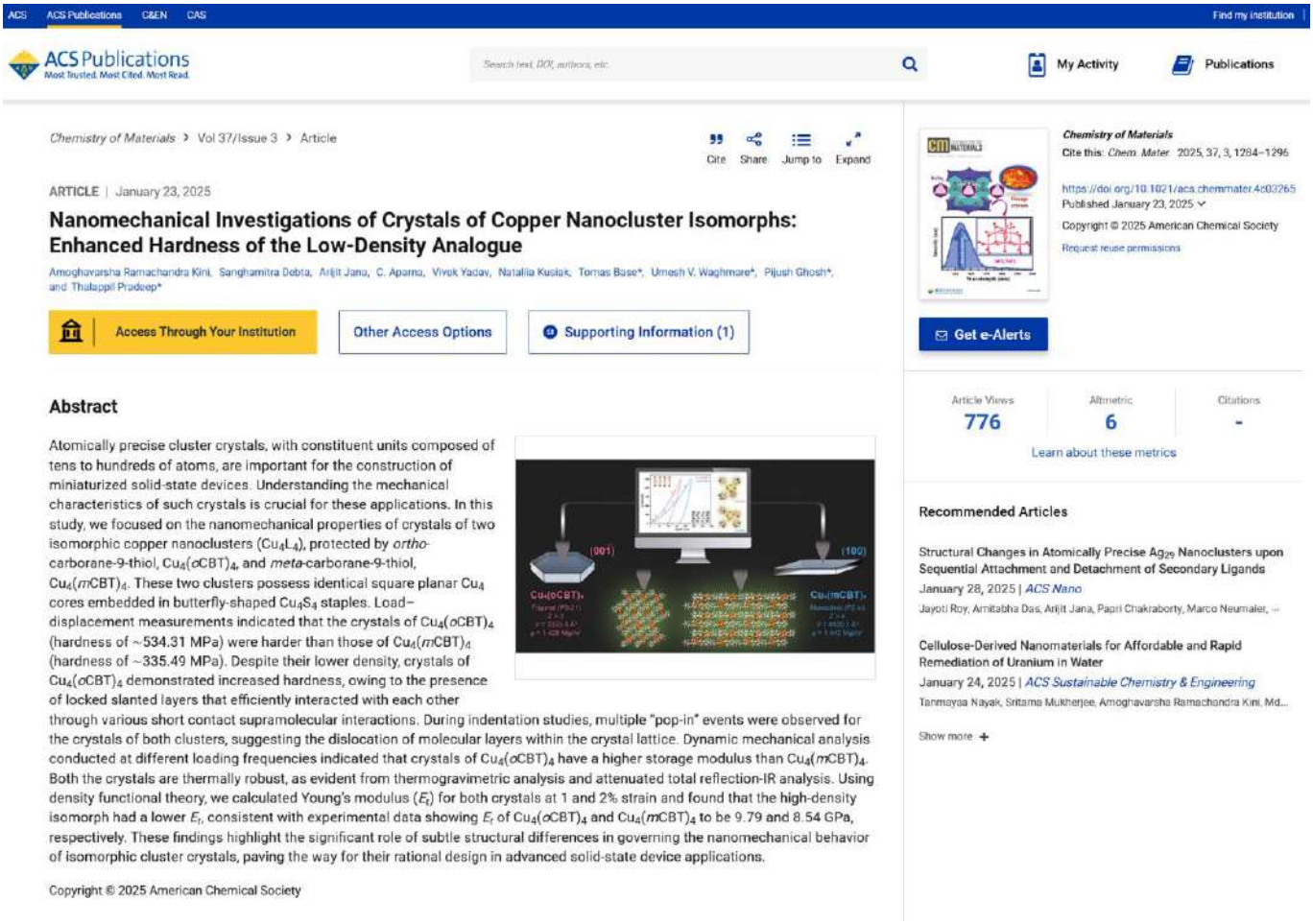
Chemistry of Materials
Cite this: *Chem. Mater.* 2025, 37, 3, 1284–1296

Nanomechanical Investigations of Crystals of Copper Nanocluster Isomorphs: Enhanced Hardness of the Low-Density Analogue

A. R. Kini, S. Debta, A. Jana, C. Aparna, V.Yadav, N. Kusiak, T.Base, U. V. Waghmare*, P. Ghosh*, T. Pradeep**

https://doi.org/10.1021/acs.chemmater.4c03265



ACS Publications
Most Trusted. Most Cited. Most Read.

Chemistry of Materials › Vol 37/Issue 3 › Article

Cite Share Jump to Expand

ARTICLE | January 23, 2025

Nanomechanical Investigations of Crystals of Copper Nanocluster Isomorphs: Enhanced Hardness of the Low-Density Analogue

Amoghavarsha Ramachandra Kini, Sangharmitra Debta, Arijit Jana, C. Aparna, Vivek Yadav, Natalia Kusiak, Tomas Base*, Umesh V. Waghmare*, Pijush Ghosh*, and Thalappil Pradeep*

Access Through Your Institution | Other Access Options | Supporting Information (1)

Abstract

Atomically precise cluster crystals, with constituent units composed of tens to hundreds of atoms, are important for the construction of miniaturized solid-state devices. Understanding the mechanical characteristics of such crystals is crucial for these applications. In this study, we focused on the nanomechanical properties of crystals of two isomorphic copper nanoclusters (Cu_4L_4), protected by *ortho*-carborane-9-thiol, $Cu_4(o\text{CBT})_4$, and *meta*-carborane-9-thiol, $Cu_4(m\text{CBT})_4$. These two clusters possess identical square planar Cu_4 cores embedded in butterfly-shaped Cu_4S_4 staples. Load–displacement measurements indicated that the crystals of $Cu_4(o\text{CBT})_4$ (hardness of ~534.31 MPa) were harder than those of $Cu_4(m\text{CBT})_4$ (hardness of ~335.49 MPa). Despite their lower density, crystals of $Cu_4(o\text{CBT})_4$ demonstrated increased hardness, owing to the presence of locked slanted layers that efficiently interacted with each other through various short contact supramolecular interactions. During indentation studies, multiple "pop-in" events were observed for the crystals of both clusters, suggesting the dislocation of molecular layers within the crystal lattice. Dynamic mechanical analysis conducted at different loading frequencies indicated that crystals of $Cu_4(o\text{CBT})_4$ have a higher storage modulus than $Cu_4(m\text{CBT})_4$. Both the crystals are thermally robust, as evident from thermogravimetric analysis and attenuated total reflection-IR analysis. Using density functional theory, we calculated Young's modulus (E_t) for both crystals at 1 and 2% strain and found that the high-density isomorph had a lower E_t, consistent with experimental data showing E_t of $Cu_4(o\text{CBT})_4$ and $Cu_4(m\text{CBT})_4$ to be 9.79 and 8.54 GPa, respectively. These findings highlight the significant role of subtle structural differences in governing the nanomechanical behavior of isomorphic cluster crystals, paving the way for their rational design in advanced solid-state device applications.

Chemistry of Materials
Cite this: *Chem. Mater.* 2025, 37, 3, 1284–1296
https://doi.org/10.1021/acs.chemmater.4c03265
Published January 23, 2025

Get e-Alerts

Article Views 776 | Altmetric 6 | Citations -

Learn about these metrics

Recommended Articles

Structural Changes in Atomically Precise Ag_{29} Nanoclusters upon Sequential Attachment and Detachment of Secondary Ligands
January 28, 2025 | *ACS Nano*
Jayoti Roy, Amitabha Das, Arijit Jana, Papri Chakraborty, Marco Neumaier, ...

Cellulose-Derived Nanomaterials for Affordable and Rapid Remediation of Uranium in Water
January 24, 2025 | *ACS Sustainable Chemistry & Engineering*
Tanmayaa Nayak, Sritama Mukherjee, Amoghavarsha Ramachandra Kini, Md...

Show more +