High-Throughput Screening for Phase-Change Memory Materials

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Phase change memory (PCM) is an emerging non-volatile data storage technology concerned by the semiconductor industry. To improve the performances, previous efforts have mainly focused on partially replacing or doping elements in the flagship Ge-Sb-Te (GST) alloy based on experimental "trialand-error" methods. Here, the current largest scale PCM materials searching is reported, starting with 124 515 candidate materials, using a rational highthroughput screening strategy consisting of criteria related to PCM characteristics. In the results, there are 158 candidates screened for PCM materials, of which ≈68% are not employed. By further analyses, including cohesive energy, bond angle analyses, and Born effective charge, there are 52 materials with properties similar to the GST system, including Ge₂Bi₂Te₅, GeAs₄Te₇, GeAs₂Te₄, so on and other candidates that have not been reported, such as TIBiTe₂, TISbTe₂, CdPb₃Se₄, etc. Compared with GST, materials with close cohesive energy include AgBiTe₂, TISbTe₂, As₂Te₃, TIBiTe₂, etc., indicating possible low power consumption. Through further melt-quenching molecular dynamic calculation and structural/electronic analyses, Ge₂Bi₂Te₅, CdPb₃Se₄, MnBi₂Te₄, and TlBiTe₂ are found suitable for optical/electrical PCM applications, which further verifies the effectiveness of this strategy. The present study will accelerate the exploration and development of advanced PCM materials for current and future big-data applications.

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1. Introduction

Phase change memory (PCM) is used in the field of new non-volatile memory by utilizing the feature that the amorphous phase and the crystalline phase of the PCM material can be quickly and reversibly switched.^[1-3] Figure 1 (left) summarizes the main applications of current PCM technology (including electrical memory, optical memory, and neuroinspired computing). Compared with other emerging memories, the PCM technology can be used in both electrical and optical storage.^[4] With the efforts of Intel and Micron, Optane memories based on 3D Xpoint technology, a PCM technology, have entered the market.^[5,6] Furthermore, PCM technology is showing a great potential in areas such as inmemory computing,^[7] artificial neuromorphic systems,^[8,9] and all-optical on-chip memory.^[10] Since Ovshinsky originally proposed this technology in the 1960s,^[11] there are some materials examined for phase-change recording applications, of which Ge-Sb-Te (GST) alloys perhaps are

the best known.^[12-14] To achieve better performance, recent research has been devoted to optimizing the PCM materials by partial substitution or doping in GST materials. There are several materials with good performance in certain properties, for instance new material candidates with low power consumption including the TiSbTe alloy,^[15,16] the ScSbTe alloy,^[17-19] C-doped GST alloy,^[20] and so on, and the ones with high thermal stability including the SiSbTe alloy,^[21] the GeCuTe alloy,^[22,23] the SbTeSe alloy^[24] and so on. Currently, the improvement of performances by searching new materials is mainly based on experimental "trial-and-error" methods. Such a systematic searching is often limited by experimental conditions and often requires very long development duration and high cost. For example, it has been more than 20 years to the discovery of current mainstream GST materials^[12] since PCM technology was proposed.^[11]

Nowadays, high-throughput methods provide opportunities for accelerating material development, which is based on computational quantum-mechanical/thermodynamic methods, database construction, and data mining.^[25] It mainly refers to automatic large-scale simulation based on current materials or hypothetical materials instead of manual input. The highthroughput computational approaches to screen and mine







Figure 1. Preliminary screening strategies for phase change memory (PCM) materials. To explore new PCM materials for a series of applications, four tiers of selection criteria including element types, electronic band gaps, structures with octahedron-like local motifs, and phase stability are employed, based on the Materials Project (MP) database. The screening starts from more than 120 000 structures and the number of selected structures at each tier is indicated. These procedures significantly raise the searching efficiency for PCM materials from a vast number of existing but still unexplored structures.

advanced materials using robustness descriptors and available computational or experimental databases have been applied in many fields, including topological insulators,^[26] lithium-ion batteries,^[27,28] solar photo-voltaics,^[29] thermoelectric materials,^[30] dielectric and optical materials,^[31,32] thermochemical water splitting perovskites^[33] and so on. Using the high-throughput screening methods can reduce the long synthetic time and accelerate the development of materials. Therefore, it offers a possibility of applications in the field of PCM materials.

In this work, we employ 124 515 inorganic crystal structures in the Materials Project^[34] (MP) database for high-throughput screening and mining PCM related materials based on the structural and electronic-property descriptors. Analysis reveals that some special materials, such as Bi₈Te₇, As₂Te₃, GePb₄Te₅ with high Born effective charge indicating good signal contrast, AgBiTe₂, TlSbTe₂, As₂Te₃, TlBiTe₂, Bi₄Te₃, Sb₂Te₃, BiSb₃Te₆, PbSb₄Te₇, GeAs₄Te₇ with special low cohesive energy indicating low power consumption, and Bi₄Te₃, Bi₂Se₂Te with relatively good data retention. In addition, we also find some unreported materials with properties that are similar to GST materials, such as TlBiTe2, CdPb3Se4, MnBi2Te4, etc. We choose these unreported candidates to perform RESET melt-quenching data encoding molecular dynamics (MD) to obtain their amorphous atomic phases. It is found that the unreported PCM materials CdPb₃Se₄ and TlBiTe₂ are guite similar to GST in both structure and properties. MnBi2Te4 is close to GST but further holds magnetic moments. At the same time, among the 158 possible materials selected in this study, ≈68% of which are still not considered as PCM materials or examined for phasechange recording applications before, to our current knowledge. Therefore, it offers a new PCM materials database for the semiconductor community. We expect this work will accelerate the discovery of PCM materials and provide potentially valuable references for the experimental development of the PCM technology.

2. Results and Discussion

2.1. Screening Strategy

Leveraging the open-source MP database^[34] (Database V2019.11) with 124 515 inorganic crystal structures, we use four tiers of criteria (see in Figure 1 (right)) which are closely related to the characteristics of PCM materials for the screening. The first tier screens the elemental compositions. It has been found that PCM materials are mainly the IVA-VIA compounds, or the VA-VIA compounds, or the compounds including the IVA. VA, and VIA elements together. That's because the p-electronbonding characteristic of these compounds often constructs a unique chemical bond between the conventional covalent and ionic bonds,^[35,36] which has been regarded as the fingerprint of PCM materials. Therefore, in this tier, we define the criterion to search the materials at least including one or two kinds of the IVA, VA, and VIA elements. In other words, materials of X-IVA-VIA, X-VA-VIA, X-VA, X-IVA, X-VIA, where X is one any kind of element, are searched. After the screening, 9592 materials meet the criterion. Here, we have excluded the oxides because of their very strong ionic bonding accompanying phase separation and destroying the p-bonding network,^[37,38] which is not suitable for PCM applications.

Next, in the second tier, the bandgap is employed as the assisted searching criterion. PCM materials usually hold narrow bandgaps, for example, the optical gap of crystal Ge₂Sb₂Te₅ is around 0.5 eV.^[39] A relatively small bandgap ensures the effective electrical current of Joule heating in electronic memory, and the optical absorption in optical memory.^[40] In fact, a large band gap is corresponding to strong chemical interactions between atoms that makes phase changes difficult, for example, a 100-nm thinness amorphous SiO₂ (with bandgap $\approx 9 \text{ eV}^{[41,42]}$) almost needs 1 h to be crystallized at 1100 K,^[43] which is impossible for actual high-speed memory devices. The screening condition of this







Figure 2. Typical structures and local atomic motifs for PCM materials. a) The structure of rhombohedral GeTe (mp-938, the id in MP database) and a corresponding Ge-centered octahedral motif with the O:6 coordination environment. b) The structure of rhombohedral Sb₂Te₃ (mp-1201) and its two local motifs. One motif is for a Sb centered O:6 coordination environment and the other is a Te centered TY:3 coordination environment. The color coding for atoms is shown as well. The expression of the coordination environments O:6 and TY:3 is from a previous reference.^[81]

tier is the calculated bandgap of material below 1 eV. The band gap data is directly collected from the MP database^[34] with the generalized gradient approximation (GGA) and GGA + U functionals.^[44] Compared to the experiments, these band gaps are underestimated by \approx 40%,^[45,46] however, it is a meaningful step to exclude the materials with an especially large gap. Finally, 1608 candidates with narrow band gaps were selected.

The third tier selects the materials with the octahedral or the similar local bonding environment. That's because the PCM p-orbital bonds tend to form the octahedral network.^[47] For example, Figure 2 displays local structures of two typical PCM materials, that is, rhombohedral GeTe (mp-938) and rhombohedral Sb₂Te₃ (mp-1201). There, most of the atomic sites belong to octahedral (O:6) coordination whereas other sites (mainly Te atoms) near the van der Waals gap can be classified as trigonal non-coplanar (TY:3) coordination or called defective octahedral coordination^[48,49] due to their bond angle still at around 90°. The unique bonding motif is beneficial to reduce the interfacial energy and accelerate crystallization.^[50] This uniqueness of motif comes from the p-orbital bonding or resonant bonding^[51] or metavalent bonding^[52] or hyperbonding^[53] of PCM materials which can also improve the electronic polarizability and optical signal contrast. Therefore, it has been considered as an important fingerprint for PCM materials. The selected materials should satisfy the condition that the coordination environment of atomic sites in the unit cell is most possible to be O:6 or TY:3. In this tier, 173 candidate materials are further selected.

In the fourth tier, we use energy above hull (ΔE_{hull}) obtained from the MP database to examine the thermodynamical phase stability^[54] at zero K and zero pressure of the 173 materials from the previous tier. ΔE_{hull} for a material can be defined as the energy of decomposition of the material into the set of most stable materials at the same chemical composition. In other words, one material with a very high ΔE_{hull} is considered to be insufficiently stable because of its strong thermodynamic driving force for decomposition. Here, we consider materials with $\Delta E_{\rm hull} < 100 \mbox{ meV}$ atom⁻¹ are stable or metastable for PCM applications. In fact, this criterion of thermodynamical stability has also been successfully employed for other material screening.^[55,56] Finally, 158 candidates pass the examination of energy above hull.

Figure 3 summarizes the elemental distribution of all the 158 materials selected from 124 515 samples after searching all the four tiers. It is clear that the dominated distribution is from the elements in IVA, VA, VIA groups. This distribution result is mainly due to the previous first tier screening. They are mainly Te, Bi, Se, S, Pb, Sb, Ge, Sn, As. This is basically consistent with the elemental sources from the ever reported PCM materials as listed in Table S1, Supporting Information. The typical PCM materials, such as Ge₂Sb₂Te₅, GeSb₂Te₄, GeSb₄Te₇, GeTe, and Sb₂Te₃ can be found without requirements of other biased selection tiers, which demonstrates the reasonability of our screening strategy. Other main-group elements also include the IA, IIA, IIIA ones, such as In, Tl, Li, Na. Some transition elements such as Ag, Ti, Ni, Cr, Mn, Y, Zr, Cd, Hf, Ta, Pt are also found in the distribution. In fact, Ag is popular for optical PCM materials, for example, Ag-In-Sb-Te.^[57] Recently, Ti,^[15,16] Y,^[58] and Ag^[59] have also been suggested to be doped in the Sb₂Te₃ material and improve the PCM performances significantly. For example, a PCM cell based on Ti doped Sb₂Te₃ can hold one order of magnitude faster SET speed and as low as one-fifth RESET power consumption, compared to GST based PCM cell at the same size.^[15,16] Unexpectedly, a certain number of rare earth elements in forms of rare earth mononitrides,^[60] such as YN, LuN, are also observed. These varieties of element distribution bring hope to the exploration of new PCM materials. However, it should need the further analyses on the properties related to the metrics of PCM performances to clarify the validity of the selected candidates.



Figure 3. Distribution of elements from the screened structures. The counts are according to the 158 candidates after the four-tier screenings as shown in Figure 1. The color bar indicates the relative intensity of the distribution. The gray background color corresponds to no contribution of the elements.

2.2. Analysis of Performance Characteristics of Screened Materials

Next, we further calculate three metrics which are related to native bonding characteristics, optoelectronic signal, data retention, phase-change behavior, and power consumption of PCM materials.^[4,61] First of all, Born effective charge (Z^*) is employed. Previous research has found that PCM materials have high electronic polarizabilities^[51] which can be quantified by Born effective charges.^[62] High Born effective charge (from 4 to 6) is also considered as one of property-based fingerprints for PCM materials due to their native p-orbital bonding characteristics.^[36,53] The calculation steps can be found in the Experimental Section. Second, we calculate cohesive energy $(E_{\rm C})$. High power consumption is one of the main problems of current PCM materials.^[63] Energy cost of phase change data memory is mainly caused by melting the crystalline phase of PCM materials before quenching the liquid into the amorphous phase.^[61] As such, high melting point (T_m) materials tend to have high power consumption. $E_{\rm C}$ can measure the bonding strength between atoms and is positively correlated to the melting point of crystalline materials.^[64] Therefore, $E_{\rm C}$ here could be a suitable descriptor for this purpose. Third, a degree of 90° bond angle deviation (D_{BAD}) is employed to correlate phase-change behavior, see the definition of D_{BAD} in Experimental Section. In general, the 90° bond angle originates from the pure p-orbital bonding. This kind of bond angle can promote fast crystallization of the PCM materials,^[50] which guarantees the fast speed of data encoding. On the other hand, due to existence of cation vacancies or hybridizations of d/s and p orbitals, the bond angle will usually deviate from 90° to a certain degree, which could benefit the fast amorphization and the stability of amorphous phase. Therefore, a suitable D_{BAD} could display a compatibility of fast crystallization and fast amorphization in a PCM material.

Figure 4a shows the performance map of Z^* , D_{BAD} , and E_C for the selected 158 candidates as well as 3 other reported cubic GST structures.^[4,65] The MP material-id (mp-id) of typical GST/ Ge-Te (GT)/Sb-Te (ST) PCM materials are shown to highlight their positions in the Z^* – D_{BAD} – E_C coordinates. In order to find more suitable candidates, we make a further screening from

the 158 candidates according to the performance ranges of the GST/GT/ST samples with a variation of \pm 5% assuming the materials similar to GST/GT/ST would be good PCM materials. The data (with light-red color) display all these chosen candidates. To watch the distribution conveniently, Figure 4b-d plots the 2D maps of Z^*-E_C , Z^*-D_{BAD} , and E_C-D_{BAD} , respectively. In fact, in Figure 4b, the Z^* of the light-red data is from 3.6 to 6.7 e which is consistent with the previously reported values (\approx 4–6 e) for the popular PCM materials.^[36] In Figure 4d, the E_C values of the light-red data are at a very low level from 2.6 to 3.4 eV atom⁻¹. This is reasonable to have as low as possible $T_{\rm m}$ for PCM applications due to the melt-quenching RESET process. In contrast, we find a series of yellow data belonging to rare earth mononitrides, have exceptional large $E_{\rm C}$ (≈ 6.5 eV atom⁻¹), indicating very high $T_{\rm m}$, such as ≈ 2943 K of YN,^[66] and very high energy cost for PCM applications. In Figure 4c,d, the D_{BAD} of the light-red data are from 2.6° to 6.4°, where the one of GeTe (6.1°) is larger than those of Ge₂Sb₂Te₅ (2.7°). This reflects the easy amorphization for GeTe but readily crystallization for Ge₂Sb₂Te₅. In fact, it is well known from the experiments^[67] that GeTe can display better amorphous stability (i.e., data retention) than Ge₂Sb₂Te₅ does. On the other hand, the D_{BAD} of 0° for the rare earth mononitrides predicts their super ease of crystallization but difficulties of amorphization, see the discussion later.

Table 1 summarizes the performance metrics of 52 materials belonging to the light-red data in Figure 4. Among them, 32 candidates are found in (or related to) previous reports for PCM applications or research, such as Ge₂Bi₂Te₅, GeAs₄Te₇, GeAs₂Te₄, and SnSb₂Te₄, while 20 of them are rarely studied for PCM applications, such as TlBiTe₂, TlSbTe₂, CdPb₃Se₄, MnBi₂Te₄, Bi₄S₃Te₃, and InBi₃Se₆. Especially, we here predict several candidates of relatively low *E*_C for potential low power consumption. This is a critical requirement for PCM applications because it not only benefits lowering cost of energy but may also benefits high-density integration.^[68] Candidates with low *E*_C are AgBiTe₂, TlSbTe₂, As₂Te₃, TlBiTe₂, Bi₄Te₃, Sb₂Te₃, BiSb₃Te₆, PbSb₄Te₇, GeAs₄Te₇ and so on. The blue data are for other candidates, of which ≈33% are generally high *E*_C sulfides, reflecting relatively high-power consumption for phase change.







Figure 4. Further screening with three calculated metrics related to performances of PCM materials. They include Born effective charge (Z^*), degree of bond angle deviation (D_{BAD}), and cohesive energy (E_c). a) The 3D displaying for the three metrics. (b–d) are the focused 2D displaying for Z^*-E_c . Z^*-D_{BAD} , and E_c-D_{BAD} , respectively. The most popular PCM crystals including Ge-Sb-Te alloys, Sb₂Te₃, and GeTe are marked out. The candidates are classified into three categories. The ones with metrics close to those of GST/GT/ST (100% ± 5%) are shown with light-red circles. The ones (rare earth nitrides) with special high cohesive energies (>6 eV atom⁻¹) are shown with yellow triangles. Other candidates are shown with blue squares. The cubic rocksalt GST with random cation vacancy distribution are also added to the metric analyses. The mp-* is the id used in the MP database.

2.3. Amorphous Phase, Signal Contrast, and Crystalline Nucleation

Amorphous phases of the PCM materials play the key role in data memory. However, compared to the crystal phases, the structure information of the amorphous phases at atomic scale is much difficult to be identified due to the complexity of atomic arrangements. In general, typical high-cost experiment methods, such as extended X-ray absorption fine structure, X-ray absorption near-edge structure, and high-resolution transmission electron microscopy, or high-computation-cost theoretical methods, such as melt-quenching MD technique are required. Due to high calculation costs, we chose four potential candidates from Table 1 and make efforts to obtain their amorphous structures via the melt-quenching MD method. The amorphous phase of the popular PCM Ge₂Sb₂Te₅ is also analyzed as a reference. The studied systems include Ge₂Bi₂Te₅ (mp-1206551), CdPb₃Se₄ (mp-1226877), TlBiTe₂ (mp-27438), and MnBi₂Te₄ (mp-1077840), of which the last three are still not reported for PCM applications in terms of our current best knowledge.

Figure 5 displays all their structures. The rationality of the amorphous models is verified in Figure S1, Supporting Information. The pair correlation functions (PCF) in Figure 6a of all the amorphous phases converge to 1 in the range of r > 10Å, which is a main characteristic of being disordered. We can directly see the disordered structures for Ge₂Bi₂Te₅, CdPb₃Se₄, TlBiTe₂, and MnBi₂Te₄ in Figure 5b-e. In contrast, even using faster quenching rate, the rare earth mononitride, such as YN, cannot form any amorphous phase but almost achieves a full crystallization after the melt-quenching MD, see Figure 5f. This is completely consistent with previous discussions on the poor amorphization ability according to the $E_{\rm C}$ and $D_{\rm BAD}$ analyses of crystalline phases for the rare earth mononitride. In the obtained amorphous phases, we can also see some local motifs of near-regular fourfold/four-membered rings, which are usually popular in GST alloys.^[69] The motif has been discussed as a kind of crystalline seed to promote fast switching www.advancedsciencenews.com



Table 1. The MP material-id (mp-id), the cohesive energy (E_C), the Born effective charge (Z^*), and the degree of 90° bond angle deviation (D_{BAD}) of the 52 materials (shown with the light-red data in Figure 4 of the $E_C = Z^* - D_{BAD}$ map) are listed in the table. To our current knowledge, the references in the table tell that the corresponding or similar compounds could be considered as PCM materials. We note that the proportion of the components in the references often deviates from the standard formula in the MP database possibly due to the complicated experimental design.

Formula	mp-id	E _C [eV atom ⁻¹]	Z*[e]	$D_{BAD}[^{\circ}]$	Reported re
Bi ₄ S ₃ Te ₃	mp-1227434	3.233	3.836	2.924	_
$Bi_{14}S_8Te_{13}$	mp-557619	3.117	3.846	2.581	-
Sb ₂ SeTe ₂	mp-1219475	2.779	4.923	4.914	[83]
InBi ₃ Se ₆	mp-1223998	3.048	3.652	4.600	-
$CdPb_3Se_4$	mp-1226877	3.088	4.361	2.673	-
Bi ₂ Se ₂ Te	mp-1227356	2.951	4.014	3.096	-
$AgBiSe_2$	mp-27916	2.886	3.927	2.684	-
Bi ₂ Se ₂ Te	mp-31406	2.918	4.591	5.985	-
KBiSe ₂	mp-36539	2.902	4.354	3.016	-
$Pb_2Bi_2Se_5$	mp-570930	3.191	4.296	3.106	-
Sb_2Se_2Te	mp-571550	2.859	4.831	5.957	[83]
PbBi ₂ Se ₄	mp-675543	3.143	4.136	3.432	-
Sb_2Se_2Te	mp-8612	2.895	4.204	2.998	[83]
PbBi ₆ Te ₁₀	mp-1106025	2.789	4.817	3.237	[84]
PbSb ₄ Te ₇	mp-1209139	2.769	5.279	3.299	[84]
PbBi ₂ Te ₄	mp-1227398	2.837	4.235	5.265	[84]
PbSb ₂ Te ₄	mp-31507	2.814	5.272	3.408	[84]
GeSb ₂ Te ₄	mp-1224348	2.836	3.866	5.106	[12]
SnBi ₄ Te ₇	mp-1101917	2.815	4.867	2.993	-
BiSbTe ₃	mp-1227340	2.721	4.875	3.449	-
$Ge_2Sb_2Te_5$	mp-1224375	2.921	6.376	2.690	[12]
PbBi ₄ Te ₇	mp-23005	2.813	4.833	3.098	[84]
TISbTe ₂	mp-4573	2.663	4.386	5.420	-
GeSb ₄ Te ₇	mp-29641	2.786	5.377	2.909	[12]
PbBi ₂ Te ₄	mp-676250	2.855	4.961	2.941	[84]
MnBi ₂ Te ₄	mp-1077840	2.885	4.004	4.830	-
$Ge_2Sb_2Te_5$	mp-3534	2.905	3.671	5.562	[12]
${\sf GeAs}_2{\sf Te}_4$	mp-14790	2.833	5.978	2.644	[85,86]
${\sf SnBi}_2{\sf Te}_4$	mp-38605	2.857	5.038	2.764	-
SnSb ₂ Te ₄	mp-27947	2.823	5.313	2.845	[87]
AgBiTe ₂	mp-1182952	2.659	4.400	3.161	-
${\sf GeSb}_4{\sf Te}_4$	mp-1224378	2.808	5.500	2.800	[12]
BiSb₃Te ₆	mp-1227403	2.714	4.917	3.373	-
TlBiTe ₂	mp-27438	2.697	4.718	4.224	-
GePb ₄ Te ₅	mp-1224514	3.109	6.027	2.670	-
Ge ₂ Bi ₂ Te ₅	mp-1206551	2.942	5.886	3.365	[88]
GeAs ₄ Te ₇	mp-8645	2.769	5.959	2.658	[85,86]
GeBi ₄ Te ₇	mp-29644	2.822	4.904	3.505	[88]
GeSb ₂ Te ₄	mp-1224350	2.843	4.400	4.841	[12]
GeBi ₂ Te ₄	mp-27948	2.874	5.338	3.427	[88]

Formula	mp-id	E _C [eV atom ⁻¹]	Z*[e]	$D_{BAD}[^{\circ}]$	Reported ref.
As ₂ Te ₃	mp-9897	2.685	6.228	2.900	[89]
As ₂ Te ₃	mp-1195735	2.686	5.716	3.063	[89]
Bi ₄ Te ₃	mp-28229	2.698	3.664	6.175	[90]
Bi ₂ Se ₃	mp-541837	3.045	3.970	3.790	[91]
Bi ₂ Te ₃	mp-34202	2.750	4.733	3.396	[90]
Bi ₈ Te ₉	mp-580062	2.731	4.512	5.265	[90]
Bi ₈ Te ₇	mp-1214397	2.710	6.659	5.581	[90]
Bi ₈ Se ₉	mp-1190284	2.986	4.379	3.388	[91]
GeTe	mp-938	3.206	3.837	6.133	[92,93]
Sn ₄ P ₃	mp-27410	3.356	4.469	3.689	-
Sb ₂ Te ₃	mp-1201	2.706	4.884	3.209	[94]
SbTe	mp-7716	2.702	4.420	5.791	[94]

Table 1. Continued.



Figure 5. The amorphous structures of four representative candidates obtained via the melt-quenching ab initio molecular dynamics to mimic the RESET data encoding compared to the case of the popular GST. The case of YN is also shown. a) $Ge_2Sb_2Te_5$ (mp-1224375). b) $Ge_2Bi_2Te_5$ (mp-1206551). c) $CdPb_3Se_4$ (mp-1226877). d) $TlBiTe_2$ (mp-27438). e) $MnBi_2Te_4$ (mp-1077840). f) YN (mp-2114).

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Figure 6. Structural/electronic properties of amorphous phases of representative candidates and their rationality for PCM applications. a) Pair correlation function, PCF. b) Bond angle distribution, BAD. c) Imaginary part of dielectric function, ε_2 .

between the two phases. This phenomenon is also reflected by the 90° main peak of bond angle distribution for the four new amorphous materials as well as GST, see Figure 6b. Next, reasonable signal contrast is essential for PCM. As such, we compare the optoelectrical signal between the crystalline phase and the amorphous phase. The imaginary parts of the dielectric function (ε_2) are calculated. Figure 6c displays all the four candidates have significant contrasts between the two phases at around 2 eV like that in GST. Here, the amorphous MnBi₂Te₄ has also a large response at low frequency, which reflects a certain metallic property in its amorphous phase. Currently, the MnBi₂Te₄ has been considered as a topological insulator and with many other interesting properties.^[70,71] However, its amorphous phase is still little studied before. Therefore, our work can be timely to recall the attention to its new application. Besides, $MnBi_2Te_4$ has also $\approx 20\%$ ferromagnetic signal contrast between the amorphous and the crystalline phase, which indicates a possible application in magnetic storage. Furthermore, if the antiferromagnetic ordering is considered for the crystalline phase,^[70] the contrast could be larger.

Last but not least, in order to verify that the candidates have the characteristics of reversible transitions between crystalline and amorphous phases, we need to simulate recrystallization process (from amorphous phase to crystalline phase). However, the ab initio MD (AIMD) simulation of the recrystallization usually requires massive calculation load due to simulating a typical duration of hundreds of picoseconds (ps). Here, we use one of typical PCM candidates, that is, CdPb₃Se₄, as an example to test the ability of recrystallization. The recrystallization AIMD is performed at 600 K from its amorphous phase. It is







Figure 7. The nucleation and recrystallization of $CdPb_3Se_4$. a) The time evolution of the number of fourfold rings for $CdPb_3Se_4$ during a recrystallization MD at 600 K for 390 ps. b) The structure at 0 ps. c) The structure at 390 ps.

well known that the fourfold ring is an important fingerprint of the crystal nucleus and crystalline phase in PCM materials^[69] as mentioned before. **Figure 7**a shows the evolution of the number of fourfold rings during the recrystallization MD. From 130 to 260 ps, the substantial increase of fourfold rings clearly indicates the crystalline nucleation has taken place. Figure 7b,c also shows the initial amorphous structure and the structure at 390 ps with significantly recrystallized, respectively. Thus, the ability of fast crystalline nucleation of the candidate material suggests the screening criteria in this work are effective.

The current difficulty in searching PCM materials on one hand is that the effective descriptors are not straightforward. In order to develop PCM materials with good performance, it is necessary to meet various requirements, such as low power consumption,^[72] rapid phase transition,^[12,73] good data retention,^[22,74] large signal contrast between the two phases,^[73] high cycling endurance,^[74,75] and so on. On the other hand, currently there is no mature database of amorphous model structures like those of crystal model structures. That's because it is still impossible to perform large-scale AIMDs like melt-quenching simulations on large number of materials with current supercomputational ability. In this work, we propose the screening strategy and the descriptors for PCM materials from the crystal database, and also confirm the amorphous structures, the signal

contrast, even the nucleation ability, for the selected candidates. Our efforts indicate high-throughput screening of PCM materials by reasonable computation cost is possible. Therefore, it would benefit searching advanced PCM materials for memory integrated circuit and optical storage applications.

3. Conclusion

In summary, by four tiers of screening strategy (including element, bandgap, local motif, and stability) for PCM materials, we obtain 158 possible candidates through high-throughput searching, of which ≈50 are considered as potential PCM materials, some of which have been examined for phase-change recording applications and some are still not. According to element distributions, most of the screened materials are ternary alloys, telluride-based alloys are the mainstream, which is consistent with current popular PCM materials. By analyzing data storage performance of the materials, we found a series of materials with good performance in one aspect, for example, some materials with lower or similar cohesive energy to common GST materials include AgBiTe₂, TlSbTe₂, As₂Te₃, TlBiTe₂, Bi₄Te₃, Sb₂Te₃, BiSb₃Te₆, PbSb₄Te₇, GeAs₄Te₇ indicating relatively low melting point (or low power consumption) for



application. Here, 3D performance metrics map $(Z^*-D_{BAD}-E_C)$ is proposed to analyze comprehensive performance of PCM materials. We found that the $E_{\rm C}$ of the phase change material is relatively low in the range of ($\approx 2.6-3.4$ eV atom⁻¹), and Z^* and D_{BAD} are in the moderate range of about (\approx 3.6–6.7 e) and ($\approx 2.6-6.4^{\circ}$), respectively. We propose several unreported materials similar to GST materials possible, such as CdPb₃Se₄, TlBiTe2, MnBi2Te4. By melt-quenching MD, the amorphous structures of CdPb₃Se₄, TlBiTe₂, MnBi₂Te₄, Ge₂Bi₂Te₅ are clearly demonstrated. Similar to GST, they offer significant optoelectrical contrasts to the corresponding crystal phases. Besides, MnBi₂Te₄ also displays a certain degree of magnetic contrast between its two phases. The work offers the first systematic high-throughput screening of PCM materials from more than 120 000 inorganic crystal structures. We note that performances of PCM materials, such as crystallization speed, cycling endurance, and amorphous stability should be further experimentally testified according to the screening suggestions. In sum, the present study will be important to help the semiconductor industry to develop PCM materials for nonvolatile memory in current and future big-data applications.

4. Experimental Section

First-Principles Calculations and AIMD: The first-principles calculations employed density functional theory as implemented in the Vienna Ab initio Simulation Package code.^[76] The electronic exchange-correlation interaction was described by the Perdew-Burke-Ernzerhof functional.^[77] The cutoff energies for plane-wave expansion were 1.3 times of the highest value of the recommended cutoff energies in pseudopotentials (i.e., 1.3×max(ENMAX)). The calculations of Z^* for the selected 158 materials were performed using conventional unit cells. A unified scheme called automatic_density in the Python Materials Genomics (pymatgen) package^[78] was used to generate k-point grids for all of the 158 materials. The generated densities of the grids were 500 per atom for structural relaxation and 1000 per atom for the Z* calculations. The Z* for an atom was averaged by the diagonal elements of the Z^* tensor in which the values of all the elements are transformed to their absolute values. Then, the final Z^* for a material was averaged by all atoms in the calculation models. The AIMD adopted the NVT canonical ensemble, in which Nośe-thermostat was used to control the temperature.^[79] The structural models for AIMD were $4 \times 4 \times 1$, $4 \times 4 \times 1$, $4 \times 4 \times 2$, $4 \times 4 \times 1$, $4 \times 4 \times 1$, $3 \times 3 \times 3$ supercell based on the unit cell of Ge₂Bi₂Te₅ (mp-1206551), CdPb₃Se₄ (mp-1226877), TlBiTe₂ (mp-27438), MnBi₂Te₄ (mp-1077840), Ge₂Sb₂Te₅ (mp-1224375) and, the conventional unit cell of YN (mp-2114), respectively. All the amorphous models were obtained by the meltquenching method.^[22,80] First, the crystal supercells were melted at 3000 K for 7.5 ps to fully diffuse the atoms. Next, they were maintained near their melting points ($\approx\!1000\text{--}1200$ K) for 12 ps to get equilibrium liquid states. Then, they were quenched to 300 K with a rate of \approx -50 to -60 K ps⁻¹. Finally, the structures were maintained for 6 ps at 300 K to achieve the equilibrium states. In addition, the YN with a very large cohesive energy was melted at 10 000 K and then maintained at 3500 K for 12 ps before it was quenched to 300 K. All the structures were fully relaxed before the electronic property calculations. The Γ -centered k-point grid of 1 \times 1 \times 1 and 2 \times 2 \times 2 were for AIMD simulations/structural relaxations and subsequent calculations of dielectric property, respectively. The octahedral structure was screened using the chemenv^[81] package of the open-source Python Materials Genomics (pymatgen) materials analysis package.^[78] The PCF and BAD were obtained by averaged by 1000 transient structures that were intercepted from the trajectory of the 300 K-MD simulations. The cutoff distance for bonding between two atoms was 1.3 times the sum of their covalent radii.

The D_{BAD} is defined by the following equation.

$$D_{\text{BAD}} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - 90)^2}$$
(1)

where X_i is the bond angle formed by bonding between atoms and n is the number of bond angles. The definition of D_{BAD} is similar to the sample standard deviation. The bond angles around 180° are excluded because they are the sum of two adjacent 90° angles.

Data Availability: The data that support the results in this paper are available at https://materialsproject.org/\#search/materials (Database V2019.11) and supplementary information. The data in this paper including bandgap, ΔE_{hull} , E_{C} , unit cell, and conventional unit cell of materials can be obtained through the open Materials Application Programming Interface^[82] and pymatgen^[78] from MP database.^[34]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

high-throughput material screening, non-volatile memory, phase change memory materials

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