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

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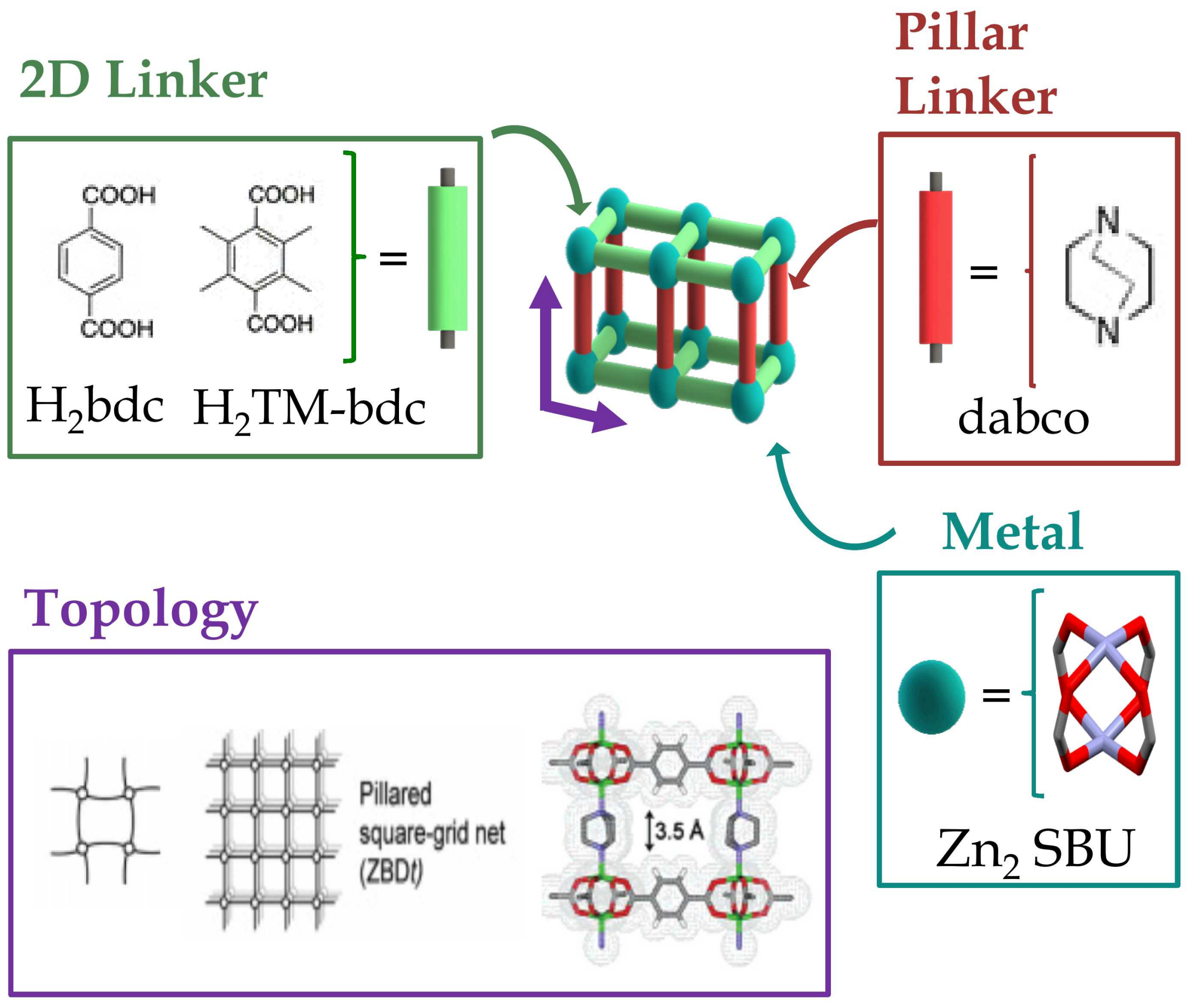
Introduction

Metal-organic frameworks (MOFs) are crystalline, nanoporous materials with exceptionally high surface areas and chemically tunable structures. The structure-property relationship has been explored by varying 2D linkers, pillar linkers, metals, and topology.[1]

Negative thermal expansion (NTE) materials contract with increases in temperature. However, existing NTE materials have only limited 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.



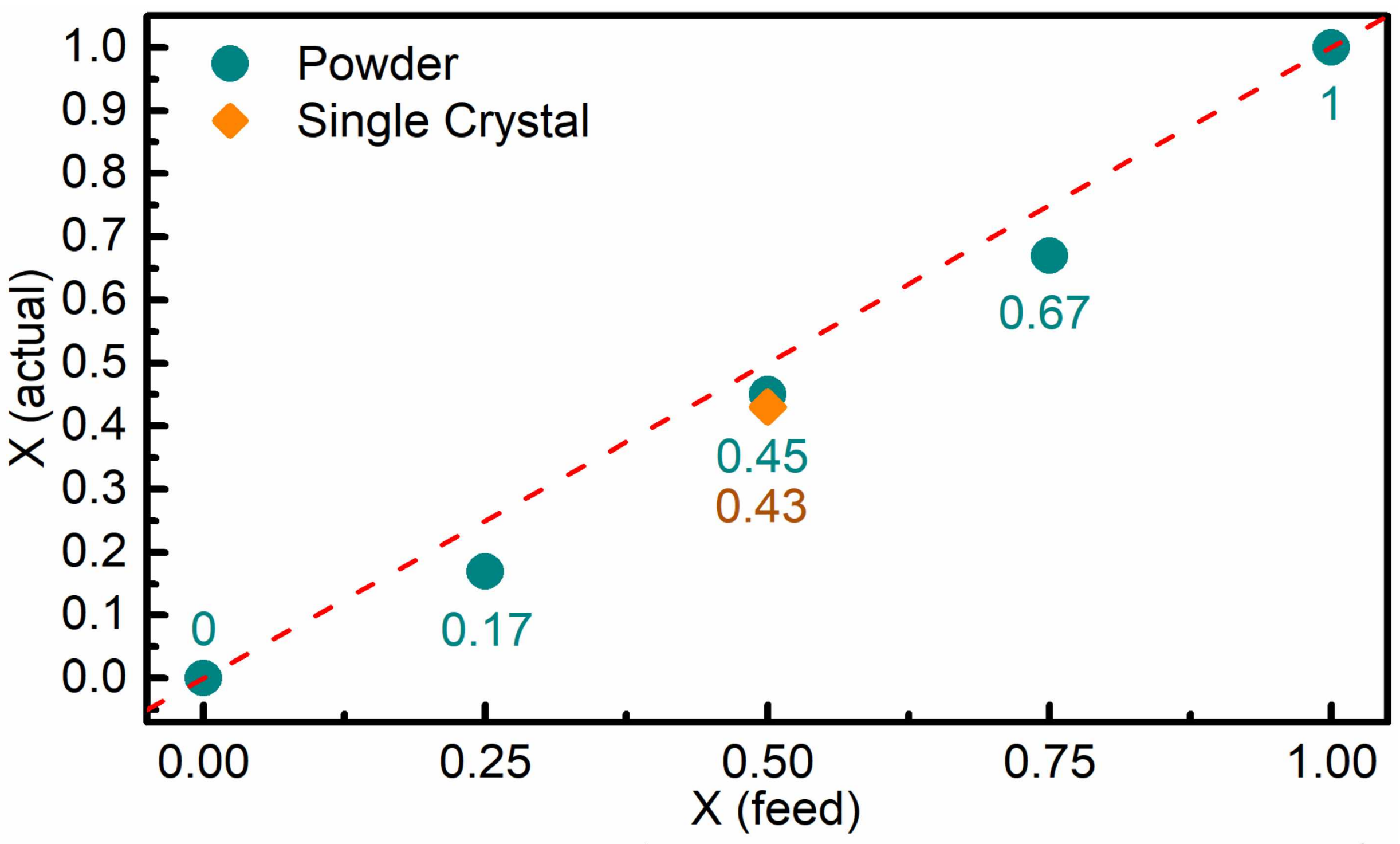
bdc^{2-} = 1,4-benzenedicarboxylate, $TM\text{-}bdc^{2-}$ = 2,3,5,6-tetramethyl-1,4benzenedicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane.

In this study, we report the preparation of $Zn_2(bdc)_{2-2x}(TM\text{-}bdc)_{2x}(dabco)$ (**Zn-DMOF-TM$_x$**) solid solutions (where x = 0.0, 0.17, 0.45, 0.67, and 1.0), and show that the TM-bdc/bdc ratio has a marked effect on the thermal expansion properties of the framework.

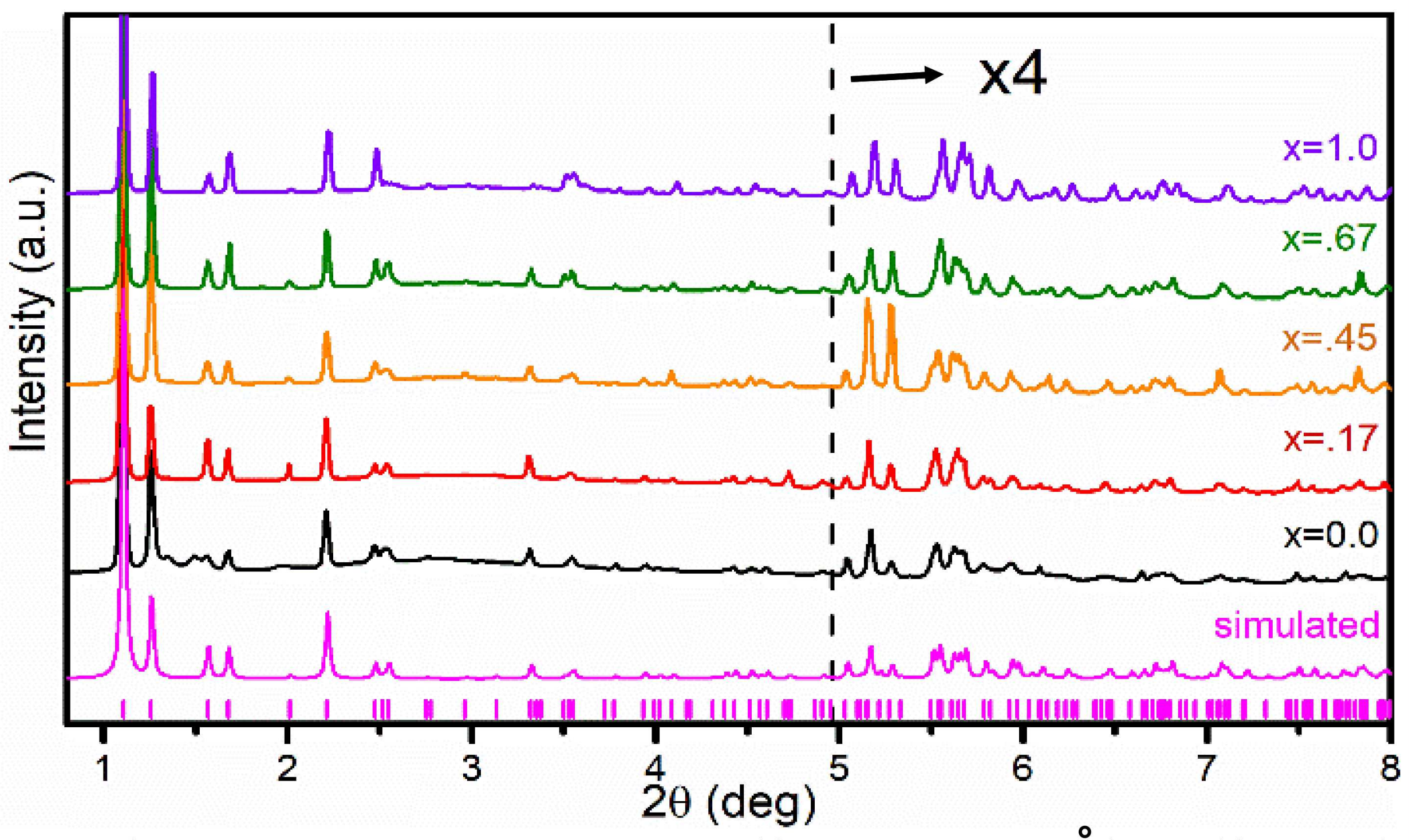
$x = [TM\text{-}bdc^{2-}] / ([TM\text{-}bdc^{2-}] + [bdc^{2-}])$

Results

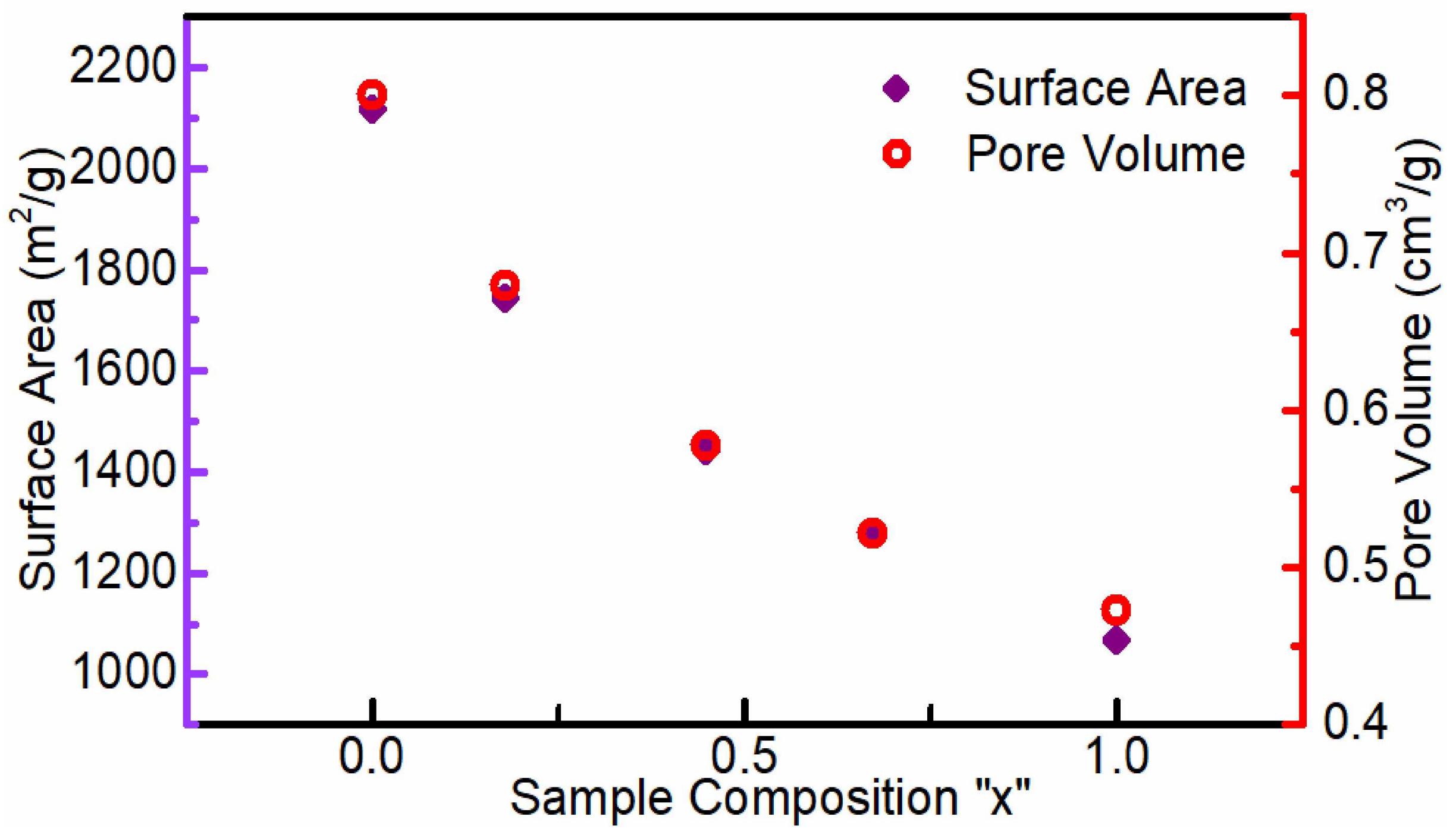
Composition, Sample Purity, and Porosity



A comparison using ^1H NMR of the $TM\text{-}bdc^{2-}$ fraction in the syntheses (feed) with that incorporated into the prepared **Zn-DMOF-TM$_x$** samples (actual) indicate that the ratio of linker units incorporated into the MOF is close to that used in the syntheses and that the ratio incorporated into a single crystal is close to that of bulk powder made under the same conditions.



Synchrotron XRD patterns (λ = 0.2113 Å) collected at room temperature for the **Zn-DMOF-TM$_x$** samples. Magenta tick marks at the bottom of the plot indicate the expected reflection positions for the *P*4/*mmm* phase simulated for the parent **Zn-DMOF** structure.

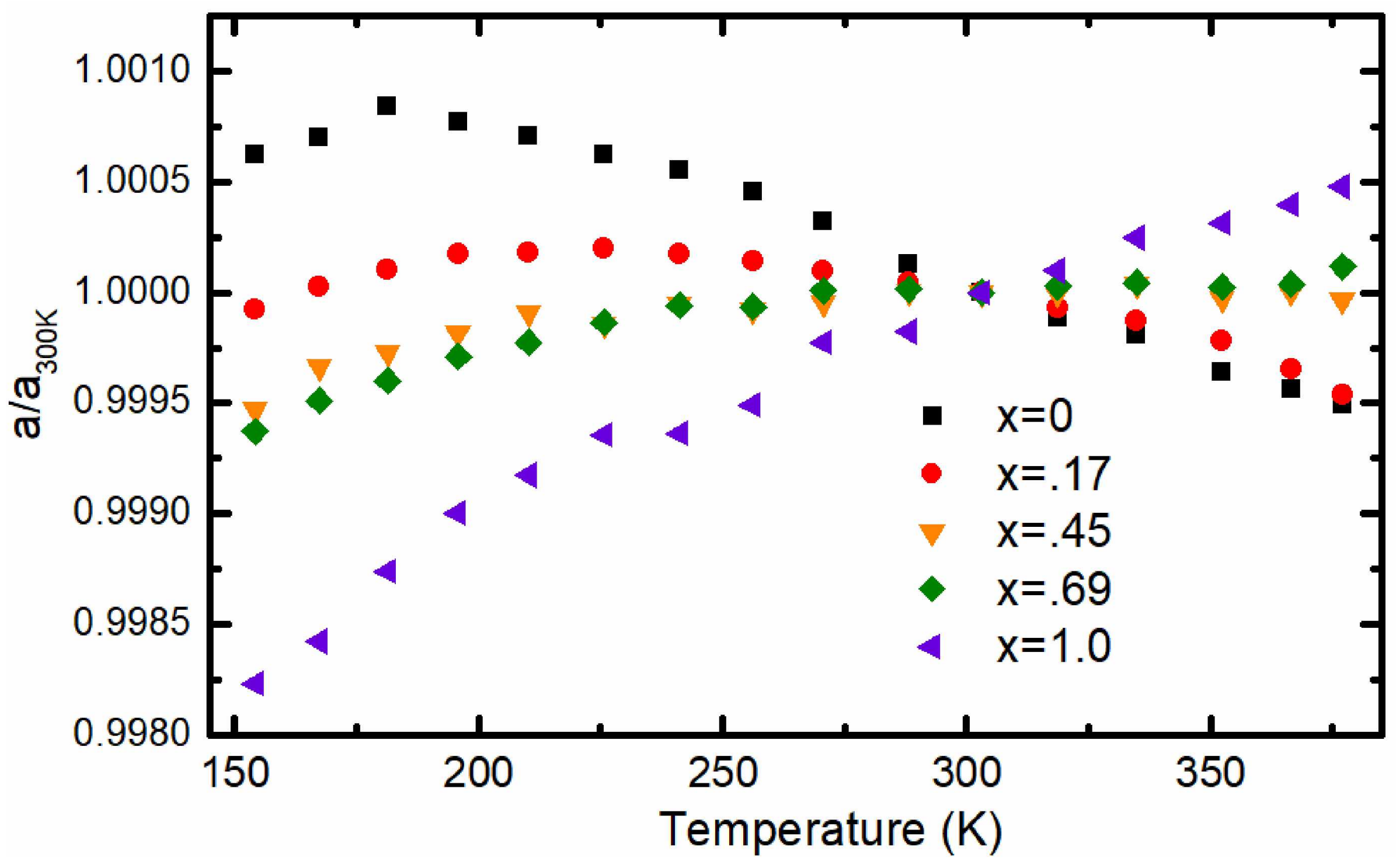


Comparison of BET surface area and pore volume.

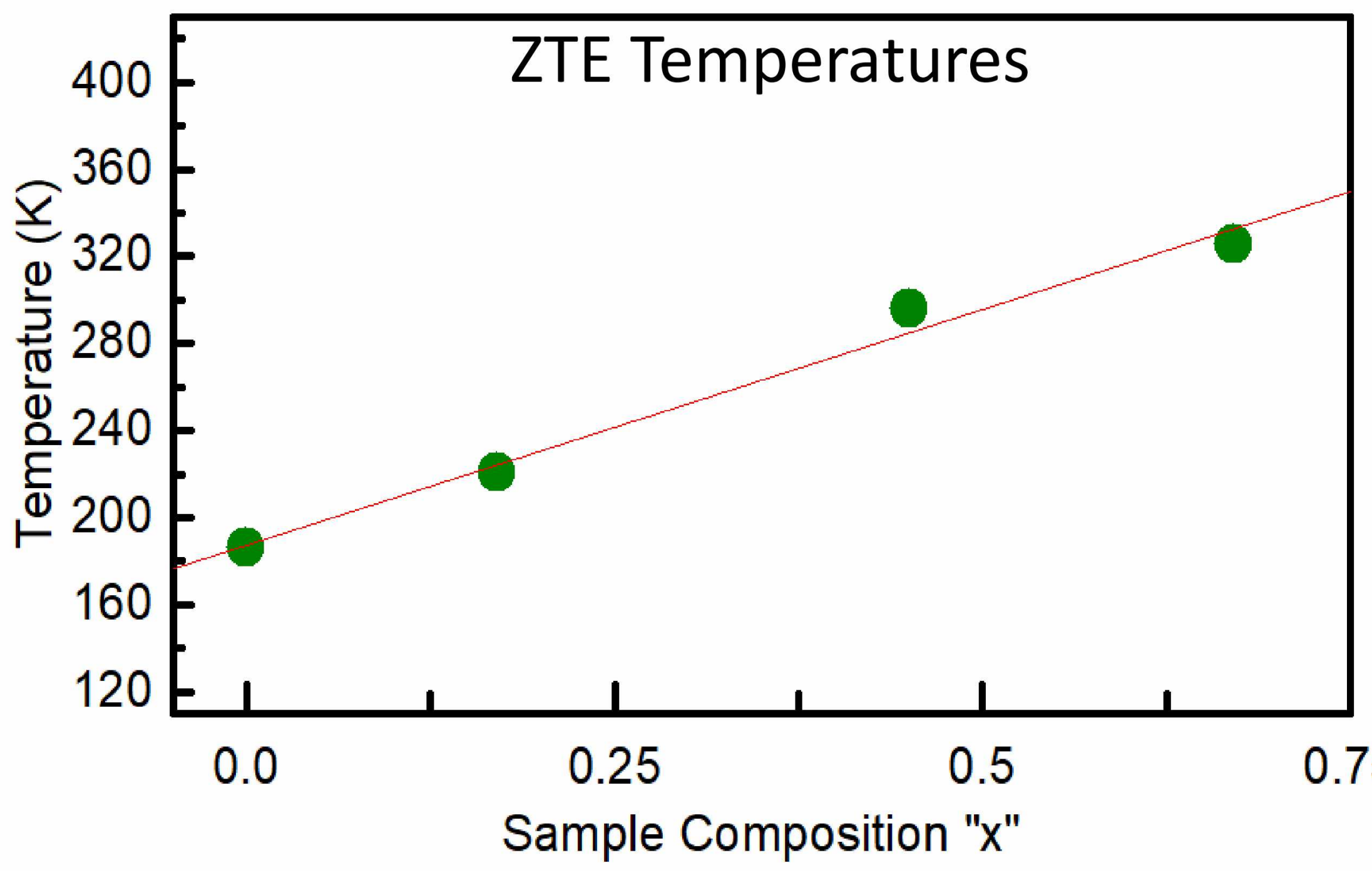
Results (cont.)

Thermal Expansion

Each sample was investigated by variable temperature powder diffraction over the temperature range150 - 375 K



Variation of normalized lattice constant a/a_{300K} for the **Zn-DMOF-TM$_x$** samples as a function of temperature and composition.



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. *Acc. Chem. Res.* **2015,** *48* (11), 2850-2857.

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