI, PHI nano TOF II) was adopted to examine the distribution of Mg, Sb, Bi, and Te at the sample surface region. Sputter etching was performed using an Ar^+ gun (2 kV, 100 nA) to obtain the desired depth profile. The area of analysis was $10 \times 10 \mu\text{m}^2$. The TOF-SIMS data were processed using TOF-DR 3.0. APT measurements were performed on a local electrode atom probe (LEAP 5000 XS) to investigate the distribution of Mg, Sb, and Bi with a laser pulse energy of 12.5 pJ, a base temperature of 40 K, a detection rate of 0.5, and a pulse repetition rate of 200 kHz. The flight path of ions was 100 mm, and the detection efficiency of the detector was 80%. The APT data were processed using AP Suite 6.3.

C. Thermoelectric transport properties measurements

Both the Seebeck coefficient and electrical resistivity were measured under a helium atmosphere from 300 to 573 K (ZEM-3, ULVAC Riko). The total thermal conductivity $\kappa_{\text{tot}} = \rho DC_p$ was calculated using the measured density (ρ) by the Archimedeian method, thermal diffusivity (D) by the laser flash apparatus (LFA 457, Netzsch), and specific heat capacity (C_p) by the relationship $C_p = 3NR/M(1 + 1.3 \times 10^{-4}T - 4 \times 10^{-3}T^{-2})$, where $3NR = 124.71 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$, M is the molecular weight ($\text{g} \cdot \text{mol}^{-1}$) of the formula unit being considered, and

T is the temperature in K. The calculation of the Hall carrier concentration n_H ($n_H = 1/[eR_H]$) and mobility μ_H ($\mu_H = \sigma R_H$), where e , σ , and R_H are the electronic charge, the electrical conductivity, and the Hall coefficient, respectively.

D. DFT calculations

DFT calculations were carried out using the semicommercial DFT code, Vienna *ab initio* simulation package [43] with plane-wave basis sets and periodic boundary conditions. The electron-core interactions were described using the Blochl projector-augmented-wave method [44] within the frozen core approximation. The plane-wave basis sets were generated with valence configurations of Mg-3s² and Sb-5s²5p². The generalized-gradient approximation of Perdew *et al.* [45] was employed for describing the exchange-correlation functionals. The energy cutoff of 360 eV and a $3 \times 3 \times 3$ Gamma-centered K -mesh for Brillouin-zone integration were tested to be sufficient for converging the total energy into 1 meV/atom. All the ground-state structures were optimized by minimizing the Hellmann-Feynman forces, until the total forces on each ion were converged to 0.02 eV Å⁻¹. COHP calculations were carried out using the LOBSTER code [46] and CI-NEB calculations were carried out using the VTST code [47].

E. MD simulations

All MD calculations were carried out in the Graphics Processing Units Molecular Dynamics package [48], with periodic boundary conditions, an isothermal-isobaric (N - P - T) ensemble with a Berendsen barostat at $p = 1013.25$ mbar and a time step of $\delta t = 1$ fs. Polycrystalline cells containing 1, 2, 5, 10, or 20 grains were constructed with the ATOMSK code [49]. In each case, the grains were created in a cubic simulation cell with cell dimensions of 100 Å $\times$ 100 Å $\times$ 100 Å, and thus with ca. 37 000 atoms. All polycrystalline cells were relaxed for 100 ps to reach equilibrium before the simulations. The cells containing symmetric-tilt GBs were constructed by rotating the lattice along the [001] axis. Considering the periodic boundary conditions, the supercells we built adopted a sandwich structure with two identical GBs, and thus with ca. 6000 atoms. To simulate the Mg-deficient environment at GB, 5% of Mg atoms were randomly removed near the GB planes. In contrast, Mg interstitial atoms were introduced by randomly adding 3% of Mg atoms into the interstitial sites within the grain regions.

F. Neuroevolution-potential training data

The training data we used are briefly listed as follows:

- (1) Ground-state structures of Mg₃Sb₂
- (2) Distorted structures constructed by applying -10 to 10% strain at 1% intervals to Mg₃Sb₂ bulk supercells

- (3) Uniaxial strained structures along lattice direction a and c at 0 K. The volume changes range from 90% to 110% with an interval of 1%.
- (4) Bulk supercells of Mg₃Sb₂ containing 1%–5% concentrations of intrinsic point defects, specifically, Mg vacancies, Sb vacancies, and Mg_{Sb}/Sb_{Mg} anti-site defects
- (5) Low-Miller-index surfaces of the Mg₃Sb₂ bulk supercells with varying slab thicknesses
- (6) Symmetric grain-boundary supercells constructed from the corresponding surfaces mentioned above
- (7) Snapshots from N - V - T *ab initio* molecular dynamics simulations of the bulk supercell at 300, 1000, and 3000 K at the equilibrium 0-K volume
- (8) Active learning strategies are employed to iteratively augment the training dataset with structures selected from MLP-MD trajectories.

G. Einstein relation

In the Einstein relation, atomic tracer diffusion coefficients (D_V^*) can be derived by

$$D_V^* = \frac{1}{6} \left(\frac{dr_{\text{Mg}}^2}{dt} \right), \quad (1)$$

where r_{Mg}^2 is the MSD of the Mg atoms.

During MD simulations, atoms may migrate away from their initial regions and spend most of their time diffusing in other regions. However, these atoms are still counted as belonging to their original regions in the MSD calculations. Consequently, the calculated D_V^* may not accurately represent the regions to which the atoms are assigned. To address this issue, the effective diffusion coefficients (D_V) were adopted in this work to represent the D_V^* obtained from polycrystalline supercells, following the approach described in previous work [36]. These D_V correspond to some average of bulk diffusion, grain-boundary diffusion, and intergranular diffusion. Nevertheless, comparing the differences in D_V between polycrystalline Mg₃Sb₂ supercells with varying GB densities and single-crystal Mg₃Sb₂ supercells is sufficient to determine whether GBs in Mg₃Sb₂ facilitate or impede Mg atomic migration.

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Y. G. wrote the original draft and conducted visualization and investigation, developed the methodology, and conducted data curation. N. Q. and S. conducted visualization and investigation, developed the methodology, and conducted data curation. Y.-K. Z. and J. Z. developed the

methodology and conducted data curation. L. W. and R. X. conducted data curation. F. G. and W. C. supervised. Y. Y. and J. S. supervised and were in charge of resources. Z. L. was responsible for writing, review, and editing, in addition to conceptualization and project administration.

DATA AVAILABILITY

The final potential of Mg_3Sb_2 and associated DFT reference data, as well as relevant structural data, are openly available in the Zenodo repository at [50]. Other necessary data are available from the authors upon reasonable request.

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