

Symmetry breaking structural phase transitions, dielectric properties and molecular motions of formamidinium cations in 1D and 2D hybrid compounds:
(NH₂CHNH₂)₃[Bi₂Cl₉] and (NH₂CHNH₂)₃[Bi₂Br₉]

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Streszczenie

Two organic–inorganic hybrid halobismuthates(III), (NH₂CHNH₂)₃[Bi₂Cl₉] (**FBC**) and (NH₂CHNH₂)₃[Bi₂Br₉] (**FBB**), have been prepared with their structures revealed by single-crystal X-ray diffraction at various temperatures. **FBC** is characterized by one-dimensional (1D) [Bi₂Cl₉]³⁻_∞ anionic chains built by edge-sharing BiCl₆ octahedra, whereas **FBB** adopts a layer structure (2D) [Bi₂Br₉]³⁻_∞. Both materials were found to exhibit a rich polymorphism in the solid state. **FBC** undergoes two reversible phase transitions (PTs) at 218/220 K and at 123/126 K (cooling/heating), respectively, whereas for **FBB** also two PTs occur close together at 196/199 K and at 190/188 K. Dielectric response around the PT temperatures of **FBC** and **FBB** reflects high disorder of dipolar groups over the high temperature phases. The ‘order–disorder’ mechanism of these PTs is assigned to the dynamics of formamidinium cations. **FBB** is considered as a ferroic material exhibiting ferroelastic domains below 196 K. The molecular motions of organic cations in a wide temperature range were studied by means of ¹H NMR (spin–lattice relaxation time). Presented findings will provide a new method to explore organic–inorganic multifunctional PT materials.

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