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Periodicity and its breaking in compressed ferroelectric dabco monosalts

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1,4-Diazabicyclo[2.2.2]octane (dabco) monosalts form a fascinating group of compounds, which exhibit exceptional dielectric properties. They can be described by a general formula: dabcoHX, where X= Br⁻, I⁻, ClO₄⁻, BF₄⁻ and ReO₄⁻. DabcoHI is the first material for which anisotropic relaxor properties were reported.[1] The ferroelectric relaxors are particularly desired for numerous practical applications in electronics, including miniature electronic devices and new methods of storing electricity in capacitors. Moreover, organic relaxors are environment friendly and easier to produce and to dispose off, than inorganic ceramic relaxors of mixed perovskites and doped with lead. DabcoHI undergoes a large number of transformations at elevated pressure and temperature, however analogous dabcoHBr exists only in three forms. Exceptionally rich phase diagram of ten phases was also revealed for dabcoHClO₄. At normal conditions in dabco monosalts the dabcoH⁺ cations are NH⁺...N bonded into linear chains, but pressure can considerably modify that pattern, and the weak hydrogen bonds are relevant for the formation of new polymorphs at high pressure.[2,3] In all dabcoHI polymorphs the NH⁺...N bonded chains of dabcoH⁺ cations are retained, however the chains are linear at 0.1 MPa and high pressure induces modulation of the chain with gradually increased periodicity. In dabcoHBr only phase III is NH⁺...N bonded. Although phase II of dabcoHClO₄ isostructural with phase II of dabcoHBF₄, it behaves differently on lowering temperature than it was observed in dabcoHBF₄. The polymorphic structures of dabco salts differ mainly in the arrangement of the chains and iodide anions, in the dabco conformation, and in the location of protons. When crystallized from methanol, above 1.70 GPa, dabcoHI forms solvates, and the high-pressure crystallization from aqueous solution leads to hydration already at 0.50 GPa.

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