SANDIA REPORT
SAND2019-10497
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Engineering Precisely Controlled Negative and Zero Thermal Expansion Behaviors in Metal-Organic Frameworks

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ABSTRACT

Positive thermal expansion can cause significant stress or even catastrophic device failure in applications where materials are placed in confined environments. At material interfaces such as coatings, thermal expansion effects can also lead to cracking and peeling behavior. The ability to impart controlled thermal expansion properties in an array of designs via additive manufacturing technologies would mitigate such problems and bring significant value to various materials science and engineering challenges. Negative thermal expansion materials are of interest for composite material applications whereby they can compensate for the behavior of a positive thermal expansion matrix. This Truman Fellowship LDRD research project presents complimentary experimental and molecular modeling results towards the fundamental understanding and development of metal-organic framework (MOF) materials with controlled thermal expansion properties. Design strategies for imparting precisely tailored negative, zero, and positive thermal expansion regimes in MOFs are studied and the implications of these design strategies for the use of MOFs as an emergent negative thermal expansion material class are examined. Challenges towards exploiting this nanoscale behavior at length scales relevant to composite material systems are introduced.

ACKNOWLEDGEMENTS

I will be forever grateful to the Truman Fellowship Selection Committee for providing me with the opportunity to pursue this research project. The unique opportunity to carry out this exciting scientific research with all of the resources and support that Sandia has to offer has been a truly rewarding experience. I would like to especially thank Yolanda Moreno for her endless assistance throughout my time as a Truman Fellow. It is hard to imagine a more supportive and stimulating scientific environment to carry out this research. I would also like to thank all of my colleagues and the individuals that have collaborated with me throughout this Fellowship, both internal and external to Sandia. Many of you appear as co-authors on the publications resulting from this LDRD, including especially fruitful collaborations with researchers at the Georgia Institute of Technology and the University of Amsterdam. I cannot express enough my gratitude for the significant role that you all played in shaping my educational experience and the success during my time at Sandia as a Truman Fellow.

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EXECUTIVE SUMMARY

Negative thermal expansion materials are of interest for an array of composite material applications whereby they can compensate for the behavior of a positive thermal expansion matrix. Three of the most significant research accomplishments of this project in terms of impact on Sandia's science, technology and engineering capabilities are the following:

(1) the first experimental proof-of-concept demonstration of design strategies for tailoring negative, zero, and positive thermal expansion regimes in metal-organic frameworks using rational structural design strategies. This thermal expansion control was achieved by independently varying the guest molecule, ligand, metal, and topological properties of structures. Insights into the origin of these behaviors were obtained through an analysis of synchrotron-radiation total scattering and diffraction experiments, as well as complementary molecular simulations.

(2) the development of a synthesis method for achieving precisely tailored thermal expansion control in metal-organic frameworks using a mixed-linker solid solution approach. Previously, there had been no reports where the thermal expansion of a metal-organic framework had been tuned continuously from negative to positive through the formation of single-phase solid solutions. We demonstrate that this is possible, and that the formation of mixed linker solid solutions is likely a general strategy for the control of thermal expansion in many metal-organic frameworks.

(3) the development of a novel computational method for enabling high fidelity thermal expansion predictions via a flexible force field parameterization scheme that involves fitting the classical model on the *ab initio* derived elastic constant tensor for the system.

We also provide perspective on the prospects of metal-organic frameworks as an emerging negative thermal expansion material class. The presentation of a selection guide (Figure 3-1) for crystalline, isotropic negative thermal expansion materials based on average coefficient of thermal expansion value reported over various temperature ranges should be useful to scientists and engineers looking to choose an appropriate negative thermal expansion material for a given application. Other application considerations, including the response of the metal-organic framework's thermal expansion to applied external pressure and the temperature dependency of its mechanical properties, are also discussed in publications resulting from this project.

Attempts were made to demonstrate that negative thermal expansion metal-organic frameworks can significantly outperform benchmark low coefficient of thermal expansion filler materials such as glass microbeads at reducing the bulk coefficient of thermal expansion of composite material systems. While this goal was not achieved in the timespan of this project, this is likely an engineering shortcoming as opposed to a fundamental limitation of metal-organic frameworks as a prospective negative thermal expansion material class.

ACRONYMS

Abbreviation	Definition
CTE	Coefficient of thermal expansion
MOF	Metal-organic framework
NTE	Negative thermal expansion
PTE	Positive thermal expansion
PXRD	Power X-ray diffraction
TGA-DSC	Thermogravimetry and differential scanning calorimetry
ZTE	Zero thermal expansion

1. INTRODUCTION

1.1. Background

Positive thermal expansion (PTE) is the norm in most materials, a behavior attributed to the increased anharmonicity of the interatomic force within a chemical bond as a function of temperature (Figure 1-1, left). Negative thermal expansion (NTE), however, has been observed in materials that include oxides, fluorides, cyanides, polymers, and carbon nanotubes.[1–5] The primary structural dynamics leading to NTE in crystals are shown in Figure 1-1, right. For a representative three-component system of components A-B-A, the average A-B distance will increase with temperature due to the standard positive thermal expansion behavior. However, if large enough in amplitude, transverse vibrations of component B can cause the average A---A distance to decrease (Figure 1-1a, right). Furthermore, these transverse vibrations can also lead to an additional mechanism in which concerted "rocking" (librational) motions between the A-B units occur to reduce their average distance (Figure 1-1b, right).

In 3D crystals, the quantized lattice vibrations of the system are described by its phonons.[6] In materials such as framework silicates and metal oxides, a rigid unit model has been proposed to describe the collective motions of the connected polyhedra building units in the systems.[7] In this model, it is assumed that the energy needed to distort the links between polyhedra is less than the energy needed to distort the polyhedra structures themselves. As a result, it is energetically favorable for the linked polyhedra within the structure to undergo transverse vibrations along with various twisting and tilting motions that lead to an overall shrinkage in the framework volume.[8] To account for systems where some internal polyhedra distortion can occur, a quasi-rigid unit model has also been proposed.[9]

A seminal discovery in the NTE field was that ZrW_2O_8[10] exhibits isotropic NTE ($\alpha_l = (1/l)\mathrm{d}l/\mathrm{d}T \approx -9$ ppm K^{-1}) over the 0.3 to 1050 K temperature range.[11] Since this finding, a number of experimental and theoretical studies have shed light on the vibrational modes leading to this behavior and their implications for the design of further NTE materials.[12,13] More recently, an increased interest has developed around tailoring thermal expansion via chemical modifications[14] and through the use of phase transitions with magnetic, ferroelectric, charge-transfer and metal-insulator origins[15] to achieve large-scale NTE. Outside of the materials science community, however, the most ubiquitous NTE substance is water. Water has an increasing density with temperature over the 0-4 °C range due to the increased entropy resulting from the breaking of its tetrahedral hydrogen bonding network.[16]

Figure 1-1. Left: Vibrational mechanism of PTE. Potential energy, U(r), as a function of interatomic distance, r, in a representative anharmonic system. Average interatomic distances, r_1 and r_2, are shown at two temperatures ($T_2 > T_1$). Right: Vibrational mechanisms of NTE. Schematic of the two primary mechanisms leading to NTE in solids: (a) transverse vibrational motions and (b) cooperative rocking (librational) motions. Black lines show actual bond lengths whereas dotted blue lines indicate the decreased perceived bond length.

Zeolites and metal-organic frameworks (MOFs) are material classes that have been predicted to exhibit widespread NTE,[17–21] due in part to their nanoporosity and flexible framework characteristics. MOFs, formed by the assembly of inorganic nodes and multitopic organic ligands,[22,23] are particularly intriguing as NTE materials because of the greater design flexibility they afford relative to zeolites. The organic constituents in MOFs also enable a larger degree of structural flexibility[24] which may further promote their potential for exhibiting large-scale NTE.

Previously, isotropic NTE had been experimentally reported in a limited number of frameworks, including in the well-studied HKUST-1 (Cu_3BTC, BTC = 1,3,5- benzenetricarboxylate)[25] and IRMOF-1 ($Zn_4O(BDC)_3$, BDC = benzene-1,4-dicarboxylate)[26] materials. Beyond computational studies on Zn_4O-based IRMOF variants,[18,19] the systematic structural engineering of MOFs as a NTE material class has not been well-explored. NTE in MOFs can also be accompanied by phase transitions, leading to discontinuities in their lattice parameters with temperature.[27] Controlled thermal expansion in the absence of such phase transitions, however, is critical to the utility of NTE materials in most applications where the PTE matrix will change dimensions in a relatively continuous fashion.

Positive thermal expansion can be problematic and lead to high-consequence mechanical failure modes in materials. Also, there are instances where highly controlled thermal expansion properties are needed to achieve temperature-independent responses or to match the CTE of two materials at an interface (see Figure 1-2). Negative thermal expansion materials can be incorporated into a PTE matrices to create ZTE or better match the CTE of two materials at an interface. More generally, a fundamental understanding of MOF thermal expansion is crucial to advancing their utility in a wide range of potential applications that include coated monoliths,[28] microcantilever sensors, and electronic devices.[29] In each of these scenarios, changes in temperature will arise, and a mismatch in the CTE of the MOF and its substrate material will produce residual stresses that can lead to cracking or peeling behavior or compromise the adhesion between the MOF and its interfaced layer.

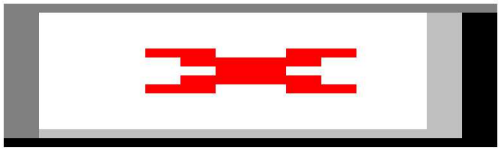

Figure 1-2. Illustrations of scenarios where a lack of thermal expansion control can lead to undesirable or unexpected consequences.

1.2. Approach

The overarching goal of this project (Figure 1-3) is to take the various building blocks present in metal-organic frameworks and, through an understanding of their nanomaterial design principles and physics, enable the synthesis of controlled NTE materials that can robustly compensate for PTE in different material designs. The progression of the primary experimental and molecular modelling techniques that were used towards addressing this challenge are shown in Figure 1-4. During the course of these investigations, additional insights into the temperature-dependent mechanical properties and response to pressure of NTE MOFs were also elucidated.

This project was formulated in response to the Department of Energy's strategic objective to "deliver the scientific discoveries … that transform our understanding of nature … and strengthen the connection between advances in fundamental science and technology innovation." The intended end result of this project is to help mature NTE materials as a viable technology by creating a more systematic understanding of their mechanism, as well as establishing viable methods to incorporate them into engineering materials.

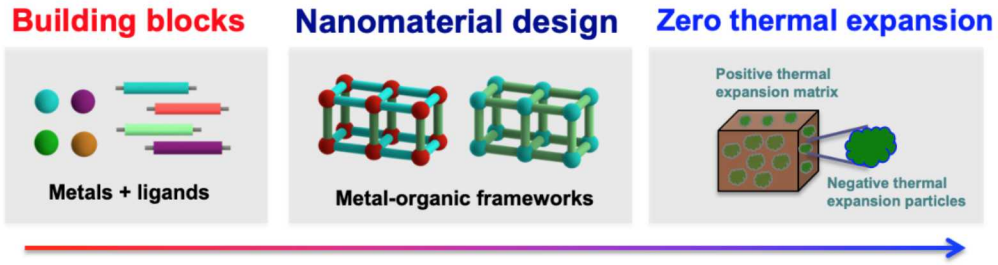

Figure 1-3. Schematic illustrations of the building blocks, constructed frameworks, and a potential application of metal-organic frameworks as negative thermal expansion materials.

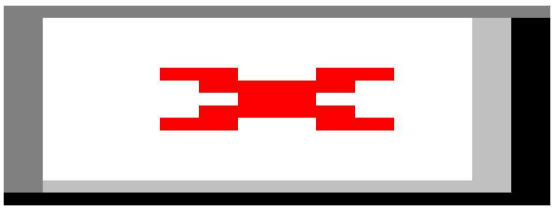

Figure 1-4. Progression of the primary characterization techniques used towards identifying and understanding candidate metal-organic framework structures for negative thermal expansion applications.

2. NEGATIVE THERMAL EXPANSION INVESTIGATIONS IN METAL-ORGANIC FRAMEWORKS

A complete list of the publications and submitted manuscripts resulting from this project can be found in Appendix A. This section provides a concise summary of the key findings from selected studies carried out throughout this project. Segments of the below text were reproduced from the corresponding peer-reviewed publications.

2.1. Negative thermal expansion design strategies

In this work, we provide the first experimental proof-of-concept demonstration of design strategies for tailoring negative, zero, and positive thermal expansion regimes in metal-organic frameworks using rational structural design strategies.[30] Thermal expansion control was achieved by independently varying the guest molecule, ligand, metal, and topological properties of structures. Insights into the origin of these behaviors were obtained through an analysis of synchrotron-radiation total scattering and diffraction experiments, as well as complementary molecular simulations.

Various design strategies for achieving thermal expansion control in MOFs were demonstrated using the structures shown in Figure 2-1. M_2L_2(DABCO) MOFs containing the 1,4-diazabicyclo[2,2,2]octane (DABCO) pillaring ligand (Figure 2-1a-c) enabled us to isolate the impact of the metal (M), topology, and steric bulk of functional groups on the linear dicarboxylate ligand (L) in the 2D M_2L_2 layered direction while keeping other structural features constant. IRMOF-1 (Figure 2-1d) is a prototypical MOF based on $Zn_4O(CO_2)_6$ clusters and benzene-1,4-dicarboxylate (BDC) ligands that has previously been shown to exhibit isotropic NTE.[18,19,26] Here, we experimentally show that the identity of its incorporated guest species can be used as a strategy to tune the magnitude of its NTE. Lastly, the dependence of thermal expansion on the thermal history and length of the dicarboxylate ligand in Zr_6O_8-based MOFs (Figure 2-1e) with minimal structural defects is presented.

The coefficients of thermal expansion in these systems were analyzed upon heating using variable-temperature synchrotron or laboratory powder diffraction experiments over a ~10 to 100 °C temperature range. This temperature range is relevant to NTE applications where MOFs would be most suitable from a mechanical and thermal properties standpoint, such as fillers in organic matrices (e.g. polymers, epoxies, and resins), and also yielded near-linear behavior that enabled comparison of average CTE values.

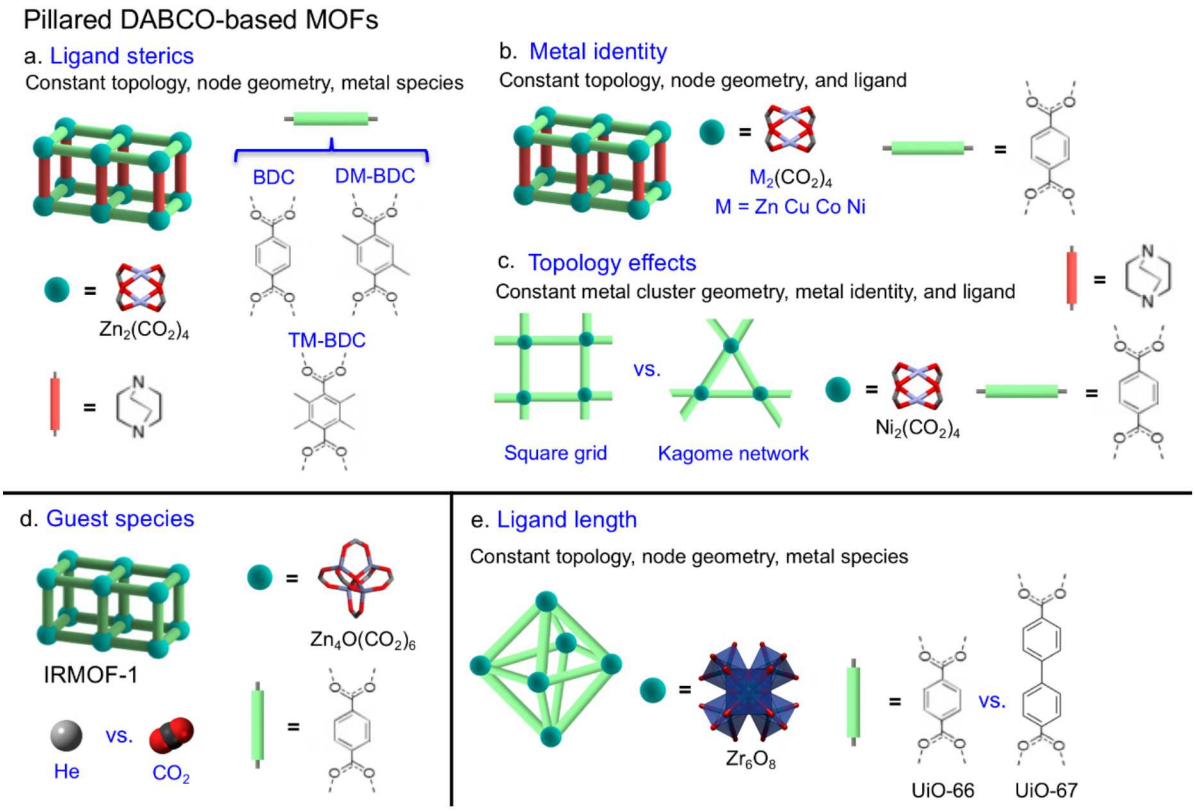

Figure 2-1. Overview of design strategies for thermal expansion control in nanoporous metal-organic frameworks. a. Modifying the steric bulk of the ligand. b. Changing the identity of the metal in the inorganic cluster. c. Altering the framework topology. d. Varying the guest species. e. Altering the length of the ligand.

2.2. Synthesis method for achieving precisely tailored thermal expansion

The development of a synthesis method for achieving precisely tailored thermal expansion control in MOFs using a mixed-linker solid solution approach is demonstrated. Previously, there had been no reports where the thermal expansion of a metal-organic framework had been tuned continuously from negative to positive through the formation of single-phase solid solutions.

In the system Zn-DMOF-TM_x, $Zn_2[(BDC)_{2-2x}(TM\text{-}bdc)_{2x}][dabco]$, the introduction of increasing amounts of TM-BDC, with four methyl groups decorating the benzene dicarboxylate linker, leads to a smooth transition from negative to positive thermal expansion in the a–b plane of this tetragonal material.[31] The temperature at which zero thermal expansion occurs evolves from ~186 K for the Zn-DMOF parent structure (x =0) to ~325 K for Zn-DMOF-TM (x = 1.0). The broader importance of these results is that the formation of mixed linker solid solutions is likely a general strategy for the control of thermal expansion in MOFs.

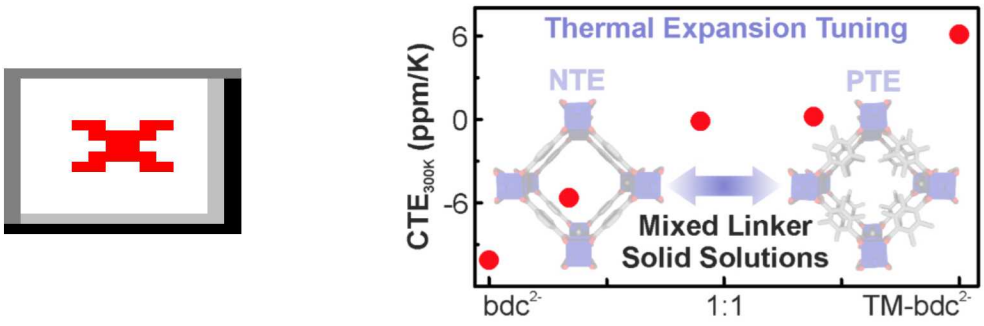

Figure 2-2. Left, Variation of the a/a_{300} lattice parameter for the Zn-DMOF-TMx samples as a function of temperature and composition. Right, comparison of CTE values for different Zn-DMOF-TM_x frameworks at 300 K.

2.3. Enabling high fidelity thermal expansion predictions

The development of a novel computational method for enabling high fidelity thermal expansion predictions is achieved via a flexible force field parameterization scheme that involves fitting the classical model on the *ab initio* derived elastic constant tensor for the system.[32]

Constructing functional forms and their corresponding force field parameters for the metal−linker interface of metal−organic frameworks is generally challenging. We propose fitting these parameters on the elastic tensor, computed from *ab initio* density functional theory calculations, using the approach shown in Figure 2-3. The advantage of this top-down approach is that it becomes evident if functional forms are missing when components of the elastic tensor are off. As a proof-of-concept, a new flexible force field for MIL-47(V) is derived. Negative thermal expansion is observed and framework flexibility has a negligible effect on adsorption and transport properties for small guest molecules. We believe that this force field parametrization approach can serve as a useful tool for developing accurate flexible force field models that capture the correct mechanical behavior of the full periodic structure

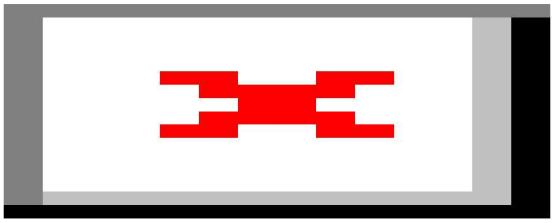

Figure 2-3. Elastic tensor-based force field parametrization approach: functional forms and corresponding parameters are changed or added until the classical force field elastic tensor agrees with the *ab initio* computed elastic tensor.

2.4. Elucidating variable-temperature mechanical properties

We report the first experimental study into the thermomechanical and viscoelastic properties of a MOF.[33] Nanoindentations show a decrease in the Young's modulus, consistent with classical molecular dynamics simulations, and hardness of HKUST-1 with increasing temperature over the 25−100 °C range (Figure 2-4). Variable-temperature dynamic mechanical analysis reveals significant creep behavior, with a reduction of 56% and 88% of the hardness over 10 min at 25 and 100 °C, respectively. This result suggests that, despite the increased density that results from increasing temperature in the negative thermal expansion MOF, the thermally induced softening due to vibrational and entropic contributions plays a more dominant role in dictating the material's temperature-dependent mechanical behavior.

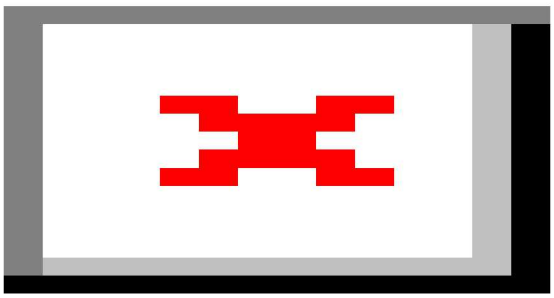

Figure 2-4. (a) Building units of HKUST-1 and ball-and-stick model of the unit cell along the ⟨100⟩ direction. Optical images of a (b) preactivated and (c) *in situ* activated HKUST-1 crystal facet with residual indents. (d) AFM images of representative residual indents (scan size: 10 × 10 μm).

3. PERSPECTIVES ON MOFS AS AN EMERGENT NEGATIVE THERMAL EXPANSION MATERIAL CLASS

One key question that this research project set out to address was, for a given temperature range, what sets of NTE materials can be considered as fillers to achieve some desired thermal expansion characteristic in a composite material system. As discussed in our work,[30] an ideal NTE material for composite material applications will have a large magnitude of NTE in order to minimize the amount of material needed to achieve the desired CTE reduction. Furthermore, in single phase polycrystalline materials such as ceramics, anisotropic thermal expansion can be problematic and lead to internal microcracking and increased stress.[34] Figure 3-1 provides a selection guide for isotropic NTE materials based on average CTE values reported for selected materials over various temperature ranges. The highest magnitude isotropic NTE materials include various Prussian blue analogs, metal cyanides and metal fluorides. Depending on the target application, MOFs can provide advantages over traditional material classes that include an extended range over which NTE is exhibited, improved chemical, mechanical, and thermal stability properties[35] and, due to their porosity, the exploitation of guest environment as a thermal expansion control strategy. On the other hand, while a lesser magnitude of NTE has been observed in material families that encompass zirconium vanadates, zirconium tungstates, and various metal oxides, their chemical and thermal stability limits can far exceed those present in MOFs. Furthermore, one should consider the compatibility between the mechanical properties, such as bulk modulus and hardness, of the NTE material and its PTE matrix. In this regard, MOFs are likely most suitable for matrices that include foams, polymers, epoxies and resins.[24]

Unique attributes of MOFs that make them promising as an emergent NTE material class are their immense degree of structural tunability[36] and the intriguing mechanical properties endowed by their hybrid organic-inorganic chemistry.[37] The mechanical properties of MOFs bode well from an NTE standpoint. Given that $\alpha_V = (1/V)(\partial V/\partial T)_P$, thermodynamics and the Maxwell relations show that $\alpha_V = 1/B_T(\partial S/\partial V)_T$ (where $B_T = -V(\partial P/\partial V)_T$), suggesting that a material with a high magnitude of NTE should also be relatively soft. In the context of other NTE materials, MOFs are promising, with B_T values from diamond anvil cell experiments and theoretical calculations in the range of low tens of GPa.[24,37] While NTE is anticipated to be more pervasive in MOFs than in many other material classes, it is notably absent in prototypical materials such as the ZIF-8 ($Zn(MeIM)_2$, MeIM = 2-methylimidazolate) framework,[38] in which we observe PTE (α_V = 19.6(9) ppm/K, Figure S34) that is consistent with previous computational predictions.[39]

The node distortion behavior of Zr_6O_8-based MOFs also suggests unique and exciting prospects for robustly compensating for the glass transition exhibited in amorphous and semi-crystalline materials that progress from a relatively brittle to a more rubbery state upon heating. The glass transition in polymers often leads to a relatively large (~3-5x of the original value) increase in the CTE upon heating and can occur at temperatures similar to where node chemistry-induced contractions occur in Zr_6O_8-based MOFs. We find that the temperature at which these contractions occur to be structure-dependent for UiO-66 and UiO-67, suggesting that design strategies for tailoring these contractions towards a desired temperature for targeted epoxies or polymer matrices can be employed.

Before becoming useful in composite material applications, studies into how the nanoscale (crystallographic) NTE found in MOFs translate to a CTE reduction at the macroscopic (bulk)

scale must be performed. This requires thermomechanical analysis techniques for studying the change in length of a bulk specimen to capture important effects not evident from diffraction, such as changes to microstructure. Such characterizations have been performed on the well-studied ZrW_2O_8 material[40] and have shed light on the importance of considerations that include particle dispersion, particle size, and appropriate surface interactions to promote adhesion between the NTE particle and its matrix. For MOFs, careful attention should also be placed on the effect of adsorbed guest species and whether confinement in the composite system gives rise to pressure-induced phase transitions.[41]

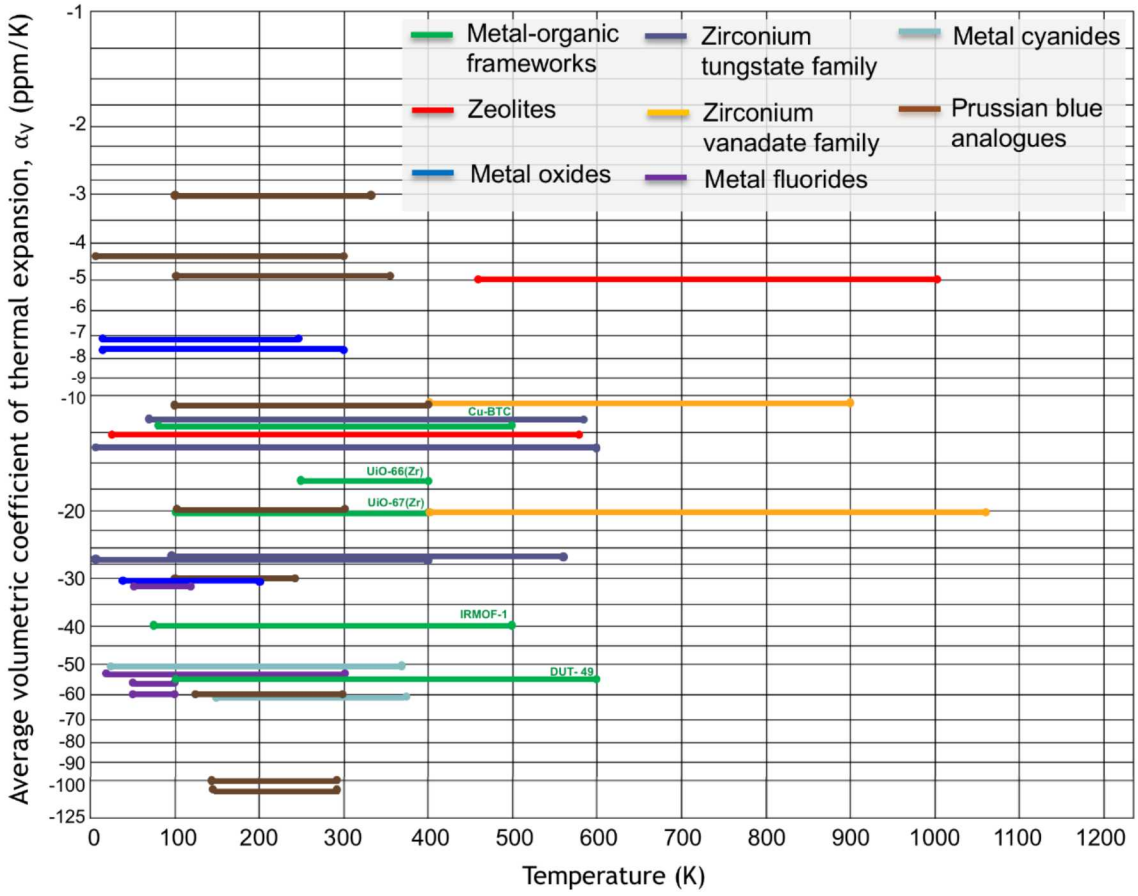

Figure 3-1. Selection guide for isotropic negative thermal expansion crystalline materials. Average experimental volumetric CTE values reported for selected materials in various negative thermal expansion material classes. Values for MOFs, zeolites, metal cyanides, Prussian blue analogues and zirconium tungstate and vanadate families values are based on literature in ref. 12. DUT-49 value obtained from ref. 42. Selected metal fluoride values were taken from ref. 43. UiO-66(Zr) and UiO-67(Zr) values from this work are for the frameworks having undergone a 95 °C heat pre-treatment.

4. RECOMMENDED FUTURE WORK

Attempts were made to demonstrate that negative thermal expansion metal-organic frameworks can significantly outperform benchmark low coefficient of thermal expansion fillers such as glass microbeads at reducing the bulk coefficient of thermal expansion of composite material systems. While this goal was not achieved in the timespan of this project (see experiments in Appendix B), this appears to be an engineering shortcoming as opposed to a fundamental limitation of metal-organic frameworks as a prospective negative thermal expansion material class.

The material that was selected for these studies was the MOF termed HKUST-1 or Cu-BTC. To avoid synthesizing the large quantities of this material that would needed for these composite material studies, the bulk material was purchased from Sigma Aldrich under the commercial name Basolite C300. This material exhibits isotropic NTE with an estimated volumetric CTE of ~ 40 ppm/K[25] and a D50 particle size distribution of ~15 microns. Its magnitude of NTE, combined with its reasonable chemical stability and relatively cheap cost to purchase at the gram-scale made it a suitable candidate for these investigations. The benchmark low CTE fillers were glass bubbles consisting of high-strength, hollow soda-lime-borosilicate glass microspheres with thin walls and characteristics that include an estimated volumetric CTE of ~ 10 ppm/K, roughly twice the density as the HKUST-1 MOF, and a similar average particle size distribution as the MOF. It was first confirmed using diffraction (Figure 4-1, left) and thermomechanical analysis (Figure 4-1, right) that the previously reported NTE in the HKUST material at the crystallographic (nano-)scale also translated to the particle (micron-)scale.

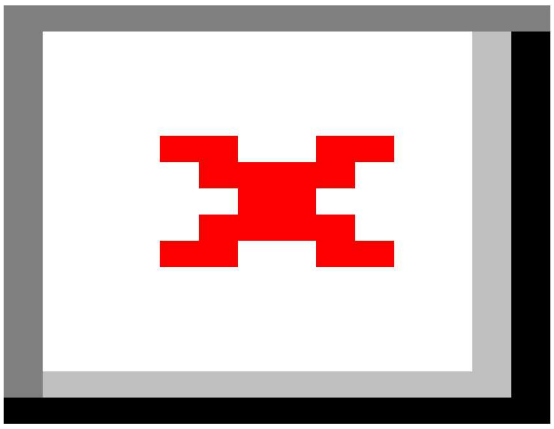

Figure 4-1. Characterization of the thermal expansion properties of the MOF HKUST-1 at the (left) nanoscale using variable temperature diffraction analysis and (right) particle length scale using thermomechanical analysis.

A photopolymer resin matrix system was selected, with assistance from Sandia staff members Greg O'Bryan and Adriana Pavia (Materials Chemistry), as a proof-of-concept proxy system for potential materials used in photolithography additive manufacturing processes. Details on the formulation and their thermal expansion results are given in Appendix B. A similar design experiments, performed on thermoset epoxy system, was also performed in collaboration with Brad Jones (Organic Materials Science). The thermomechanical analysis results suggest that the inability of the NTE MOF to outperform the benchmark glass bead material at reducing the CTE of the composite system is primarily due to poor surface adhesion as opposed to poor matrix dispersion, as indicated by comparison of particle distributions in SEM cross section images of the systems. Further investigations into the degree of chemical crosslinking, nature of the MOF-matrix adhesion, and possibilities for alternative epoxy and resin matrices are recommended. Alternatively, other NTE MOFs with tailored surface chemistry characteristics could be chosen, or the surface chemistry of the existing MOF could be modified using previously developed crystal procedures.[44] From an applications standpoint, optimal mechanical properties and facile incorporation with additive manufacturing material feeds is expected when the particle sizes are as small and monodisperse as possible.

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APPENDIX A. LIST OF PUBLICATIONS

1. Heinen, Burtch, Walton, Dubbeldam, "Flexible force field parameterization through fitting on the ab initio derived elastic tensor," *Journal of Chemical Theory and Computation*, 2017, 13 (8), 3722.

2. Stassen, Burtch, Talin, Falcaro, Allendorf, Ameloot. "An updated roadmap for the integration of metal-organic frameworks with electronic devices and chemical sensors," *Chemical Society Reviews*, 2017, 46 (11), 3185.

3. Burtch, Heinen, Bennett, Dubbeldam, Allendorf, "Mechanical properties in metal-organic frameworks: emerging opportunities and challenges for device functionality and technological applications*," Advanced Materials*, 2018, 30 (37), 1704124

4. Heinen, Ready, Bennett, Dubbeldam, Friddle, Burtch, "Elucidating the variable-temperature mechanical properties of a negative thermal expansion metal-organic framework," *ACS Applied Materials & Interfaces*, 2018, 10 (25), 21079.

5. Baxter, Schneemann, Ready, Wijeratne, Wilkinson, Burtch, "Tuning Thermal Expansion in Metal-Organic Frameworks using a Mixed Linker Solid Solution Approach," *Journal of the American Chemical Society*, 2019 (DOI: 10.1021/jacs.9b06109).

6. Burtch, Baxter, Heinen, Bird, Schneemann, Dubbeldam, Wilkinson, "Negative thermal expansion design strategies in a diverse series of metal-organic frameworks," under revision in *Advanced Functional Materials*.

7. Baxter, Schneemann, Ready, Wilkinson, Burtch,* "Reversible High-Pressure Amorphization and Pressure-Dependent Thermal Expansion Behavior of a Guest-Filled MOF-5 Framework." Submitted.

These findings also led to the filing of a non-provisional patent for the use of MOFs as NTE materials in additive manufacturing technologies (Burtch. Method for Tuning Thermal Expansion in an Additive Manufacturing Feedstock Material. U.S. Patent Serial No. 15/717,265 filed Sept. 27, 2017).

APPENDIX B. COMPOSITE MATERIAL STUDIES

Procedure. A UV-activated resin was mixed with a photo initiator solution and loaded with either Glass Micro Balloons (GMB) or the MOF HKUST-1 (Basolite C300), according to the following procedure

Bisphenol-A glycerolate dimethacrylate was thawed after removing from a fridge. 1.73g was added to a centrifuge dish and heated in an oven at 35ºC for a few minutes to allow the chemical to settle

A photo initiator solution was created by adding 10.50 mg methyl piperidine and 511 mg camphorquinone to 4 mL dry THF

60 μL of the photo initiator solution was added by Eppendorf pipette to the BisGMA and hand mixed, heated, and centrifuged for 60 seconds

The required volume of GMB or MOF was then added to achieve a volume loading of 0%, 10%, 20%, 30%, or 40%, based off calculations using the densities of the fillers (1.161 g/mL BisGMA, 0.607 g/mL GMB, and 0.35 g/mL MOF)

Each mixture was hand mixed, heated, centrifuged for 60 seconds, heated, and hand mixed again in order to ensure thorough mixing of the filler. Centrifuging was tested at various rpms and with or without vacuum, but neither had a noticeable effect on the filler dispersion. Due to the viscosity of the BisGMA, centrifugation did not seem to visually improve the filler dispersion but was still performed for all samples for consistency.

Next, molds were clamped in place and the cylindrical openings were sprayed with non-stick spray. Mixtures were scooped into the molds while warm. Attempts were made to avoid air bubbles and to ensure a flat surface by scraping the top of the mold with a spatula. Molds were then placed in the oven again at 35ºC for a few minutes to flatten and then placed into the UV chamber to cure. Cure times varied depending on filler and vol% loading, but attempts were made to reach consistent extents of curing at the cores of the samples. The GMB and MOF samples were subjected to thermomechanical analysis (TMA), with repeats of the results for the 3rd heating cycle shown below.

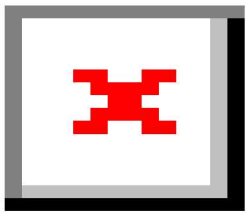

Figure 4-2. Images of cured MOF composite material samples ranging from 10 to 40% loading by volume, from left to right.

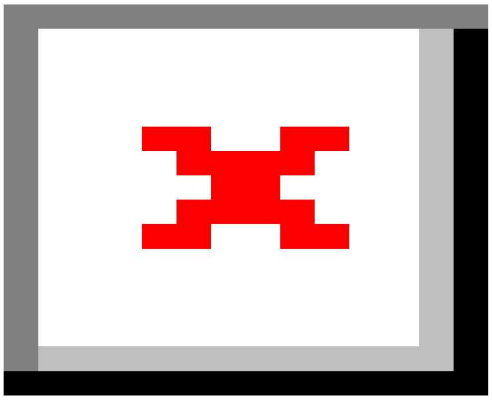

Figure 4-3. CTE values derived from the 3rd Heating Cycle of the composite materials containing GMB.

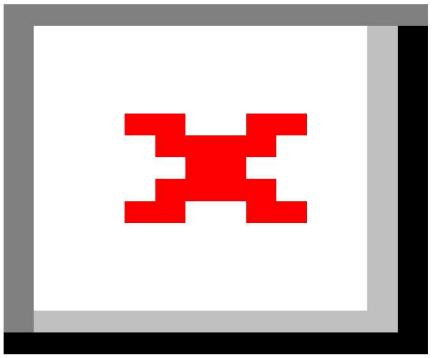

Figure 4-4. CTE values derived from the 3rd Heating Cycle of the composite materials containing the HKUST-1 MOF.

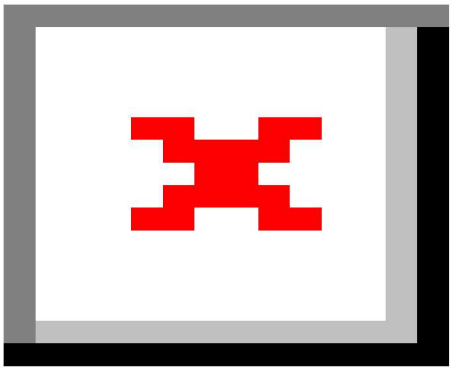

Figure 4-5. SEM images of the MOF composite at 30% volume loading

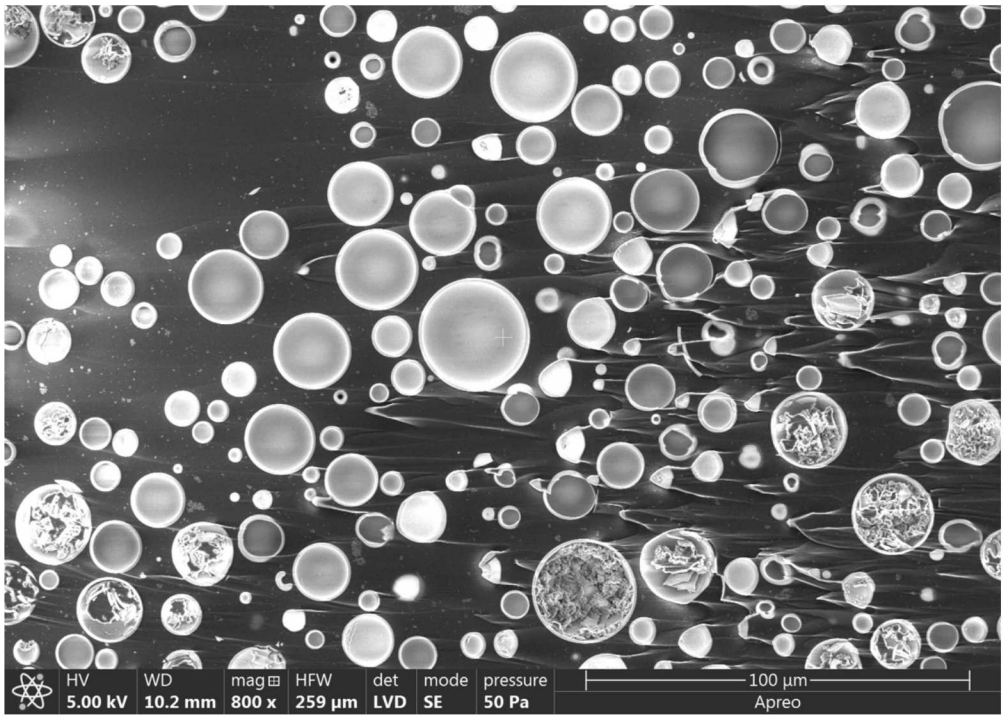

Figure 4-6. SEM images of the GMB composite at 40% volume loading

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