

Structure, phase transitions and molecular dynamics of $[C(NH_2)_3]_3[M_2I_9]$, $M=Sb, Bi$.Autorzy

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Streszczenie

Two novel guanidinium iodoantimonate(III) and iodobismuthate(III) crystals, $[C(NH_2)_3]_3[Sb_2I_9]$ and $[C(NH_2)_3]_3[Bi_2I_9]$, have been synthesized and their structures have been determined by means of single-crystal x-ray diffraction studies at three temperatures (293, 348 and 362 K). Both compounds appeared to be isomorphous in corresponding phases. The crystal structure of the title compounds is composed of discrete $M_2I_9^{3-}$ ($M = Sb, Bi$) anions and $C(NH_2)_3^+$ guanidinium cations. A non-equivalence of two guanidinium cations has been found. Both guanidinium analogs exhibit a rich sequence of phase transitions. In $Gu_3Sb_2I_9$, three solid-solid structural phase transformations of the first order type are detected at 119/121, 341/344 and 355/362 K (on cooling/heating) by the DSC and dilatometric techniques. $Gu_3Bi_2I_9$ displays four first order phase transitions: 179/185, 202/215, 287/291 and 358/368 K. The low temperature phases appear to have ferroic (ferroelastic) properties. The prototypic paraelastic phase for both compounds belongs to hexagonal symmetry (space group $P6_3/mmc$). The dielectric response has been measured in a wide frequency region (100 Hz–1 MHz), but no dielectric dispersion has been detected. Possible mechanisms of the phase transitions in $Gu_3M_2I_9$ ($M = Sb, Bi$) are discussed on the basis of the presented results.

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