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Filled Skutterudites: from Single to Multiple Filling

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ABSTRACT

This paper shortly reviews our recent work on filled skutterudites, which are considered to be one of the most promising thermoelectric (TE) materials due to their excellent power factors and relatively low thermal conductivities. The filled skutterudite system also provides a platform for studying void filling physics/chemistry in compounds with intrinsic lattice voids. By using *ab initio* calculations and thermodynamic analysis, our group has made progresses in understanding the filling fraction limit (FFL) for single fillers in $CoSb_3$, and ultra-high FFLs in a few alkali-metal-filled $CoSb_3$ have been predicted and then been confirmed experimentally. FFLs in multiple-element-filled $CoSb_3$ are also investigated and anonymous filling behavior is found in a few specific systems. The calculated and measured FFLs, in both single and multiple-filled $CoSb_3$ systems, show good accordance so far. The thermal transport properties can be understood qualitatively by a phonon resonance scattering model, and it seems that a scaling rule may exist between the lattice thermal resistivity and the resonance frequency of filler atoms in filled system. Even though a few things become clear now, there are still many unsolved issues that call for further work.

Key words*: *Filled skutterudites, ab initio calculations, Thermoelectric materials, Resonance scattering of phonons

1. Introduction

The thermoelectric (TE) performance of a material is characterized by its dimensionless figure of merit ZT given by $ZT=T\sigma^2S/\kappa$, where σ is the electrical conductivity, S is the Seebeck coefficient and κ is the total thermal conductivity. σ^2S is called power factor and usually used to evaluate the electrical transport performance. The high ZT value is the result of high power factor and low thermal conductivity. Filled skutterudite materials are one group of the most attracting thermoelectric materials due to their potential applications for thermometric power generation in the intermediate temperature range. Binary skutterudite $CoSb_3$ crystallizes in a body-centered-cubic structure with space group *Im3* and has two interstitial voids at the 2*a* positions (12-coordinated) in the lattice. The pure $CoSb_3$ has good electrical performance, but thermal conductivity is relatively high. Based on the concept of "phonon-glass-electrical-crystal" that was introduced by G. Slack for optimizing materials performance,[1,2] various void-filling impurities (La, Ce, Nd, Eu, Yb, Ba, Sr, Ca, In, Tl, Sn, Ge, K, Na, etc.) have been reported to be filled into the voids of $CoSb_3$ to form partially filled skutterudites,[3-16] although some of them are thermodynamically unstable. The filler atoms "rattle" inside the oversized cages, interact with the lattice phonons, and reduce the lattice thermal conductivity.[17-19]

The filling fraction (FF) of filler atoms in the voids of skutterudites greatly influences not only the electrical transport but the thermal transport properties.[1-16] Systematic investigating on the filling faction limits (FFLs), i.e. the maximum filling fractions of different fillers, is of great importance for further studying of the transport properties. The FFLs for rare-earths,[20,21] alkaline-earths[21] and alkaline metals[22,23] single-element-filled skutterudites have been estimated using the density functional *ab initio* method, and they show good agreement with experiments. Based on our calculations, the FFL of an impurity filling into the crystal voids is 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 host atoms. A simple electronegativity selection rule was found to determine the impurities that can be filled into the voids.[21]

Recent work showed that multiple-element-filling in skutterudites is an effective approach to further decrease lattice thermal conductivity.[25-28] Multiple filling in the voids is expected to create various localized vibration modes, scatter lattice phonons at different frequencies, lead to much lower lattice thermal conductivity,[26] and enhance TE performance. Therefore, we chose to study the filling systematics in nearly 20 representative dual-element-filled $CoSb_3$ via *ab initio* calculations.[24] The two filling impurities are selected from rare-earths (La, Ce, Eu, Yb), alkaline-earths (Ba, Sr), and alkaline metals (Na, K) with different chemical natures.

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2. Computational methods

Projector augmented wave (PAW) method, as implemented in the Vienna *ab initio* Simulation Package (VASP),[30,31] is utilized for this study, and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) for the exchange-correlation potential is used for all the calculations.[32] Projector augmented plane-wave method was used to span out the electron density.[30] Please refer to our earlier publications for computational details.[20,24] All calculations of lled-$CoSb_3$ skutterudites were carried out on a supercell (2×2×2 primitive cell) with a total of 128 atoms and 8 voids of pure $CoSb_3$.

The resonance frequency of fillers was calculated by using a simple harmonic oscillator model. All the calculations were carried out with displacement of the filler atom *I* along a trigonal axis in $I_{0.125}Co_4Sb_{12}$ by ±0.2 Å range from its equilibrium position, the center of the void. In the simple harmonic oscillator model, the spring constant *k* of *I* in the filled skutterudite can be obtained by using $\Delta E=1/2kx^2$, where ΔE is the change of total energy and *x* is the displacement of *I*. The resonance frequency, for various *I* in corresponding materials can, therefore, be generated by $\omega_0=\sqrt{k/m}$, where m is the mass of *I*. The displacement of *I* along a cubic axis was also computed and the final frequency results show slight difference.[26]

3. Results and discussions

3.1. Filling fraction limits of impurities in single-filled $CoSb_3$

Our previous work proved that the FFLs of impurities in filled $CoSb_3$ are determined by the competition between the formation of the filled skutterudites and that of secondary phases, the total reaction formula can be expressed as:[20-23]

$$nI+4CoSb_3\rightarrow\frac{2-n}{2-y}I_yCo_4Sb_{12}+$$

$$\frac{2(n-y)}{2-y}ISb_2+\frac{4(n-y)}{2-y}CoSb_2 \quad (1)$$

At a finite temperature, the corresponding Gibbs formation energy per impurity is

$$\Delta G_3=\frac{2(n-y)}{n(2-y)}\Delta H_2+\frac{y(2-n)}{n(2-y)}$$

$$\left\{\Delta H_1(y)+kT\left[\ln y+\frac{1-y}{y}\ln(1-y)\right]\right\} \quad (2)$$

where ΔH_1 is the formation energy of the filled skutterudite phase, ΔH_2 corresponds to that of the secondary phases,[21] and the last term in Eq. (2) is the configurational entropy contribution caused by the random distribution of filler atoms in the voids. *y* is the filling fraction of the impurity atoms entering the voids to form the filled skutterudite phase. By minimizing ΔG_3 with respect to the filling fraction *y* based on Eq. (2), the FFL values can be obtained in terms of ΔH_1 and ΔH_2. Shi *et al.* studied the FFLs of various filler atoms, and the results agree well with the measured data (see Fig. 1).[21] Detailed physical analysis revealed that the FFL turns out to be sensitive to the filler atom's electronegativity, and there exists a simple selection rule ($x_{Sb}-x_I>0.80$) for an impurity atom to be able to form a stable filled skutterudite. The selection rule not only leads to the discovery of alkaline-metal-filled $CoSb_3$[23] but also concludes the time-consuming experimental search for novel filled phases.

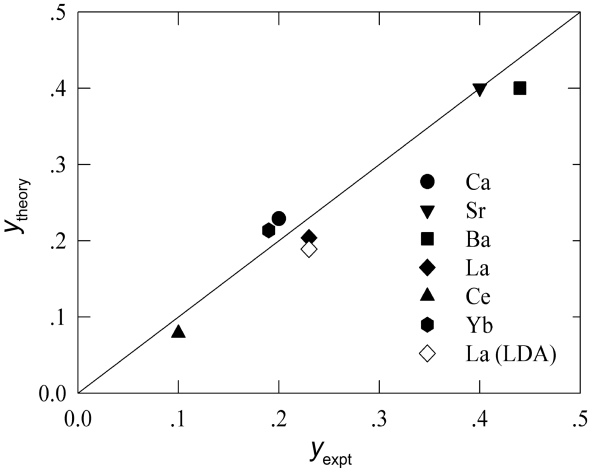

Fig. 1. Comparison of filling fraction limits between theoretical and experimental values.

Heavy element filling were considered to be the most effective way to improve the thermoelectric performance of $CoSb_3$ because lattice thermal conductivity could be reduced significantly. Generally speaking, because alkali atoms are so light, they have not attracted much attention as candidate void fillers. Our recent density functional calculations, however, showed that K has an ultrahigh filling fraction limit (more than 60%), and ZT=1 at 850 K for $K_{0.38}Co_4Sb_{12}$ was later achieved experimentally.[16,22,23] Based on the simple selection rule, the other alkaline atoms could also be filled into the voids. Mei et al investigated the FFLs of rare-earth and alkaline metals (see Fig. 2),[20,23] and found that Eu and Yb have relatively high FFLs compare to other rare-earth atoms, because of the low charge state (+2). What is more important is that the calculations showed 65% FFL for Na, much higher than those of the rare-earth and alkali-earth atoms. This result was experimentally validated later, and the Na-filled $CoSb_3$ has a surprisingly good performance of ZT=1.2 at 850 k, highest among all pure phases of single-filling CoSb3.[16,23] Even though the filling of Na atom is not so effective in reducing thermal conductivity, the Na filling introduces extra electronic states close to the bottom of the conduction band,[23] which could affect the electron mobility, and lead to enhanced power factor and improved ZT in comparison with other filled phases.[16]

The previous work proved that the FFLs of impurities in single-filled $CoSb_3$ are determined by the competition

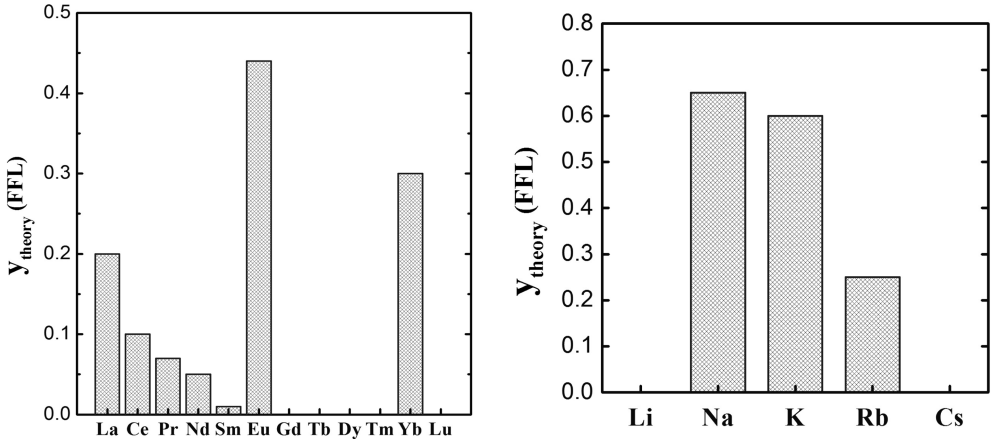

Fig. 2. Filling fraction limits of rare-earths and alkaline metals filled $CoSb_3$.

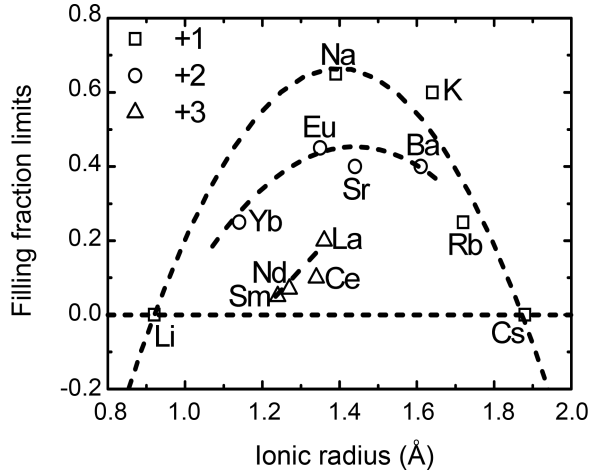

Fig. 3. Relations between the ionic radii and charge states of various filler atoms and the corresponding filling fraction limits for single filling. The dashed curves are guides for the eye.

between the formation of the filled skutterudites and that of secondary phases. Whether the impurities can be filled into the crystal voids correlates to a simple electronegativity selection rule and is determined by the chemical nature of the impurities such as their ionic radius and effective valence charge states. Fig. 3 plots the FFLs of all reported filler impurities with the correlation to the corresponding ionic radius and charge states. It can be seen that the impurity with low valence state and proper ionic radius may have relatively large FFL.

3.2. Filling fraction limits in multiple filling

There are only about ten more different types of stable single filling $CoSb_3$ as proved by both theory and experiment with filling impurities from rare-earths, alkaline-earths, and alkaline metals. However, when moving onto the double or triple filling phases, there are hundred of possibilities, which will be very difficult to study one by one experimentally. Therefore, the filling systematic of impurities in nearly 20 representative dual-element-filled skutterudites was investigated.[24] By taking the K-Ba filled $CoSb_3$ as an example, the formula of the final chemical reaction for the formation of a dual-element-filled $CoSb_3$ can be written as:

$$K+Ba+4CoSb_3 \rightarrow \frac{1}{A}K_xBa_yCo_4Sb_{12}+\frac{A-x}{A}KSb$$

$$+\frac{A-y}{A}BaSb_2+\frac{4(A-1)}{A}CoSb_2 \quad (3)$$

A is a parameter that is given by A=4–x–2y. x (y) is the filling fraction for impurity atom K (Ba). The Gibbs free energy corresponding to Eq. (3) at a finite temperature for dual-filling $CoSb_3$ is given by

$$\Delta G_3=\frac{A-x}{A}\Delta H_2^K+\frac{A-y}{A}\Delta H_2^{Ba}$$

$$+\frac{1}{A}\{\Delta H_1(x,y)+kT[x\ln x+y\ln y+(1-x-y)\ln(1-x-y)]\} \quad (4)$$

ΔH_1(x,y) is the formation energy of the co-filled phase, and ΔH_2 corresponds to that of secondary phases[20-24] for the elements as indicated by the superscripts. The last term in Eq. (4) is the configurational entropy contribution caused by the random distribution of the multiple filler atoms in the voids.

When taking alkaline-earths and alkaline metals as co-filler impurities, the filling fraction of one element decreases linearly as the other element's increases, and the total FFL, defined as the summation of the FFs of the two fillers, is in between the two end FFL values that correspond to the two separated fillings [see Fig. 4 (a)]. When rare-earths and alkaline-earths (or alkali metals) jointly fill into the crystal voids, usually one element dominates the filling [Fig. 4 (b)]. However, to our surprise, the total FFL is found to possibly exceed both individual FFLs (separated filling) in a few co-filled systems, such as Na-Eu dual-filled $CoSb_3$ [see Fig. 4 (c)].[24] This is due to that fact that the Na-Eu co-filling introduces anisotropic local structure distortions, affects the electron density states of both Na and Eu atoms in the filled

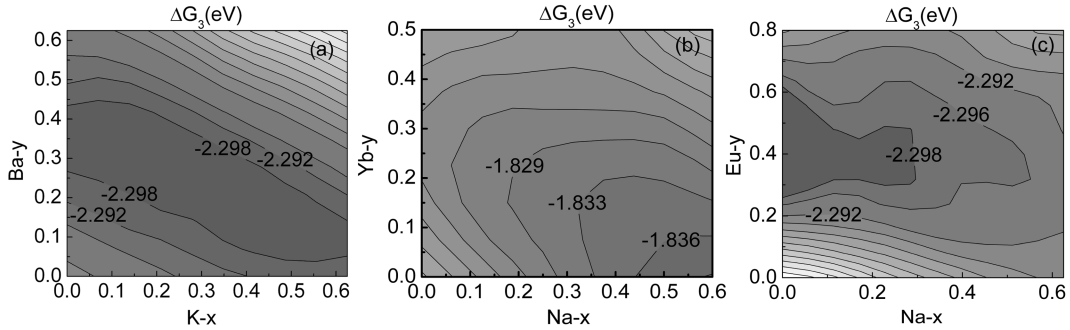

Fig. 4. Gibbs free energy pattern for some dual-element-filled $CoSb_3$ systems at 1000 K.

states, lowers the Na and Eu charge states and then the Na-Eu columbic interaction, and leads to the anomalous dual-element filling.

Fig. 4(a) is an example for co-filled skutterudites with the filler atoms being alkaline-earths and alkali metal atoms. The lower ΔG_3 values, as indicated by darker region in the figure, represent more stable dual-element filling at the filling fractions. This indicates that the alkaline-earths and alkaline metals could be jointly filled into the crystal voids at any rates, and the sum of filling fraction follows a linear correlation rule.

The ΔG_3 of the Na-Yb co-filled $CoSb_3$ is plotted in Fig. 4(b). It leads to a Na-dominant filled skutterudites. This is the co-filling behavior for the combinations of rare-earth with alkaline-earths (or alkali) or that of rare-earth with rare-earth atoms. Adding rare-earth fillers into the voids usually increases the Gibbs free energy, leads to the decomposition of the co-filled systems, and leaves only the dominant alkali-filled $CoSb_3$ or one rare-earth dominant filled $CoSb_3$.

An anomalous behavior is plotted in Fig. 4(c) for the Na-Eu filled $CoSb_3$. It can be seen that increasing the filling fraction of Na does not decrease that of Eu significantly, and the total FFL for this system could be very large. Detailed analysis could be found in Ref. 24.

3.3. Effect of impurity filling on the reduction of lattice thermal conductivity

With the partial filling of different guest impurities (called rattler sometimes), these impurities rattle inside the oversized cages and strongly interact with heat-carrying acoustic phonons. The rattler-induced local vibration modes were experimentally determined in filled skutterudites by inelastic neutron scattering measurements and by nuclear inelastic scattering.[34,35] These localized phonon modes are mostly harmonic, close to be of the nature of resonant phonon scattering.[34,35] Only those phonons with frequencies close to the localized rattling frequency would strongly interact with the local mode. By assuming a local phonon scattering, we may derive a relationship for the dependence of lattice thermal resistivity on vibrational frequency and the filler filling fraction y,

$$W_L = K_L^{(-1)} \quad W_L^0 \quad \frac{C}{[K_L^0]^2}\frac{Y}{W_0^2} \tag{5}$$

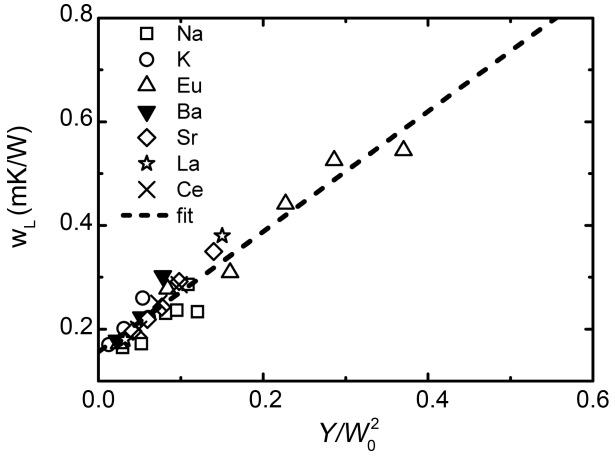

Fig. 5. Relationship between thermal resistivity and Y/W_0^2 . The dashed line is the linear fitting.

Where W_L is the lattice thermal resistivity, reciprocal of lattice thermal conductivity K_L. W_L^0 is lattice thermal resistivity of pure skutterudites and the contribution of the defect scattering. W_0 is the resonant scattering frequency of filler atoms. Fig. 5 plots the experimental relationship between the lattice thermal resistivity and Y/W_0^2, and it shows a linear correlation for various single fillers. It indicates to some extent that there exists a scaling law between thermal resistivity and resonant phonon scattering. The coefficient of Y/W_0^2 is close to be a constant for impurities with different properties, which most likely implies that the resonant phonon scattering is the dominant mechanism for the lattice thermal conductivity reduction in void-filling $CoSb_3$ systems. In principle, random distribution of filler impurities may also introduce point defect effect as pointed out before, but seems not significant in this case.[26,36] How to describe the quantitative relationship between lattice thermal conductivity reduction and rattling is still an unsolved problem.

The rattling or resonant scattering frequency of filler atoms could be calculated by a lattice-dynamical model based on density-functional calculations.[26] The most simple approximation is to take the coupling between the central filler and surrounding host atoms as a classical spring, described by a spring constant k (see Table 1).[26] Our calculations show that the filler impurities in filled skutterudites

Table 1. Spring Constant k and Resonant Frequency ω_0 of the Filler Impurity, When Simplifying the Interaction Between the Filler and Surrounding Atoms as a Spring, in the [111] and [100] Directions of $I_{0.125}Co_4Sb_{12}$. I Represents the Filler Element.[26] Available Experiments Data are Also List in the Table

		[111]		[100]		expt[34,35,37,38]
I	Mass (10^{-26} kg)	k (N/m)	ω_0 (cm^{-1})	k (N/m)	ω_0 (cm^{-1})	ω_0 (cm^{-1})
La	23.07	36.10	66	37.42	68	55
Ce	23.07	23.72	54	25.18	55	55
Eu	25.34	30.16	58	31.37	59	
Yb	28.74	18.04	42	18.88	43	40
Ba	22.81	69.60	93	70.85	94	
Sr	14.55	41.62	90	42.56	91	
Na	3.819	16.87	112	17.18	113	
K	6.495	46.04	141.	46.70	142	

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 amongst different groups. All the calculated frequency results are list in the Table 1. The resonant scattering frequencies of filler impurity along the two crystallography directions ([111] and [100]) of $I_{0.125}Co_4Sb_{12}$ are given, and they show essentially the same results, mainly due to the nearly isotropic crystal symmetry.[26] Sophisticated full phonon spectrum calculations give the same rattling frequency.[37] Experimental results using inelastic neutral scattering also proved that the calculated results are in a good agreement with the measured data (See Table 1).[34,35,37,38]

The above rattling frequencies provide the basis for designing promising multiple-filling $CoSb_3$. In principle, if one could create multiple localized phonon modes at frequencies sufficiently different from one another, these localized modes would scatter a broader range of heat-carrying lattice phonons, and then lead to even lower K_L.[26] This suggests that multiple filling using elements from different groups can be an effective method for additional K_L reduction in filled skutterudites. Experiment studying on the thermal conductivity of dual-element-filled skutterudites confirmed that filling atoms from different groups such as the Ba-Ce and Ba-Yb combinations did lead to lower thermal conductivity than that from the same group such as the Ba-Sr combinations.[26,27,29] The K_L of the Ba-Sr filled $CoSb_3$ is relatively higher compare to other dual-element-filled $CoSb_3$, such as Ba-La, Ba-Ce and Ba-Yb dual-filled $CoSb_3$.[26,27,29] This is consistent with our theoretical prediction that multiple fillers from different group reduce more thermal conductivity than that of from the same group. With that, the ZT value of the Ba-Yb dual-filled $CoSb_3$ was pushed up to reach 1.36 at 850 K.[27] The selection rule is also expected to be valid for filling two or more than two types of filler impurities in caged compounds more than $CoSb_3$. Further work need to be done in the future.

4. Summary

The FFLs of single and dual-element-filled $CoSb_3$ have been investigated by density functional *ab initio* method. A simple electronegativity selection rule was found to determine whether filler impurities can be stably filled into the crystal voids. Based on the rule, we predicted a few novel filled skutterudite compounds, such as Na- and K-filled skutterudites. It has been confirmed by experimentalists that the Na FFL in the Na-filled $CoSb_3$ reaches an ultra high limit of 65%, and the filled systems show excellent thermoelectric performance. The FFLs of dual-element-filled skutterudites have also been studied using the similar method. Most of the impurity atoms could jointly fill into the voids with a linear FFL behavior, and anomalous filling behaviors exists in a few dual-filled systems such as Na-Eu filled $CoSb_3$. 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. Differently categorized filler atoms can scatter lattice phonons with different frequencies, implying that multiple filling using atoms from different groups could realize much lower thermal conductivity and then enhance TE performance further. This scattering model of reducing thermal conductivity using the combination of fillers of different rattling frequencies is also expected to be general and effective for other cage-structure compounds, such as clathrates.

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