Growth and characterization of halogenobismuthates of amino acids

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In the search for new materials to overcome the disadvantages of perovskite materials (insufficient stability and the presence of a toxic metal), one of the directions is compounds based on halogenobismuthates [1]. Salts of amino acids with these anions are promising. We conducted a systematic hunt for such representatives and discovered more than 50 new crystalline salts of glycine, sarcosine, dimethylglycine, betaine, *β*-alanine, L-alanine, L-leucine, L-proline, L-ornithine, L-lysine, L-arginine, L-histidine with BiX_4^-, BiX_5^{2-}, BiX_6^{3-}, $Bi_2X_8^{2-}$, $Bi_2X_9^{3-}$, $Bi_2X_{10}^{4-}$,$Bi_3X_{13}^{4-}$, $Bi_4X_{16}^{4-}$ and $Bi_6X_{22}^{4-}$ anions, where X is Cl, Br and mainly I.
Single crystals were grown by slow evaporation using various solvents (H_2O, CH_3CN, ethanol, acetone, DMF, DMSO, and their mixtures). Crystal structures of obtained salts were determined by X-Ray diffraction and characterized by IR and Raman spectroscopy. Bandgaps (E_g) of the salts were established through the diffuse reflectance method and determined from electronic structures calculated based on crystal structures by the DFT method, using the generalized gradient approximation.
The incorporation of iodine (I_2) molecules and triiodide (I_3^-) anions into the structure of halogenobismuthate salts allows to significantly narrow the bandgap [2,3]. The use of halogeno-bismuthate anions made it possible to synthesize members with dimeric cations of the ($A^+\cdots A^+$) type for glycine, sarcosine, betaine, L-proline, and L-leucine, for which salts with such cations were not previously known [4]. Additionally, due to the use of amino acids, it was possible to obtain hitherto unknown anions $Bi_3Br_{13}^{4-}$ and $Bi_3I_{13}^{4-}$.
We managed to form halogenobismuthate salts of amino acids with incorporation of iodine molecules and I_3^-, I_5^- anions into their structures, which made it possible to reduce the bandgaps to optimal values.

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References

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