The Mystery of Hybrid Perovskites: Why Some Crystals Act Like Both Solids and Liquids

From dual incommensurate phases in $MAPbBr_3$ to crystal-liquid thermal transport in $MAPbCl_3$, organic cation rotation emerges as the key control parameter.

Hybrid organic–inorganic perovskites, with the general formula $MAPbX_3$ (MA = methylammonium, X = halide), have emerged as revolutionary materials for solar cell applications, achieving power conversion efficiencies above 25%.[1] However, the fundamental mechanisms underlying their exceptional optoelectronic properties remain unclear. The interaction between rotatable organic cations and the dynamically disordered inorganic framework generates a complex phonon landscape that traditional characterization techniques cannot readily resolve.

To address this challenge, researchers from National Central University and National Cheng Kung University employed X-ray and neutron diffraction and inelastic neutron scattering instruments at both NIST **SPINS** and Australian Nuclear Science and Technology Organisation's **SIKA** to investigate the atomic-scale dynamics of $MAPbBr_3$ and $MAPbCl_3$ single crystals. Neutron scattering was essential for this investigation. Unlike X-rays, which primarily probe electron density, neutrons interact directly with atomic nuclei and are especially sensitive to hydrogen—a key component of the MA^+ cations. This sensitivity enables neutrons to map the orientational disorder and rotational dynamics of organic molecules buried within the dense PbX_6 octahedral framework. Furthermore, inelastic neutron scattering directly measures phonon energies and lifetimes across the entire Brillouin zone, providing a complete picture of how heat-carrying vibrations propagate through both the rigid inorganic lattice and the mobile organic sublattice.

Building on earlier observations of an incommensurate phase in $MAPbBr_3$,[2] Wen-Hsien Li's team at National Central University discovered that this complexity extends to dual incommensurate phases persisting across a much broader temperature range using neutron diffraction data.[3] Two distinct phases coexist below 150 K: a low-temperature phase (ICM_{LT}) that remains stable down to 75 K, and a high-temperature phase (ICM_{HT}) appearing between 134 and 150 K. Remarkably, the transition between these phases induces extremely large lattice distortions—a 0.25% contraction followed by a 0.42% expansion of the tetragonal basal plane within just 9 K. These structural changes arise from the reorientation of MA^+ ions, which form an incommensurate sublattice with spatial periodicity different from the $PbBr_3^-$ framework.

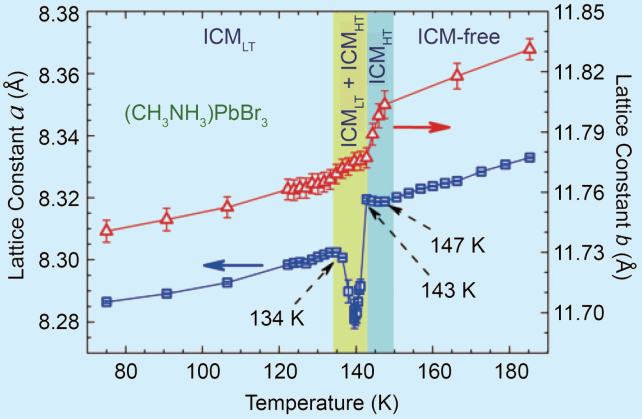

Fig. 1: Temperature dependencies of the lattice constants *a* (open squares) and *b* (open triangles). Large negative thermal expansions followed by large positive thermal expansions are seen for *a* in the regime where ICM_{LT} and ICM_{HT} coexist (yellow shaded region). Large positive thermal expansion of *b* in the ICM_{HT}-solely regime (blue shaded region) is also visible. [Reproduced from Ref. 3]

Phonon dispersion measurements at 75 K revealed six definitive acoustic-like phonon branches in $MAPbBr_3$, indicating that the MA^+ sublattice is solid enough to support its own vibrational modes. Upon warming to 200 K, these six branches reconstruct into just two, with significantly enhanced frequencies. This phonon reconstruction reflects the thermal disordering of MA^+ ions, which progressively reduces the degree of atomic disorder in the $PbBr_3^-$ framework—a counterintuitive effect where heating actually improves lattice perfection.

The investigation of $MAPbCl_3$ by Pai-Chun Wei's team (National Cheng Kung University) uncovered an even more striking phenomenon: dual crystal-liquid thermal transport behavior.[4] The team employs high-resolution powder X-ray diffraction at **TPS 19A**. The result shows that below 168.9 K in the orthorhombic phase, $MAPbCl_3$ exhibits crystal-like thermal conductivity that decreases with temperature—typical for crystalline solids dominated by phonon-phonon scattering. However, upon transitioning to the cubic phase above 174.8 K, thermal conductivity begins to increase with temperature, resembling the behavior of liquids or gases where enhanced molecular motion improves heat transfer.

This unusual transition is driven by the onset of rotational jumps in MA^+ cations, which shift the lattice distortion

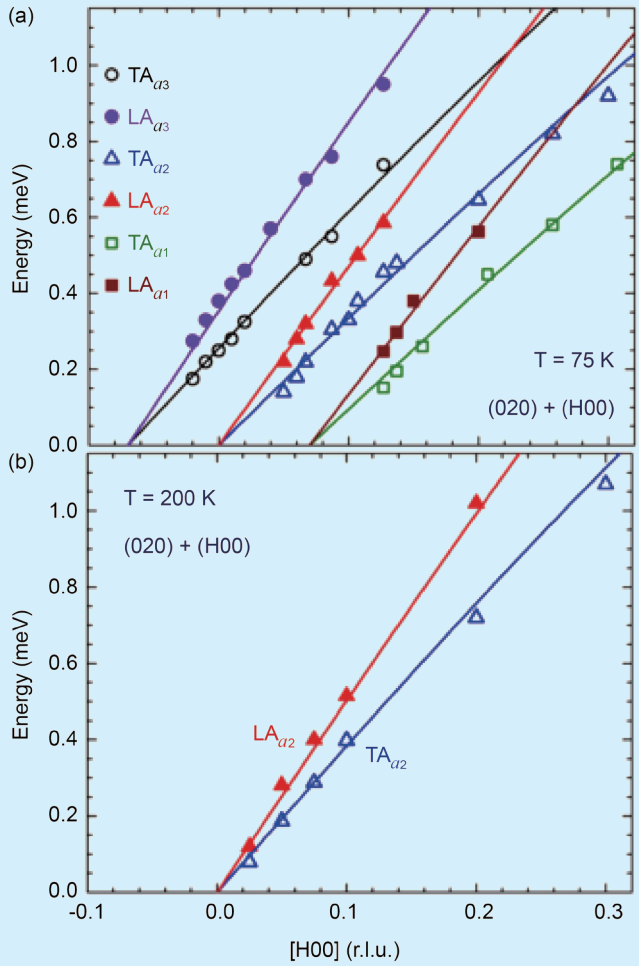

Fig. 2: Phonon dispersion curves of $(CH_3NH_3)PbBr_3$ along the [H00] crystallographic direction at (a) 75 K and (b) 200 K. The solid curves show the results of fitting the data to harmonic expressions, as discussed in the text. Six phonon branches are present at 75 K, grouped as follows: two branches originate from the zone center at H = 0, labeled LA_{a2} (solid triangles) and TA_{a2} (open triangles); two originate from H = 0.07, labeled LA_{a1} (solid squares) and TA_{a1} (open squares); and two originate from H = –0.07, labeled LA_{a3} (solid circles) and TA_{a3} (open circles). At 200 K, the four ICM branches disappear, while the two CM branches remain. [Reproduced from Ref. 3]

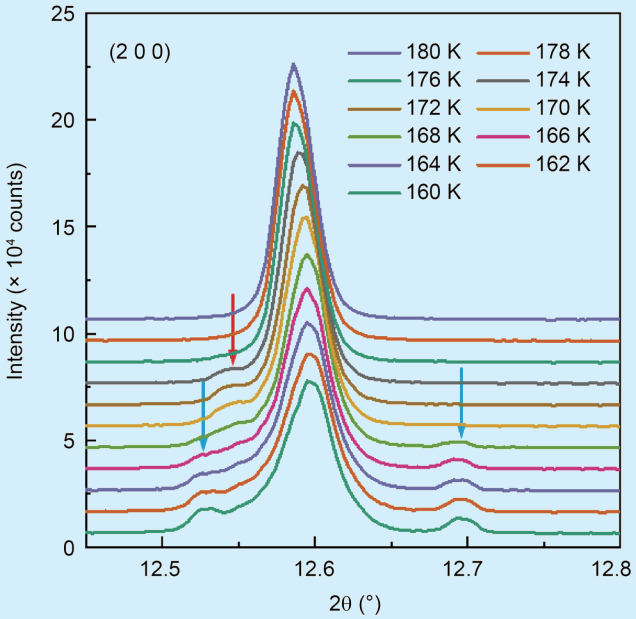

Fig. 3: Evolution of the (2 0 0) diffraction peak during phase transitions. [Reproduced from Ref. 4]

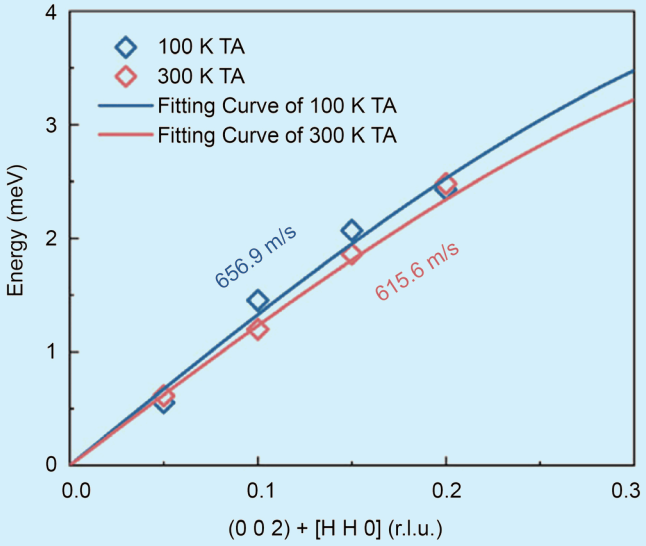

Fig. 4: Phonon dispersion relations in $MAPbCl_3$ measured at 100 K and 300 K: Transverse acoustic (TA) phonon dispersions along the [H H 0] direction. [Reproduced from Ref. 4]

from a static to a dynamic regime. Using the **SIKA** spectrometer, the team measured exceptionally low phonon velocities (656.9 m/s for transverse acoustic modes at 100 K) and ultrashort phonon lifetimes (0.788–8.67 ps at 300 K). The phonon mean free paths approach the Regel-Ioffe limit of just 5–10 Å—comparable to the Pb–Cl bond length itself—indicating that phonons are scattered so frequently that they can barely propagate.

The combination of low phonon velocities, short lifetimes, and minimal mean free paths leads to thermal conductivity near the theoretical amorphous limit (0.211 W/m·K) over a wide temperature range. This ultralow thermal conductivity is lower than that of well-known thermoelectric materials such as SnSe and GeTe, demonstrating the potential of hybrid perovskites for thermal management applications.

Both studies reveal that the rotational freedom of MA^+ cations is the key parameter controlling thermal transport in hybrid perovskites. In the orthorhombic phase, restricted MA^+ rotation preserves static lattice distortions, and Umklapp scattering dominates phonon resistance. In the cubic phase, dynamic MA^+ rotations generate time-dependent lattice distortions that induce resonant scattering and higher-order phonon interactions—phenomena that are extremely challenging to capture through computational modeling alone.

These findings elucidate the fundamental physics underlying the "soft" lattice dynamics of hybrid perovskites and suggest strategies for engineering thermal properties through compositional tuning or structural modifications. Understanding how organic cations mediate heat transport

may guide the design of more stable perovskite solar cells with improved thermal management, advancing their commercialization. (Reported by Yu-Chun Chuang)

*This report features the work of Jia-Kai Hu, Pai-Chun Wei and their collaborators published in Small **21**, 2408773 (2025).*

TPS 19A High-resolution Powder X-ray Diffraction
ANSTO SIKA – Cold Neutron Triple-axis Spectrometer
NIST SPINS – Spin-polarized Triple-axis Spectrometer

- Inelastic Neutron Scattering
- Hybrid Perovskites, Lattice Dynamics, Thermal Transport, Incommensurate Structures

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Shining X-rays into the Heart of Catalytic Complexity

Seeing through the spinel, element-selected XAS unveils the secret physics that drive high-entropy catalysts.

In the fast-moving field of materials science, researchers are turning chaos into opportunities. A new generation of catalysts, called high-entropy catalysts (HECs), is challenging the traditional notion that simplicity leads to stability. Traditional catalysts typically rely on one or two principal elements, sometimes enhanced by dopants or supports to tailor activity or stability. By contrast, HECs are defined by the deliberate incorporation of multiple principal components—metals, oxides, nitrides, carbides, or sulfides—into a single-phase matrix. The key principle lies in maximizing configurational entropy ($\Delta S_{config} = R \ln N$), where R is a constant and N is the number of constituent elements. A high ΔS_{config} value can offset the positive enthalpy of mixing, stabilizing otherwise phase-separated systems into uniform crystalline phases. By blending more elements in different proportions, scientists are discovering materials that are not only more robust but also remarkably efficient in driving critical energy reactions. Among these, spinel (AB_2O_4), rock-salt (MO), layered (P2-type), and perovskite (ABO_3) structures are the most widely adopted for HECs as they provide a perfect balance between entropy stabilization and functional versatility. The spinel structure features an entropy-friendly lattice that supports multiple transition metals, high-temperature synthesis, and strong electrochemical stability. Within spinel HECs, this framework enhances thermodynamic stability and improves functional performance, enabling effective charge transfer, reversible redox processes, and extended durability.

Gaining insights into the local environments of spinel structures, including the atomic bonding and oxidation at different sites and electron exchange during reactions, is essential for improving catalyst design. This is where X-ray absorption spectroscopy (XAS) is utilized. Often referred to as a "fingerprint," the XAS technique enables researchers to examine specific elements in complex materials and observe their changes over time. By scanning the energy of X-rays across an element's absorption edge, scientists can identify its oxidation state, coordination geometry, and local bonding environment. This highlights the role of the XAS technique in revealing active sites, oxidation state evolution, and electronic structure modulation. Recent studies conducted this year have demonstrated the effectiveness of using XAS beamlines at the NSRRC. The studies revealed how certain metals can dynamically switch between oxidation states during oxygen evolution reactions,

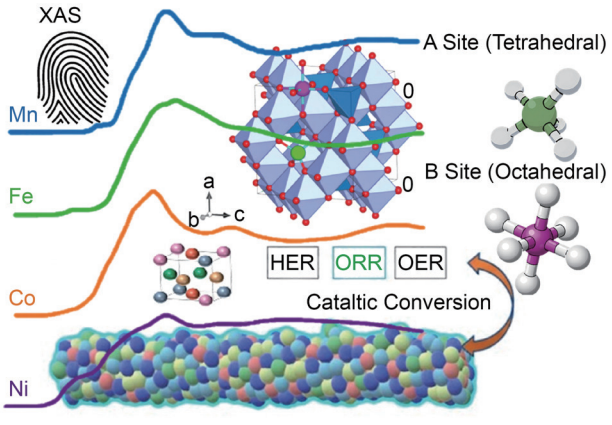

Fig. 1: An in-depth analysis of the AB_2O_4 spinel-type high-entropy catalyst utilizing element-selected XAS techniques reveals significant insights into its catalytic performance and stability.