2384 *Chem. Mater.* **2010,** *22,* 2384–2394
DOI:10.1021/cm903717w

CHEMISTRY OF
MATERIALS
Article

Systematic Study of the Multiple-Element Filling in Caged Skutterudite $CoSb_3$

Lili Xi,[†] Jiong Yang[†] Caifei Lu,[†] Zhigang Mei,[‡] Wenqing Zhang,*,[†] and Lidong Chen[†]

[†]*State Key Laboratory of High Performance Ceramics and Superfine Microstructure,
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China, Graduate School,
Chinese Academy of Sciences, Beijing, China, and* [‡]*Department of Materials Science and Engineering,
Pennsylvania State University, University Park, Pennsylvania 16802*

Received December 11, 2009. Revised Manuscript Received February 7, 2010

Impurity filling fraction limits (FFLs) in nearly 20 dual-element-filled $CoSb_3$ are investigated via ab initio density functional calculations. The two types of filling impurities are selected from rare-earths (La, Ce, Eu, Yb), alkaline-earths (Ba, Sr), and alkaline metals (Na, K) with different chemical nature. Our results show that alkaline-earth and alkaline metal atoms can be jointly filled into the crystal voids, and the total filling fraction limits follow a linear correlation rule, that is, the filling fraction of one element decreases linearly whereas the other element's increases. Cofilling of alkaline-earth (or alkaline metal) with rare-earth shows one filler dominant, usually alkaline-earth (or alkaline metal), or the one with relatively high filling fraction limit. Rare-earth impurities as cofilling atoms have relatively lower filling fractions than alkaline-earth (or alkaline metal) atoms. Eu has a relatively high FFL comparable to the FFLs of alkaline-earths, and the total FFL for the Na−Eu cofilled $CoSb_3$ may be higher than that of the Na-single-filled $CoSb_3$ (65%, the highest FFL). A model to estimate the FFLs for the filling with more than two types of elements in filled skutterudites is also discussed.

1. Introduction

As a group of promising thermoelectric (TE) materials, filled skutterudites (i.e., caged $CoSb_3$ with filling impurities in its crystal voids) have attracted great attentions in recent years.[1,2] The performance of TE materials is determined by the figure of merit ZT value. ZT can be expressed as $ZT = T\sigma S^2/\kappa$, where σ is the electrical conductivity, S is the Seebeck coefficient, and κ is the thermal conductivity. Binary skutterudite $CoSb_3$ crystallizes in a body-centered-cubic structure with space group $Im3$ and has interstitial voids at the $2a$ positions (12 Sb-coordinated) in the lattice. Unfilled $CoSb_3$ exhibits good electrical transport performance, but its thermal conductivity is relatively high, and therefore does not show good TE performance. According to the concept "phonon-glass-electron-crystal" introduced by G. Slack,[3,4] the thermal conductivity of $CoSb_3$ could be reduced by impurity filling, so various void-filling impurities[5−18](La, Ce, Nd, Eu, Yb, Ba, Sr, Ca, In, Tl, Sn, Ge, K, Na, etc.) have been used to fill the voids of $CoSb_3$ to form partially filled skutterudites. The filler atoms "rattle" inside the oversized cages, acting as additional phonon scattering centers, and therefore reduce the lattice thermal conductivity.[19−21] This makes the filled $CoSb_3$ skutterudites one kind of potential excellent TE materials.

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*Corresponding author. E-mail: wqzhang@mail.sic.ac.cn.

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A lot of theoretical works on electronic structures and other properties have been carried out on skutterudites. Singh and co-workers studied various properties of $IrSb_3$, $CoSb_3$, $CoAs_3$, CoP_3, $LaFe_4P_{12}$, and $(La,Ce)Fe_4Sb_{12}$ by using the linearized augmented plane wave method within the local density approximation.[22−24] Løvvik et al. and Bertin et al. investigated the thermodynamic stabilities and electronic properties of CoP_3- and $CoSb_3$-based filled skutterudites.[25,26] Ab initio calculations combined with classical Boltzmann transport equation under constant relaxation time approximation have been used to study electrical transport properties in our previous work,[27,28] and they are successful in evaluating transport properties of thermoelectric materials, such as Seebeck coefficients.

The filling fraction limits (FFLs) of impurities in $CoSb_3$ have significant effects on both the electrical and thermal transport properties.[1−18] In recent years, a theoretical method for FFL prediction has been developed on basis of the density functional calculations. The FFL of an impurity is found to be determined not only by the interaction between the impurity and host atoms but also by the formation of secondary phases between the impurity atoms and one of the host atoms. The FFLs for rare-earths (RE),[29,30] alkaline-earths (AE),[30] and alkaline metals (AM)[31,32] in single-element-filled skutterudites have been estimated using the ab initio method, and they show great agreement with experiments.[29−32] So far the reported lattice thermal conductivities of the filled $CoSb_3$ are still higher than those of the traditional TE materials, such as Bi_2Te_3 and PbTe.[33] To improve their thermoelectric performance, it is necessary to reduce the thermal conductivity, which is inversely proportional to ZT.

Recent work showed that multiple-element-filling in skutterudites could be an effective approach to further decrease the lattice thermal conductivity.[34−37] Multiple-filling atoms in the voids can create various localized vibration modes that can scatter the lattice phonons with different frequencies, and thus lattice thermal conductivity could be expected to be further reduced. However, the diversity and complexity of filling multiple elements in skutterudites introduce great difficulties in experiments. So far, only a few experimental reports on multiple-element-filled skutterudites are available. Therefore, it is critical to theoretically study the filling systematic of impurities in multiple-element-filled $CoSb_3$ and understand the factors that determine the FFLs.

Using the density functional ab initio method,[30−32] the FFLs of impurities in nearly 20 dual-element-filled skutterudites have been investigated. In our previous work, an anomalous Na−Eu dual-filling has been studied in detail.[38] The present work presents a systematic study on the FFLs in dual-element-filled $CoSb_3$. In the following parts, we will briefly describe the computational method in Section II. In Section III, we will first discuss the numerical results as well as some experimental validations, and then introduce the models for estimating the FFLs for the filling with more than two types of elements, and last discuss the implication of our work for the thermoelectric performance improvement of the filled $CoSb_3$. In Section IV, we will give a summary.

2. Computational Methods

The projector augmented wave (PAW) method and Perdew−Burke−Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange-correlation potential, as implemented in the Vienna ab initio simulation package (VASP), are utilized in the study.[39−41] A plane-wave cutoff energy of 350 eV and an energy convergence criterion of 1×10^{-4} eV for self-consistency are adopted. All calculations are carried out in a supercell ($2 \times 2 \times 2$ primitive cell) with 128 atoms and 8 voids. All the ions are relaxed toward equilibrium until the calculated Hellmann−Feynman forces on each atoms are $< 1 \times 10^{-2}$ eV/Å, and lattice parameters are optimized by fitting the Birch−Murnaghan equation of state.[42] Only gamma point is used for both the pure and filled $CoSb_3$ in the supercell, and a $6 \times 6 \times 6$ Monkhorst-Pack uniform k-point sampling is used for other compounds,[43] such as secondary phases and simple elements. The above computational methods and parameter settings have been proved to be reliable in predicting the filling fraction limits for impurities in single-element-filled $CoSb_3$.[29−32] Test calculations also show that denser k-points for filled $CoSb_3$ (e.g., $2 \times 2 \times 2$ k-points sampling) only lead to minor changes to the final results.

The body-centered cubic skutterudite contains large voids at the positions of $2a$, and atoms Co and Sb locate at the positions of $8c$ and $24g$, respectively.[30] The conventional crystallography unit cell and the primitive cell are plotted in figure 1, where A and B represent different impurity atoms filled into the large

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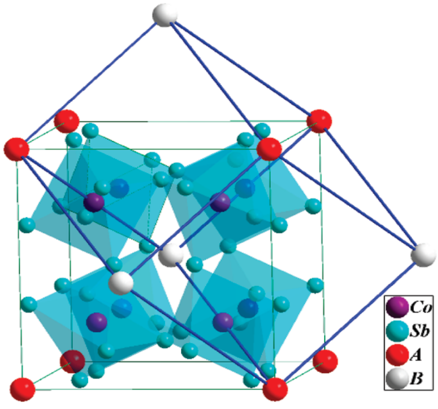

Figure 1. Conventional crystallography unit cell (light dashed line) and the primitive cell (thick solid blue line) of skutterudite structure. A and B represents different filler atoms. This figure shows a full filling pattern (A, B, 2*a*; Co, 8*c*; Sb, 24*g*).

cages. Within a conventional unit cell, there are only two different filling patterns: null filling (filling fraction = 0) or full filling (A, 0.5; B, 0.5). To study various filling fractions of the $CoSb_3$ voids, calculations are carried out in a supercell ($2 \times 2 \times 2$ primitive cell). There are 128 atoms and 8 voids for pure $CoSb_3$ within the supercell, which has nine different filling fractions from 0 to 1 differing by 0.125 for single filling $CoSb_3$.

As for dual-element filling, the configuration problem is much more complicated than that of single filling. The number of possible filling configurations for each composition is much larger than that of single filled systems, and they are not just limited to the 9 filling patterns (from 0 to 1 differed by 0.125). When two different elements are filled into the crystal voids together, such as K and Ba atoms, there are 31 different filling patterns even without considering the configuration problems at the same filling fraction. All kinds of different occupation configurations are optimized to obtain the most stable structure. Nearly 20 different dual-element cofilling cases are studied using the above approach, and multiple filling fractions can then be approximately evaluated based on the calculation results for the dual-element fillings.

3. Results and Discussion

3.1. Crystal Structure. In all calculations, both the lattice constants of each supercell and the positions for ions are fully optimized. In certain filling fraction, the lattice constant remains the same for each configurations,[29,30,32] and we use the one that has the lowest energy. Based on our results, lattice constants increase linearly with increasing filling fractions for all the dual-element-filled $CoSb_3$. Similar phenomena were also found in previous work for single-filling systems.[29,30,32] As for the dual-element-filled $CoSb_3$, it was found that the lattice constants with the same filling fractions but different filling combinations also exhibit a linear relationship. This is shown in Figure 2, where the relationship between lattice constant and filling fraction y for one of the two filler atoms is plotted. The total filling fraction is set to be 0.5. x and y are the filling fractions of the two types of filler atoms.

Our previous work showed that the FFLs of impurities in filled $CoSb_3$ are determined by the competition between the formation of the filled skutterudites and that of

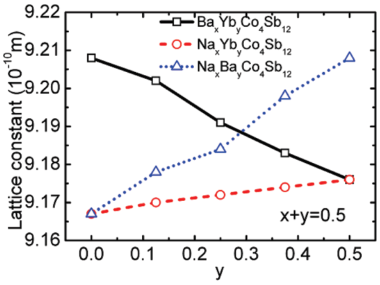

Figure 2. Calculated lattice constants as a function of filling fraction y for the Ba−Yb, Na−Yb, and Na−Ba dual-element-filled $CoSb_3$. The total filling fraction is fixed at 0.5.

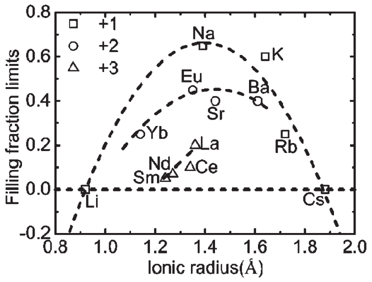

Figure 3. Relations between the ionic radii and charge states[29,30,32] of various filler atoms and the corresponding filling fraction limits for stable single filling. The dashed curves are guides for eyes.

secondary phases, and is independent of the initial quantity of filler atoms.[30] It has been shown that the ionic radius and valences of the filling impurities affect their FFLs greatly based on the final FFL data.[32] Figure 3 plots the FFLs of the reported filler impurities with the correlation to the corresponding ionic radius and valence charge states. There are 12 Sb atoms around each filler impurity, so the coordination number is twelve, and the 12-coordination (CN = 12) ionic radius[44] are used in figure 3. But only the 8-coordination (CN = 8) radius for Li ion could be found in ref 44., so the radius of CN = 8 for Li ion is used. It is seen that to form a stable filled skutterudite the ionic radius of the filler atom comes from a lower limit 1.2 Å to a upper limit 1.65 Å. Below the lower limit (1.2 Å), the size of the voids in $CoSb_3$ is too large for the fillers, and they can not form stable bonding between the filler atoms and the surrounding Sb atoms. In contrast, filler atoms with ionic radii larger than the upper limit 1.65 Å (but smaller than the void radius) are too large for the voids in $CoSb_3$, and therefore, the interaction between the filler ions and antimony atoms would lead to repulsion because of a strong overlap of the valence electrons. That could explain the reason why Li and Cs impurities can not fill into the voids of $CoSb_3$ (see Figure 3). Because of the same reason, the rare-earths after Sm (except Eu and Yb) can not be filled into the voids of $CoSb_3$. In addition to the ionic radii, the valence of a filler atom also affects its filling fraction. Figure 3 indicates that with the similar ionic radius a lower charge state leads to a higher FFL. The fillers Na and K with charge state +1 have relatively large FFLs compared to

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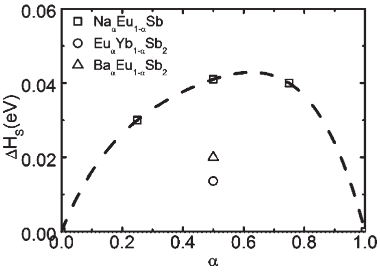

Figure 4. Formation enthalpies of forming solid solutions (see eq 4 in text) related to the Na−K, Ba−Eu, and Eu−Yb dual-element-filled $CoSb_3$ systems.

the alkaline-earths and rare-earth metals at the comparative ionic radii. Eu (+2) and Yb (+2) atoms have higher filling fractions than other rare-earth atoms, such as La (+3), Ce (+3).[29−32]

3.2. Filling Fraction Limit. Similar to our previous work, by considering the formation of both the filled skutterudite and secondary phases,[29,30] the formula of the final chemical reaction for the formation of a dual-element-filled $CoSb_3$ can be written as following

$$\mathrm{K} + \mathrm{Ba} + 4\mathrm{CoSb}_3 \rightarrow \frac{1}{A}\mathrm{K}_x\mathrm{Ba}_y\mathrm{Co}_4\mathrm{Sb}_{12} + \frac{A-x}{A}\mathrm{KSb} + \frac{A-y}{A}\mathrm{BaSb}_2 + \frac{4(A-1)}{A}\mathrm{CoSb}_2 \qquad (1)$$

The corresponding reaction of the filled skutterudite and secondary phases can be expressed as

$$x\mathrm{K} + y\mathrm{Ba} + 4\mathrm{CoSb}_3 \rightarrow \mathrm{K}_x\mathrm{Ba}_y\mathrm{Co}_4\mathrm{Sb}_{12} \qquad (2)$$

$$\mathrm{K} + \mathrm{Ba} + 3\mathrm{CoSb}_3 \rightarrow \mathrm{KSb} + \mathrm{BaSb}_2 + 3\mathrm{CoSb}_2 \qquad (3)$$

Note that the K−Ba-filled $CoSb_3$ has been taken as an example to simplify the expression. For other filler-atom combinations, the differences are the coefficients before the compounds and the subscripts of the secondary phases. In eq 1, x (y) is the filling fraction for impurity atom K (Ba) and is independent of the coefficient of pure K (Ba) phase, which has been set as one. A is a parameter that is given by $A = 4 - x - 2y$. The formula of other filling reactions can be written in a similar way. Notice that only the x (y) fraction of the impurity atoms go into the voids and the rest form the secondary phases.

Consider that there may be solid solutions, e.g., $(M_{1-\alpha}N_\alpha)Sb_2$ as an example, in the reaction of secondary phase formation (eq 3) when two or more different elements get involved in the filling. The reaction can be written as $(1 - \alpha)MSb_2 + \alpha NSb_2 \rightarrow (M_{1-\alpha}N_\alpha)Sb_2$, and the formation enthalpy of the solid solutions is

$$\Delta H_S = E_{(\mathrm{M}_{1-\alpha}\mathrm{N}_\alpha)\mathrm{Sb}_2} - (1-\alpha)E_{\mathrm{MSb}_2} - \alpha E_{\mathrm{NSb}_2} \qquad (4)$$

The formation enthalpies of Na−K, Ba−Eu, and Eu−Yb systems have been calculated by using the ab initio method. Some of the results are shown in Figure 4. The results indicate that the formation enthalpy ΔH_S is usually positive, implying that it is easy to form pure secondary phases instead of solid solutions. Experimentally, there were also no secondary phases at any solid solution states observed in dual-element filling of different combinations, which is consistent with our calculations.

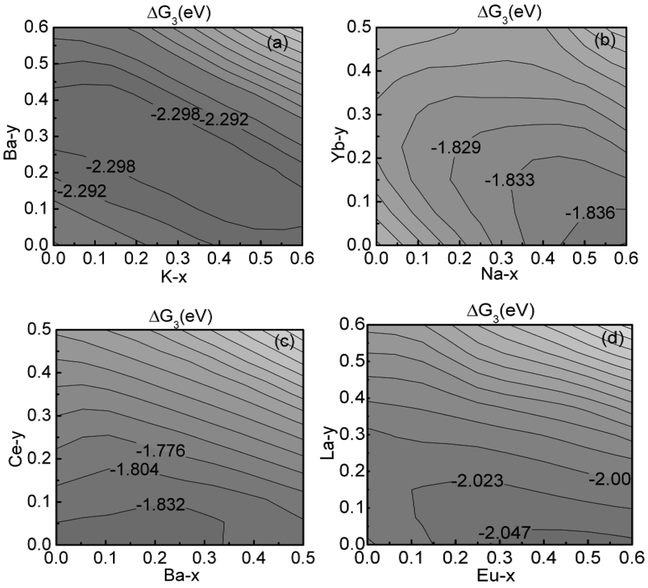

Figure 5. Gibbs free energy patterns for some dual-element-filled $CoSb_3$ systems ($M_xN_yCo_4Sb_{12}$) at 1000 K.

By considering the random distribution of fillers in $CoSb_3$ and introducing the configurational entropy, the Gibbs free energy corresponding to eq 1 at a finite temperature for dual-element filling is given by

$$\Delta G_3 = \frac{A-x}{A}\Delta H_2{}^{\mathrm{K}} + \frac{A-y}{A}\Delta H_2{}^{\mathrm{Ba}} + \frac{1}{A}\{\Delta H_1(x,y) + kT[x\ln x + y\ln y + (1-x-y)\ln(1-x-y)]\} \qquad (5)$$

Where$\Delta H_1(x, y)$ is the formation energy when impurity atoms fill into lattice voids corresponding to eq 2. $\Delta H_2{}^{K}$-(or $\Delta H_2{}^{Ba}$) is the formation energy of secondary phases corresponding to eq 3 with only K (or Ba) phase (superscript) being involved in the reaction. k is the Boltzmann constant and T is the absolute temperature. The detailed explanation of these parameters can be found elsewhere.[29−32]

The two filling impurities are selected from RE (La, Ce, Eu, Yb), AE (Ba, Sr), and AM (Na, K), which differ in chemical nature by categories. Nearly 20 typical dual-element-filled $CoSb_3$ systems are studied by using ab initio calculations. Unlike the single-element-filled $CoSb_3$ systems, the Gibbs free energy for a dual-element-filled $CoSb_3$ is related to both x and y values. By searching for the minimum ofΔG_3 with respect to the filling fractions x and y, the FFL in multiple-filled $CoSb_3$ can be obtained in terms of ΔH_1, $\Delta H_2{}^{M}$, and $\Delta H_2{}^{N}$. M and N represent different types of filler atoms (M, N = K, Ba, ...).

Figure 5 shows a few typical contour plot patterns of the iso-energy surface of ΔG_3, as functions of both x and y at T = 1000 K for some representative dual-element-filled $CoSb_3$. The lower ΔG_3 values, as indicated by the

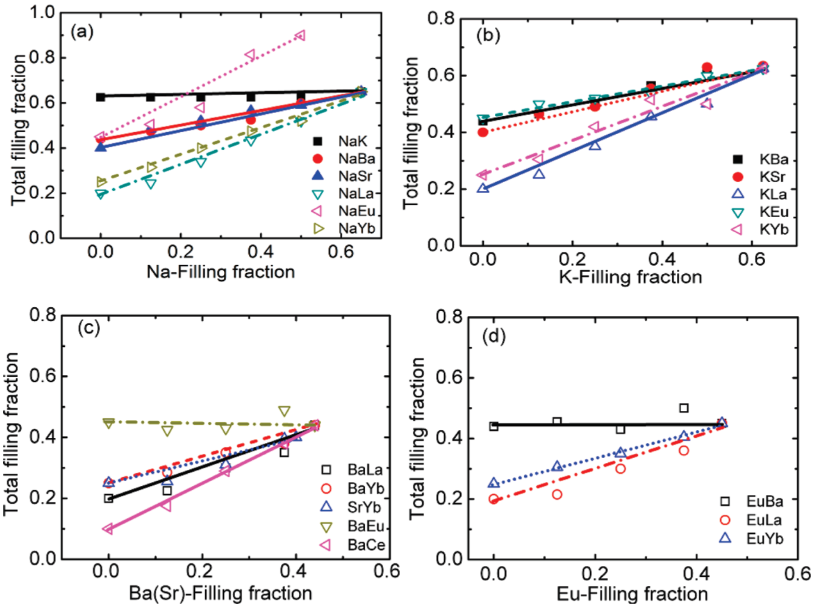

Figure 6. Relationship between the total filling fraction and the corresponding filling fraction of one of the cofiller atoms. (a–d) Filling fractions of Na-, K-, Ba- (Sr-), and Eu-related cofilling $CoSb_3$ systems, respectively. The lines are guides for the eyes.

darker regions in the plots, represent more stable dual-element filling at the filling fractions. Most of the dual-element-filled systems have the linear band pattern as shown in Figure 5a. The filling fraction of one filler decreases linearly as that of the other increases, and the total FFL, i.e., maximum $x + y$, falls in between the two single-element FFLs. Figure 5a is for the K–Ba-filled systems and the values in the plot indicate theΔG_3 of contour lines. There is a large black band which means that stable dual-element filled skutterudite can be obtained in this area (see Figure 5a). It indicates that impurity atoms K and Ba could be jointly filled into the crystal voids at almost any rates, and the sum of filling fractions follows a linear correlation rule. Panels b and c in Figure 5 show the ΔG_3 contour plots for the Na–Yb and Ba–Ce dual-filled systems. It can be seen that adding RE fillers into the voids usually increases Gibbs free energy. From panels b and c in Figure 5, we can expect that given adequate filler atoms, the final products are dominant AE (or AM)-filled $CoSb_3$. However, the final products may also contain a small amount of RE fillers. With the lowering of the filling fractions of the dominant fillers (AE or AM), the filling fractions of RE fillers increases slightly. The filler atoms that have relatively high FFLs in single-filled $CoSb_3$ usually dominate the filling when they are filled into the voids together with other elements. Figure 5d is for the Eu–La cofilled system; the dominant filler atom is Eu, as expected.

We also calculate the total filling fractions when fixing the filling fraction of one of the two filler atoms at a given value. All the calculated filling fraction results are shown in Figure 6a–d. Figure 6a plots the relationship between the total filling fraction of Na–-M dual-filling $CoSb_3$ and the filling fraction of Na atoms, where M represents one of the other filler impurities (M = K, Sr, Ba, La, Eu, Yb). Figure 6b–d plot the total filling fraction of K–M, Ba–M (or Sr–M), and Eu–M dual-filling systems versus the given filling fraction of K, Ba (Sr), and Eu atoms, respectively. For the systems cofilled with AE–AE, AE–AM, or AM–AM combinations, such as K–Ba cofilling, the filling fraction can change continuously, and is marked by solid symbols in Figure 6. For the other cofilled systems, the filling fraction is marked by open symbols, indicating that the stable dual-filling skutterudites show one filler dominant, usually the AE or AM fillers, or the one with relatively high single-filling fraction limit. Experimentally, when controlling the filling fractions of AM or AE at lower values, the total filling fractions also follow a nearly linear trend.

Our calculations show that the FFL of one element decreases substantially as the other element's increases, and the total FFL value usually falls in between the values of the two single FFLs, or is dominated by one FFL. One exception is the Na–Eu dual-filling $CoSb_3$ system (Figure 6a), in which the increasing filling fraction of Na atoms does not cause decreasing of the filling fraction of Eu atoms. Therefore, the total FFL of the Na–Eu cofilled $CoSb_3$ can reach a very high value, almost close to full filling. This anomalous filling has been studied in a previous paper.[38] The AM atoms Na and K have the relatively high dual filling fractions because of their low valence charge states (+1). Because of the high valence charge states, RE metals as cofillers usually lead to relatively low total filling fractions, whereas Eu as cofiller atom has similar filling fraction to that of AE atoms (see Figure 6c,d). The Ce impurity has a low filling fraction when filled into the structure voids together with other impurity atoms, as shown in Figure 5c,d for Ba–Ce dual-filled systems.

On the basis of the above results, we can summarize the following findings:

(1) When selecting AE and AM as cofiller impurities, the filling behaviors are simple linear because of the similar electronic structures of the fillers. The filling

fraction of one element decreases linearly as the other element's increases, and the total FFL falls in between the two end FFL values that correspond to the two elements filling into the cages separately. They could be jointly filled into the crystal voids at any rates.

(2) When RE and AE (or AM) jointly fill into the $CoSb_3$ cages, the total filling fraction is lower than that of the cofilling of AE and AM. They could not be jointly filled into the crystal voids at arbitrary rates though the fillings also follow a linear correlation rule, as shown in panels b and c in Figure 5b for Na−Yb and Ba−Ce dual-filled $CoSb_3$. Usually, the AE or the AM atoms dominate the filling. There is only a limited filling fraction of RE atoms that can be filled into the crystal voids, especially for Ce, when they act as cofiller atoms. When Eu atoms fill into the voids together with AE or AM atoms, Eu may have a relatively large filling fraction compared to other RE atoms (See Figure 6d). This is consistent with the higher FFL of Eu in single-filled $CoSb_3$ in comparison with other RE because of its lower charge state and proper ion radius (see Figure 3).

(3) When taking two different RE elements as cofiller impurities, the filling behavior is similar to the second case, that is, one of the two elements dominates the cofilling, usually the one with relatively high single FFL, as shown in Figure 5d for the Eu−La cofilled system.

The dual-element cofilling behaviors could be approximately divided into the three categories as discussed above. One special case needs to be addressed, that is the Na−Eu cofilling system. The Na−Eu cofilling shows an anomalous filling behavior, and details have been discussed elsewhere.[38]

3.3. Factors Determining FFL. *A. Analysis of* ΔH_1. Factors that determine the FFLs for dual-element-filled $CoSb_3$ are more complicated than those for single-element-filled $CoSb_3$. The formation of filled $CoSb_3$ by filling two different impurities, such as K and Ba, can be described by eq 2. The corresponding formation enthalpy $\Delta H_1(x, y)$ can be defined in the form of $\Delta H_1(x, y) = E_{K_xBa_yCo_4Sb_{12}} - xE_K - yE_{Ba} - 4E_{CoSb_3}$, which includes the interactions between the same types of elements, ΔE_2^K for K−K pairs and ΔE_2^{Ba} for Ba−Ba pairs, and that between different types of elements, ΔE_2^{K-Ba} for K−Ba pairs (see eq 6 below). Within a reasonable approximation, the formation enthalpy $\Delta H_1(x, y)$ could be decomposed into three parts

$$\Delta H_1(x,y) \approx x\Delta H_1^K + y\Delta H_1^{Ba} + xy\Delta E_2^{K-Ba}$$
$$= x\left(\Delta E_1^K + x\Delta E_2^K\right) + y\left(\Delta E_1^{Ba} + y\Delta E_2^{Ba}\right) + xy\Delta E_2^{K-Ba} \quad (6)$$

Here, $\Delta H_1^K(\Delta H_1^{Ba})$ represents the formation enthalpy of the pure K-filled (Ba-filled) $CoSb_3$,[29−32] and it has nearly a linear dependence on $\Delta E_1^K(\Delta E_1^{Ba})$ and $\Delta E_2^K(\Delta E_2^{Ba})$, as proved before.[29−32] $\Delta E_1^K(\Delta E_1^{Ba})$ represents the formation energy of filling an single impurity K (Ba) into the crystal void of $CoSb_3$ and is determined by the interaction between the filler impurity and its neighboring host atoms.[29−32] Note that a simple electronegativity selection rule ($x_{Sb} - x_I > 0.80$) was found to determine whether an impurity can be filled into the crystal voids for single filling. Because $\Delta E_1^K(\Delta E_1^{Ba})$ mainly comes from the K−Sb (Ba−Sb) bonding energy and relates to the electronegativity difference, and it shows no difference from the single filling case. Generally speaking, the simple electronegativity selection rule is still valid for dual- or multiple-filled skutterudites.$\Delta E_2^K(\Delta E_2^{Ba})$ mainly comes from the Coulombic interactions between K−K (Ba−Ba) atoms screened by crystal environment and could be related to impurity valence charge state q_X by

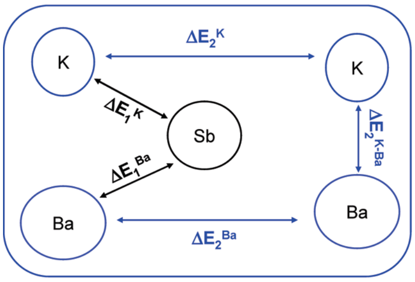

Figure 7. Schematic diagrams of various interactions in dual-element-filled $CoSb_3$. K−Ba cofilling $CoSb_3$ is taken as an example.

$$\Delta E_2^X \propto \frac{q_X^2}{R_X} e^{-2R_X/R_0}$$

, where R_X is the distance between impurities X and relates closely to the lattice constant of the filled $CoSb_3$.[29−32] The filling-induced change of lattice constants is small in filled systems,[29] so R_X could be reasonably taken as a constant. Using this relationship forΔE_2^X, the effective charge states of the single filling impurity atoms were estimated.[29−32]is the effective screening length describing the screening effect of the $CoSb_3$ crystal environment around a charged filler, and was estimated to be around 12.58 Å for single-filled $CoSb_3$ systems. This value is much larger than those (typically ~2−3 Å) for metals, suggesting a weak charge screening effect in $CoSb_3$.[30] The last term in eq 6, $xy\Delta E_2^{K-Ba}$, counts approximately the total K−Ba interactions in the dual-filled system and thus depends on x and y.

Figure 7 plots the schematic diagrams of various interactions in K−Ba dual-filled $CoSb_3$, in which the interaction ΔE_2^{K-Ba} between different types of elements is clearly indicated together with all other quantities. The Sb atoms represent the host atoms in the filled skutterudites in Figure 7. The arrows indicate the different interactions between the filler atoms and those between the fillers and the host atoms.

In *ab initio* scheme, the total interaction energy between different types of filler atoms could be estimated by

$$\Delta E_{K-Ba} = E_{K_xBa_yCo_4Sb_{12}} + 4E_{CoSb_3} - E_{K_xCo_4Sb_{12}} - E_{Ba_yCo_4Sb_{12}} \approx xy\Delta E_2^{K-Ba} \quad (7)$$

Where ΔE_2^{K-Ba} is the effective interaction energy per pair of K−Ba atoms. The interaction ΔE_2^{K-Ba} plays a key role

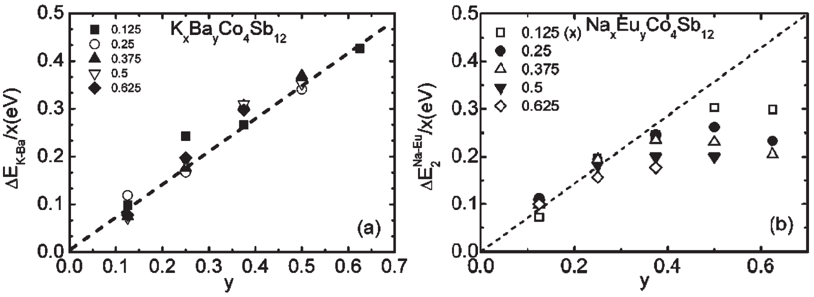

Figure 8. Interaction energy $\Delta E_{M-N}/x$ as a function of y at different x values for dual-element-filled $M_xN_yCo_4Sb_{12}$: (a) K−Ba system, (b) Na−Eu system. The dashed lines are guides for the eyes.

in determining the cofilling behavior. Considering the fact that the interaction between filler impurities was proven to be primarily Coulombic in single-filled $CoSb_3$,[29,30] we may reasonably infer that the ΔE_2^{K-Ba} also comes from the Coulombic interaction between different fillers screened by crystal environment. Generally, the interaction could be written as ΔE_2^{M-N}, and M and N represent different types of filler atoms. Therefore, this interaction can be expressed as

$$\Delta E_2^{M-N} \propto \frac{Z q_M q_N}{R_{M-N}} e^{-2R_{M-N}/R_0}$$

R_{M-N} is the distance between fillers M and N. q_M and q_N are the effective charge states of M and N. R_0 is the effective screening length as mentioned before. Z is the coordination number of the nearest neighbor of crystal voids. In the filled $CoSb_3$, the value of Z is 8. If there is no interaction ΔE_2^{M-N}, the filling of the two different elements is independent. Figure 8 plots $\Delta E_{M-N}/x \approx y$ for K−Ba- and Na−Eu-filled $CoSb_3$. Results for K−Ba cofilled systems (See Figure 8a) show a linear relationship, which means that the interaction ΔE_2^{K-Ba} is close to be a constant. On the basis of our calculations, all the ΔE_{M-N} data using alkaline earths and alkaline metals as cofiller atoms follow a similar linear behavior, indicating that the effective charge states of the fillers and the crystal structure parameters keep almost unchanged in these systems, even with change from single to multiple filling. This can explain why the alkaline-earths and alkaline atoms could be jointly filled into the crystal voids following a linear correlation rule (see Figure 5a). The $\Delta E_{M-N}/x$ curves for the cofilling systems with RE and AE (or AM) deviate from the linear correlation trend, and with the Na−Eu cofilled system as a very special case (see Figure 8b).[38]

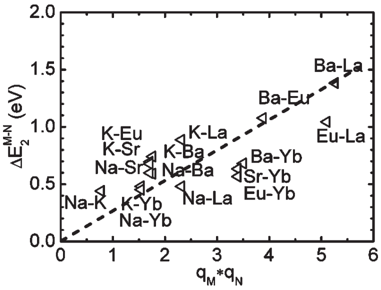

Figure 9. Relationship between the interaction energy ΔE_2^{M-N} and the product of the effective valence charge states of fillers M and N. The dashed line is a guide for the eyes.

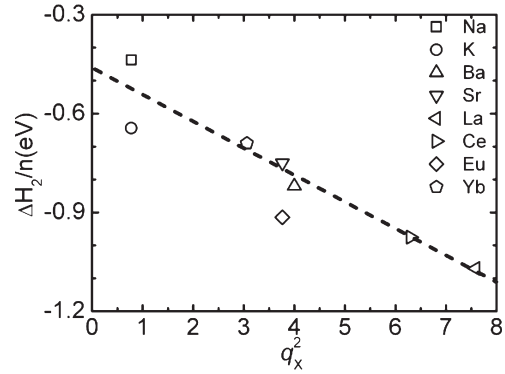

Figure 10. Relationship between the formation energies $\Delta H_2/n$ of secondary phases for different filler impurities and the square of the valence charge states (q_X^2) of the corresponding fillers. The dashed line is a linear fit.

For single-filled $CoSb_3$, the distance between filler impurities (R_X) and the effective screening length (R_0) are close to be constants. Therefore, the Coulombic interaction ΔE_2^X shows a good linear dependence on q_X^2.[30] With the estimated ΔE_2^{M-N} using eq 7, we plot the relationship between ΔE_2^{M-N} and the product of valence charge states (q_Mq_N) for various dual-element-filled systems in Figure 9. Higher charge states, such as Ba (+2) and La (+3), lead to higher interaction energy ΔE_2^{M-N}, which may result in an unstable filled skutterudite and then the dominant filling of the filler with relatively low charge state. Most of the rare-earth-related systems have relatively high ΔE_2^{M-N} values, so the FFLs of RE-filled $CoSb_3$ systems are low based on our calculations except for filler atoms Eu. The correlation between theΔE_2^{M-N} and q_Mq_N for the series of dual-filled $CoSb_3$ systems investigated seems to be close to linear in general trend, even with deviation for a few systems, which also indicates that the decomposition of formation energy in an approximate linear way (eqs 6 and 7) is reasonable.

B. Factors Determining ΔH_2. In principle, there are no differences in the derivation for the formation energy of secondary phases ΔH_2 in single-filled system and dual-filled $CoSb_3$. However, considering the different chemical formula for secondary phases of AM, AE, and RE elements, for instance, the NaSb for Na and $BaSb_2$ for

Table 1. Various Interaction Energies in Dual-Filled $M_xN_yCo_4Sb_{12}$ Obtained by Fitting the Ab initio Data to Model Equations; See Eq [6] and Explanation in the Corresponding Text

	ΔE_1^{M} (eV)	ΔE_1^{N} (eV)	ΔE_2^{M} (eV)	ΔE_2^{N} (eV)	ΔE_2^{M-N} (eV)	ΔH_2^{M} (eV)	ΔH_2^{N} (eV)
K−Na	−0.875	−0.662	0.188	0.164	0.440	−0.644	−0.437
K−Ba	−0.875	−2.133	0.188	0.775	0.742	−0.644	−1.64
K−Sr	−0.875	−1.964	0.188	0.685	0.677	−0.644	−1.5
K−La	−0.875	−2.668	0.188	1.471	0.887	−0.644	−2.14
K−Eu	−0.875	−2.341	0.188	0.634	0.695	−0.644	−1.83
K−Yb	−0.875	−1.822	0.188	0.828	0.481	−0.644	−1.38
Na−La	−0.662	−2.668	0.164	1.471	0.481	−0.437	−2.14
Na−Yb	−0.662	−1.822	0.164	0.828	0.452	−0.437	−1.38
Na−Sr	−0.662	−1.964	0.164	0.685	0.598	−0.437	−1.5
Na−Ba	−0.662	−2.133	0.164	0.775	0.592	−0.437	−1.64
Ba−La	−2.133	−2.668	0.775	1.471	1.383	−1.64	−2.14
Ba−Yb	−2.133	−1.822	0.775	0.828	0.681	−1.64	−1.38
Ba−Eu	−2.133	−2.341	0.775	0.634	1.077	−1.64	−1.83
Sr−Yb	−1.964	−1.822	0.685	0.828	0.634	−1.5	−1.38
Eu−La	−2.341	−2.668	0.634	1.471	1.044	−1.83	−2.14
Eu−Yb	−2.341	−1.822	0.634	0.828	0.566	−1.83	−1.38

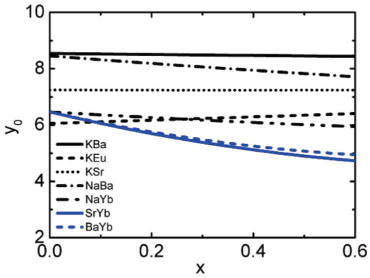

Figure 11. Relationship between y_0 and x in eq 12. x is the filling fraction of one of the filling atoms. In general, y_0 does not change substantially with increasing x.

Ba, we re-express the formation reaction and formation energy in a general way as

$$\begin{aligned} X + nCoSb_3 \rightarrow nCoSb_2 + XSb_n \quad \Delta H_2 \\ = E_{XSb_n} + nE_{CoSb_2} - E_X - nE_{CoSb_3} \\ = (E_{XSb_n} - nE_{Sb} - E_X) - n(E_{CoSb_3} - E_{Sb} - E_{CoSb_2}) \end{aligned} \quad (8)$$

where n equals 1 or 2 for different impurities. The net result of the terms in the first bracket represents the cohesive energy of XSb_n, and that in the secondary bracket is a constant with a coefficient n. The term $(E_{XSb_n} - nE_{Sb} - E_X)$ could be considered to be approximately proportional to q_X^2 based on our earlier analysis,[30] where q_X is the effective charge state of the filler atom X in the void. So the formation energy for the secondary phases should satisfy

$$\Delta H_2/n = (E_{XSb_n} - nE_{Sb} - E_X)/n - (E_{CoSb_3} - E_{Sb} - E_{CoSb_2}) \approx C_1 q_X^2 + C_2 \quad (9)$$

where C_1 and C_2 are presumed to be constants. Though the equation is not a rigorous description, the correlation between $\Delta H_2/n$ and q_X^2, as plotted in Figure 10, shows a reasonably good linear relationship.

C. Analysis of the Dual-Element Filling Fractions. By using eqs 5 and 6, the Gibbs free energy ΔG_3 can be simplified to be

$$\Delta G_3 = \left(\frac{A-x}{A}\Delta {H_2}^{K} + \frac{x}{A}\Delta H_1^{K}\right) + \left(\frac{A-y}{A}\Delta {H_2}^{Ba} + \frac{y}{A}\Delta H_1^{Ba}\right) + \frac{1}{A}xy\Delta E_2^{K-Ba} \quad (10)$$

where the configuration entropy term has been neglected for a simplified analysis. The first term in eq 10 corresponds to the K single filling, and the second term to the Ba single filling. The last term $xy\Delta E_2^{K-Ba}$ describes the interactions between the filler impurities K and Ba. Though we can not obtain an analytical solution of the groups of (x, y) values corresponding to the minimum of ΔG_3, at each predefined x, the relationship between y_m and x, together they define all extremes of ΔG_3, can be obtained analytically as

$$y_m = \frac{(4-x)}{2} - \frac{1}{2\sqrt{\Delta E_2^{Ba}}} y_0^{1/2} \quad (11)$$

$$\begin{aligned} y_0 = \left(\Delta E_2^{Ba} + 4\Delta E_2^{K} - 2\Delta E_2^{K-Ba}\right)x^2 + 16\Delta E_2^{Ba} + \\ 8\left(\Delta E_1^{Ba} - \Delta {H_2}^{Ba}\right) + \Big[4\left(\Delta E_1^{K} - \Delta {H_2}^{K}\right) - \\ 2\left(\Delta E_1^{Ba} - \Delta {H_2}^{Ba} - \Delta E_2^{Ba}\right) + 8\Delta E_2^{K-Ba}\Big]x \end{aligned} \quad (12)$$

eq 6 has been inserted into eq 10 for the above derivation. Note that the parameters, except for the parameter ΔE_2^{K-Ba}, can be approximately obtained from the calculated energies for single-filling $CoSb_3$.[29−32] The parameters of those energy quantities (ΔE_1, ΔE_2, ΔH_2) for filled skutterudites are given in Table 1. Numerical values of ΔE_1^{K}, ΔE_1^{Ba}, ΔE_2^{K}, ΔE_2^{Ba}, ΔH_2^{K}, and ΔH_2^{Ba} are obtained from the calculations for single-element-filled $CoSb_3$.[29−32] The parameter ΔE_2^{K-Ba}, an extra term in dual-element-filled $CoSb_3$, is obtained by using eq 7 and calculations for dual-element-filled $CoSb_3$. The relationship between y_0 and x can be calculated by using the fitting data list in Table 1. This correlation is plotted in Figure 11 for some dual-element-filled $CoSb_3$. Generally speaking, y_0 does not change substantially with the increasing x. From Figure 11, we can see that the coefficient of x^2 in eq 12 is very small, which leads to a linear relationship between y_0 and x. Detailed analysis of the data in Table 1 indicates

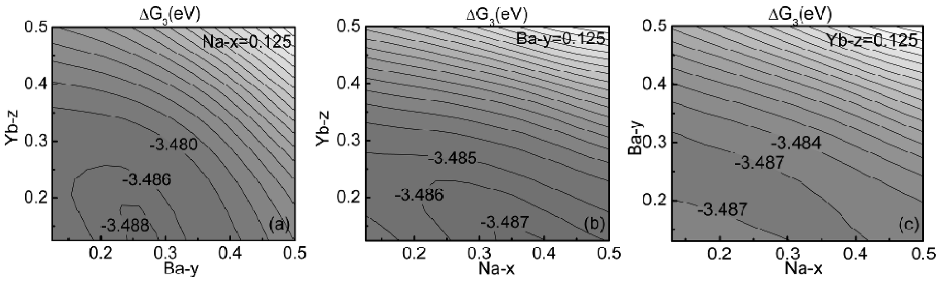

Figure 12. Gibbs free energy contour for Na−Ba−Yb triple-element-filled $CoSb_3$ systems at 0 K. (a) Na, $x = 0.125$; (b) Ba, $y = 0.125$; (c) Yb, $z = 0.125$.

that the filler atoms with different charge states (such as K−Ba) do give almost zero coefficient of x^2, whereas the filler atoms with the same charge states (such as Ba−Yb) lead to a nonzero coefficient of x^2 (with a value slightly bigger than zero). The constant term in eq 12 is much bigger than zero (8.546 eV for K−Ba, 8.456 eV for Na−Ba). Therefore, based on eq 11, we may understand that the filling fraction y for one of the filling elements decreases with the increased filling fraction x for the other filling element in dual-filled $CoSb_3$.

D. Model to Predict FFLs in Multiple Filling. The FFLs of single- and dual-element-filled $CoSb_3$ have been studied systematically. Through the detailed study on FFLs, we expand our knowledge about the void filling in typical caged compound, e.g., the $CoSb_3$. On the basis of the aforementioned results and theory, a model to predict the FFLs for triple- and even multiple-filled $CoSb_3$ can be approximately developed. In the approach, the formula reaction for the triple-element-filled $CoSb_3$ is expressed as

$$\mathrm{Na} + \mathrm{Ba} + \mathrm{Yb} + 4\mathrm{CoSb_3} \rightarrow \frac{1}{B}\mathrm{Na}_x\mathrm{Ba}_y\mathrm{Yb}_z\mathrm{Co_4Sb_{12}} + \frac{B-x}{B}\mathrm{NaSb} + \frac{B-y}{B}\mathrm{BaSb_2} + \frac{B-z}{B}\mathrm{YbSb_2} + \frac{4(B-1)}{B}\mathrm{CoSb_2} \quad (13)$$

Where x, y, and z are the filling fractions of Na, Ba, and Yb. The parameter $B = 4 - x - 2y - 2z$. If we ignore the high order interactions that involve three different atoms (such as $\Delta E_{\mathrm{Na-Ba-Yb}}$), the formation energy with three different impurities filling into the voids can be written as

$$\Delta H_1(x,y,z) \approx x\Delta H_1^{\mathrm{Na}} + y\Delta H_1^{\mathrm{Ba}} + z\Delta H_1^{\mathrm{Yb}} + xy\Delta E_2^{\mathrm{Na-Ba}} + xz\Delta E_2^{\mathrm{Na-Yb}} + yz\Delta E_2^{\mathrm{Ba-Yb}} \quad (14)$$

The corresponding Gibbs free energy can be written in the following form

$$\Delta G_3 = \left(\frac{B-x}{B}\Delta H_2{}^{\mathrm{Na}} + \frac{x}{B}\Delta H_1^{\mathrm{Na}}\right) + \left(\frac{B-y}{B}\Delta H_2{}^{\mathrm{Ba}} + \frac{y}{B}\Delta H_1^{\mathrm{Ba}}\right) + \left(\frac{B-z}{B}\Delta H_2{}^{\mathrm{Yb}} + \frac{z}{B}\Delta H_1^{\mathrm{Yb}}\right) + \frac{1}{B}xy\Delta E_2^{\mathrm{Na-Ba}} + \frac{1}{B}xz\Delta E_2^{\mathrm{Na-Yb}} + \frac{1}{B}yz\Delta E_2^{\mathrm{Ba-Yb}} + \frac{1}{B}kT[x\ln x + y\ln y + z\ln z + (1-x-y-z)\ln(1-x-y-z)] \quad (15)$$

There are many types of interactions in filled skutterudites (See Figure 7). Generally speaking, it is only the effective interactions from the filler pairs at the nearest neighbor that play an important role when filling atoms into the crystal voids. The eq 14 shows that the interactions in triple-filled $CoSb_3$ are similar to those in dual-filled $CoSb_3$. Therefore, it is reasonable to predict the FFLs in multiple-filled $CoSb_3$ by using the fitting data from single- and dual-filled $CoSb_3$ as listed in Table 1. Using the parameters given in Table 1, the Gibbs free energy of triple-element-filled $CoSb_3$ can be obtained, and then the filling fractions of multiple filling systems can be predicted.

As an example, Figure 12 plots the Gibbs free energy patterns for Na−Ba−Yb triple filling $CoSb_3$ at $T = 0$ K. Figure 12 shows that fixing the filling fraction of Na (Ba) atoms leads to the dominant Ba (Na) filling, while Yb has small filling fraction. The filling behavior is in general similar to those in the dual-element filling. The filling of Ba and Na follows a linear way at a fixed Yb filling. Multiple-element filling in $CoSb_3$ is expected to be more effective in reducing thermal conductivity, but there are more diversity and complexity in experiment. A systematic study on FFL of multiple-element-filled $CoSb_3$ is of great importance in theory and experiment. Further work will be carried on in the future.

3.4. Implications for Materials Synthesis.

By using ab initio calculations and thermodynamic analysis, the FFL of single-element-filled $CoSb_3$ has been understood very well. All calculated results agree well with the measured data. A simple electronegativity selection rule was found to determine whether a filler impurity can be stably filled into the crystal voids. The simple selection rule leads to the discovery of the alkaline-metal-filled $CoSb_3$,[29−32] and ultrahigh FFLs in a few AM-filled $CoSb_3$ have been predicted and then confirmed experimentally. This is favorable in searching for novel filled phases by experimentalist. Comparing with the single filling, the FFL study in dual-element-filled $CoSb_3$ is more important because of the diversity and complexity in experiment.

Filler atoms locating at the crystal voids not only interact with lattice phonons in a resonant scattering way to reduce thermal conductivity but also regulate the current carrier to improve electrical transport properties. Our analysis shows that the filler-projected density of states usually falls well above the Fermi level, and therefore, the donated electrons mainly tune Fermi level and thus carrier concentration for n-type. That is why the charge states of those fillers do not change much from

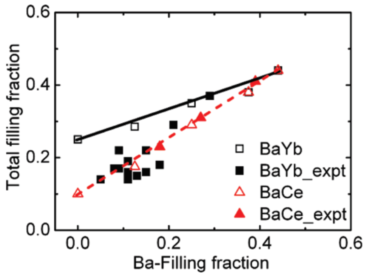

Figure 13. Comparison between the measured total filling fractions (solid symbols) and the corresponding calculated values (lined with open symbols). The open (theory) and solid (experiment) black squares are for the Ba−Yb-filled $CoSb_3$. The open (theory) and solid (experiment) triangles are for the Ba−Ce-filled $CoSb_3$. The lines are guides for the eyes.

single filling. We did some analysis on the electrical transport properties of single filling systems and concluded a rule of "0.5 electrons per unit cell" for optimizing performance of n-type $CoSb_3$ skutterudites.[28] As for the thermal properties, we found that the reduction of thermal conductivity depends critically on the rattling frequencies of the filling atoms.[35] Our calculations show that the filler impurities in filled skutterudites can be approximately categorized into three groups according to their resonant phonon frequencies: rare earths, alkaline earths, and alkali metals. The phonon resonant frequencies are comparable for filler elements within the same group of similar chemical nature; however, they are significantly different among different groups. It is shown that multiple filling using elements from different groups can be an effective method for additional k_L reduction in filled skutterudites. Such as the Ba−Ce and Ba−Yb combinations may be more effective than Ba−Sr combinations. This has been proved by experiments.[35] As for most effective combinations of the multiple filling with more than two different types of fillers, although we may still follow the same qualitative way of selection as we have done for dual filling, an quantitative guidance with predetermined filler types and filling fractions will be much helpful. But, that is not an easy job and we are working on that now.

The reported total filling fractions in Ba−Yb and Ba−Ce dual-filled $CoSb_3$ systems are shown in figure 13. The open squares and triangles are calculated results, whereas the solid symbols are measured data.[36,45] The sum of the measured filling fractions are usually slightly lower than the theoretically predicted value. For Ba−Yb cofilled systems, a few of experimental data are very close to the theoretical limit. The results for the Ba−Ce dual-filled systems seem to have a good agreement. On the one hand, the consistency comes from the fact that the theoretical results are the upper limits as proven by experiments. On the other hand, it also reveals that a careful synthesis process can truly realize the ultimate filling to maximum filling fractions.

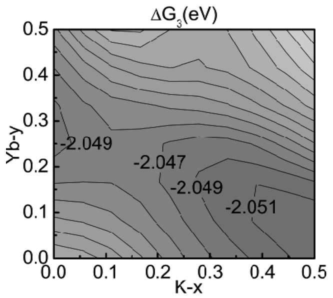

Figure 14. Gibbs free energy for K−Yb dual-element-filled $CoSb_3$ system at 1000 K.

All the studies above correspond to the case that the multiple-filled skutterudites form homogeneous compounds. However, in fact, formation of compounds with inhomogeneous compositions distribution or phase splitting is also possible when filler atoms go into the crystal voids. In our calculations, there are a few cases in which the dual-filled phase may form two different phases, such as K−Yb dual-filled $CoSb_3$ (See Figure 14). There are two extremes in the contour plot of ΔG_3, one is the K-dominant filled $CoSb_3$ and the other is the Yb-dominant filled phase. It might imply that when K and Yb are cofilled into the crystal voids, they do not form a stable homogeneous dual-element-filled $CoSb_3$; on the contrary, they prefer to form two single-element filled $CoSb_3$. This may due to the large difference in radius between K (1.65 Å) and Yb (1.18 Å) and different charge states in the filled skutterudites. If this can be controlled, the splitting phases may form certain nanostructures or even superlattice, which is potentially important to search for new thermoelectric materials.

4. Summary

In conclusion, the filling fraction limits of dual-element-filled $CoSb_3$ are systematically investigated by ab initio density functional calculations. Our results show that The AE and AM atoms could be jointly filled into the crystal voids, and the total filling fraction limits follow a linear correlation rule, that is, the filling fraction of one element decreases linearly while the other element's increases. This can be understood reasonably from their similar electronic configuration, lower ionic valence charge states and comparable ionic radius (Na^+, 1.34 Å; K^+, 1.65 Å; Ba^{2+}, 1.61 Å; Sr^{2+}, 1.44 Å),[44] and relatively high single-filling fraction limits comparing to that of rare-earth atoms (K, Na $>$60%, Ba, Sr 40%). Cofilling of AE (or AM) with RE shows one filler dominant, usually the AE (or AM), or the one with relatively high filling fraction limit. RE impurities as cofilling atoms have relatively lower filling fractions than AE (or AM) atoms. Eu atoms as a cofiller has comparable filling fraction to that of alkaline-earth atoms. This is reasonable because Eu^{2+} has radii (Eu^{2+}, 1.35 Å)[44] comparable to that of other AE (Ba, Sr) and AM (Na, K) elements. This may explain why Eu atom has higher filling fraction limit than other RE atoms, especially for Na−Eu dual-element-filled $CoSb_3$ system with a very high total FFL. Comparison with the existed experimental data is made, and the agreement seems reasonable.

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(45) Bai, S. Q.; Pei, Y. Z.; Chen, L. D.; Zhang, W.; Zhao, X. Y.; Yang, J. *Acta. Mater.* **2009**, *57*, 3135.

Model to predict the FFLs for filling with more than two types of fillers in $CoSb_3$ is also discussed. Filler atoms in the crystal voids not only interact with lattice phonons as a resonant phonon scattering centers to reduce thermal conductivity but also regulate the current carriers to optimize electrical transport properties. Theoretical systematic study on the FFLs in filled skutterudites, including single-element, dual-element, and multiple-element-filling $CoSb_3$, could speed up the searching for novel thermoelectric materials and save costs for blind trying in experiments at the same time.

Acknowledgment. This work is partially supported by National Basic Research Program (973-program) of China under Project 2007CB607503 and NSFC Grants (50825205, 50821004, 50672118, 50820145203, and 10634070) and CAS project (KJCX2-YW-H20, KGCX2-YW-206). Discussion with Mr. SQ. Bai is sincerely acknowledged.