Highlights

RESEARCH AREA 2 - **Functional and Complex Materials for Innovative Electronics and Sensing** - 2022

"Origin of Ferroelectricity in Two Prototypical Hybrid Organic–Inorganic Perovskites"

Kai Li[1], Zhi-Gang Li[1], Jun Xu[1], Yan Qin[1], Wei Li[1], Alessandro Stroppa[2], Keith T. Butler[3], Christopher J. Howard[4], Martin T. Dove[5], Anthony K. Cheetham[6], and Xian-He Bu[1]

[1]School of Materials Science and Engineering & Tianjin Key Laboratory of Metal and Molecule-Based Material Chemistry, Nankai University, Tianjin 300350, China
[2]CNR-SPIN, c/o Dip. to di Scienze Fisiche e Chimiche, Universitàdegli Studi dell'Aquila, 67100 Coppito (AQ), Italy
[3]Department of Chemistry, University of Reading, Reading RG6 6AD, U.K.
[4]School of Engineering, University of Newcastle, Newcastle, New South Wales 2308, Australia
[5]College of Computer Science, Sichuan University, Chengdu, Sichuan 610065, China
[6]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB3 0FS, U.K.

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Hybrid organic–inorganic perovskite (HOIP) ferroelectrics are attracting considerable interest because of their high performance, ease of synthesis, and lightweight. However, the intrinsic thermodynamic origins of their ferroelectric transitions remain insufficiently understood. Here, we identify the nature of the ferroelectric phase transitions in displacive $[(CH_3)_2NH_2][Mn(N_3)_3]$ (Fig. 1) and order–disorder type $[(CH_3)_2NH_2][Mn(HCOO)_3]$ via spatially resolved structural analysis and ab initio lattice dynamics calculations. Our results demonstrate that the vibrational entropy change of the extended perovskite lattice drives the ferroelectric transition in the former and also contributes importantly to that of the latter along with the rotational entropy change of the A-site (Fig. 2). This finding not only reveals the delicate atomic dynamics in ferroelectric HOIPs but also highlights that both the local and extended fluctuation of the hybrid perovskite lattice can be manipulated for creating ferroelectricity by taking advantages of their abundant atomic, electronic, and phononic degrees of freedom.

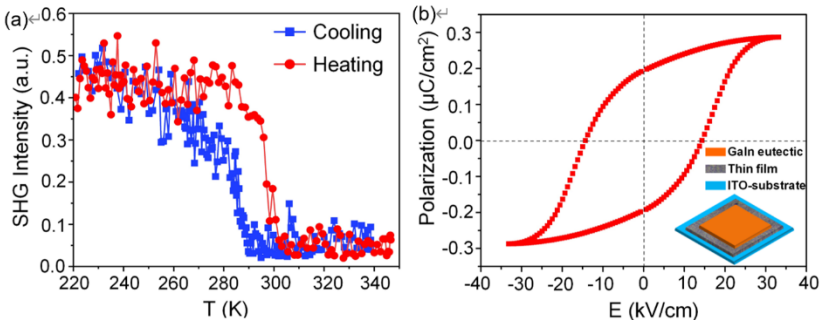

Fig. 1: SHG and ferroelectric characterizations of $[DMA][Mn(N_3)_3]$.
(a) Temperature-dependent SHG upon both heating and cooling. (b) The macroscopic polarization versus external voltage hysteresis loop. The inset in (b) shows the GaIn/$[DMA][Mn(N_3)_3]$ thin film/ITO capacitor architecture.

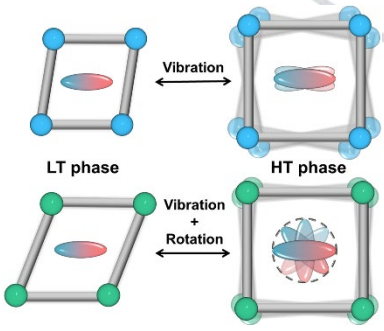

Fig. 2: Angular dependence Jc(θ) in semi-log scale (a) and pinning force (b), at 8 K and in fields of 2 and 16 T. The huge peak at H//ab is the signature of the pinning mechanism related to the 2D GB // ab defects. The small peak detectable at 16 T correlates with the 2D GB ⊥ ab observed defects, and indicates that c-axis correlated defects might become active as pinning centers at high fields.