Lead-free hybrid ferroelectrics under high pressure: record-low compressibility in $[N(C_2H_5)_3CH_3]FeCl_4$

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Progress in hybrid organic-inorganic ferroelectrics (HOIFs) has stagnated. High-pressure investigations offer robust methodologies to clarify structure-property correlations and facilitate systematic phase engineering of lead-free HOIFs as feasible inorganic substitutes [1,2]. Prior research concentrated on metal-organic frameworks (MOFs) and toxic lead-based HOIFs, which were limited in stability and pressure range.
We investigate the lead-free HOIF $[N(C_2H_5)_3CH_3]FeCl_4$ (EMAFC), which is stable and mechanochromic up to 51.5 GPa, featuring a reversible $P6_3mc$-to-$P1$ transition at 0.75 GPa. Synchrotron powder X-ray diffraction, Raman, UV-Vis, dielectric, and second-harmonic generation data under pressure reveal coupling between structural changes and bandgap modulation. EMAFC exhibits a record-high bulk modulus K_0=42.0(5) GPa. Most HOIFs generally display bulk moduli of up to approximately 18 GPa and often exhibit pronounced mechanical anisotropy, which stands in stark contrast to the much higher bulk moduli – typically ranging from 100 to 200 GPa – and low isotropic behavior observed in inorganic ferroelectrics [3]. No molecular ferroelectric or hybrid organic-inorganic perovskite has been reported to have a bulk modulus as high as this, with most values ranging from 7 to 12 GPa (Figure 1). Our research and direct comparison with an isostructural equivalent demonstrate that the choice of inorganic anion (e.g., $[FeCl_4]^-$ vs. $[FeBr_4]^-$) has a significant impact on bulk modulus. This property is determined by the inorganic component, specifically the metal center and halide (F, Cl, Br, I). The halide can be tailored to successfully tune compressibility in hybrid organic-inorganic molecular systems. These findings establish structure-compressibility relationships, enabling advanced phase and property control in lead-free hybrid ferroelectrics.

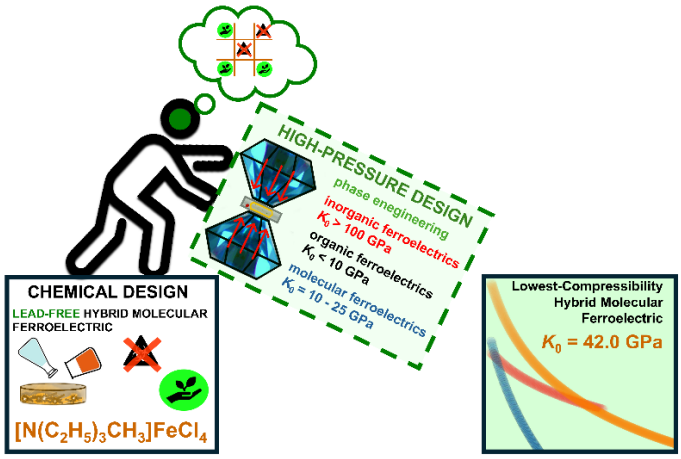


Figure 1. *Record-low compressibility in lead-free hybrid ferroelectric* $[N(C_2H_5)_3CH_3]FeCl_4$ *under high pressure.*

[1] T. Nakagawa et al, Small (2026). 0:e14648.
[2] T. Nakagawa et al, Inorg. Chem. (2023). 62, 19527-19541.
[3] X.-B. Han et al, CrystEngComm (2022). 24, 1507-1517.

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