

Tunable Thermal Expansion in Metal-Organic Frameworks Through a Mixed Linker Solid Solutions Approach

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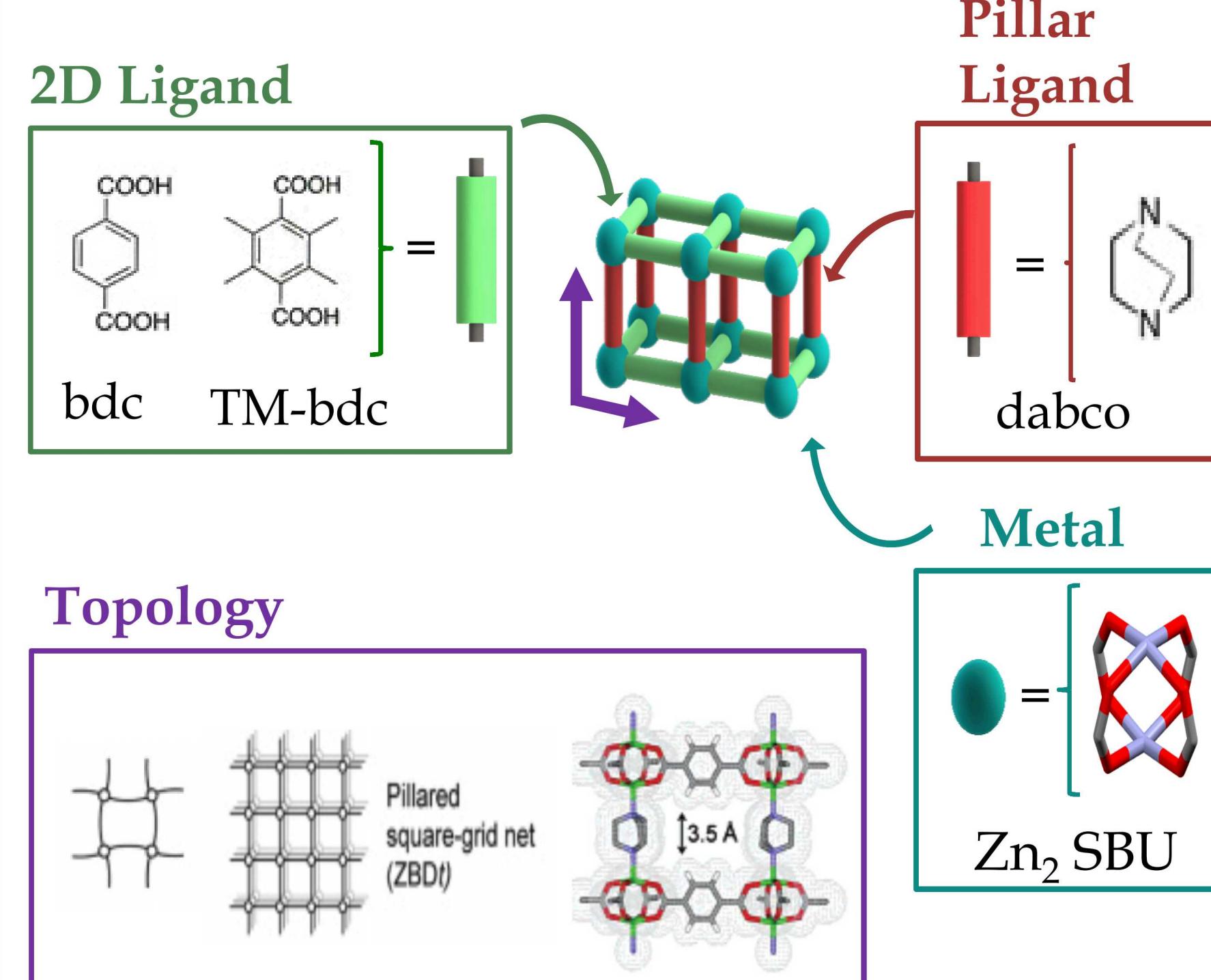
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Introduction

Metal-organic frameworks (MOFs) are crystalline, nanoporous materials with exceptionally high surface areas and chemically tunable structures. The structure-property relationship is explored by varying 2D ligands, pillar ligands, metals, and topology.

Negative thermal expansion (NTE) materials contract with increases in temperature. However, existing NTE materials are limited by tunability.

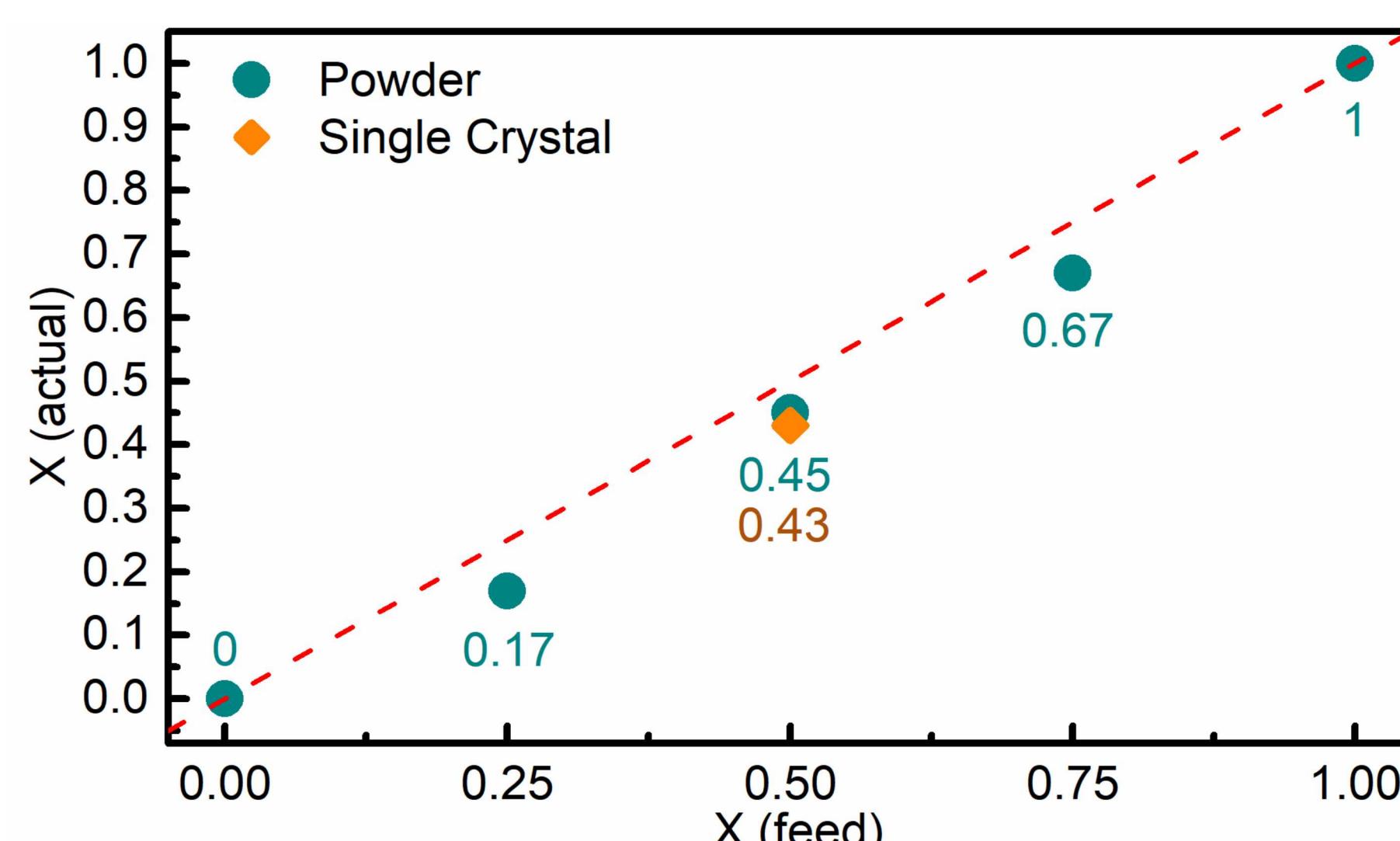
MOFs are desirable candidates for important technological applications involving thermal expansion composites as well as stand-alone zero thermal expansion (ZTE) materials; however, studies pertaining to tunable thermal expansion from negative to positive in MOFs are scarce.



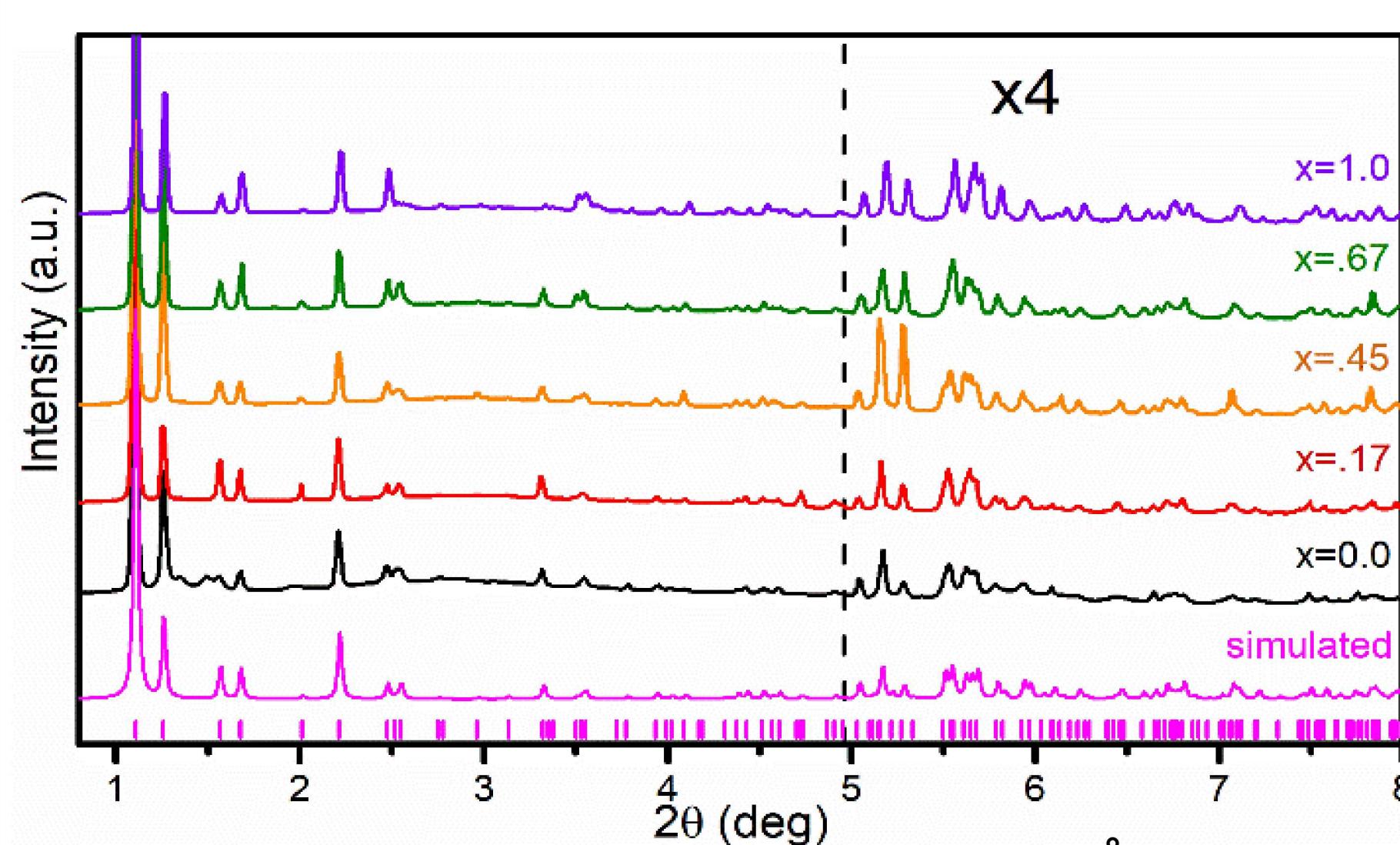
Tunable thermal expansion in Zn-DMOF-TM_x [Zn(bdc)_{2-2x}(TM-bdc)_{2x}(dabco); bdc²⁻ = 1,4-benzenedicarboxylate; TM-bdc²⁻ = 2,3,5,6-tetramethyl-1,4-benzenedicarboxylate; dabco = 1,4-diazabicyclo[2.2.2]octane], which comprises the previously reported parent structures Zn-DMOF and Zn-DMOF-TM, have been studied by varying the organic linker compositions with x = 0.0, 0.17, 0.45, 0.67, and 1.0.

$$x = [\text{TM-bdc}^{2-}] / ([\text{TM-bdc}^{2-}] + [\text{bdc}^{2-}])$$

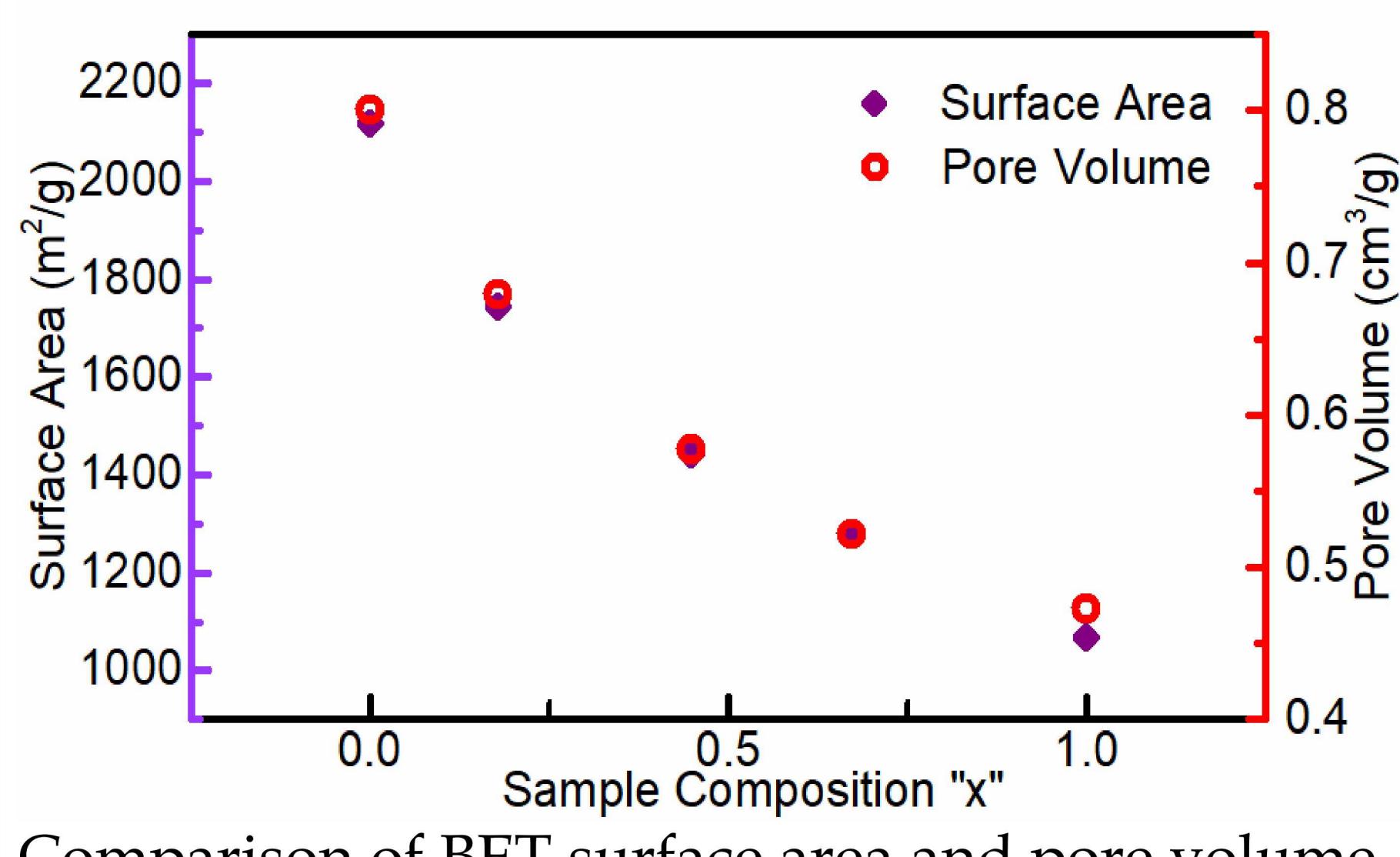
Results



A comparison of the TM-bdc₂ fraction in the syntheses (feed) with that incorporated into the prepared Zn-DMOF-TM_x samples (actual). Red dashed line - Exact equivalence between the fraction used in the syntheses and that incorporated into the samples.

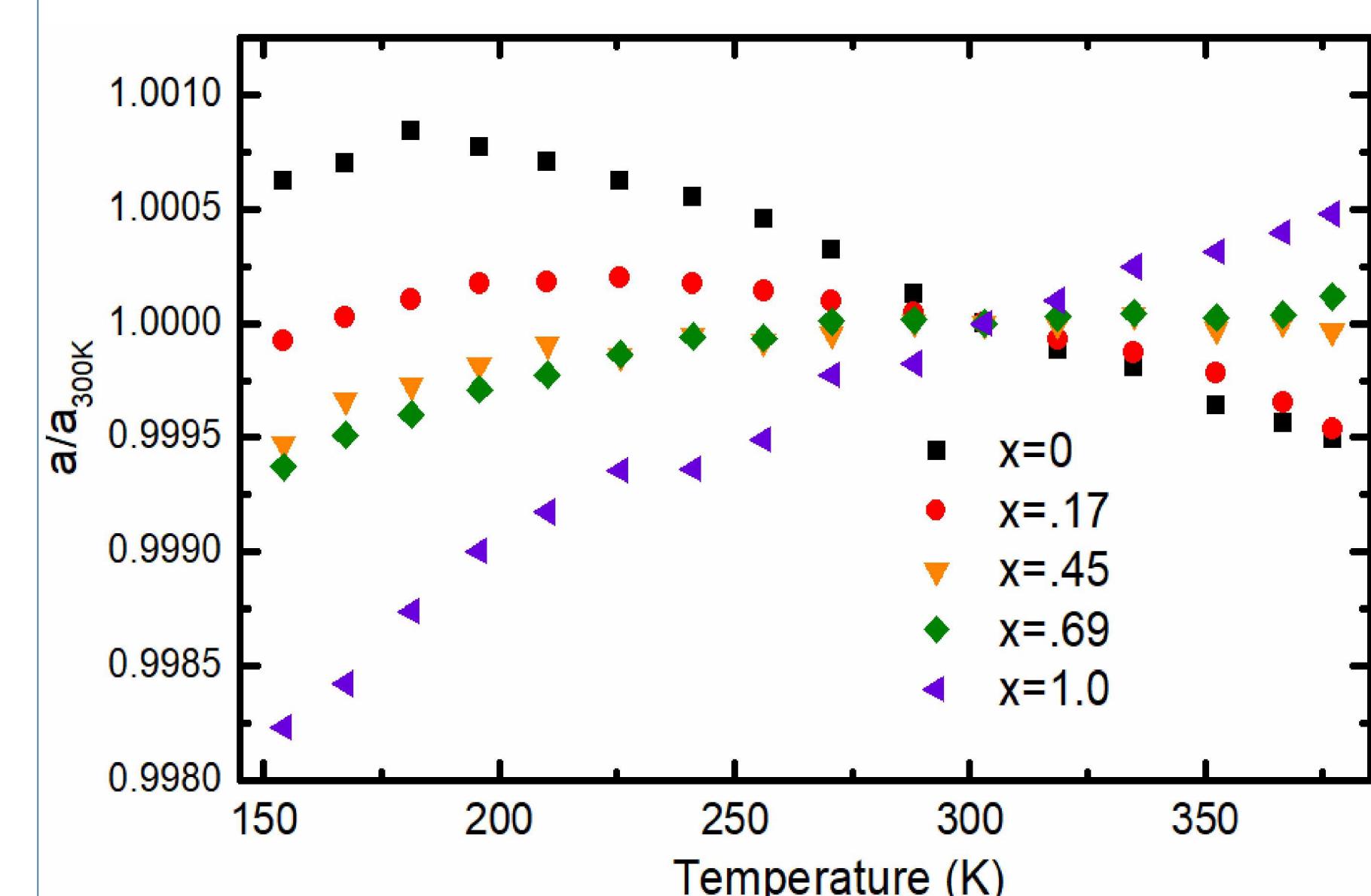


Synchrotron XRD patterns ($\lambda = 0.2113 \text{ \AA}$) collected at room temperature for the Zn-DMOF-TM_x samples. Magenta tick marks at the bottom of the plot indicate the expected peak positions for the $P4/mmm$ phase simulated for the parent Zn-DMOF structure.



Comparison of BET surface area and pore volume.

Results (cont.)



Variation of a/a_{300} for the Zn-DMOF-TM_x samples as a function of temperature and composition.

Summary and Outlook

- Solvothermal synthesis of single phase mixed linker Zn-DMOF-TM_x ($x = 0.0, 0.17, 0.45, 0.67$, and 1.0) solid solutions.
- A decrease in both pore volume and BET surface area with increasing incorporation of the bulkier TM-bdc²⁻ ligand.
- Prepared compositions crystallize in the tetragonal space group $P4/mmm$ at room temperature.
- Thermal expansion in the a-b plane changes predominantly from negative to positive for $x=0$ to $x=1$.

This high level of tunability for the Zn-DMOF-TM_x system indicates that the systematic substitution of functionalized ligands into other MOF frameworks will provide access to many different families of controlled thermal expansion materials.

Acknowledgements

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References

Burtch, N. C.; Walton, K. S., Modulating Adsorption and Stability Properties in Pillared Metal-Organic Frameworks: A Model System for Understanding Ligand Effects. *Accounts of Chemical Research* 2015, 48 (11), 2850-2857.