SUMMARY

Synthesis and physicochemical characterization of organic-inorganic hybrid materials based on combinations of divalent and trivalent metal halides with amines are currently one of modern science's most dynamically developing fields. This is related to the possibility of using the materials mentioned above in many industrial fields (e.g., optoelectronics or photovoltaics). Halobismuthates(III) and haloantimonates(III) create an attractive group of molecular-ionic compounds exhibiting ferroelectric, ferroelastic, piezo-, and pyroelectric properties. These compounds are simple and cheap to synthesize, and are characterized by high thermal stability and resistance to external stimulus. They are also a promising alternative to hybrid compounds based on toxic lead.

The subject of research of the presented doctoral dissertation was organic-inorganic hybrids based on metal halides (BiX_3 and SbX_3; where X = Cl, Br) containing the 1,2,4-triazolium cation in the crystal structure. The main aim of the work was to analyze the obtained compounds in the context of phase transitions and correlation between crystal structure and physicochemical (macroscopic) properties, with particular emphasis on electrical characteristics.

The developed synthetic methodology along with optimized crystal growing approach allowed obtaining six novel hybrids. All of them were characterized in terms of a single X-ray analysis, while physicochemical properties, in a wide temperature-range, (e.g., thermal, dielectric) were determined for three of them. Additionally, pyroelectric current measurements, recording of ferroelectric hysteresis loop and second harmonic generation (SHG) have been carried out for the crystal adopting a non-centrosymmetric space group. Based on the obtained results, the nature of phase transition was determined, as well as an attempt was made to explain the molecular mechanisms of their occurrence.

The most important achievement of the presented doctoral thesis was the discovery of the unique ferroelectric compound, that is $(C_2N_3H_4)_3[SbBr_6]$. The obtained hybrid is one of the few examples of a ferroelectric in the group of haloantimonates(III) and halobismuthates(III) among R_3MX_6 stoichiometry. Based on the performed analyses it was concluded that the occurrence of polar properties is a consequence of a significant deformation of the isolated octahedrons (activity of a lone pair ($5s^2$) on antimony atom) as well as dynamics of 1,2,4-triazolium cations. Thus the ferroelectric phase transition has been classified as a rarely observed ‘displacive’ and "order-disorder" mix-type. Surprising results were also obtained from the physicochemical analysis of the derivatives described by the following formula: $(C_2N_3H_4)_3[SbBr_5][Br]$ and $(C_2N_3H_4)_3[SbBr_6]\cdot(C_2N_3H_4)[Br]\cdot H_2O$. Due to the irreversible phase transition, a substantial reconstruction of the crystal structure occurs, leading to obtaining a material with a dominant ferroelectric R_3MX_6 phase.