Origin of the Disparity between the Stability of Transmutated Mix-Cation and Mix-Anion Compounds

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Transmutation is an efficient approach for material design. For example, ternary compound $CuGaSe_2$ in chalcopyrite structure is a promising material for novel optoelectronic and thermoelectric device applications. It can be considered as formed from the binary host compound ZnSe in zinc-blende structure by cation transmutation (i.e., replacing two Zn atoms by one Cu and one Ga). While cation-transmutated materials are common, anion-transmutated ternary materials are rare, for example, Zn_2AsBr (i.e., replacing two Se atoms by one As and one Br) is not reported. The physical origin for this puzzling disparity is unclear. In this work, we employ first-principles calculations to address this issue, and find that the distinct differences in stability between cation-transmutated (mix-cation) and anion-transmutated (mix-anion) compounds originate from their different trends of ionic radii as functions of their ionic state, i.e., for cations, the radius decreases with the increasing ionic state, whereas for anions, the radius increases with the increasing absolute ionic state. Therefore, for mix-cation compounds, the strain energy and Coulomb energy can be simultaneously optimized to make these materials stable. In contrast, for mix-anion systems, minimization of Coulomb energy will increase the strain energy, thus the system becomes unstable or less stable. Thus, the trend of decreasing strain energy and Coulomb energy is consistent in mix-cation compounds, while it is opposite in mix-anion compounds. Furthermore, the study suggests that the stability strategy for mix-anion compounds can be controlled by the ratio of ionic radii r_3/r_1, with a smaller ratio indicating greater stability. Our work, thus, elucidates the intrinsic stability trend of transmutated materials and provides guidelines for the design of novel ternary materials for various device applications.

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By conducting cation or anion transmutation, many novel materials with tunable properties can be obtained from a simple material.[1–5] For example, as shown in Fig. 1, by substituting two unary group-Ⅳ Ge atoms in the original diamond structure with one group-Ⅲ (group-Ⅱ) element and one group-V (group-Ⅵ) element, binary zinc-blende materials such as GaAs (Ⅲ–V) or ZnSe (Ⅱ–Ⅵ) can be obtained. Similarly, ternary compounds can be generated from binary materials through elemental transmutation. For instance, using one group-I and one group-Ⅲ atom to substitute two group-Ⅱ element Zn atoms in ZnSe (with band gap of $\sim$2.8 eV), mix-cation chalcopyrite $CuGaSe_2$ (with reduced band gap of $\sim$1.7 eV) can be obtained, which preserves the octet rule and possesses the lowest formation energy among the ordered structures and has many applications in solar cells and thermoelectrics.[1,6–13] Similar stable compounds with the chalcopyrite structure such as I–Ⅲ–$Ⅵ_2$ (where I = Cu, Ag, or Au, Ⅲ = Al, Ga, or In, and Ⅵ = S, Se, or Te) and Ⅱ–Ⅳ–V_2 (where Ⅱ = Zn, Cd, or Hg, Ⅳ = Si, Ge, or Sn, and V = P, As, or Sb) have received significant attention for their applications in optoelectronic devices[6–8] and thermoelectrics.[9,14–16]

Although a large number of transmutated mix-cation compounds with interesting properties are known,[6–26] transmutated mix-anion compounds are rare, despite their similarity to mix-cation compounds in terms of Coulomb interaction. For example, mix-anion chalcopyrite compounds, such as $Ⅱ_2$–V–Ⅶ (Ⅱ = Zn or Cd; V = N, P, As or Sb; Ⅶ = F, Cl, Br or I), do not yet exist.[27] Currently, studies on mix-anion chalcopyrite compounds are notably scarce, suggesting significant differences from mix-cation counterparts.[28–30] Therefore, it is crucial to carefully investigate the physical mechanism behind this stability disparity.

In this work, by calculating and analyzing the mixing enthalpies of the various mix-anion ternary chalcopyrite compounds and comparing to those of the mix-cation ones, the thermodynamic stabilities of ternary chalcopyrite compounds are investigated. A general trend about their stability is derived and the physical origin behind the trend is unveiled. We find that because the radius decreases with the increasing ionic state for cations, for transmutated mix-cation compounds, the strain energy

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and Coulomb energy can be simultaneously optimized to make these materials stable. In contrast, for mix-anion systems, because the radius increases with the increasing absolute ionic state for anions, the minimization of Coulomb energy contradicts the optimization of the strain energy, thus the system becomes unstable or less stable. These insights improve our understanding of stability of ternary and multinary compounds and greatly accelerate the future screening and design of ternary and multinary compounds for specific applications.

To investigate the stability of ternary chalcopyrite compounds, the total energy and material properties of the chalcopyrites and related compounds are calculated using density functional theory (DFT) with projector-augmented wave[31] potentials as implemented in the Vienna *ab initio* simulation package (VASP).[32] The volume and shape of the cell, and internal atomic positions are fully relaxed using the Perdew–Burke–Ernzerhof (PBE) functional[33] until the total energy is converged to 10^{-6} eV and the residual forces are below 0.01 eV·Å^{-1}. All valence d electrons involved in metal elements are treated in the same footing as other valence electrons. An energy cutoff of 520 eV for the plane-wave basis and a k-point mesh of $5 \times 5 \times 4$ for sampling the Brillouin zone of the chalcopyrite primitive cell is used. The lattice parameters, bond lengths, and electronic structures are calculated using a hybrid functional as constructed by Heyd, Scuseria, and Ernzerhof (HSE) with the screening range set to 0.2 Å^{-1}, and the fraction of the nonlocal Fock exchange is set to be 0.25.[34]

The thermodynamic stability of each chalcopyrite structure is determined by its mixing enthalpy $H_{\rm m}$, which is calculated as the total energy difference between the ternary compound and its most stable binary constituting compounds. For example, the stability of $CuGaSe_2$ is determined by comparing with both Cu_2Se and Ga_2Se_3, while that of Zn_2AsBr is determined by comparing with both $ZnBr_2$ and Zn_3As_2. Therefore, the mixing enthalpies per atom of chalcopyrite $CuGaSe_2$ and Zn_2AsBr are defined by

$$H_{\rm m}(\mathrm{CuGaSe_2}) = \frac{1}{4}\Big[E_{\rm t}(\mathrm{CuGaSe_2}) - \frac{1}{2}E_{\rm t}(\mathrm{Cu_2Se}) - \frac{1}{2}E_{\rm t}(\mathrm{Ga_2Se_3})\Big], \quad (1)$$

$$H_{\rm m}(\mathrm{Zn_2AsBr}) = \frac{1}{4}\Big[E_{\rm t}(\mathrm{Zn_2AsBr}) - \frac{1}{2}E_{\rm t}(\mathrm{ZnBr_2}) - \frac{1}{2}E_{\rm t}(\mathrm{Zn_3As_2})\Big], \quad (2)$$

where $E_{\rm t}$ represents the total energy per formula unit. A negative value of $H_{\rm m}$ means that decomposition into these stable binary products from ternary chalcopyrite compound requires external energy, hence the ternary chalcopyrite is thermodynamically stable. On the other hand, a positive value of $H_{\rm m}$ indicates that the chalcopyrite structure is unstable.

As an example, we first investigate the prototype mix-cation and mix-anion chalcopyrite crystals $CuGaSe_2$ and Zn_2AsBr, respectively, which are derived from zinc-blende ZnSe by atomic transmutation with neighboring atoms in the Periodic Table, that is, for mix-cation systems, two Zn atoms are replaced by a pair of Cu and Ga atoms, and for mix-anion chalcopyrite systems, the Se atoms are replaced by a pair of As and Br atoms. The lowest energy structures of binary compounds involved in the calculation of mixing enthalpy include Zn_3As_2, $ZnBr_2$, Ga_2Se_3, and Cu_2Se. The ternary chalcopyrite structures are depicted in Fig. 1. The lattice parameters (a and c), bond lengths (r_{12}, r_{32}, and r_{22}), the displacement parameters ($u = (1/4) + [(r_{12}^2 - r_{32}^2)/a^2]$), Bader charges ($q$), and mixing enthalpies ($H_{\rm m}$) are listed in Tables 1 and 2.

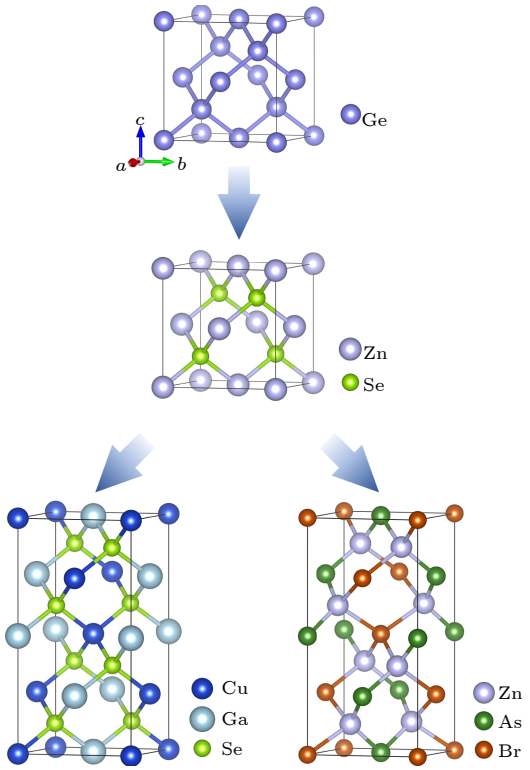

Fig. 1. An example of generating binary and ternary compounds through elemental transmutation.

Table 1. Calculated basic physical properties of ternary compounds $CuGaSe_2$ and Zn_2AsBr as well as the host binary compound ZnSe, including lattice parameters a and c (Å), the displacement parameter u, bond lengths r_{12}, r_{32}, and r_{22} (Å), Bader charge q on each atom (e), and mixing enthalpy $H_{\rm m}$ (eV/atom).

Compound	a	c	u	r_{12}	r_{32}
$CuGaSe_2$	5.64	11.09	0.2515	2.43	2.42
Zn_2AsBr	5.84	11.94	0.3057	2.75	2.38
ZnSe	5.69	–	–	$r_{22} = 2.47$	
Compound	q_1	q_2	q_3	$H_{\rm m}$	
$CuGaSe_2$	0.41	−0.76	1.11	−0.099	
Zn_2AsBr	−0.62	0.72	−0.82	0.008	
ZnSe	–	±0.72	–	–	

Although we put both $CuGaSe_2$ (mix-cation) and Zn_2AsBr (mix-anion) compounds into the same chalcopyrite configuration, their stabilities are significantly different. As shown in Table 1, $CuGaSe_2$ has a negative mixing

enthalpy (−99 meV/atom), thus is stable again decomposition to its binary constitutes, but Zn_2AsBr has a positive mixing enthalpy (8 meV/atom), thus is unstable. The origin of this disparity in their stability is explained below.

To facilitate the understanding and discussion, we consider the transmutation process in three steps to form the ternary compounds.

Step 1. In this step, we fulfill the transmutation procedure by replacing the Zn atoms in mix-cation structures with Cu and Ga, or the Se atoms in mix-anion structures with As and Br. As a result, the atomic charges in the structures changed from q_2 to q_1/q_3, as shown in Table 1 and Fig. 2. The average Coulomb energy between two nearest neighbor cations and anions (q_1q_2 and q_3q_2) in the ternary compounds remains the same as that in the original ZnSe compounds (q_2q_2), while the different charges on the q_1 and q_3 sites leads to an extra negative Coulomb energy that is proportional to $(\delta q)^2$, where (δq) is the charge difference between q_1 and q_3.[35] Meanwhile, because the q_1 and q_3 ions have different sizes while the bond lengths are constrained to be the same in this step, the systems have positive strain energy. Furthermore, the mixing enthalpy is now referenced to the binary compounds with "ideal" bond lengths. Therefore, in this step, the change of mixing enthalpy ΔH_1 depends on the bond length matching and the extra Coulomb energy. For $CuGaSe_2$, the difference in bond length between Cu–Se and Ga–Se bonds is small (see Table 2) because the bonds are partially covalent and partially ionic, and both are close to the Zn–Se bond length, so the increase in strain energy is limited and the extra Coulomb energy becomes dominant. This is reflected by the fact that the mixing enthalpy of $CuGaSe_2$ is negative in this step, as shown in Fig. 3. On the other hand, for Zn_2AsBr, as the mismatch of bond lengths between its Zn-As bonds and those in the corresponding binary compounds (Zn_3As_2) is large, i.e., the lengths of Zn–As and Zn–Se bond do not match (Table 2), there is a larger increase in strain energy. Even though the change in Coulomb energy of Zn_2AsBr is also negative, due to the significant increase in its strain energy, the mixing enthalpy is positive in this step, as shown in Fig. 3.

Table 2. Crystal system, space group, and bond lengths (Å) of the selected binary compounds related to formation of $CuGaSe_2$ and Zn_2AsBr.

Compound	Crystal system	Space group	Average bond length (Å)
Zn_3As_2	tetragonal	$P4_2/nbc$	2.59
$ZnBr_2$	tetragonal	$I4_1/acd$	2.45
Ga_2Se_3	monoclinic	$C1c1$	2.46
Cu_2Se	monoclinic	$P12_1/c1$	2.47

Step 2. We adjust the volume of $CuGaSe_2/Zn_2AsBr$ cell from its original value $V = V_0 = V_{ZnSe}$ to that of the fully relaxed chalcopyrite structural $CuGaSe_2/Zn_2AsBr$ cell, as shown in Fig. 2. The change of enthalpy ΔH_2 obtained in this step reflects the impact of volume change of $CuGaSe_2/Zn_2AsBr$ cell on its mixing enthalpy. In this step, since the volume of $CuGaSe_2/Zn_2AsBr$ has relaxed towards the value of the fully relaxed structure, ΔH_2 is definitely negative, as shown in Fig. 3 and Table 3. For $CuGaSe_2$ and Zn_2AsBr, the values of ΔH_2 are small because these structures are both transmutated from ZnSe with neighboring atoms in the Periodic Table.

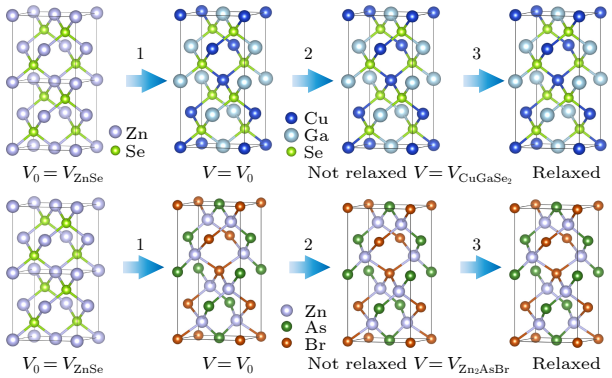

Fig. 2. Three steps of the elemental transmutation process. Step 1: element transmutation without relaxation. Step 2: volume change without relaxation. Step 3: relaxation.

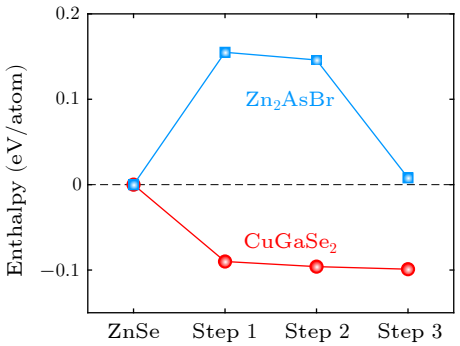

Fig. 3. The changes of mixing enthalpies during the three-step processes from ZnSe to $CuGaSe_2$ and to Zn_2AsBr.

Table 3. The mixing enthalpy variations in the three-step processes.

Structure	ΔH_1 (eV/atom)	ΔH_2 (eV/atom)	ΔH_3 (eV/atom)
$CuGaSe_2$	−0.090	−0.005	−0.004
Zn_2AsBr	0.155	−0.009	−0.138
Structure	$H_m = \Delta H_1 + \Delta H_2 + \Delta H_3$ (eV/atom)		
$CuGaSe_2$	−0.099		
Zn_2AsBr	0.008		

Step 3. We fully relax the structures obtained from step 2. This process reveals the mixing enthalpy differences caused by the changes of bond lengths, denoted as ΔH_3. In this step, the Coulomb interaction and the strain between ions occur simultaneously, attempting to find the balanced structure with the lowest energy. As shown in Fig. 3(a), for the chalcopyrite compounds, according to the crystal symmetry, the Coulombic forces applied by the two nearest trivalent ions (group-Ⅲ/V ions carrying charge q_3) on the bivalent ion (group-Ⅱ/Ⅵ ions carrying charge q_2) is along the C_2 principal rotation axis; the resultant force

of the two nearest monovalent ions (group-I/VII ions carrying charge q_1) on the central bivalent ion is also along the C_2 axis but in opposite direction. When the bivalent ion is fixed at the tetrahedral center in step 2, i.e., the symmetric position of the zinc-blende structure, the magnitude of the Coulombic attraction between q_3 and q_2 (F_{32}) is greater than that (F_{12}) between q_1 and q_2, i.e., $|F_{32}| > |F_{12}|$, because the charge on the trivalent ion q_3 is larger than q_1 ($|q_3| > |q_1|$, see Table 1). This behavior is the same for mix-cation and mix-anion compounds because the Coulomb interaction depends on the product of the charges.

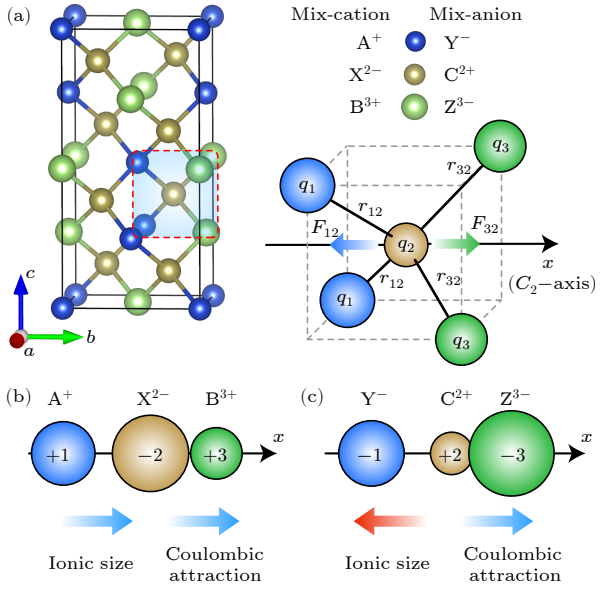

Fig. 4. Schematic plots of the influence of Coulombic attractions and ion size on the stability of ternary chalcopyrite compounds (mix-cation ABX_2 or mix-anion C_2ZY). (a) The resultant Coulomb force F_{32} (F_{12}) acting on the valence II ion with q_2 charge by the two nearest neighbor ions with q_3 (q_1) charges, with its magnitude determined by the charge state and the distance between the ions. (b) For a typical mix-cation ternary chalcopyrite compound, the nominal charge states of cations on both sides of the central anion are +1 and +3, where the cation with higher valence usually has a smaller ionic radius, and a shorter bond length. (c) For a typical mix-anion ternary chalcopyrite compound, the anion with higher absolute valence has a larger ionic radius and usually a longer bond length. The imbalance of the Coulombic attraction and size in the mixed-anion system will eventually force the bond lengths to be further away from the ideal values, leading to the instability.

In the case of a mix-cation structure, i.e., $CuGaSe_2$, the ionic radius of Cu^+ is greater than Ga^{3+} because more electrons are removed from Ga, but the atomic/covalent radius of Cu is smaller than Ga. The system is actually partially covalent and partially ionic, consequently, the Cu–Se bond length is only slightly longer than the Ga–Se bond, consistent with that observed in their corresponding binary compounds, as shown in Table 2. Therefore, for $CuGaSe_2$, the movement of divalent ions towards their neighboring trivalent ions caused by the Coulombic attraction in step 3 also reduces the strain energy, that is, resulting in decreases in both Coulomb energy and strain energy simultaneously during this process, as shown in Fig. 4(b). Because for $CuGaSe_2$, the bond lengths change a little during the relaxation in step 3, ΔH_3 ($CuGaSe_2$) ~ -0.004 eV/atom has a relatively small negative value, where both the changes of Coulomb energy and of strain energy are negative.

On the contrary, in the case of mix-anion structure, i.e., Zn_2AsBr, Coulomb energy and strain energy cannot be simultaneously optimized. This is because As^{3-} ion is much larger than Br^- ion since more electrons are added to As, therefore the "ideal" Zn–As bond is much longer than the Zn–Br bond, as shown in Table 2. In step 3, the Coulombic interaction brings the divalent ions closer to the trivalent ions, i.e., the bond length of Zn–As and that of Zn–Br both deviate further from the "ideal" bond lengths of Zn–As bond and Zn–Br bond, leading to an additional increase in the strain energy. This contradiction between strain and Coulombic interactions is, therefore, the origin of instability of mix-anion compounds, i.e., the stability of the Zn_2AsBr structure is worse than that of $CuGaSe_2$.

The above analysis shows that besides the Coulombic interaction, the trend of strain energy due to the different sizes of the mixed ions is critical in determining the stability of the ternary compounds. The mix-anion and mix-cation compounds show different trends in their relationship between the size and absolute ionic charge state, so they show very different stability.

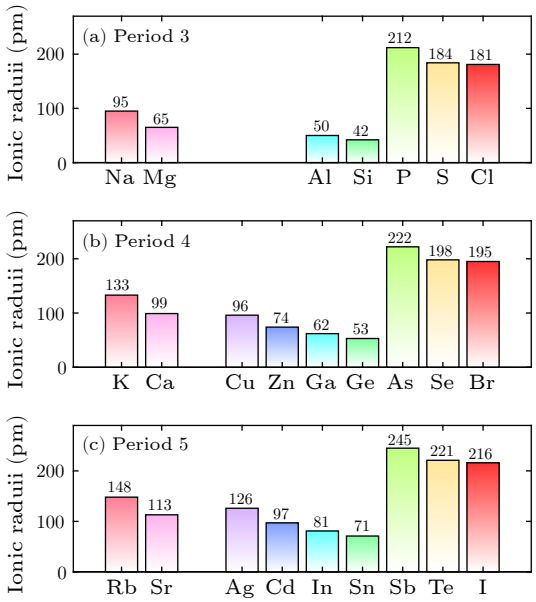

Fig. 5. Trends of ionic radius of elements in third, fourth, and fifth periods.

For elements within the same period of the Periodic Table, cations with higher valences possess smaller ionic radii than those with lower valences because they lose more electrons (Fig. 5), whereas anions with higher absolute valences have larger ionic radii than those with lower absolute valences because more electrons are added to the anions. For isovalent elements in the same column of the Periodic Table, atomic size usually increases with the atomic num-

ber.

In a ternary crystal such as the chalcopyrites, the Coulombic interaction always tends to pull the ion with q_2 charge closer to that with q_3 charge. In a mix-cation chalcopyrite, the trend of ionic sizes coincides with the Coulomb interaction that pulls q_2 ion closer to q_3 ion. Consequently, the bond lengths of the ternary compounds are close to the ideal bond lengths, i.e., the strain energy is small. Therefore, the mixing enthalpy is usually negative (stable) due to the Coulomb interaction for the mix-cation compounds. On the contrary, in a mix-anion structure, the q_2 ion also tends to move toward the q_3 ion due to the large Coulomb interaction. However, since q_1 ion is relatively smaller than q_3 ion, the shift of the q_2 ion towards the q_3 ion will cause the distance between q_1 and q_2 ions to be much longer than that in the binary compounds, and the distance between q_3 and q_2 ions to be shorter (see Tables 1 and 2). This leads to an obvious increase of the strain energy. Therefore, mix-anion ternary chalcopyrites have relatively higher strain energies, thus higher mixing enthalpy, deteriorating their thermodynamic stability.

Our above analysis suggests that, for ternary chalcopyrite structures, the smaller (larger) of the trivalent (monovalent) anion atomic number, the stabler of the compounds. We validated this by calculating the bond lengths and formation enthalpies of $Zn_2X^{VA}X^{VIIA}$ (X^{VA} = P, As, or Sb; X^{VIIA} = Cl, Br, or I) compounds. The results are shown in Fig. 6, confirming our expectations.

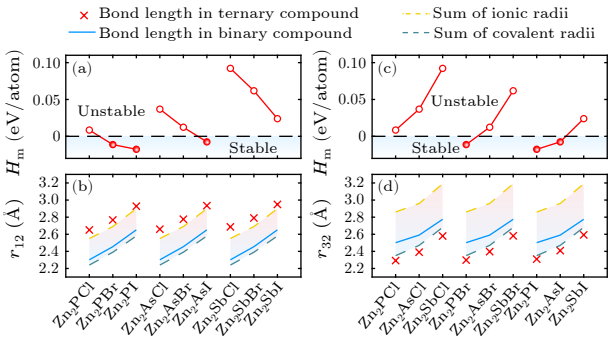

Fig. 6. Comparison of the bond lengths in ternary chalcopyrite crystals versus those in binary compounds, where r_{12} is the bond length of monovalent ion and divalent ion, and r_{32} represents that of trivalent ion and divalent ion. The mixing enthalpies (H_m) indicate the stabilities of ternary structures. Stable binary phases have their bond lengths (marked by blue lines) always fall between the sum of ionic radii (yellow dashed lines) and that of covalent bond radii (green dashed lines). The more its bond length (marked by × shape) of the ternary compound exceeds this range between the dotted lines, the higher its mixing enthalpy is, and the structure becomes less thermodynamically stable.

From the reasoning mentioned above, to achieve more stable mix-anion chalcopyrite crystals, one can replace the (−3) valence anion with smaller anions and the (−1) valence anion with larger ones. To further verify this inference, a series of ternary chalcopyrite structural compounds are constructed and their mixing enthalpies are calculated, as shown in Fig. 7. More detailed results are listed in the Supplementary Materials. We find that the ratio of ionic radii (r_3/r_1) can be employed as a descriptor for predicting stability, where r_3 represents the ionic radii of trivalent ions; r_1 represents the ionic radii of monovalent ions. This guideline simplifies the stability estimation for many materials and serves as a helpful reference for future high-throughput calculations. Figure 7 shows the trend of the ratio (r_3/r_1) versus the mixing enthalpy. The scattered data points can be well captured by a linear fit, with an interception line dividing the diagram into two regions: (i) a stable region with (r_3/r_1) smaller than 1.12, and (ii) an unstable region with (r_3/r_1) larger than 1.12. Figure 7 confirms our conclusion that reducing the radii of cations or anions with higher absolute valences will stabilize the crystal structures. This understanding enables us to design mix-anion compounds: choosing smaller trivalent anion and larger monovalent anion will construct a more stable mix anion structure.

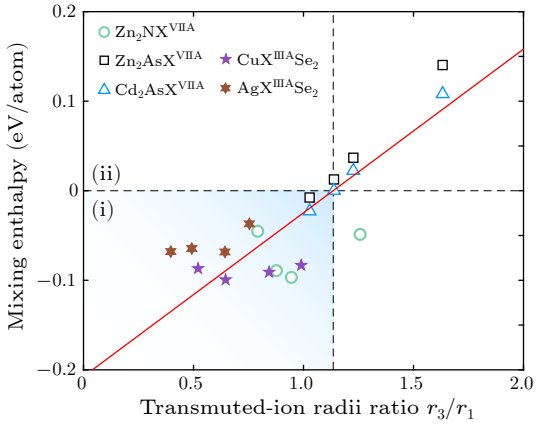

Fig. 7. Mixing enthalpy of ternary chalcopyrite compounds versus the ratio of ionic radii of transmuted ions (r_3/r_1). The constructed ternary compounds include Zn_2NX^{VIIA}, Zn_2AsX^{VIIA}, Cd_2AsX^{VIIA} as mix-anion chalcopyrite structures, and $CuX^{IIIA}Se_2$, $AgX^{IIIA}Se_2$ as mix-cation chalcopyrite structures, where X^{VIIA} = Cl, Br, or I; X^{IIIA} = Al, Ga, or In. The red line is the linear fit of the scattered points.

In summary, we have revealed that the stability of ternary chalcopyrite compounds is determined by whether the strain energy and Coulomb energy can be simultaneously optimized in the structure, and explained the puzzling experimental observation that mixed-cation compounds are more stable than the mixed-anion compounds. A simple descriptor of stability is the relative ratio of ionic radii of the transmuted ions. When ions with higher absolute valences have smaller ionic radii than those of ions with lower absolute valences, the structures are more stable. Increasing the size of the high-valence ion will result in higher strain energy, which is the major cause of the instability of such crystals. Given that most cations with high valences possess smaller ionic radii than those with lower valences, mix-cation chalcopyrite crystals are more likely to be stable. On the contrary, mix-anion chalcopyrite crystals often have oversized high absolute valence anions; thus, they are more likely being unstable. A few exceptions exist, such as Zn_2AsI, Zn_2PI, Zn_2PBr, Zn_2NCl,

Zn_2NBr, and Zn_2NI, where group-VII ions are larger than the group-V ions, leading to their relatively better stabilities. This work elucidates the stability mechanisms of ternary chalcopyrite crystals. The understanding constitutes the basis for designing novel ternary or multinary materials for various applications.

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