

Unravelling the interplay of local structure and physical properties in phase-change materials

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ABSTRACT

In general, semiconductors exhibit similar local arrangements in the crystalline and the amorphous phase, since the chemical bonds in a covalent semiconductor are independent of long range order. On the contrary, the covalent compound $\text{Ge}_2\text{Sb}_2\text{Te}_5$, which is a prototype phase change material employed in optical and electronic data storage, has recently been shown by Kolobov et al. to exhibit a profound change in local order upon amorphisation. We have employed ab initio ground state calculations to unravel the origin of the local order in phase change alloys and the resulting physical properties. This investigation shows that the p-electrons of Te and Sb play a crucial role for the local order favouring a cubic like arrangement. In particular, it can be shown that for average valence numbers above four an octahedral arrangement is stabilized in the crystalline phase as found for many phase change alloys. The consequences of this bonding characteristic for the properties of these materials will be discussed.

Keywords: local order, structure, electronic properties, design rules

1. INTRODUCTION

Phase-change (PC) materials show a truly remarkable property combination. They can be stabilized in an amorphous and a crystalline state with different optical properties, which implies that there has to be a difference in the atomic arrangement in both phases. At the same time the transition from the amorphous to the crystalline phase is very fast, indicating that short range rearrangements are sufficient for the transformation. Until recently it has been tacitly assumed, that the absence of long range order is the main difference between the amorphous and the crystalline state. This assumption goes back to the work of Zachariasen¹, who built the foundation for the theory of covalent random networks. In this model for amorphous materials the atoms adopt the same number of nearest neighbours as in the corresponding crystalline state. Recent findings by Kolobov et al.² demonstrate, however, that there is a significant difference in the local atomic arrangement between the amorphous and crystalline state. Their observation implies that phase change materials are characterized by a remarkable interplay between atomic arrangement and electronic structure. To unravel this interplay electronic structure calculations are ideal, since they determine both the atomic arrangement and the electronic states responsible for the structure.

We have tried to identify generic trends observed in phase change materials and then have tried to explain those using density functional theory. With trial- and error strategies and empirical rules, a considerable number of suitable PC materials have been identified. Table 1 lists some successful and unsuccessful PC materials and their crystalline structures as observed after laser induced crystallization.

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Table 1: Some successful and unsuccessful PC materials, their structures and their average number N_{sp} of covalence electrons. Please note that both $\text{Ge}_1\text{Sb}_2\text{Te}_4$ and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ each have one vacancy per unit cell in the cubic structure, but not in the hexagonal structure. This explains the different average number of valence electrons for $\text{Ge}_1\text{Sb}_2\text{Te}_4$ with cubic and hexagonal structure.

	Material	Structure	N_{sp}
	GeTe	Rocksalt	5
	$\text{Ge}_1\text{Sb}_2\text{Te}_4$	Rocksalt (metastable)	4.75
		Hexagonal (stable) ³	5.4
	$\text{Ge}_2\text{Sb}_2\text{Te}_5$	Rocksalt ⁴	4.8
	$\text{Ge}_4\text{Sb}_1\text{Te}_5$	Rocksalt ⁵	5.1
Successful samples	In_3SbTe_2	Rocksalt ⁶	4.3
	AgSbTe_2	Rocksalt ⁷	4.5
	AuSbTe_2	Rocksalt ⁸	4.5
	$\text{Au}_{25}\text{Ge}_4\text{Sn}_{11}\text{Te}_{60}$	Cubic ⁹	4.5
	$\text{Ag}_3\text{In}_4\text{Sb}_{76}\text{Te}_{17}$	Cubic ⁹	4.45
	$\text{Ag}_{5.5}\text{In}_{6.5}\text{Sb}_{59}\text{Te}_{29}$	Cubic-like/hexagonal ¹⁰	4.93
Unsuccessful samples	AgInTe_2	Chalcopyrite ⁷	4
	AuInTe_2	Chalcopyrite ⁸	4

Here, ‘successful’ means that the material has sufficient optical contrast between the crystalline and amorphous state and can recrystallize rapidly. We notice some distinct differences between successful and unsuccessful PC materials: (1) most of the successful materials have a cubic or cubic-like structure; (2) successful materials have a higher coordination number Z in the undistorted state. Please note, however, that in the distorted structure, Z is typically considerably smaller than 6. While $Z = 6$ for the rocksalt and cubic structure, it equals 4 for the chalcopyrite structure, which is unsuitable for phase change recording. Though some rocksalt structures are only metastable, i.e. rearrange after prolonged heating to a new and more stable structure, they often appear in laser induced crystallization processes due to the rapid cooling rate⁴. Table 1 implies that materials with a metastable or stable cubic or cubic-like structure, including the rocksalt phase, are suitable for phase change recording. Matsunaga and Yamada⁹ have already pointed out that cubic structures are preferable in high speed phase change materials since they enable particularly fast crystallization due to their simple crystalline structure. However, the chalcopyrite or the related wurzite structure are also relatively simple. Nevertheless, as table 1 reveals, they are not suitable for phase change recording. In a recent publication we have demonstrated that only alloys with cubic structure have the necessary density contrast between the amorphous and crystalline structure that is required to give sufficient contrast for optical recording⁷. In this paper it will be demonstrated which compounds are characterized by such cubic structures using first principle calculations based on density-functional theory (DFT). Furthermore the electronic origin of cubic structures in these covalent semiconductors will be discussed. From these results a map is derived, which predicts the stability regime for suitable phase change materials.

2. EXPERIMENTAL

DFT calculations have been performed for a series of ternary ABTe_2 alloys where element A is either group-11 or group-13, while B covers elements from group-13 to group-15. In a first step, AuSbTe_2 and AuInTe_2 have been considered to compare the energy difference between the rocksalt and chalcopyrite structure for different compounds. These calculations were performed as a benchmark test of our DFT computations to prove whether they can reproduce the experimentally observed ground state structure and lattice constants. The results of DFT calculations for AuInTe_2 and AuSbTe_2 are presented in Fig. 1 showing the total energy E per single atom versus lattice size a for the two different structures. We find in agreement with experiment⁸ that the chalcopyrite structure is stable for AuInTe_2 , while the rocksalt structure is stable for AuSbTe_2 . By a least-square fit of the Murnaghan equation of state,

$$E(V) = \frac{B_0 V}{B'(B'-1)} \left[B' \left(1 - \frac{V_0}{V} \right) + \left(\frac{V_0}{V} \right)^{B'} - 1 \right] + E_0(V_0) \quad , \quad (1)$$

we obtain a lattice constant a_0 which is a function of volume V_0 , minimum energy E_0 and bulk modulus $B_0 = V d^2 E / dV^2$ at $V = V_0$. In this equation, the pressure derivative of the bulk modulus $B' = dB/dP$ is assumed to be a constant. As can be seen from Fig. 1 the Murnaghan equation of state describes the results of the DFT calculations extremely well. Hence we can use the corresponding fit to determine the minimum energy E_0 with high precision.

3. RESULTS

The energy differences $\Delta E = E_0^R - E_0^C$ between the two structures are listed in Table 2. In this paper, superscripts R and C represent the rocksalt and the chalcopyrite structure, respectively. While for AuInTe_2 the chalcopyrite structure is more stable by 0.12 eV/atom, for AuSbTe_2 the rocksalt structure is preferred by 0.42 eV/atom.

DFT can also explain the density of the ground state structure for AuInTe_2 (chalcopyrite) and the ground state for AuSbTe_2 (rocksalt). The density of AuSbTe_2 is about 1.3 times larger than that of AuInTe_2 , which is also in good agreement with the experiment which finds a density 1.28 times larger for AuSbTe_2 than for AuInTe_2 ⁸. Hence we can summarize that the DFT calculations do not only reproduce the experimentally observed ground state structure but also correctly reproduce the density difference between the rocksalt and chalcopyrite structure. We can now ask the question if other related alloys have the same crystalline ground state. Therefore the stable structure for two other pairs of ternary materials: CuInTe_2 and CuSbTe_2 , as well as AgInTe_2 and AgSbTe_2 was determined. The ternary alloys Cu(In,Sb)Te_2 and Ag(In,Sb)Te_2 have similar energy-lattice size curves as that of Au(In,Sb)Te_2 shown in Fig 1.

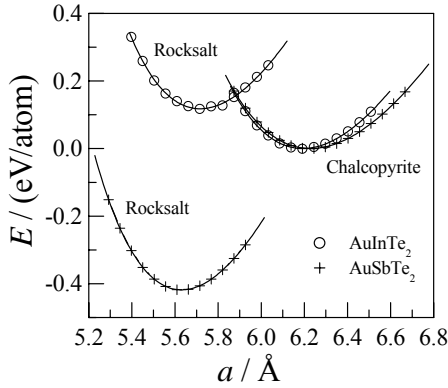


Figure 1: Dependence of total energy per single atom E on lattice constant a for different structures of AuInTe_2 and AuSbTe_2 . Open circles and crosses are DFT calculation results, and solid curves are least-square fits of the Murnaghan equation of state. The minimum energy of the chalcopyrite structure serves as the reference point for the energy scales, i.e. was set to zero.

It is interesting to note that the energy difference between the rocksalt and the chalcopyrite structure is almost identical for isoelectronic compounds. For (group-11) InTe_2 , where the group-11 element is Cu, Ag or Au, the energy difference ΔE between the rocksalt and the chalcopyrite structure is 0.13, 0.11, and 0.12 eV/atom for Cu, Ag, and Au, respectively. For (group-11) SbTe_2 , the energy difference ΔE between the rocksalt and the chalcopyrite structure is -0.41, -0.37, and -0.42 eV/atom for Cu, Ag, and Au, respectively. Again, the energy difference hardly differs for the three isoelectronic compounds. It is found that alloys containing In always prefer the chalcopyrite structure, while those containing Sb always prefer the rocksalt structure. Hence, the difference between the In and Sb series stems from the difference between In and Sb atoms. Further calculations show that the stable structure even holds if In is replaced by the same group atom such as Ga, or Sb is replaced by the same group atom such as As or Bi. That is, replacing one kind of element with another element from the same group

does not influence the stable structure. It is important to note that replacing Au with Cu or Ag does not influence the stable structure of the ternary alloy, though it does change the lattice constant, bulk modulus, etc. For any pair of ternary alloy, we find that the lattice constant of the rocksalt structure is about 10% smaller and the density is correspondingly about 30% higher.

Thus, we conclude that the change of ground state structure from chalcopyrite to rocksalt upon replacing In by Sb stems from their different electronic properties, that is their different number of valence electrons. In this paper, we only consider atoms from group-11 to group-16, i.e. elements having one to six valence electrons, respectively. Here, the d-shell of group-11 metals is assumed to be full and is not counted when determining the average number of valence electrons. Then the average number of valence electrons per single atom N_{sp} is determined to be 4 for AuInTe₂ and 4.5 for AuSbTe₂. Our results imply that ternary alloys prefer the chalcopyrite structure when $N_{sp} = 4$, while the rocksalt structure is preferred when $N_{sp} = 4.5$. To understand this change of structure with the number of valence electrons the ABINIT code has also been employed to investigate the electronic structure of the different alloys. Fig. 2 presents the electronic density in the (001) plane for AuSbTe₂ with rocksalt structure and in the (110) plane for AuInTe₂ with chalcopyrite structure. The electronic density diagrams show p-bonding in the rocksalt structure and sp^3 -bonding in the chalcopyrite structure, i.e. a bond angle of 90° in the former case and a bond angle of 109.5° in the latter case.

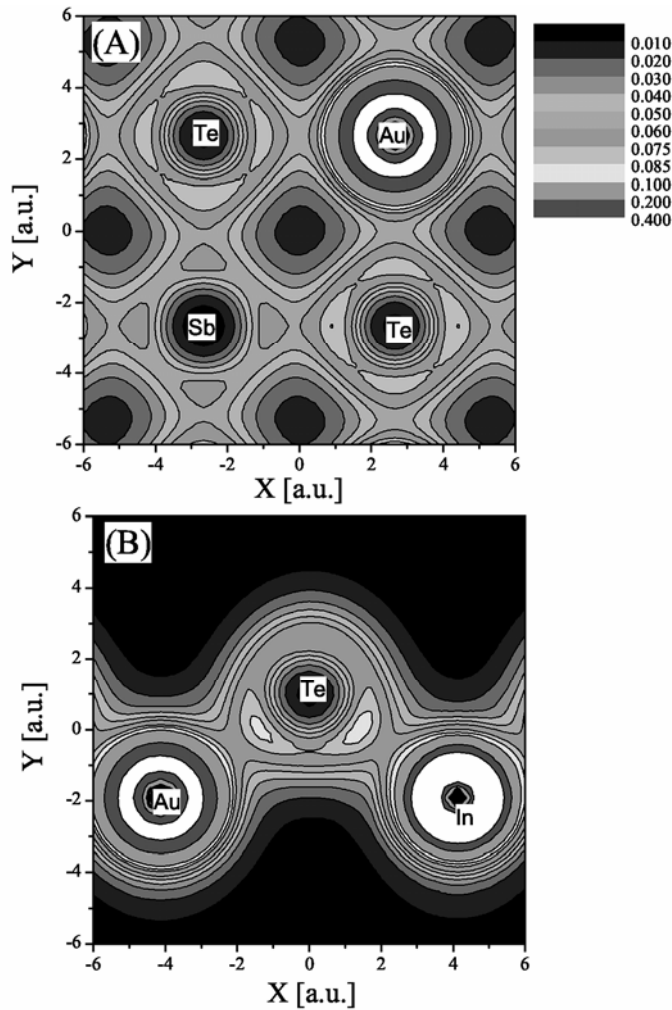


Figure 2: The electronic density in (A) for the (001) plane of AuSbTe₂ with rocksalt structure and in (B) for the (110) plane of AuInTe₂ with chalcopyrite structure. We consider the following electrons as valence electrons: $5d^{10}6s^1$, $4d^{10}5s^25p^1$, $5s^25p^3$, $5s^25p^4$ for Au, In, Sb and Te to create the pseudopotential used in the DFT calculation. The electronic density is in unit of $e/a.u.^3$, where $a.u.$ corresponds to Bohr's radius.

Hence we find in agreement with previous work¹¹ that the ideal situation for the diamond-like (in our case it is the chalcopyrite) structure is $N_{sp} = 4$. In this case the bonding part of the sp^3 hybrid has optimum filling while the antibonding part is not occupied. $AuInTe_2$ satisfies this condition. Increasing N_{sp} , however, will destabilize the chalcopyrite structure since now the antibonding part of the sp^3 orbital will become occupied. Therefore, for $N_{sp} = 4.5$ the alloy prefers p bonding which leads to the rocksalt structure. For this structure with the coordination number $Z = 6$, the perfect situation is that each atom provides three p electrons for p bonding, or $N_{sp} = 5$, even though we expect a weaker dependence since the crucial part of the p-orbital, or p-band, respectively is neither bonding nor anti-bonding but rather non-bonding. Calculations for $InSbTe_2$ whose N_{sp} is 5 indeed show that the rocksalt structure is more stable by an energy difference $\Delta E = -0.53$ eV/atom. This raises the question for which alloys the rocksalt structure is preferred. The corresponding materials would be suitable candidates for phase change recording. We expect the border between sp^3 bonding and p bonding and hence chalcopyrite and rocksalt structure to occur somewhere between an average valence electron number of N_{sp} of 4 and 4.5.

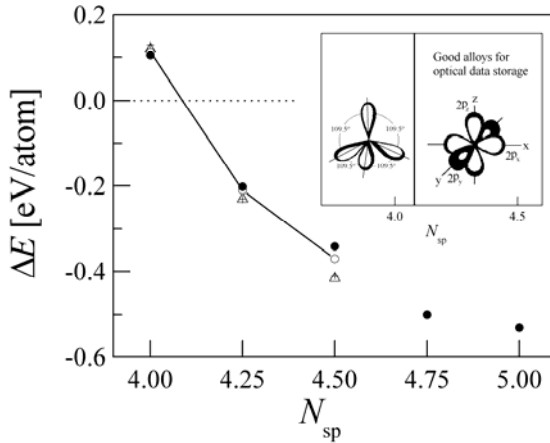


Figure 3 Plot of energy difference per single atom ΔE for different average number of valence electrons N_{sp} . Open triangles (Δ) represent $Au(In,Sn,Sb)Te_2$; Open circles (\circ) represent $Ag(In,Sn,Sb)Te_2$; Crosses ($+$) represent $Cu(In,Sn,Sb)Te_2$; Solid circles (\bullet) represent $AuGaTe_2$, $AuGeTe_2$, $AuAsTe_2$, $InSnTe_2$, and $InSbTe_2$, respectively. Solid line is the link for Ag series of alloys. The border separating the chalcopyrite and rocksalt structure is estimated as about $N_{sp} = 4.1$. The insert shows the different bonding in materials crossing the border.

Therefore we present in Fig. 3 the energy difference per single atom ΔE as a function of N_{sp} . For all calculated Te based ternary alloys, we find that when $N_{sp} = 4$ the alloys prefer the chalcopyrite structure with a relatively large ΔE . Increasing N_{sp} will decrease ΔE . When $N_{sp} = 4.25$, the change of sign for the energy difference ΔE indicates that the alloy prefers the rocksalt structure. Even though this result does not imply that alloys like $AgSnTe_2$ and $AuSnTe_2$ ($N_{sp} = 4.25$) will have a rocksalt structure since other crystalline phases might even have a lower energy, we can exclude the chalcopyrite structure. Hence materials such as $CuSnTe_2$, $AgSnTe_2$ as well as $AuSnTe_2$ might also be suitable candidates for good PC materials. Indeed we have recently obtained experimental evidence which confirms that $AgSnTe_2$ is suitable for PC recording⁸. This is the first case where a phase change material has been developed based upon density functional simulations rather than trial- and error preparation procedures. In addition, we also expect that materials with N_{sp} above 4.25 will also be good PC materials. This is in excellent agreement with the data compiled in Table 1. In this table we have collected all known phase change alloys that show good properties in rewritable optical data storage ('successful samples') and also two samples, which are not suitable. Consistent with the arguments presented above, we note from Table 1 that the N_{sp} of successful PC materials is always larger than 4, and usually between 4.3 and 5. From Fig. 3, we estimate that the critical value of N_{sp} distinguishing the rocksalt and the chalcopyrite structures is about 4.1.

4. SUMMARY

In summary, the DFT calculations presented here help to identify new and possibly superior phase change materials. All phase change materials reported are characterized by a cubic or near-cubic coordination which is caused by the dominance of the p-electron bonding. The average number of valence electrons plays the crucial

role in determining the structure of the semiconductor alloys studied here. For $N_{sp} = 4$, we find that the stable structure of (Cu, Ag, Au)InTe₂ is the chalcopyrite phase with sp³ bonding, while for $N_{sp} = 4.5$, the stable structure of (Cu, Ag, Au)SbTe₂ ternary alloys is the rocksalt structure with p bonding. Results show that Te based ternary materials will favor the suitable rocksalt structure if their N_{sp} is bigger than 4.1. This simple criterion facilitates the search for new phase change materials and opens the way to a more fundamental understanding of phase change materials¹².

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