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## Control of thermal expansion in a low-density framework modification of silicon

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The low-density clathrate-II modification of silicon, Si<sub>136</sub>, contains two distinct cage-like voids large enough to accommodate various types of guest atoms which influence both the host structure and its properties. Although the linear coefficient of thermal expansion of Si<sub>136</sub> (293 K < T < 423 K) is only about 20% larger than that of the ground state  $\alpha$ -Si (diamond structure), the coefficient of thermal expansion monotonically increases by more than 150% upon filling the framework cages with Na atoms in Na<sub>x</sub>Si<sub>136</sub> (0 < x < 24), ranging from  $\alpha = 2.6 \times 10^{-6} \text{K}^{-1}$  (x = 0) to  $6.8 \times 10^{-6} \text{K}^{-1}$  (extrapolated to x = 24) by only varying the Na content, x. Taken together with the available heat capacity and bulk modulus data, the dramatic increase in thermal expansion can be attributed to an increase in the mode-averaged Grüneisen parameter by a factor of nearly 3 from x = 0 to x = 24. These results highlight a potential mechanism for tuning thermal expansion, whereby guest atoms are incorporated into the voids of rigid, covalently bonded inorganic frameworks to influence the lattice dynamics.

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From bridges to thin films, thermal expansion plays a critical role in the functional behavior of materials both large and small. In many high-precision technological applications, including optical components, micro- and nano-electronics, solid-state energy conversion, and aerospace engineering, thermal expansion must be carefully accounted for when devices are subjected to temperature fluctuations and/or gradients.<sup>1,2</sup> For these reasons, the identification of mechanisms by which thermal expansion can be controlled or tuned in technologically useful materials could have a significant impact on device functionality, reliability, and longevity.<sup>1-3</sup> The discovery of materials with very large negative coefficients of thermal expansion (CTEs) over wide temperature ranges ushered in prospects of creating positive/negative CTE composites with specific thermal expansion behavior, including zero thermal expansion, which can be tuned by the composition and volume ratio of the constituents.<sup>1-4</sup> However, since such composites can be challenging to prepare and can also mechanically fail after repeated thermal cycling due to unwanted local stresses, control of CTE in a single homogeneous phase provides a more robust solution.<sup>3,5</sup>

Since the thermal expansion of solids in most temperature ranges of interest has its origin primarily in the anharmonic nature of interatomic interactions, influencing the lattice dynamics by chemical and/or structural modifications can provide an effective pathway for controlling the CTE of single-phase materials.<sup>1</sup> In particular, the atypical lattice vibrations present in negative thermal expansion (NTE) materials present opportunities to engineer CTE. This has been evidenced in

various NTE materials, including ReO<sub>3</sub>-type fluorides,<sup>6</sup> metal organic frameworks,<sup>7</sup> and zeolites,<sup>8</sup> where the volume-reducing lattice vibrations are directly linked to the open framework crystal structure of the material. The frameworks in some of these structures accommodate low energy transverse vibrations (phonons) in which one or more constituent atoms can oscillate into the open space of the voids in the framework, reducing the overall volume as the vibrational displacement increases.<sup>1-3</sup> These low energy vibrations, which are typically transverse acoustic modes, are often characterized by large, negative mode Grüneisen parameters  $\gamma_i = -d \ln \omega_i / d \ln V$ , where  $\omega_i$  is the frequency of the *i*th phonon mode and V is the volume of the crystal, which can in turn produce negative CTE or small positive CTE in these materials.

It has recently been demonstrated that chemical modifications, e.g., framework substitution and/or intercalation of framework voids, can significantly suppress the lattice vibrations responsible for NTE, providing a mechanism for controlling CTE in a single homogeneous phase by adjusting the content of one or more constituents in the composition of oxides,<sup>9,10</sup> cyanides,<sup>11</sup> and fluorides.<sup>12</sup> It is reasonable to expect that other types of open-framework materials with different chemistries, structures, and physical properties, e.g., low-density, covalently bonded frameworks of group 14 elements,<sup>13-15</sup> might have similar features allowing the CTE to be tuned by filling the open-structured voids of the framework. In the present work, we explored this possibility by investigating the effect on thermal expansion when filling the framework cages of the Si<sub>136</sub> allotrope of silicon with Na in Na<sub>x</sub>Si<sub>136</sub> (type II clathrate crystal structure, Pearson symbol Si(cF136), 0 < x < 24) and have found that the linear CTE can be tuned from  $\alpha = 2.6 \times 10^{-6} \text{K}^{-1}$  for x = 0 to near

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$6.8 \times 10^{-6} \text{ K}^{-1}$  for  $x = 24$  by only adjusting the guest content, without modification of the  $\text{Si}_{136}$  framework composition.

Microcrystalline powder samples of  $\text{Na}_x\text{Si}_{136}$  ( $x = 1.1, 5.5, 12.6, 17.3, \text{ and } 21.9$ ) were synthesized by thermal decomposition of the precursor  $\text{Na}_4\text{Si}_4$  under high vacuum, according to the procedure reported in detail elsewhere.<sup>16</sup> Synchrotron powder X-ray diffraction (XRD) data were collected at the Advanced Photon Source, beam line 11-BM, measured from powder-filled capillaries. Measurements at 293 K were performed using the photon energy of 30.0 keV ( $\lambda = 0.414167 \text{ \AA}$ ). Measurements at 373 K, 423 K, and 473 K were performed using the photon energy of 24.0 keV ( $\lambda = 0.517039 \text{ \AA}$ ) under nitrogen Cryostream. Crystal structure refinement (type II clathrate, space group  $Fd\bar{3}m$ ) by the Rietveld method<sup>17</sup> using the GSAS analysis package<sup>18,19</sup> yielded both the Na content  $x$  from the refined site occupancies and the refined cubic lattice parameter  $a$  [see Fig. 1(c) for representative XRD data and fit]. All samples contained approximately 2–3 wt. % of clathrate-I  $\text{Na}_8\text{Si}_{46}$ , which was refined as a secondary impurity phase. Below 500 K, no significant changes in the Na or Si occupations were observed from our refinements, indicating that the Na content did not change during the high temperature experiments and that the silicon framework does not bear vacancies in any of the samples.

Before discussing the influence of Na content on CTE, we briefly highlight a few relevant features of the host  $\text{Si}_{136}$  framework. Despite the expanded framework geometry (approximately 15% increase in the volume per atom), which is accompanied by conspicuous differences in the phonon

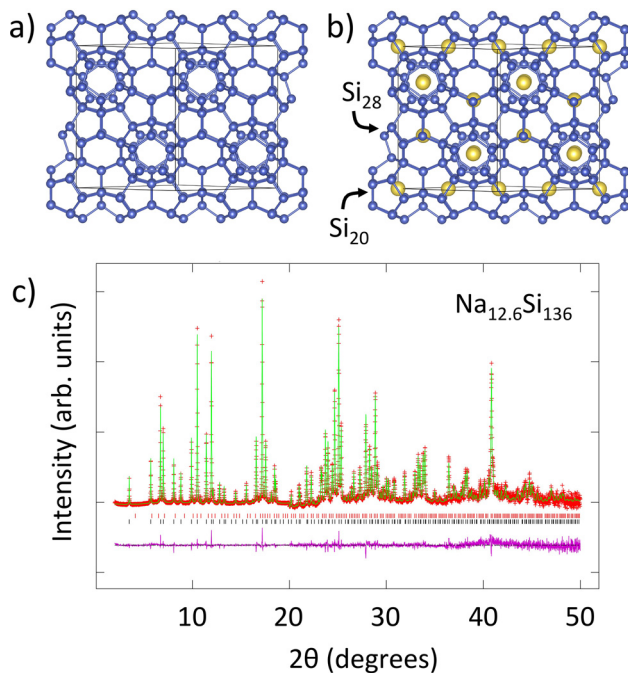


FIG. 1. (a) Crystal structure of the low-density clathrate-II allotrope of silicon,  $\text{Si}_{136}$ . (b) The eight  $\text{Si}_{28}$  and sixteen  $\text{Si}_{20}$  cages per conventional cubic unit cell can each be occupied by Na (yellow spheres), with the maximum occupation corresponding to the composition  $\text{Na}_{24}\text{Si}_{136}$ . (c) Observed (red “+” symbols), calculated (green curve), and difference patterns (lower purple curve) from Rietveld refinement against synchrotron X-ray diffraction data at  $T = 473 \text{ K}$  for  $\text{Na}_{12.6}\text{Si}_{136}$  ( $\lambda = 0.517039 \text{ \AA}$ ; intensity data multiplied  $\times 5$  for  $20^\circ < 2\theta < 30^\circ$  and  $\times 10$  for  $30^\circ < 2\theta < 50^\circ$ ).

spectra and corresponding vibrational density of states,<sup>20</sup> a number of the thermodynamic properties of  $\text{Si}_{136}$  are remarkably similar to the ground state of silicon,  $\alpha\text{-Si}$  [diamond structure, Pearson symbol  $\text{Si}(cF8)$ ]. For example, the metastable  $\text{Si}_{136}$  is only slightly higher in energy than  $\alpha\text{-Si}$ ,<sup>20</sup> the bulk modulus is only about 8% smaller,<sup>21,22</sup> and the specific heats for the two different modifications (on a per atom basis) are very similar, with the Debye temperature of  $\text{Si}_{136}$  only about 5% lower.<sup>20,23,24</sup> The room temperature coefficients of thermal expansion for both  $\text{Si}_{136}$  and  $\alpha\text{-Si}$  are comparable and relatively small (with  $\alpha$  of  $\text{Si}_{136}$  being slightly larger), and the temperature profiles of  $\alpha$  for the two modifications are quite similar.<sup>20,25,26</sup> Negative thermal expansion behavior below 125 K and relatively small positive CTE values at higher temperatures for both modifications have been attributed to a preponderance of phonon modes at low energy which have negative Grüneisen parameters.<sup>20,26</sup>

The effect on the thermal expansion behavior induced by filling the  $\text{Si}_{136}$  cages with Na is shown in Fig. 2. In general, the refined lattice parameters at room temperature for all five samples [Table I and inset to Fig. 2(a)] are in very good agreement with those reported previously for  $\text{Na}_x\text{Si}_{136}$ .<sup>16,27,28</sup> In particular,  $a$  first decreases slightly for  $0 < x < 8$  but then increases for  $8 < x < 24$ , in agreement with prior work.<sup>16,27,28</sup> This can be attributed to selective occupation of the eight

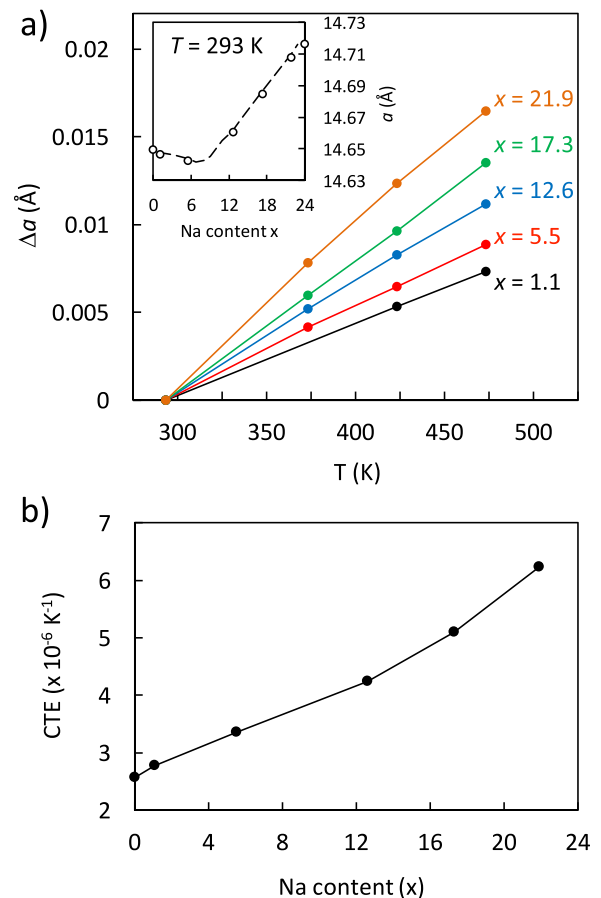


FIG. 2. (a) Relative change in the lattice parameter as a function of temperature for  $\text{Na}_x\text{Si}_{136}$ . (Inset: Lattice parameter as a function of Na content  $x$  at 293 K. The dashed curve shows the trend reported in Ref. 16. Lattice parameter values for  $x = 0$  and  $x = 24$  were taken from Refs. 20 and 33, respectively.) (b) Linear coefficient of thermal expansion as a function of Na content  $x$ .

TABLE I. Experimental Na content ( $x$ ) and fractional occupancy (occ.) of Na atoms in large ( $\text{Si}_{28}$ ) and small ( $\text{Si}_{20}$ ) cages, room temperature lattice parameter ( $a$ ) as determined from Rietveld refinement for the five  $\text{Na}_x\text{Si}_{136}$  compositions, as well as  $\text{Si}_{136}$ . Also given are linear CTE ( $\alpha$ ), specific heat per unit volume ( $c_p$ ), and bulk modulus ( $B$ ). An occupancy factor near 1.0 indicates that all cages of that type are occupied. The number of significant figures reported reflects the estimated experimental uncertainty in each quantity.

$x$	$\text{Si}_{28}$ occ. <sup>a</sup>	$\text{Si}_{20}$ occ. <sup>a</sup>	$a$ (Å)	$\alpha$ ( $10^{-6} \text{ K}^{-1}$ )	$c_p$ ( $\text{MJ m}^{-3} \text{ K}^{-1}$ )	$B$ (GPa)
0	...	...	14.649 <sup>20</sup>	2.6 <sup>20</sup>	1.83 <sup>34</sup>	90 <sup>21</sup>
1.1	0.12	0.01	14.64600(2)	2.8	1.60 <sup>34</sup>	...
5.5	0.65	0.02	14.64209(2)	3.4	1.70 <sup>34</sup>	...
12.6	0.94	0.32	14.66047(2)	4.2	1.79 <sup>34</sup>	...
17.3	0.96	0.60	14.68414(2)	5.1	1.85 <sup>34</sup>	...
21.9	0.96	0.89	14.70752(2)	6.2	1.76 <sup>34</sup>	...

<sup>a</sup>Na position in the  $\text{Si}_{20}$  cage is the 16c site at the cage center. The Na atom in the  $\text{Si}_{28}$  cage was refined using a fourfold split site which models the Na atom displaced from the center of the  $\text{Si}_{28}$  cage (32e position).<sup>16</sup> The reported  $\text{Si}_{28}$  cage occupancy is four times the occupancy of the 32e site.

larger, oversized  $\text{Si}_{28}$  cages for  $x < 8$ , whereas the sixteen smaller  $\text{Si}_{20}$  cages become significantly occupied only once the larger  $\text{Si}_{28}$  cages are near full occupation ( $x > 8$ ) (Table I). The non-monotonic response to filling is also reflected in the evolution of local Na-Si distances for the two cages, suggesting very different guest-framework interactions for the two cages.<sup>16,27,28</sup> The change in lattice parameter as a function of temperature for  $\text{Na}_x\text{Si}_{136}$ ,  $\Delta a(T) = a(T) - a(293 \text{ K})$ , is shown in Fig. 2(a). All compositions show positive thermal expansion, with  $a$  increasing nearly linearly with temperature in the measured temperature range. The linear coefficient of thermal expansion in the range of 273 K to 473 K [referenced to  $a_0 = a(293 \text{ K})$ ], calculated as  $\alpha = (1/a_0)(da/dT)$ , is shown in Fig. 2(b). In contrast to the non-monotonic response of  $a(293 \text{ K})$  to filling the Si framework cages,  $\alpha$  increases monotonically with  $x$ , from  $2.6 \times 10^{-6} \text{ K}^{-1}$  ( $x = 0$ ) to  $6.8 \times 10^{-6} \text{ K}^{-1}$  ( $x = 24$ ). The 150% increase in  $\alpha$  occurs only by filling the framework cages without changing the framework composition or symmetry: our refinements indicate that all framework sites are fully occupied by silicon and the structure maintains the  $Fd\bar{3}m$  symmetry for all samples at all temperatures.

To discern the underlying reason for the large increase in  $\alpha$  induced by filling the cages with Na, we turn to the Grüneisen expression for the linear coefficient of thermal expansion of a material in terms of its other thermodynamic properties<sup>29</sup>

$$\alpha = \frac{\gamma C_V}{3BV}, \quad (1)$$

where  $C_V$  is the sample heat capacity at constant volume (in J/K),  $V$  is the sample volume (so that  $c_V = C_V/V$  is the specific heat per unit volume), and  $B$  is the bulk modulus. The overall Grüneisen parameter  $\gamma$  is defined as a weighted average of the mode Grüneisen parameters,  $\gamma = \sum_i c_i \gamma_i / \sum_i c_i$ , where  $\gamma_i$  is the mode Grüneisen parameter for the  $i$ th phonon mode, and  $c_i$  is the contribution to the lattice specific heat from the  $i$ th phonon mode.<sup>30</sup> We first examine the influence of the guest content on the specific heat  $c_V$  of  $\text{Na}_x\text{Si}_{136}$ . It is well established that guest atoms in intermetallic clathrates

contribute low energy “rattle” modes to the phonon spectrum, due to the relatively weak bonding between the guest and the framework.<sup>13</sup> Low energy vibrations associated with the Na guests in  $\text{Na}_x\text{Si}_{136}$  have been clearly observed by inelastic neutron scattering,<sup>31,32</sup> consistent with the large and strongly temperature dependent atomic displacement parameters for Na guest atoms obtained from crystallographic refinements.<sup>32,33</sup> In addition, the Si framework modes are shifted to lower energy upon filling the cages.<sup>31,32</sup> Both of these effects tend to enhance the specific heat, especially at lower temperatures, but not to such an extent to produce a very large enhancement in the thermal expansion coefficient near room temperature and above. Indeed, the specific heat at constant pressure  $c_p$  ( $\approx c_V$  at 293 K) for a series of  $\text{Na}_x\text{Si}_{136}$  samples has recently been reported;<sup>34</sup> data for  $x = 0$  and  $x = 24$  are also available.<sup>20,23,24,33</sup> The values at 293 K are listed in Table I. In cases where data were unavailable for a given composition examined in the present work, the heat capacity values were interpolated using the two nearest Na contents for which  $c_p$  was measured. The experimental  $c_p$  values at 293 K are relatively similar for all compositions, i.e., all are within 20% of each other and do not show a significant monotonic increase with  $x$ .

We next evaluate the effect of guest content on the bulk modulus,  $B$ . The room temperature bulk modulus for  $\text{Si}_{136}$  was experimentally measured to be 90 GPa, about 8% smaller than  $\alpha\text{-Si}$ .<sup>21,22</sup> Although experimental data on the bulk modulus for  $\text{Na}_x\text{Si}_{136}$  have yet to be reported, we infer the likely effect of Na filling on  $B$  by examining available results from first principles calculations. Using density functional theory (DFT) in the local density approximation (LDA), Xue *et al.* calculated the (0 K) bulk modulus for  $\text{A}_8\text{Si}_{136}$  (A = guest atom), where the A atoms occupy only the large cages in  $\text{Si}_{136}$ , to be 84 GPa, 84 GPa, 83 GPa, and 83 GPa for A = Na, K, Rb, and Cs, respectively.<sup>35</sup> In comparison to the (0 K) bulk modulus of 81 GPa for  $\text{Si}_{136}$  also calculated within the LDA<sup>22</sup> (which we note is somewhat lower than the corresponding experimental value obtained at room temperature), the calculations for  $\text{A}_8\text{Si}_{136}$  suggested that filling the larger  $\text{Si}_{28}$  cages with guest atoms only slightly increases the bulk modulus, perhaps by a few percent at most. Although we are unaware of any first principles evaluation of the effect of filling the smaller  $\text{Si}_{20}$  cages on the bulk modulus of  $\text{A}_x\text{Si}_{136}$ , Zhang *et al.* calculated the bulk modulus for clathrate-I  $\text{Na}_8\text{Si}_{46}$  (in which Na occupies all of the  $\text{Si}_{24}$  and  $\text{Si}_{20}$  cages in a similarly 4-bonded  $\text{Si}_{46}$  framework) using LDA-DFT and found an increase of only a few percent over the value of  $B$  predicted for the  $\text{Si}_{46}$  allotrope.<sup>36</sup> Conversely, filling the cages of the clathrate-VIII  $\text{Si}_{46}$  with Na appears to slightly reduce the bulk modulus.<sup>37</sup> A crude estimation of the relative bulk moduli for  $\text{Si}_{136}$  and  $\text{Na}_{24}\text{Si}_{136}$  from their respective mass density  $\rho$  and speeds of sound  $v_s$  estimated from their respective Debye temperatures (where  $B = v_s^2 \rho$ ) suggests only a 1% increase in  $B$  upon filling all of the cages with Na. From all of these considerations, we infer that filling of the  $\text{Si}_{28}$  and  $\text{Si}_{20}$  cages likely has relatively little influence on the bulk modulus.

The 150% increase in the coefficient of thermal expansion in  $\text{Na}_x\text{Si}_{136}$  can thus only be associated with a large increase in the overall Grüneisen parameter [cf. Eq. (1)] as the cages in  $\text{Si}_{136}$  are occupied by Na. Using the experimental heat capacities, measured thermal expansion coefficients,

and a common value of  $B = 90$  GPa (experimental value for  $\text{Si}_{136}$ ), we estimated the overall Grüneisen parameter as a function of  $x$  using Eq. (1). The resulting values are plotted in Fig. 3. Also shown (dashed line) is the room temperature value of  $\gamma$  for  $\alpha\text{-Si}$ ,<sup>26</sup> which we note is quite similar to that for  $\text{Si}_{136}$ . The large increase in  $\gamma$  by more than a factor of 2 from  $x = 0$  to  $x = 24$  suggests that the Na atoms have a significant impact on the lattice dynamics in these materials, not only contributing new low energy vibrational modes but also significantly influencing the average character of the lattice vibrations as well.

Considering that the overall Grüneisen parameter is a weighted average of the mode Grüneisen parameters,  $\gamma = \sum_i c_i \gamma_i / \sum_i c_i$ , potential underlying sources of the observed large increase in the overall Grüneisen parameter upon filling the cages with Na can be suggested. New modes with significant anharmonicity, perhaps associated with the Na guests, may contribute large, positive mode Grüneisen parameters not present in  $\text{Si}_{136}$ . It is also conceivable that the other vibrational modes involving primarily the  $\text{Si}_{136}$  framework atoms become more anharmonic, either through hybridization with the guest atom modes or perhaps due to increased metallic character of the framework bonding due to charge transfer from Na to the silicon framework.<sup>27</sup> Another possible explanation for the large increase in  $\gamma$  is a suppressed influence of low energy phonon modes that have negative Grüneisen parameters, to which the low temperature NTE in  $\text{Si}_{136}$  has been attributed. It is conceivable that the presence of Na atoms inside the  $\text{Si}_{28}$  and  $\text{Si}_{20}$  cages may cause steric hindrance of transverse oscillations of Si framework atoms, perhaps strongly influencing those modes with  $\gamma_i < 0$  and reducing their influence on thermal expansion. A similar mechanism was recently observed in  $\text{ScF}_3$ , whereby intercalation of Li within voids of the  $\text{ScF}_3$  framework drastically reduces the amplitude of F atom oscillations, dramatically suppressing the negative thermal expansion in that material.<sup>38</sup> It is interesting to note that increasing the occupation of either the larger  $\text{Si}_{28}$  cage ( $x < 8$ ) or smaller  $\text{Si}_{20}$  cage ( $x > 8$ ) causes a comparable increase in the CTE. Experimental determination and/or first principles calculations of the mode Grüneisen parameters

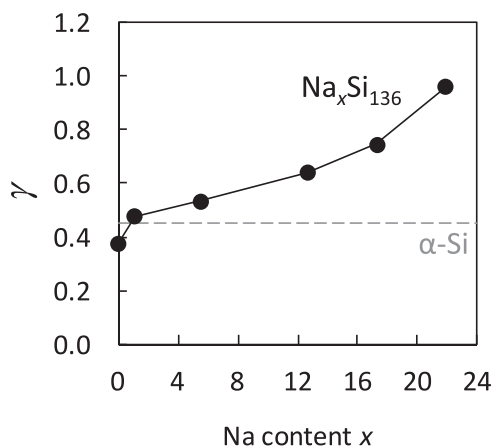


FIG. 3. Overall room temperature Grüneisen parameter of  $\text{Na}_x\text{Si}_{136}$  as a function of Na content,  $x$ . The dashed solid line indicates the overall Grüneisen parameter of  $\alpha\text{-Si}$  at room temperature.<sup>26</sup>

and/or atomic displacement patterns for  $\text{Na}_x\text{Si}_{136}$  as a function of Na content would be very informative, as such studies would likely allow the microscopic mechanism(s) underlying the large increase in the overall  $\gamma$  to be discerned.

In summary, filling the polyhedral voids of the clathrate-II  $\text{Si}_{136}$  framework with Na guest atoms dramatically increases the linear coefficient of thermal expansion. The increase in CTE is accompanied by an increase in the overall Grüneisen parameter by nearly a factor of 3, suggesting increased anharmonicity in the interatomic interactions and/or decreased influence of phonon modes that have negative mode Grüneisen parameters as the cages are filled with Na. The results highlight a potential approach to tuning thermal expansion by filling the intrinsic voids of inorganic materials that have open-framework crystal structures. Of particular interest is to understand how filling the voids of similar structures, e.g., other covalent frameworks that also display negative thermal expansion,<sup>39</sup> might be used to control the thermal expansion in such materials.

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