



Self-diffusion in Zn_4Sb_3 from first-principles molecular dynamics

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ABSTRACT

The Zn_4Sb_3 system is promising for thermoelectric applications due to its very low thermal conductivity coupled with a good power factor. Molecular dynamics calculations based on density functional theory were carried out for different stoichiometries of Zn_4Sb_3 , corresponding to three situations: the composition $\text{Zn}_{3.6}\text{Sb}_3$ (actually Zn_6Sb_5 with only one Zn site occupied), a slightly higher Zn content $\text{Zn}_{3.8}\text{Sb}_3$ (with some of the Zn atoms in interstitial sites), and a slightly lower Zn content $\text{Zn}_{3.4}\text{Sb}_3$ (with some Zn vacancies). The diffusivity was calculated for different temperatures and the diffusion coefficient plotted in Arrhenius plots. The results compare well with experimental data, and point to a highly mobile Zn species with a very high diffusion coefficient prefactor.

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1. Introduction

Zinc antimonide Zn_4Sb_3 is one of the more promising materials for thermoelectricity, partly due to a very low thermal conductivity; this has been linked to the existence of several interstitial Zn sites [1]. The presence of nano-inclusions and voids has also been suggested as a mechanism for reducing thermal conductivity, based on recent high-resolution transmission electron microscope studies [2–4]. The formation of these nanostructures can be understood from a temperature-dependent solubility of Zn on interstitial sites in the Zn_4Sb_3 phase, combined with the diffusivity of Zn being higher than that of Sb [3,4]. It is already known from a tracer diffusivity experiment that Zn is highly mobile in Zn_4Sb_3 [5], but it is not known how the diffusivity of Sb compares to that of Zn. We have in the present study used first-principles molecular dynamics (FPMD) to quantify the diffusion coefficient of both Zn and Sb as a function of temperature in Zn_4Sb_3 .

2. Methodology

Density functional theory (DFT) at the PBE-GGA level [6] was used to provide self-consistent electronic structures as source for the calculations of Hellman–Feynman forces. Plane-waves were used as basis functions according to the projector augmented wave method [7], as implemented in the Vienna *ab initio* Simulation Package (vasp) [8,9]. The cut-off energy of the plane wave expansion was 208 eV, and only the Γ point was used for the \mathbf{k} -space integrals. The criterion for electronic convergence was a change in calculated total energy of less than 1 meV between two consec-

utive iterations. This level of precision was sufficient to achieve errors in the calculated forces <0.05 eV/Å, thus giving reliable MD results. Three different models were employed in order to compare situations with varying Zn content. The simplest structure had only the crystallographic site Zn1 fully occupied, with the stoichiometry $\text{Zn}_{3.6}\text{Sb}_3$. An alternative model was created by removing Zn atoms, thus forming Zn vacancies ($\text{Zn}_{3.4}\text{Sb}_3$), while the last model had Zn interstitial sites occupied ($\text{Zn}_{3.8}\text{Sb}_3$). The standard $R-3c$ unit cell was used, which consisted of 64–68 atoms. A Boltzmann distribution of velocities corresponding to the given temperature was automatically provided by vasp. The time step used for molecular dynamics (MD) was 1 fs, and the simulations were run for 5000 time steps.

3. Results and discussion

The mean square displacement (MSD) of Zn and Sb in Zn_4Sb_3 is shown in Fig. 1. It is evident that it generally takes 2–3 ps before the MSD starts growing linearly for all the compositions. This linear growth is a sign of solid state diffusion, confirmed by inspection of the ionic movements. Also, most of the temperatures of this study were below the melting point of Zn_4Sb_3 (836 K [10]). Furthermore, melting did not occur at the highest temperatures; this was confirmed by assessing the total electronic energy as a function of time and temperature (not shown here). Such overheating is quite common in molecular dynamics, and is in our case convenient – it gives access to a larger range of temperatures than would otherwise be accessible (*i.e.* only below the melting point).

Another signature of solid state diffusion can be seen in a plot of the diffusion coefficient D as a function of time (Fig. 2). After 1–4 ps the diffusion coefficient takes on a more or less constant value. This value (calculated as the average of D during the last ps of the

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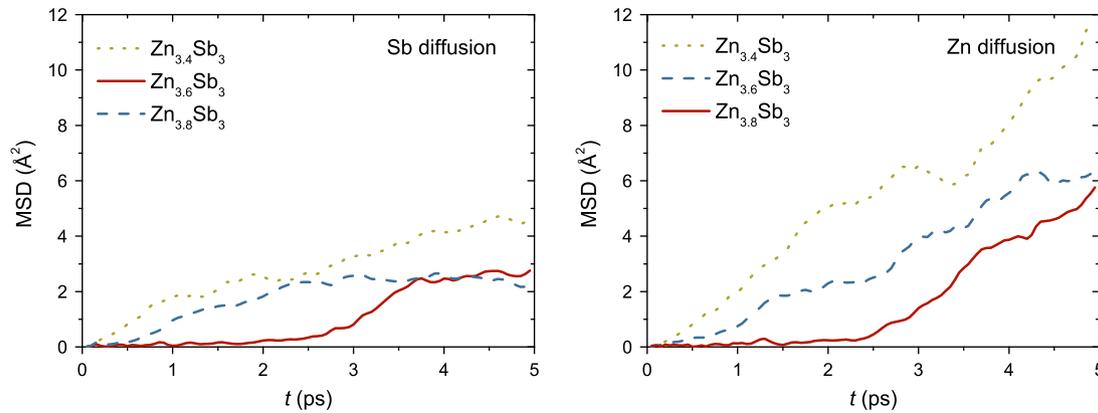


Fig. 1. The mean square displacement (MSD) as a function of time for Sb diffusion (left) and Zn diffusion (right) in Zn_4Sb_3 . Results for the compositions $\text{Zn}_{3.4}\text{Sb}_3$, $\text{Zn}_{3.6}\text{Sb}_3$ and $\text{Zn}_{3.8}\text{Sb}_3$ are shown as dotted, solid, and dashed curves, respectively. The temperature was 700 K.

simulation time) was used to create Arrhenius plots of D as a function of the temperature.

This is shown in Fig. 3 for the three different Zn_4Sb_3 compositions. Despite the rather large uncertainty of the methodology, we see that a linear fit to the logarithm of D versus reciprocal temperature is reasonable. The linear fits in Fig. 3 were used to estimate the activation energy Q , which is the slope of the curve. Furthermore, the diffusion coefficient prefactor D_0 , which is the point of interception between the trend line and the ordinate axis, was obtained by extrapolating the linear trend line as shown in Fig. 3.

The results are summarized in Table 1, where D_0 and Q are given for Zn and Sb for all the compositions. They are also compared to experimental results from Ref. [5]. We first note that the quality of the linear fit (quantified by R^2) is relatively high for most of the curves, except that of Sb diffusion in $\text{Zn}_{3.4}\text{Sb}_3$ – we will therefore neglect these results in the following discussion. It is then interesting to see that the activation energy is quite similar for Zn and Sb for all three compositions; between 11 and 15 kJ/mol. This compares very favorably with the experimental result for Q , which is 11 kJ/mol [5]. This means that the activation energy is quite accurately predicted with this technique, and that we can quite safely conclude that Q is similar for Sb and Zn. We can also see that Q consistently increases with increasing Zn content. This is probably due to local distortions of the lattice close to the interstitial Zn atoms, effectively increasing the diffusion barrier.

However, when we turn to the diffusion coefficient prefactor D_0 , the picture is different. First of all, D_0 for Zn is approximately twice as large as that for Sb, leading to a very high overall mobility of Zn. But we also note that the calculated prefactors are two orders of

magnitude higher than the experimental one. This is not unusual for calculated prefactors [11,12], and can be rationalized by the relatively short simulation times being used by MD calculations. The prefactor is determined by jump frequencies and correlation factors; [13] the latter designate the deviation from true random walk due to correlated jumps. As an example, a jump from a lattice site to an interstitial site can be strongly correlated with a jump back to the lattice site, which would lead to a correlation factor considerably smaller than unity. The jump frequencies and correlation factors may have significantly different time signatures. The jump frequencies are undoubtedly well described by the MD calculations, where several jumps are seen within the simulation times. However, there are most probably correlation effects which hinder long-distance diffusion; such effects can have significantly longer time constants than the jump frequencies, and may thus not be seen until considerably longer simulation times are employed. When comparing our study with the experiments, we should note that we have studied self-diffusion, while Ref. [5] used diffusion of a tracer species to quantify the diffusivity – this is a possible additional contribution to the discrepancy between the theoretical and experimental results.

The question is then whether we can trust the relative size of the calculated prefactors for Sb and Zn – is really D_0 larger for Zn, or can the correlation factors change the relative mobility of the two species? It is difficult to give a definite answer to this question, but one can speculate that the various interstitial Zn sites can provide more opportunities for the Zn atoms to escape through non-correlated jumps. This can possibly change the correlation factor in favor of Zn, increasing rather than decreasing the difference between Zn and Sb. This remains of course speculative, and only

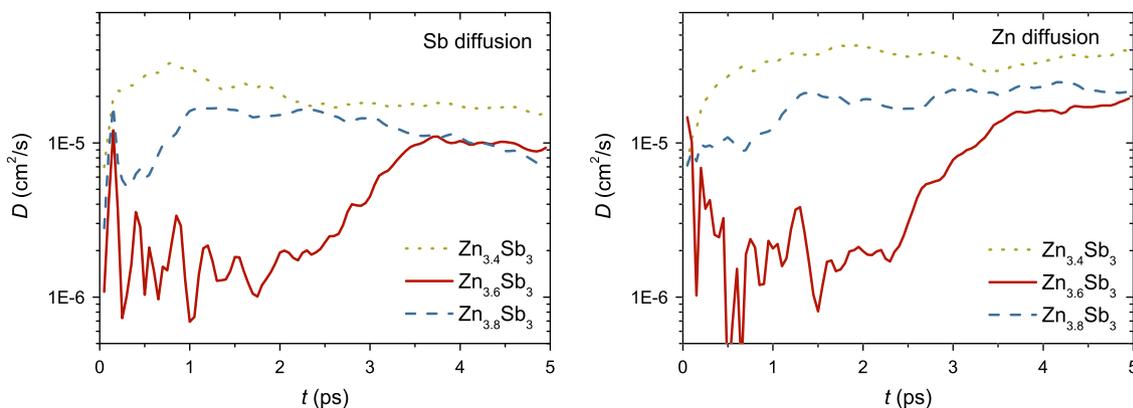


Fig. 2. The diffusion coefficient D as a function of time for Sb diffusion (left) and Zn diffusion (right) in Zn_4Sb_3 . Results for the compositions $\text{Zn}_{3.4}\text{Sb}_3$, $\text{Zn}_{3.6}\text{Sb}_3$ and $\text{Zn}_{3.8}\text{Sb}_3$ are shown as dotted, solid, and dashed curves, respectively. The temperature was 700 K.

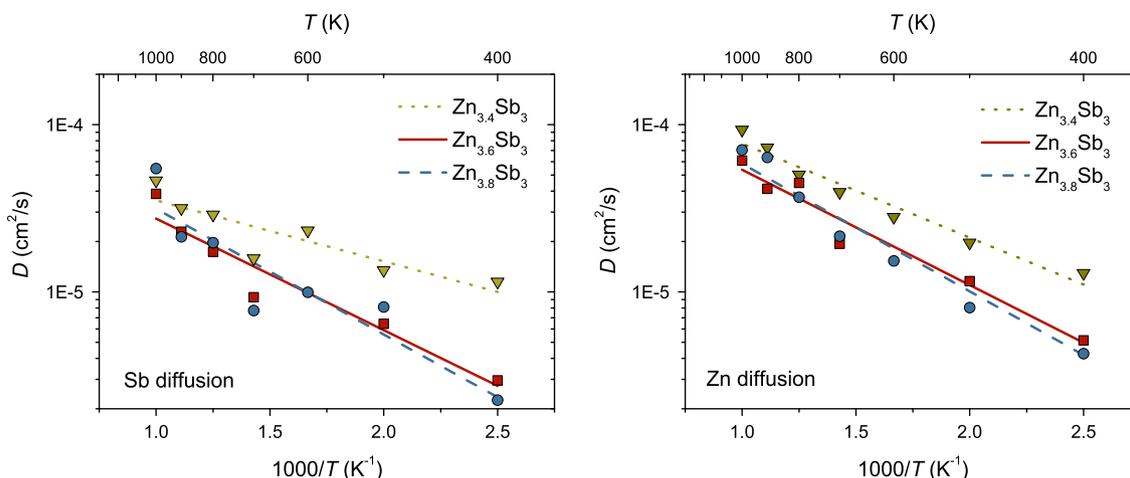


Fig. 3. The logarithm of D as a function of reciprocal temperature for Sb diffusion (left) and Zn diffusion (right) in Zn_4Sb_3 . Linear trends for the compositions $\text{Zn}_{3.4}\text{Sb}_3$, $\text{Zn}_{3.6}\text{Sb}_3$ and $\text{Zn}_{3.8}\text{Sb}_3$ are shown as dotted, solid, and dashed lines, respectively. The temperature was varied between 400 and 1000 K.

Table 1

The Diffusion Coefficient Prefactor D_0 and the activation energy Q for the Different Compounds in this Study, compared with experimental results for Zn diffusion in Zn_4Sb_3 [5]. The quality of the linear fit (the straight lines in Fig. 3) is measured by the coefficient of determination R^2 .

Compound	D_0 (10^{-4} cm ² /s)		Q (kJ/mol)		R^2 (1)	
	Sb	Zn	Sb	Zn	Sb	Zn
$\text{Zn}_{3.4}\text{Sb}_3$	0.82	2.8	7	11	0.79	0.96
$\text{Zn}_{3.6}\text{Sb}_3$	1.3	2.6	13	13	0.93	0.96
$\text{Zn}_{3.8}\text{Sb}_3$	1.8	3.4	14	15	0.85	0.98
Expt. [5]		0.13		11		

experiments or a thorough calculation of the correlation factors can resolve this matter properly.

4. Conclusions

We have shown that Zn has a very high mobility in Zn_4Sb_3 , based on first-principles molecular dynamics calculations. The activation energies of Zn and Sb jumps are quite similar, and close to the experimental value. A very high prefactor D_0 makes Zn diffusion significantly faster than Sb diffusion, but this is quite speculative, since the experimental value of D_0 for Zn is two orders of magnitude smaller than the calculated one. We nevertheless believe that the results support the assumptions of recent articles [3,4], where it was proposed that rapid diffusion of Zn can lead to Zn precipitates and subsequently nanovoids.

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