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Complex doping of group 13 elements In and Ga in caged skutterudite $CoSb_3$

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Abstract—The complex doping behavior of Ga and In in $CoSb_3$ has been investigated using ab initio total-energy calculations and thermodynamics. The formation energies of void filling, Sb substitution and complex dual-site occupancy defects with different charge states, and their dependence on chemical potentials of species, were studied. Results show that Ga predominantly forms dual-site $2Ga_{VF}$–Ga_{Sb} defects and substitutes for Sb only at very high Fermi levels or electron concentrations. In, on the other hand, can play multiple roles in skutterudites, including filling in the crystalline voids, substituting for Sb atoms or forming dual-site occupancy, among which the fully charge-compensated dual-site defects ($2In_{VF}$–In_{Sb} and $4In_{VF}$–$2In_{Sb}$) are dominant. The equilibrium concentration ratio of impurities at void-filling sites to those at Sb-substitution sites for Ga-doped $CoSb_3$ is very close to be 2:1, while this value markedly deviates from 2:1 for In-doped $CoSb_3$. The 2:1 ratio of Ga doping in $CoSb_3$ leads to low electron concentration ($\sim 2 \times 10^{19}$ cm^{-3}) and makes the doped system a semiconductor.

Keywords: Defect; Thermoelectric; Ab initio calculations; Skutterudites

1. Introduction

There has been great progress in filled-skutterudite thermoelectric (TE) materials in recent years [1,2]. Studies on filling fraction limits (FFLs) for various impurities in skutterudite $CoSb_3$ are important not only for understanding the transport properties but also for predicting novel systems and compositions. The FFLs for rare-earth (REs), alkaline-earth (AEs) and alkaline metal (AMs) single-element-filled skutterudites have been studied using the density functional ab initio methods and the results show good agreement with experiments [3–15]. A simple electronegativity rule (x_I–$x_{Sb} > 0.8$, where the xs are the electronegativities of the filler, I, and Sb) was proposed to determine whether a filler impurity can be stably filled into the crystal voids [3]. This rule has predicted ultra-high FFLs for certain AMs in $CoSb_3$, and these have been confirmed experimentally [13–15]. FFLs in multiple-element-filled $CoSb_3$ have also been investigated [16,17]. The calculated and measured FFLs are in good accord for these electropositive filling elements. In any case, the effect of filling with these elements includes electron doping (partially compensated by defects), strong thermal conductivity reduction, and modification of the band structure including opening of the gap [18], though not by enough to completely eliminate bipolar effects at low doping [19]. This last fact, among others, suggests that further optimization is possible, leading to still higher *ZT*.

Interestingly, there are elements that can be incorporated in skutterudites but do not satisfy this electronegativity rule, including Ga and In. Specifically, although based on electronegativity one would predict that these elements are not stable fillers in $CoSb_3$, there are several reports that Ga and In can be doped into the $CoSb_3$ structure. Furthermore, it is reported that these elements affect the electrical and thermal transport properties, and that these doped skutterudites even show improved TE performance. Harnwunggmoung et al. investigated Ga-filled $CoSb_3$ and the results showed that only a small amount of Ga can be filled into the crystal voids [20]. He et al. and Mallik et al. reported In-filled skutterudites, seemingly showing a FFL of 0.22 [21–23]. Grytsiv et al. investigated the phase equilibria of In-doped $CoSb_3$, and the maximum solubility of In in skutterudites was reported to be 0.22 when the compound is in equilibrium with $CoSb_2$ and InSb, while the solubility limit is reduced to 0.09 when it coexists with Sb [24].

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The maximum reported thermoelectric figure of merit *ZT* value of single In-filled $CoSb_3$ is 1.2 at 575 K [21]. There have also been reports of double-filled $CoSb_3$ with In. These give FFLs of In in $CoSb_3$ of <0.2 and *ZT* values of 1.43, 1.4 and 1.3 for In–Ce, In–Yb and In–Ba double-filled $CoSb_3$ at 800 K, respectively [25–27]. Recently Sesselmann et al. found that besides the void sites, In can also occupy the Sb sites [28]. In contrast, electropositive elements such as AM, AE and RE clearly cannot substitute for Sb. This is in accord with our first-principles calculations and experiments, which showed that Ga and In atoms could occupy both the voids and Sb sites in $CoSb_3$ and that these two elements behave differently with respect to carrier doping [29–31].

Here we extend this work to develop understanding of the substitution, filling and doping behavior of these group 13 elements in $CoSb_3$ based on thermodynamic doping theory and energetics obtained from first-principles defect calculations. We systematically study the single impurity induced complex doping properties for Ga- and In-containing $CoSb_3$ skutterudites. The formation energies of many complex defects with different structures and charge states are studied. The results show that both Ga and In mainly form complex dual-site defects. The defect concentrations are studied by using the grand canonical ensemble approximation. We find that the carrier concentration of Ga- and In-doped skutterudites should be very low due to the charge compensation by Sb substitution.

2. Theoretical methods

The present calculations were carried out within density functional theory using the calculation projector augmented wave method, as implemented in the Vienna Ab initio Simulation Package (VASP), and the Perdew–Burke–Ernzerhof generalized gradient approximation [32]. The narrow band gap of $CoSb_3$ is reasonably reproduced with this functional, unlike oxides or other common semiconductors where gap corrections or hybrid functionals need to be used for defect calculations. The calculations with Ga and In doping are carried out on a supercell ($2 \times 2 \times 2$ primitive cell) containing a total of 128 atoms and 8 voids from the $CoSb_3$ plus the additional dopant atoms. A $3 \times 3 \times 3$ Monkhorst–Pack uniform k-point sampling is used for supercell energy calculations, and $15 \times 15 \times 15$ Monkhorst–Pack uniform k-point sampling is used for other compounds. Lattice constants and ion positions were optimized, and the configuration that has the lowest energy is chosen for further analysis. Details are similar to our prior work on related systems [16,17].

3. Results and discussions

3.1. Crystal structures and complex defect structures

The skutterudite compounds TMX_3 (TM = Co, Rh, Ir; X = P, As, Sb), are body-centered cubic materials, space-group *Im*3. The conventional cubic cell contains 8 formula units, for a total of 32 framework atoms and 2 voids. The TM occupy the 8*c* sites and the pnictogen atoms X occupy the 24*g* sites. The voids at the 2*a* positions are 12-fold coordinated by X atoms. It is these sites that can be filled with RE, ME and AM, satisfying the electronegativity selection rule [3]. As mentioned, Ga and In do not satisfy the electronegativity selection rule, and furthermore the ionic radii of trivalent Ga and In would seem to be too small for these void sites [33]. Thus other sites, including framework substitutions for Co and Sb, should also be considered. Additionally, more complex compound defects such as void-filling substitution complexes are possible. Here we consider a wide range of possible defect structures including void filling, Co and Sb substitution, and complex defects containing different numbers of void fillers and substitution atoms. The detailed structures of these defects are described below.

Four of the possible defect types are particularly favorable. The first of these is filling of the void sites (labeled as M_{VF}, M = Ga, In), and the second is the Sb substitution defect (M_{Sb}). The third and fourth are complex defects, all involving dual-site occupancy of doping atoms but at different ratios. One has a 1:1 ratio for void-site to Sb-site occupancy (labeled as M_{VF}–M_{Sb}), and the other has a ratio of 2:1 (labeled as $2M_{VF}$–M_{Sb}). The other complex defects can be obtained by combining these four defects. Fig. 1 depicts the stable structures of these four defects. Note that these defects may show different charge states as discussed below. The simple void filling, M_{VF}, and the Sb substitutional, M_{Sb}, have only one configuration. However, for those defects with dual-site occupancy, there are several possible configurations due to the different occupations of M_{VF} and M_{Sb} and thus varying distances between doping atoms. Based on the total energy calculations, we find that the complex defect has the lowest energy when the distance between the Sb-substitution impurity M_{Sb} and the void-filling impurity M_{VF} is minimized (Fig. 1c), regardless of the charge states of the defects. This is reasonable both because of the Coulomb interactions between the negative acceptor-like M_{Sb} and the positive donor-like M_{VF}, and also from the point of view of lattice strain (Ga and In take up space upon void filling, but are smaller than Sb). Our calculations show that the Co substitutional, M_{Co} defect gives much higher formation energy than the other types of defects. Thus this defect type is excluded and is not considered further. Native point defects in ideal $CoSb_3$ were recently studied by Park et al. [34]. Their results showed that all possible native defects in $CoSb_3$ have high positive formation energies, among which the Co interstitial (Co_i) defect has the lowest. We hence include consideration of Co_i here.

Skutterudite structure $CoSb_3$ is cubic with equivalent 12 Sb atoms icosahedrally coordinating the void site. However, the symmetry is greatly reduced when defects are added. With one M impurity replacing a Sb (M_{Sb}), the void distorts and the symmetry is thus reduced. The filler impurity (M_{VF}) shifts away from the center, reflecting the small sizes of In and Ga. In the complex defects it moves to a position that is relatively closer to the impurity substituting for Sb than to other Sb atoms. The distance of this shift depends on the radius of impurity elements as well as on the chemical bonding between M_{VF} and M_{Sb}. The structure distortion is especially severe for doping with Ga which has a very small size compared both to the available volume of the void and the Sb size. Fig. 2 shows the relaxed positions of several atoms surrounding one specific void site with both the void-filling and Sb-substitution impurities (Ga or In) indicated. It can be observed that Ga_{VF} significantly shifts away from the void center and moves very close to