Temperature symmetry breaking and properties of lead-free organic–inorganic hybrids: bismuth(III) iodide and antimony(III) iodide: $(S(CH_3)_3)_3[Bi_2I_9]$ and $(S(CH_3)_3)_3[Sb_2I_9]$

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Streszczenie

We have synthesized and characterized two novel lead-free organic–inorganic hybrid crystals: $(S(CH_3)_3)_3[Bi_2I_9]$ (**TBI**) and $(S(CH_3)_3)_3[Sb_2I_9]$ (**TSI**). Thermal DSC, TG, and DTA analyses indicate structural phase transitions (PTs) in both compounds; **TBI** undergoes two structural phase transitions at 314.2/314.8 K (cooling/heating) and at 181.5 K of first (**I** ↔ **II**) and second order (**II** ↔ **III**), respectively. The crystal structures of **TBI** are refined for phases **I** (325 K), **II** (200 K) and **III** (100 K). **TBI** exhibits ferroelastic properties since both PTs are accompanied by a change in the symmetry of crystals: $P6_3/mmc \rightarrow C2/c$ (**I** → **II**) and $C2/c \rightarrow P$ (**II** → **III**). The presence of a ferroelastic domain structure has been confirmed by optical observations. In turn, **TSI** also reveals two PTs: **I** ↔ **II** (at 303.9/304.1 K) and **II** ↔ **III** (212.9/221.4 K). To compare and obtain insight into the mechanism of the PTs of **TBI**, we have carried out temperature dependent single crystal X-ray diffraction studies. Additionally, to confirm the change in the dynamical states of molecules in PTs, dielectric measurements have been carried out between 100 K and 400 K in the frequency range of 200 Hz to 2 MHz. Moreover, the measurements of the ^{1}H NMR spin–lattice relaxation time, T_1, and a second moment, M_2, of the ^{1}H NMR line have been undertaken in the temperature range between 100 and 300 K.

Adres publiczny

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