Structural studies of zero-dimensional perovskite guanidinium iodobismuthate(III)

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Since perovskite materials were initially implemented in solar cells, substantial advances have been achieved in their power conversion efficiency. At present, research efforts focus not only on true 3D perovskite materials defined by the ABX_3 formula (where A is a monovalent cation, B is a divalent metal, and X is a halogen anion) but also on similar perovskite-related materials. Lead constitutes the most frequently utilized divalent metal in these materials, which creates issues concerning its toxicity. Therefore, numerous efforts have been undertaken to substitute it with more environmentally-friendly and nontoxic elements such as bismuth or antimony. In this work, we present our investigations on guanidinium iodobismuthate(III), $[C(NH_2)_3]_3Bi_2I_9$, a lead-free perovskite-related material.

The compound crystallizes in the form of dark red plates. Its crystal structure consists of $Bi_2I_9^{3-}$ bioctahedra connected with guanidinium cations by a dense network of hydrogen bonds. The phase situation of the crystal is very complicated and depends on the temperature history of the sample, as well as the crystallization method. At room temperature in phase IIa the compound crystallises in the space group *Cmcm* [1, 2]. In this phase, some of the guanidinium cations are disordered. When heated above 361 K, the crystal undergoes a transition to phase I of the space group $P6_3/mmc$, associated with further disordering of the cations. When cooled, the sample can follow four separate paths of phase transitions.

If the sample has never been heated to phase I, then at 288 K a transition to phase IIIa of the space group $P2_1/m$ occurs. This transition is associated with a complete ordering of the guanidinium cations. At 240 K, part of the sample undergoes a transition to phase IV, the space group $P2_1/m$, associated with rearrangement of the guanidinium cations, while the rest of the sample remains in phase IIIa. The coexistence of phases occurs over a wide temperature range. At 190 K, phase IIIa undergoes isostructural transition to phase IIIb, while phase IV transforms to phase IIIb at 178 K.

If the sample was previously heated to phase I, then at 287 K, an isostructural transition to phase IIb occurs. The transition is associated with a complete ordering of the guanidinium cations. At 199 K and 178 K, part of the sample undergoes consecutive transitions to phases IV and IIIb, respectively, while the rest of the sample transforms directly to phase IIIb at 190 K.

In this study, we present detailed crystal structures of all six phases, temperature dependence of the unit-cell parameters, and temperature changes in the bond lengths and angles, including hydrogen bonds. We also discuss the mechanisms of the phase transitions associated with the formation and transformation of hydrogen bonds.

[1] Szklarz, P., Pietraszko, A., Jakubas, R., Bator, G., Zieliński, P. & Gałązka, M. (2008). *J. Phys.: Condens. Matter,* **20**, 255221.

[2] Szklarz, P., Śmiałkowski, M., Bator, G., Jakubas, R., Cichos, J., Karbowiak, M., Medycki, W. & Baran, J. (2021). *J. Mol. Struct.*, **1226**, 129387.