Hybrid Bismuth(III)-Halide Double Perovskite-Derived Ferroelastic $(Pip)_2[KBiBr_6]$ with Excitonic and Bi(III) Luminescence due to Electronic Confinement along Inorganic Pillars

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Streszczenie

Organic–inorganic halide double perovskites with the $A_2MM'X_6$ composition are considered a more stable and environmentally friendly alternative to lead-based $APbX_3$ compounds (3D HOIPs). Herein, we report the synthesis, crystal structure, physicochemical characterization, and the results of density functional theory (DFT) calculations for a double-perovskite-related $(piperidinium)_2[KBiBr_6]$. Inorganic structure is built of 1D inorganic pillars composed of $Bi(III)Br_6$ octahedra face shared with trigonal KBr_6 antiprisms. It undergoes a room-temperature order–disorder phase transition at T_c = 300/303 K (cooling/heating), associated with molecular dynamics and formation of stable hydrogen-bond interactions. Dielectric relaxation in the vicinity of T_c indicates gradual ordering of piperidinium. The $C2/m$ to $P1-$ symmetry reduction leads to the formation of a switchable ferroelastic domain structure. The material shows purplish-blue photoluminescence from high-energy excitons and Bi(III) emission due to the electronic confinement along the inorganic pillars. DFT calculations of the density of states confirm that the electronic properties are governed by the electronic states of $Bi(III)Br_6$ octahedra and reveal that electron and hole migration occur between neighboring chains, being quenched along the inorganic part. The optical band gap E_g is 2.8 eV.

Słowa kluczowe

Anions, Cations, Halogens, Inorganic compounds, Phase transitions