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Thermal Properties of the Element and Binary Oxides toward Negative Thermal Expansion: A First-Principles Lattice-Dynamics Study

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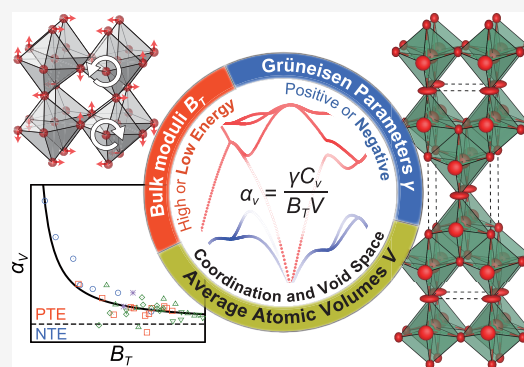


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Supporting Information

ABSTRACT: To establish the design principles of thermal properties of solids, we performed comprehensive calculations of volume thermal expansion coefficients α_V , bulk moduli B_T , average atomic volumes V , and Grüneisen parameters γ in the finite temperature for the 46 elements and 45 binary oxides using first-principles lattice-dynamics calculations. We clarified that (i) a crystal possessing large V tends to have small B_T ; (ii) the major role of γ is the determination of the sign of α_V , the value of which is ruled by the crystal structures and coordination numbers; (iii) the transverse-acoustic (TA) and/or low-frequency phonons are responsible for the negative thermal expansion (NTE) behaviors; (iv) the NTE materials prefer the relatively large V with the void space, possessing negative mode-Grüneisen parameters γ_{qv} ; and (v) the common feature of the NTE materials is the phonons vibrating forward to the void space. Our study provides a wide perspective on designing low and/or negative thermal expansion materials.



1. INTRODUCTION

Negative thermal expansion (NTE) materials have been vigorously studied for more than a century and are applied to many industrial applications such as heat resistance fillers, microdevices in light-emitting diodes (LED), large-scale integration (LSI), power semiconductors, and micropositioners in the telescopes. The first low thermal expansion (LTE) material (Fe–Ni alloy) and the first NTE material (SiO₂) were reported in 1897^{1,2} and 1907,^{3,4} respectively. The equation of states for solids was proposed by Mie and Grüneisen in 1903⁵ and 1912,⁶ respectively, governing the thermal expansion behaviors of harmonic solids. Many representative NTE materials, ZrW₂O₈,⁷ ZrV₂O₇,⁸ PbTiO₃,⁹ ScF₃,¹⁰ and Cd(CN)₂,¹¹ have been reported from the mid-20th century to recent 2010. Although a tremendous amount of work on LTE and NTE materials has been dedicated so far,^{12–24} a comprehensive study showing the chemical aspects and materials-design concepts for realizing LTE and NTE behaviors is lacking. Specifically, it remains unclear as a nontrivial problem how we design LTE or NTE materials with various combinations of the elements. These fundamental uncertainties stem from unclear correlations between the thermal expansion coefficients and related parameters of crystals.

In this study, we present the systematic calculation results of thermal properties, namely, volume thermal expansion coefficients α_V , bulk moduli B_T , average atomic volumes V , and Grüneisen parameters γ for the 46 unary solids and 45 binary

oxides through first-principles lattice-dynamics calculations using quasi-harmonic approximation (QHA). We provide a formulation of α_V based on the Mie–Grüneisen equation of states. From the analytic formulation of α_V , we thoroughly analyze the correlations between α_V , B_T , V , and γ using the calculation results. Some chemical trends of the thermal properties of unary solids and binary oxides are provided and discussed.

2. COMPUTATIONAL DETAILS

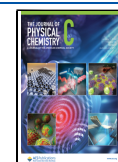
The first-principles calculations were carried out using the projector augmented-wave (PAW) method²⁵ and the PBEsol functional within the generalized gradient approximation²⁶ as implemented in VASP.^{27,28} The cutoff radii and valence electronic configurations of the PAW data sets used in the calculations are given in Table S1 in the Supporting Information. The cutoff energy was set as 550 eV. The phonon dispersions were derived from the calculated force constants using PHONOPY.^{29–31} Here, to derive the force constants, we

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adopted a $2 \times 2 \times 2$ supercell for the cubic, rhombohedral, tetragonal, orthorhombic, and monoclinic structures, while a $3 \times 3 \times 2$ supercell was used for the hexagonal structures. As an exception, we calculated the force constants of Cu_2O ($Pn3m$) by expanding the supercell as $4 \times 4 \times 4$ because the negative α_V were largely overestimated in the results from the $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells. We did not calculate the thermal properties when a crystal structure has imaginary phonon modes because free energy calculations are unavailable. For the calculations through QHA,³² we isotropically changed the relaxed lattice constants as -5 to $+5\%$ in the unary solids and -0.66 to $+0.66\%$ in the binary oxides. Here, in the calculations for the partially occupied $3d$ transition-metal oxides, we used the Dudarev formulation of $+U$ correction³³ with the antiferromagnetic configurations to obtain the dynamically stable phases. We applied the $+U$ corrections for the on-site $3d$ electrons in V, Cr, Fe, and Ni as 3, 3, 4, and 7 eV, respectively, the values of which were used in the previous studies.^{34–36} The atomic displacement parameters were calculated using PHONOPY.^{37,38}

All of the initial crystal structures used in the present study were extracted from Materials Project.³⁹ The band paths were determined by the seekpath code⁴⁰ and from the Brillouin-zone database.⁴¹ The space-group symmetry analyses were performed by SGPLIB⁴² as implemented in PHONOPY. Further, the symmetry modes and irreps were analyzed through AMPLIM-ODES^{43,44} and ISODISTORT,⁴⁵ respectively.

3. RESULTS AND DISCUSSION

3.1. Thermal Expansion Coefficients of the Elements.

We present the calculated and experimentally reported thermal expansion coefficients α_V , bulk moduli B_T , and Grüneisen parameters γ of the elements at 300 K as shown in Figure 1a–c (see Table S2 for the details in the Supporting Information). The calculated and experimental values validate the predictability and accuracy of the QHA employed in this work.

Within the scheme of QHA, the volume thermal expansion coefficient α_V in a solid is given as^{12,13,17,52–54}

$$\alpha_V = \frac{\gamma C_V}{B_T V} \quad (1)$$

where γ , C_V , V , and B_T are the Grüneisen parameter, heat capacity at constant volume, volume per one atom (average atomic volume), and bulk moduli, respectively (see Section 3 in the Supporting Information for the detailed derivation of the eq 1). At first, we discuss the correlation between the α_V and B_T based on eq 1 for unary solids as illustrated in Figure 1d. It is shown that the α_V is inversely proportional to the B_T , which is in accordance with eq 1. Here, we present the curves of α_V as a function of B_T by substituting the C_V , γ , and V as $3k_B$, 1, and $25 \text{ \AA}^3$ (mean value of average atomic volume for the unary solids), respectively in eq 1. It is apparent that the most crucial factor for determining the thermal expansion coefficients α_V is the bulk moduli B_T : low (high) α_V are owing to high (low) B_T , the chemical trend of which is natural and intuitive. In contrast, it should be denoted that α_V and V are not inversely proportional, as will be discussed in Section 3.2. Moreover, from the calculation results, we found that the higher principal quantum number n of the peripheral electron in s - and p -block (d -block) elements gives rise to lowering (heightening) their bulk moduli. In other words, the s - and p -block (d -block) with a low (high) principal quantum number n possess rigid chemical bonding. This chemical trend would explain the reason why LTE and

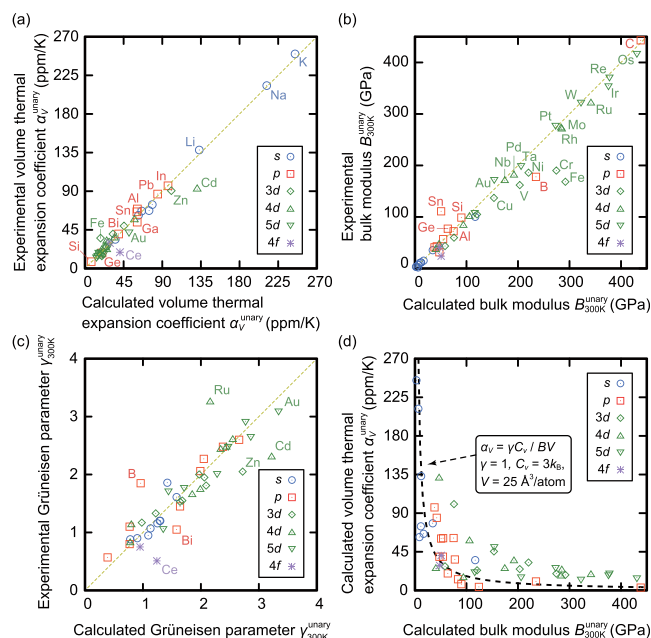


Figure 1. Validations of the calculated (a) volume thermal expansion coefficients α_V , (b) bulk moduli B_T , and (c) Grüneisen parameters γ by using QHA compared to the experimental values. Note that α_V , B_T , and γ are the calculation results in the condition of $T = 300 \text{ K}$. Experimental values of α_V , B_T , and γ are referred from refs 46–51. (d) Our calculated volume thermal expansion coefficients as a function of the bulk modulus. The dashed line depicts the relation of α_V and B_T as presented in eq 1 with assuming the C_V , γ , and V as $3k_B$, 1, and $25 \text{ \AA}^3$, respectively (see text for the detail).

NTE materials usually include $2p$ -, $3p$ -, $3d$ -, $4d$ - and $5d$ -block elements exhibiting rigid bonding such as ZrW_2O_8 ,^{7,55} ZrV_2O_7 ,⁸ $\text{Y}_2\text{Mo}_3\text{O}_{12}$,⁵⁶ $\text{Sc}_2\text{W}_3\text{O}_{12}$,⁵⁷ NbPO_5 ,⁵⁸ TaVO_5 ,⁵⁹ $\text{Zn}(\text{CN})_2$,⁶⁰ $\text{Cd}(\text{CN})_2$,¹¹ $\text{Cu}_2\text{P}_2\text{O}_7$,⁶¹ LiAlSiO_4 ,⁶² $\text{Zr}_2\text{SP}_2\text{O}_{12}$,⁶³ and $\text{KZr}_2(\text{PO}_4)_3$.^{64,65}

Let us see the chemical trends of calculated bulk moduli B_T , average atomic volumes V , and Grüneisen parameters γ of the elements. The B_T , V , and γ are found to have periodicity (Figure 2a–c). From Figure 2a,b, one can see that the B_T tends to increase as the V decreases. Additionally, as given in Figure 2c, we can also see some chemical trends of the Grüneisen parameters $\gamma_{300 \text{ K}}$ as follows: (i) $\gamma_{300 \text{ K}}$ of s -block elements are not large compared to the other elements; (ii) $\gamma_{300 \text{ K}}$ of p -block elements tends to increase with larger principal quantum number; and (iii) $\gamma_{300 \text{ K}}$ of d -block elements increases from left to right in the periodic table. To show the validity of our calculated Grüneisen parameters $\gamma_{300 \text{ K}}$, we also compared the previously reported anharmonic parameter η by Rose et al.⁶⁶ (Figure 2d). We can also see that our calculated Grüneisen parameters have a positive correlation with the previously reported anharmonic parameters, which reconfirms the validity of our QHA calculations, including the degree of anharmonicity.

3.2. Thermal Properties of Binary Oxides. We also present the calculation results of volume thermal expansion coefficients at 300 K for 45 binary oxides via QHA (Figure 3a, see also Table S3 in the Supporting Information for the numerical data). We note that some binary oxides with imaginary phonon modes were excluded from the analyses due to their ill-defined free energies under QHA. For instance, four typical SiO_2 species are found to have imaginary phonon modes (see Figures S1 and S2 in the Supporting Information).

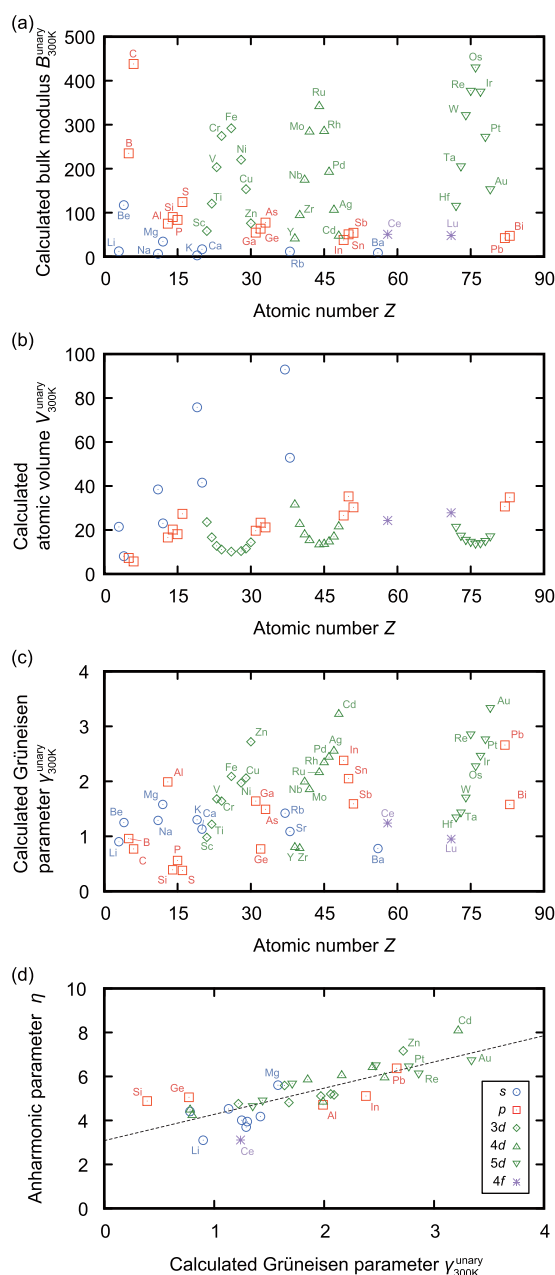


Figure 2. Calculated (a) bulk moduli, (b) atomic volumes, and (c) Grüneisen parameters of the elements with the condition of $T = 300$ K using quasi-harmonic approximation, which are aligned with the atomic number. (d) Comparison of our calculated Grüneisen parameters of the elements with the previously reported anharmonic parameter η by Rose et al.⁶⁶ The black dashed line was derived by least-squares linear fitting.

The accuracy of calculation results in the binary oxides becomes lower compared to that in the elements for reproducing the experimental results (compare Figures 1a and 3a). Particularly, we observe a large inconsistency of α_V for B_2O_3 between the calculations and experiments, which should be attributed to the phase difference between crystal and amorphous: the experimental α_V of B_2O_3 was measured in glass phase,⁶⁷ while our calculated α_V of B_2O_3 was derived from the ideal crystal ($P3_121$ phase).

We then examine the correlation between thermal expansion coefficients α_V and bulk moduli B_T for the binary oxides similar to the unary solids based on eq 1. In Figure 3b, we observe an

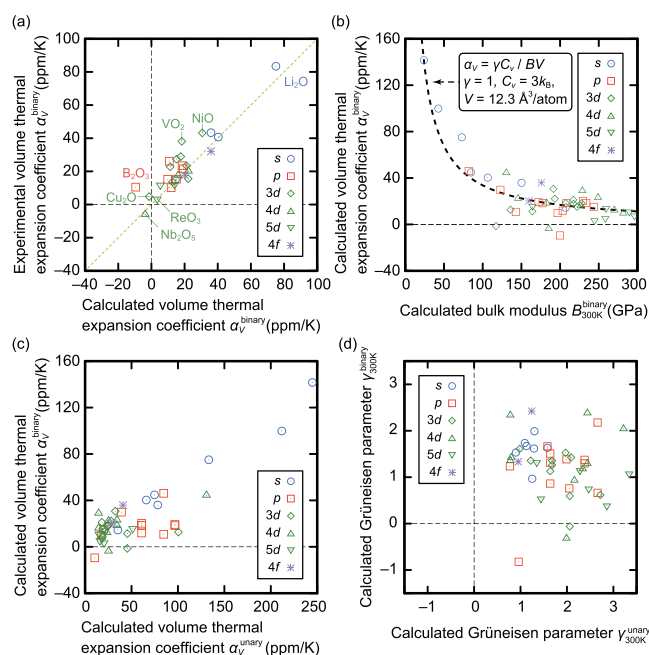


Figure 3. (a) Comparison of experimental and calculated volume thermal expansion coefficients α_V of binary oxides. (b) Calculated volume thermal expansion coefficients as a function of bulk modulus B_T for binary oxides. Experimental thermal expansion coefficients are from refs 67–89. Comparisons of (c) volume thermal expansion coefficients α_V and (d) Grüneisen parameters γ between the elements and binary oxides. α_V , B_T , and γ are the calculation results in the condition of $T = 300$ K.

inverse proportional correlation between α_V and B_T similar to Figure 1d, indicating that eq 1 is also applicable to the binary oxides. This indeed indicates that the most dominant factor in determining α_V is B_T . Originating from this inverse proportional correlation, as discussed further, a larger negative thermal expansion would be obtained in a material exhibiting a negative γ and a smaller B_T .

Figure 3c shows the positive correlation for the thermal expansion coefficients α_V of binary oxides (M_xO_y) and unary counterparts of the element M . On the other hand, the correlation for Grüneisen parameters γ of the elements and binary oxides is less clear (Figure 3d). These results imply that a compound containing an element with large α_V tends to have large thermal expansion coefficients, whereas the degree of anharmonicity in a compound is unrelated to that in the elements. These results indicate the two essential features: (i) the binary oxides composed of the elements with large α_V in their unary solids tend to have large thermal expansion coefficients and (ii) the degree of anharmonicity in the binary oxides is not directly correlated to that of the unary solids. From these results, we conclude that the degree of γ is mainly dependent on crystal structures and coordination environments rather than the element species. In other words, structural polymorphs with a single chemical composition result in different degrees of anharmonicities and thermal expansion coefficients. We demonstrate this behavior with MgO , CaO , and ZnO of rock-salt (RS) and zincblende (ZB) polymorphs as a case study (Figure 4a,b). While the relatively small α_V values were obtained from the ZB structures compared to those of RS structures (Figure 4a), the B_T values of ZB structures were smaller than those of RS structures (Figure 4b). Intriguingly, the metastable ZB phase of CaO is predicted to exhibit an NTE

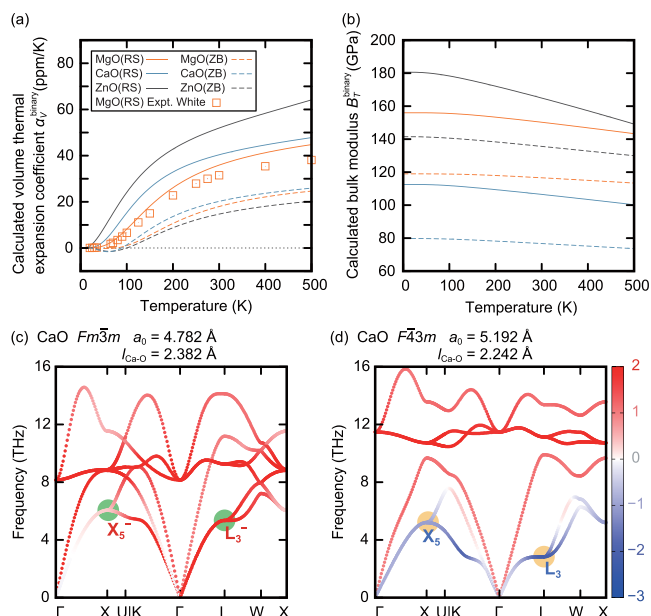


Figure 4. Calculated (a) volume thermal expansion coefficients α_V and (b) bulk moduli B_T for MgO, CaO, and ZnO of rock-salt and zincblende structures as functions of temperature. The experimental values are referred from ref 90. The phonon bands with Grüneisen parameters for CaO of (c) rock-salt and (d) zincblende structures are also shown. The red and blue indicate the positive and negative mode-Grüneisen parameters, respectively. The lattice constants and bond lengths of the RS and ZB structures at 0 K are also indicated.

behavior at low temperatures, while the ground-state RS phase of CaO has large positive thermal expansion (PTE) behavior. The crucial differences in α_V between RS and ZB structures originate from the existence of the negative mode-Grüneisen parameters, which are strongly structure dependent (Figure 4c,d).

We also compared bulk moduli B_T of the unary solids and binary oxides as a function of average atomic volume V (Figure 5a,b). In both systems, B_T has inverse proportional correlations with V and vice versa. As aforementioned in the previous discussion, α_V and B_T have a robust inverse proportional correlation, and hence we can expect a proportional correlation between α_V and V . In fact, a weak proportional correlation can be shown between them (Figure 5c). From eq 1, it may seem to be an inverse proportional correlation between α_V and V ; however, actually, they have a weak proportional correlation. In the research field of NTE, it is empirically known that the larger average atomic volume V tends to generate large negative thermal expansion,⁹¹ the reason for which can be explained by the correlation between α_V and V . Let us assume that the Grüneisen parameter γ in eq 1 is negative and α_V is inversely proportional to V as given in eq 1. Then, we get the positive correlation between α_V and V , which contradicts the previous report showing the negative correlation between α_V and V .⁹¹ Considering that B_T and V are dominant for determining α_V , we can catch a glimpse that the major role of Grüneisen parameter in eq 1 is to determine a sign (PTE or NTE). Furthermore, we also show the difference in bulk moduli B_T between the elements and binary oxides (Figure 5d). In the transition metals exhibiting high B_T , such as Cr, Fe, Ni, Cu, Ru, Rh, Re, Os, and Ir, additionally including B, the oxidation of them decreases the B_T , whereas B_T of the other relatively soft metals increases by the oxidation.

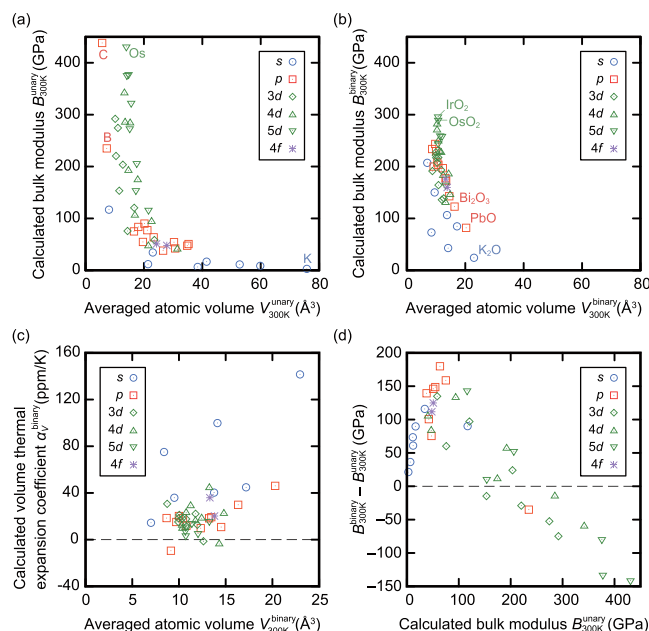


Figure 5. Calculated bulk moduli of (a) the unary systems and (b) binary oxides as a function of average atomic volume. (c) Scatter plot of the volume thermal expansion coefficient of binary oxides and the average atomic volume. (d) Difference of bulk moduli between the elements and the binary oxides as a function of the bulk moduli of the elements.

3.3. Negative Thermal Expansion Materials among the Elements and Binary Oxides. From eq 1, as is widely known, the negative α_V (NTE) can be explained only from negative γ because negative values of C_V , B_T , and V cannot be realized. This NTE mechanism is known as the *tension effect*.¹⁷ The role of Grüneisen parameters can also be seen in another aspect of the formula of inner pressure P in crystal. In this case, the static total energy of a crystal E , which is identical to the elastic energy, is given as

$$E(V) = \frac{1}{2} B_T \frac{(V - V_0)^2}{V_0} \quad (2)$$

where V_0 is the average atomic volume in a crystal at 0 K and V is the equilibrium volume per one atom at the finite temperature T . Then, the inner pressure P at finite temperature in a crystal will be given as

$$P + B_T \frac{V - V_0}{V_0} = \frac{1}{V} \sum_{q,\nu} \gamma_{q\nu} U_{q\nu} \quad (3)$$

Assuming that the inner pressure at a finite temperature T is zero with the equilibrium volume V , the volume change $V - V_0$ will be expressed as

$$V - V_0 = \frac{V_0}{BV} \sum_{q,\nu} \gamma_{q\nu} U_{q\nu} \quad (4)$$

On the other hand, in the case of the constant volume ($V = V_0$) at finite temperature, which is a non-equilibrium state, the inner pressure of a crystal will be expressed as

$$P = \frac{1}{V} \sum_{q,\nu} \gamma_{q\nu} U_{q\nu} \quad (5)$$

Both eqs 4 and 5 provide the driving forces of NTE and PTE behaviors. In eq 4, the NTE ($V - V_0 < 0$) is triggered when γ_{qv} is negative because the phonon internal energy U_{qv} is always positive. On the other hand, eq 5 indicates that the driving force of negative (positive) thermal expansion is the phonons with negative (positive) Grüneisen parameters. The phenomena of PTE and NTE in terms of free energy are illustrated in Figure 6a,b. Conclusively, the volume change (NTE and PTE) with

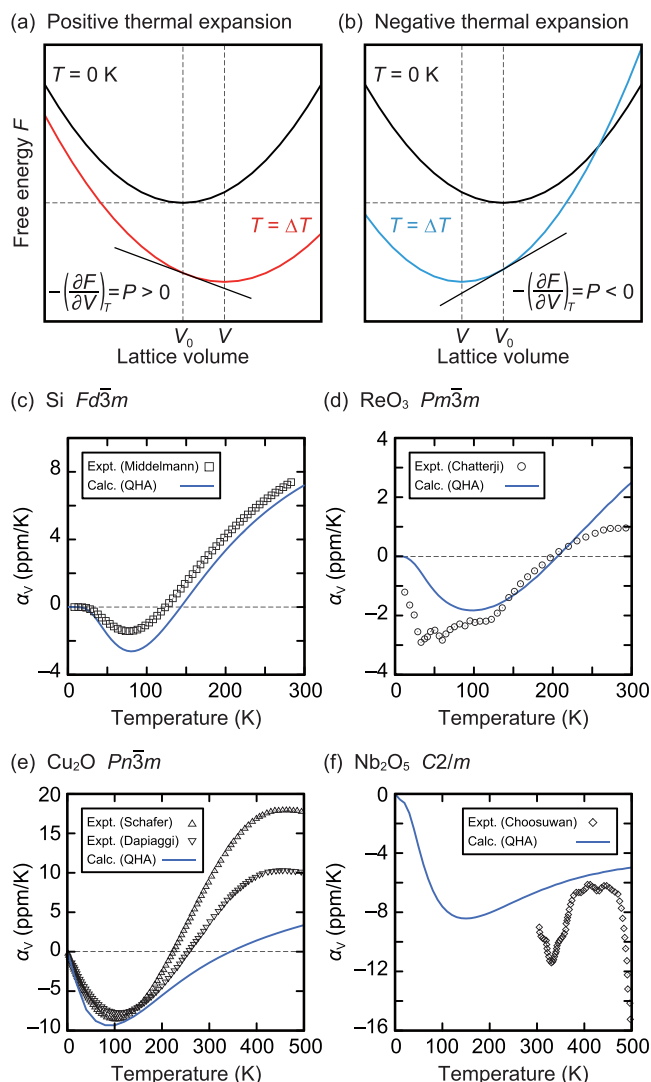


Figure 6. Schematic diagram of Helmholtz free energy as a function of lattice volume in (a) positive and (b) negative thermal-expansion materials. Temperature dependences of calculated thermal expansion coefficients α_V via QHA for (c) Si, (d) ReO_3 , (e) Cu_2O , and (f) Nb_2O_5 . The experimental α_V were extracted from refs 92–96.

varying temperatures originates from the minimization of free energy, where phonons are extensively involved, whose contribution is determined with the Grüneisen parameter depending on the crystal structure.

We present the calculation results of several NTE materials, Si, ReO_3 , Cu_2O , and Nb_2O_5 (Figure 6c–f). The calculation results of these materials via QHA are in good agreement with the experimental results, especially in low temperatures. Some inconsistencies of α_V in high temperatures might be attributed to the anharmonicity, which is not sufficiently captured by QHA (see Section 3 in Supporting Information). QHA considers only

the volume dependency of phonon frequencies, while phonon frequencies also depend on the temperature, even with a constant volume. While some limitations of QHA can be overcome with several advanced methods, such as the self-consistent phonon theory,⁹⁷ it is still convincing that QHA is one of the most well-balanced methods to capture the nature of thermal expansion with considerably high accuracy and computational cost.³² The accuracy of QHA was confirmed in the previous computational studies for binary oxides such as Li_2O ,⁹⁸ w- BeO ,^{99–101} Na_2O ,¹⁰² MgO ,^{103–106} CaO ,^{106,107} SrO ,^{107,108} Al_2O_3 ,^{109,110} Ga_2O_3 ,^{111,112} ZnO ,¹¹³ Cu_2O ,^{114–119} and ReO_3 .^{93,120,121}

We show phonon bands and mode-Grüneisen parameters of several representative phonon modes of Si, ReO_3 , Cu_2O , and Nb_2O_5 in Figure 7a–d. It has been shown that the acoustic phonons play an important role in inducing the NTE behaviors, the phonon modes of which transform like irreducible representations (irreps) X_4^- and L_3^- in Si, M_3^+ , and R_4^+ in ReO_3 , X_4^- in Cu_2O , and L_1^- , M_2^- , and A_2^- in Nb_2O_5 . Note that all of the aforementioned phonon modes except the M_3^+ mode of ReO_3 are transverse acoustic (TA) phonon modes, while the M_3^+ mode of ReO_3 is a longitudinal acoustic (LA) phonon mode. It has been suggested that the TA phonon modes are responsible for the NTE behavior of ZrW_2O_8 ,^{18,55,122,123} while transverse phonon modes are reported to be crucial for various NTE materials such as ZrV_2O_7 , NbPO_3 , $\text{Cu}_2\text{P}_2\text{O}_7$, Zn_2GeO_4 , and CuScO_2 .^{8,58,61,124–126} The reason is that TA phonons ordinarily have the lowest frequency among the acoustic branches, leading to large negative Grüneisen parameters. In fact, in 1957, Blackman and Barron suggested that low energy (low frequency) transverse phonons give rise to negative Grüneisen parameters and NTE behaviors.^{12,13} Moreover, the TA and/or low-energy phonons with negative Grüneisen parameters should be generally essential for realizing NTE behavior because the phonon lifetime tends to increase with low frequency.^{127,128} It is noteworthy that the number of acoustic phonon bands is only 3, whereas that of optical phonon bands is $3N - 3$ (N is the number of atoms in a primitive cell), implying that the acoustic phonons become relatively less important when a unit cell is composed of a large number of atoms. Thus, we consider that the NTE behaviors, the unit cells of which contain a large number of atoms such as ZrW_2O_8 and $\text{Y}_2\text{Mo}_3\text{O}_{12}$, might be attributed to a large number of low-frequency transverse optical (TO) phonons with negative mode Grüneisen parameters, the discussion of which is analogous to that of the previous reports.¹⁷

Recently, Dove et al. have shown that the NTE behavior of ScF_3 should be explained not only by the phonons at R and M points (rigid unit mode, RUM) but also by the phonons between R and M points (quasi-RUM).¹²⁹ Inspired by the previous report,¹²⁹ we show the three-dimensional distribution of averaged mode-Grüneisen parameters in half of the first-Brillouin zone for Si, ReO_3 , Cu_2O , and Nb_2O_5 as illustrated in Figure 7e–h (see the three-dimensional distribution of averaged mode-Grüneisen parameter for the other oxides in the Supporting Information). We can see through the crucial phonons that contribute to the NTE behavior in Figure 7e–h: the phonons in X and L points contribute to the NTE behavior in Si, while those between R and M points do in ReO_3 , which is consistent with the previous report of ScF_3 .¹²⁹ Additionally, one can see that the phonons around the X (L) point contribute to the NTE behavior in Cu_2O (Nb_2O_5). These results indicate that

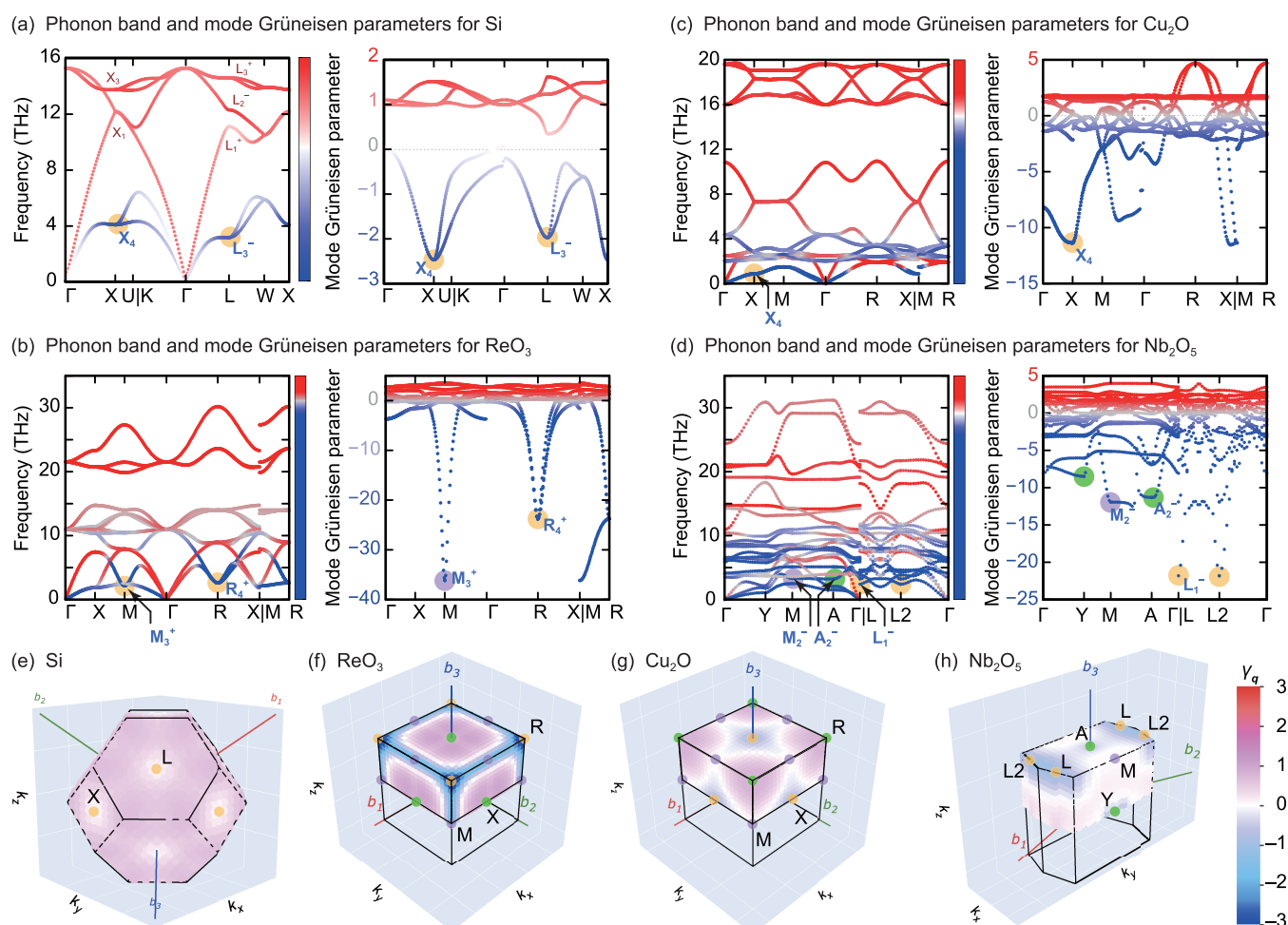


Figure 7. Phonon bands and mode-Grüneisen parameters of (a) Si, (b) ReO₃, (c) Cu₂O, and (d) Nb₂O₅. The red and blue points in the phonon bands indicate the positive and negative mode-Grüneisen parameters, respectively. The three-dimensional distributions of averaged mode-Grüneisen parameters in half of the first Brillouin zone for (e) Si, (f) ReO₃, (g) Cu₂O, and (h) Nb₂O₅ are also illustrated.

not only ScF₃ but also the oxides in Figure 7 have phonon modes, which can be regarded as RUM and quasi-RUM.

We finally present the visualized representative phonon modes of Si, ReO₃, Cu₂O, and Nb₂O₅ with large negative Grüneisen parameters in Figure 8a–d. It is shown that the phonon modes transforming like irreps X_4 and L_3^- of Si, M_3^+ of ReO₃, L_1^- , M_2^- , and A_2^- of Nb₂O₅ are rigid unit modes, while those transforming as irreps R_4^+ of ReO₃ and X_4 of Cu₂O are guitar string modes (see the Supporting Information). Recently, the guitar string effect of ScF₃ was experimentally reported,¹³⁰ the structure of which is the same as that of ReO₃. We also present the conventional crystal structures with the calculated atomic displacement parameters at 500 K of the four compounds (Figure 8e), which were visualized by using VESTA.¹³¹ The ellipsoids indicate that the relevant atoms are located in the volume, with a probability of 98%. We can see that the ellipsoidal shapes of Si and those of Cu and O in Cu₂O are close to spherical shapes, indicating that the thermal vibrations in Si and Cu₂O are isotropic. On the other hand, the ellipsoidal shapes of oxygens in ReO₃ and Nb₂O₅ are flat and pancake-shaped, indicating that the thermal vibrations of oxygens in ReO₃ and Nb₂O₅ are anisotropic. The anisotropic thermal vibration might contribute to creating the order of phonons with negative Grüneisen parameters, leading to NTE. Recently, Ritz and Benedek recently suggested that the NTE behavior of

PbTiO₃ can be attributed to the interplay between phonons and anisotropic elasticity, not to the negative Grüneisen parameters,¹³² the discussion of which is still under debate.^{133,134} Finally, let us see the isotropic atomic displacement parameters (B parameters) of the relevant compounds. We found that the B parameter is large in the order of Cu₂O, Nb₂O₅, Si, and ReO₃. Note that the large B parameter indicates a drastic thermal vibration. The order of degree of the B parameters should be attributed to the coordination numbers, bond strengths, and atomic masses. For instance, the coordination number of Cu in Cu₂O is 2, while those of Re and Nb in ReO₃ and Nb₂O₅, respectively, are 6. The B parameter of the former is larger than that of the latter.

At last, we compare the NTE behaviors in SiO₂, ReO₃, and metastable ZB CaO. Even in these simple binary oxides, grasping a big picture that unifies the NTE behaviors is challenging. Indeed, the NTE behaviors of SiO₂ (zeolites)¹³⁵ and ReO₃ are much different in terms of (i) the existence of pure RUM, which stems from the different number of atoms in their primitive cells, and (ii) the deformation stiffness of SiO₄ tetrahedra and ReO₆ octahedra, as discussed in the previous report.¹³⁵ However, considering with another perspective, we can also see the similar characteristics of SiO₂ and ReO₃: both of them have the flexible RUMs that bend the bond angles Si–O–Si and Re–O–Re, stemming from the low-frequency phonon modes, the modes of

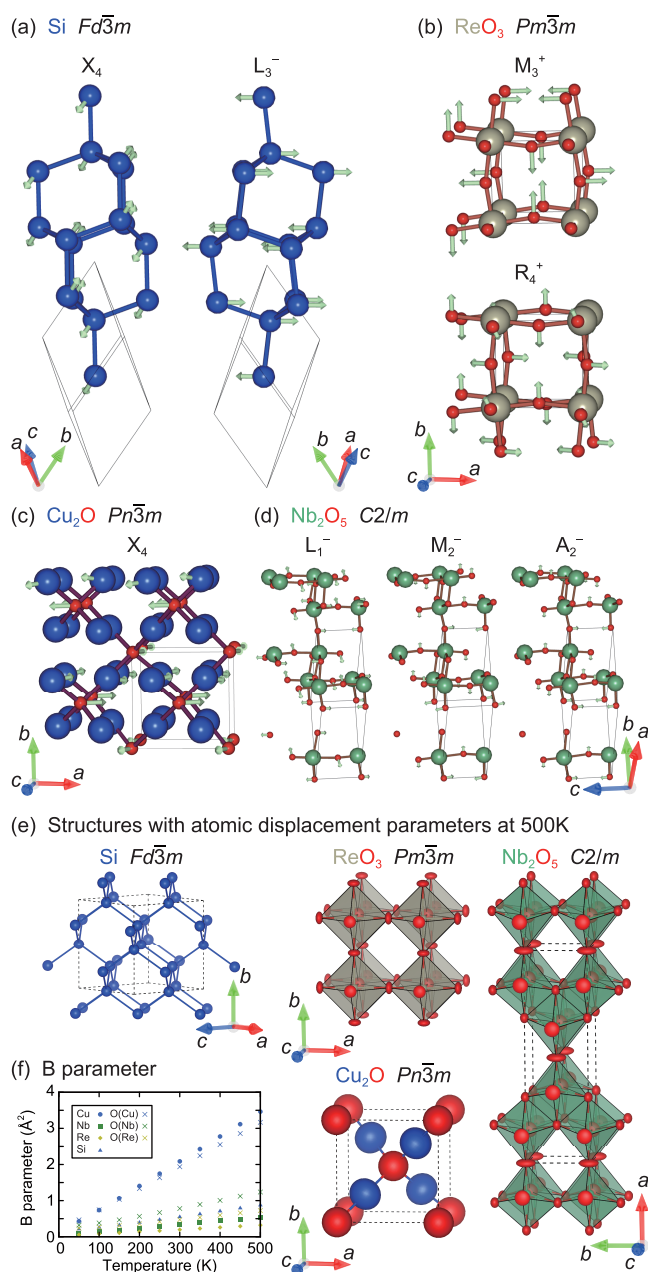


Figure 8. (a–d) Visualized phonon modes transforming like irreps (a) the X_4 and L_3^- of Si, (b) the M_3^+ and R_4^+ of ReO_3 , (c) the X_4 of Cu_2O , and (d) the L_1^- , M_2^- , and A_2^- of Nb_2O_5 . The black solid lines indicate the relevant primitive unit cells. (e) Conventional crystal structures with calculated atomic displacement parameters at 500 K. (f) Calculated B parameters as a function of temperature.

which are rotational atomic vibrations.¹³⁵ Such low-frequency phonon modes that give rotational atomic vibrations do not exist in alkaline earth oxides, such as MgO , CaO , SrO , and BaO , which have RS structures. Interestingly, the metastable ZB CaO and ZnO exhibit the NTE behavior in low temperatures, while the metastable ZB MgO possesses low thermal expansion coefficients compared to RS MgO (Figure 4a). We consider that the low-thermal expansion coefficients of metastable ZB CaO , MgO , and ZnO are attributed to the low-frequency transverse acoustic phonon modes transforming as irreps X_3 and L_3 (Figure 4d), which are analogous to the phonon modes transforming as irreps X_4 and L_3^- in Si (Figure 8a). However, we should be

cautious that even the metastable ZB structures do not have low-frequency rotational phonon modes. Thus, the NTE behavior of the ZB structure is far different from those of SiO_2 and ReO_3 . Then, what is the common feature that can be observed in all these compounds exhibiting NTE?

Together with all the discussions, we would establish a design concept for achieving phonons with negative mode Grüneisen parameters. The common feature of phonons visualized in Figure 8a–d is that the atomic displacements are toward void spaces in the relevant unit cell. Thus, the key factor in realizing NTE would be the existence of void space and relatively small coordination numbers to utilize the transverse phonons, which have small energies for dynamic lattice distortion. This is also the reason why materials with large average atomic volumes and small bulk moduli are usually preferred for NTE materials. This behavior is observed in the case of the RS and ZB structures for CaO (Figure 4), the results of which indicate that the acoustic (optical) phonon modes are softened (hardened) by the coordination-environment modification from relatively dense edge-sharing octahedra (RS structure) into wide corner-sharing tetrahedra (ZB structure).

4. CONCLUSIONS

To establish unified pictures of thermal expansion coefficients and design concepts of negative-thermal expansion (NTE) materials, we performed systematic first-principles lattice-dynamics calculations for the 46 elements and 45 binary oxides via quasi-harmonic approximation (QHA) to examine their thermal properties, that is, thermal expansion coefficients α_V , bulk moduli B_T , average atomic volumes V , and Grüneisen parameters γ . As a result, we have shown that (i) the α_V is determined mainly by the B_T , which has an inverse correlation with α_V ; (ii) a crystal possessing large V tends to have small B_T ; (iii) the α_V of complex compounds tend to be large (small) when they are composed of the element with large (small) α_V ; (iv) the major role of γ , which is ruled by the crystal structures and coordination environment, is the determination of the sign of α_V ; (v) the transverse-acoustic (TA) and/or low-frequency phonons are responsible for the negative thermal expansion behaviors; and (vi) the NTE materials prefer the relatively large V , possessing negative mode Grüneisen parameters γ_{qv} . We believe that our results would offer an essential perspective on the development of low- and/or negative thermal expansion materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.3c06507>.

Derivation of eq 1 and the discussion of anharmonicity; crystal structure schematics of four SiO_2 polymorphs and their phonon bands; calculated and experimentally reported α_V , B_T , and γ at 300 K for the unary solids and binary oxides; cutoff radii and valence electronic configurations of the PAW data sets (PDF)

Visualized phonons with negative mode-Grüneisen parameters for Si, ReO_3 , Cu_2O , and Nb_2O_5 (ZIP)

Three-dimensional distribution of averaged mode-Grüneisen parameter for Si and 46 oxides (ZIP)

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Notes

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ABBREVIATIONS

NTE, negative thermal expansion; LTE, low thermal expansion; PTE, positive thermal expansion; QHA, quasi-harmonic approximation; RS, rock-salt; ZB, zincblende; irreps, irreducible representations; TA, transverse acoustic; LA, longitudinal acoustic; TO, transverse optical

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