Discovering Large Isotropic Negative Thermal Expansion in Framework Compound AgB(CN)₄ via the Concept of Average Atomic Volume

Qilong Gao, Jiaqi Wang, Andrea Sanson, Qiang Sun, Erjun Liang,*, Xianran Xing, and Jun Chen*

ABSTRACT: Exploring isotropic negative thermal expansion (NTE) compounds is interesting, but remains challenging. Here, a new concept of “average atomic volume” is proposed to find new NTE open-framework materials. According to this guidance, two NTE compounds, AgB(CN)₄ and CuB(CN)₄, have been discovered, of which AgB(CN)₄ exhibits a large NTE over a wide temperature range (αᵥ = −40 × 10⁻⁶ K⁻¹, 100–600 K). The analysis by extended X-ray absorption fine structure spectroscopy and first-principles calculation indicate that (i) the NTE driving force comes from the transverse vibrations of bridge chain atoms of C and N, corresponding to the low-frequency phonon modes; and (ii) the same transverse vibration direction of C and N atoms is a key factor for the occurrence of strong NTE in AgB(CN)₄. The present concept of “average atomic volume” can be a simple parameter to explore new NTE compounds especially in those open-framework materials.

Negative thermal expansion (NTE) as an interesting behavior has promising applications for tuning the coefficient of thermal expansion (CTE).¹,² Taking into consideration the alleviation of thermal stress in composites, isotropic NTE compounds are the best choice, but are very rare. So far, some interesting isotropic NTE compounds have been found, such as electron-driven functional materials of magnetic transitions³,⁴ and electronic transitions⁵ and low-frequency phonon-driven framework materials of oxides,⁶,⁷ fluorides,⁸–¹⁰ cyanides,¹¹ Prussian blue analogues (PBAs),¹²,¹³ zeolites,¹⁴ and metal–organic frameworks (MOFs).¹⁵ It has been known that those phonon-driven NTE compounds commonly exhibit a wide NTE temperature range.¹⁶

In open-framework structures, the NTE mechanism has been widely considered based on the fact that low-frequency phonon modes result in negative Grüneisen parameters, and transverse vibrations of linking atoms result in lattice contraction.¹⁷ Even though we know the mechanism, it is not easy to design or explore new NTE compounds under its guidance. By the analysis of the available NTE open-framework materials, it is known that their structure exhibits some lattice structure flexibility, which also generally means that the more flexibility a structure has, the stronger the NTE that could occur. Hence, in order to explore potential NTE in the open-framework materials, we propose here a new concept of “average atomic volume (AAV)”, which is a simple parameter to indicate the average volume of atoms occupying a unit cell. The value of AAV is calculated via the equation AAV = V/(Z × N), where V is unit cell volume, Z is cell formula units, and N is the number of atoms in the chemical formula. The larger value of AAV means more flexibility of the structure and so, in principle, larger NTE. Similarly, a strict relationship between NTE and lattice parameter was evidenced in the cubic MZrF₆ and Sc₁₋ₓTiₓF₃ series,¹⁸ suggesting the reasonableness of the AAV concept introduced here.

As illustrated in Figure 1, we have plotted the CTE as a function of AAV in the isotropic open-framework materials.
including oxide, fluorides, cyanides, and Prussian blue analogues. One can clearly see that there seems to be a strong correlation between CTE and AAV. As the value of AAV increases, NTE takes place. It is interesting to note that there seems to be a critical point of AAV ($\sim 16$ Å$^3$) for the occurrence of NTE. As the value of AAV is larger than this critical point, NTE occurs for all types of systems shown in Figure 1. Otherwise, positive thermal expansion (PTE) occurs.

Inspired by the concept of AAV, we screened the possible compounds in the Inorganic Crystal Structure Database (ICSD). Fortunately, we have found an existing cubic PBA of AgB(CN)$_4$ reported in 2000. The AAV value of AgB(CN)$_4$ is 18.83 Å$^3$, which is much larger than the critical point of 16 Å$^3$, indicating the high probability of occurring NTE behavior. Hence, in this study, the crystal structure and thermal expansion of AgB(CN)$_4$ were investigated by synchrotron XRD (SXRD). Then, to confirm the NTE, a combined study was carried out by extended X-ray absorption fine structure (EXAFS) and first-principles calculations. Finally, with the help of the present new concept of AAV, we have found another new NTE cubic compound, CuB(CN)$_4$, thus confirming that the AAV parameter is really useful for the discovery of new framework NTE materials.

The sample of AgB(CN)$_4$ was prepared with KB(CN)$_4$ and AgNO$_3$ using the conventional co-precipitation method with the size of 100–200 nm (Figure S1). The FT-IR spectrum clearly shows the vibrations of $\nu_{BC}$ and $\nu_{CN}$ which is consistent with the previous results (Figure S2a). The XPS results indicate that Ag and B atoms are single valence state (Figure S2c,d). Interestingly, the TG–DSC curve suggests that the presence of AgB(CN)$_4$ merits a water-free behavior, which is very good for applications. It is known that the hygroscopic behavior is quite common in the open-framework NTE compounds such as most PBAs of YFe(CN)$_6$ and other oxides of Y$_2$Mo$_3$O$_{12}$. Moreover, AgB(CN)$_4$ exhibits a good thermal stability up to 600 K (Figure S2b).

The crystal structure is investigated by high-energy synchrotron XRD with the cubic space group $P4_3m$ (Figure 2a and Table S2), which is consistent with that previously reported. The structure of AgB(CN)$_4$ consists of AgN$_4$ and BC$_4$ tetrahedra via bridging CN units. The value of AAV of AgB(CN)$_4$ is calculated to be 18.83 Å$^3$. As shown in Figure 2b, it is interesting to observe that the present AgB(CN)$_4$ exhibits a large isotropic NTE behavior in a wide temperature range ($\alpha_v = -40 \times 10^{-6}$ K$^{-1}$, 100–600 K). The NTE behavior of AgB(CN)$_4$ is stronger than the most popular NTE materials ZrW$_2$O$_8$ and ScF$_3$ and stronger than most PBAs, such as GaFe(CN)$_6$, but smaller than (Zn,Cd)(CN)$_2$. Furthermore, the present AgB(CN)$_4$ shows a wide NTE range, which can be comparable to those in the electronic-driven functional...
materials. As shown in Figure 1, the present NTE AgB(CN)$_4$ follows the correlation between CTE and AAV. The AAV value of AgB(CN)$_4$ is 18.83 Å$^3$, which is much larger than the critical point of 16 Å$^3$ and that of the prototype ScF$_3$ and ZrW$_2$O$_8$. That is why AgB(CN)$_4$ shows a stronger NTE than ScF$_3$ and ZrW$_2$O$_8$. Furthermore, the relationship between CTE and AAV is more obvious in the same structure system of NTE materials, such as MIIPt(CN)$_6$ (MII = Ni or Cd) and M(CN)$_2$ (M = Zn or Cd).

Due to its sensitivity to the correlation of atomic motion, EXAFS spectroscopy allows us to extract the so-called "true" bonds length (i.e., the average of the atomic pair distance) between Ag and N atoms, which is different from the "apparent" bond length (i.e., the distance between the atomic average positions) extracted from SXRD. As shown in Figure 3a, an optical thermal expansion behavior of the "apparent" and the "true" Ag–N bond lengths appears in AgB(CN)$_4$. The "apparent" bond length of Ag–N displays strong NTE ($\alpha_l = -1.49 \times 10^{-5}$ K$^{-1}$), while the "true" bond length of Ag–N displays strong PTE ($\alpha_l = -4.4 \times 10^{-5}$ K$^{-1}$). The PTE of the "true" Ag–N bond length comes from the nature of the bond-bending effect. Based on the results of EXAFS and SXRD, the mean-square relative displacements (MSRDs) parallel and perpendicular to the Ag–N bond can be calculated to reveal the NTE mechanism (Figure 3b). Interestingly, the perpendicular MSRD of Ag–N atomic pairs are much larger than the parallel ones, which directly and clearly shows that the transverse thermal vibrations of N atoms are much larger than the longitudinal ones. The anisotropy ($\gamma = \text{MSRD}_\perp/\text{MSRD}_\parallel$) is large, about $\gamma = 20$ at high temperatures, similarly to the behavior of other NTE materials such as ScF$_3$ ($\gamma = 20$ for the Sc–F bond) and ZrW$_2$O$_8$ (about $\gamma = 29$ for the Zr–O bonds, about 35 for the W–O bonds). Accordingly, the NTE behavior of the "apparent" bond length of Ag–N derives from the transverse vibration effect.

The phonon dispersion curves of C and N atoms show that the vibrations of N atoms play a leading role below 400 cm$^{-1}$ (Figure 4a), and most vibrational modes in the low-frequency region have negative Grüneisen parameters (Figure 4b). These results indicate that the NTE of AgB(CN)$_4$ is mainly due to the contribution of low-frequency phonon modes. Here, all mode Grüneisen parameters, including the high-symmetry directions, have been calculated to weigh the NTE contribution of transverse vibrations of C and N atoms (Figure 4c). Whether along either of the high-symmetry directions, these phonon modes with the largest negative

![Figure 4](https://pubs.acs.org/jacs/2020/142/6937)

Figure 4. (a) Phonon dispersion curves and (b) frequency dependence of the mode Grüneisen parameters. (c) Mode Grüneisen parameters and (d) schematics of representative transverse vibrational modes at low frequencies. Arrows are proportional to the amplitude of the atomic motion.
Grüneisen parameter show the same vibration directions for both C and N atoms. Along the high-symmetry R point, it has the largest negative Grüneisen parameter at 46 cm⁻¹ (~15.3 cm⁻¹/Å³), compared to the opposite vibrational mode at 320 cm⁻¹, yielding only ~1 cm⁻¹/Å³. Therefore, it clearly indicates that the strong NTE of AgB(CN)₄ derives mainly from the same direction transverse thermal vibrations of C and N atoms.

Under the guidelines of the present proposed concept of AAV, we have also discovered another NTE compound, CuB(CN)₄, which locates at the boundary between NTE and PTE for the open-framework materials shown in Figure 1. CuB(CN)₄ is isostuctural with AgB(CN)₄ (space group: P43m). The AAV value of CuB(CN)₄ is 16 Å³, which is much lower than that of AgB(CN)₄. Accordingly, CuB(CN)₄ displays a much weakened NTE (αₜ = −3 × 10⁻⁶ K⁻¹, 100–400 K). Compared with all Zn(CN)₂-type compounds, the larger the value of AAV is, the stronger the NTE (Figure 1). AgB(CN)₄, as a new type of NTE compound, can be extended to other possible NTE compounds with a similar structure, such as AM(CN)₄ (A = Li, Na, K, Ag, Cu, etc.; M = B, Al, Ga, In, etc.). As for the development of NTE, the prototype NTE material of ZrW₂O₈ was first reported in 1959. However, its interesting NTE property obtained wide attention four decades later in 1996. In a future study, we can adopt the concept of AAV to reveal those possible NTE compounds that are hidden in the database, thus to accelerate the development of NTE compounds and their potential applications.

In summary, the concept of AAV is proposed to explore isotropic NTE in open-framework materials. A strong isotropic NTE has been found in AgB(CN)₄. The EXAFS analysis indicates that the transverse thermal vibrations of N atoms are much larger than the longitudinal ones. Combined with the results of DFT calculations, the low-frequency phonon modes of transverse vibrations of C and N atoms are the driving force for NTE. Especially, the same direction of transverse thermal vibrations of C and N atoms accounts for the strong NTE behavior. The present work not only reports the new isotropic NTE materials of AgB(CN)₄ and CuB(CN)₄ but also provides a simple way to research NTE in framework compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/ doi/10.1021/jacs.0c02188.

Experimental details, computational methods, and more experimental data (PDF)

AUTHOR INFORMATION

Corresponding Authors

Erjun Liang — International Laboratory for Quantum Functional Materials of Henan, School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450001, China; Email: ejliang@zzu.edu.cn

Jun Chen — Beijing Advanced Innovation Center for Materials Genome Engineering and School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, China; orcid.org/0000-0002-7330-8976; Email: junchen@ustb.edu.cn

Authors

Qilong Gao — International Laboratory for Quantum Functional Materials of Henan, School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450001, China; Beijing Advanced Innovation Center for Materials Genome Engineering and School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, China; orcid.org/0000-0002-8871-8329

Jiaqi Wang — International Laboratory for Quantum Functional Materials of Henan, School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450001, China

Andrea Sanson — Department of Physics and Astronomy, University of Padova, Padova 35131, Italy; orcid.org/0000-0003-3218-3553

Qiang Sun — International Laboratory for Quantum Functional Materials of Henan, School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450001, China

Xianran Xing — Beijing Advanced Innovation Center for Materials Genome Engineering and Institute of Solid State Chemistry, University of Science and Technology Beijing, Beijing 100083, China; orcid.org/0000-0003-0704-8886

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/jacs.0c02188

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21825102, 21905252, 11574276) and China Postdoctoral Science Foundation (2019M652558). Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE), Office of Science, by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. The SXRD experiments were performed at the BL02B2 and BL04B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; proposal nos. 2019A1167, 2019A1095, 2019A1340). We acknowledge the great help from the beamline scientists Dr. Shogo Kawaguchi and Dr. Koji Ohara (SPring-8). We thank the BL14W beamline at SSRF and the 1W1B beamline at BSRF for providing beam time. One of the authors, J.C., acknowledges the financial support of the University of Padova through the Visiting Scientist Program 2019.

REFERENCES


