ABSTRACT

Physical properties and mechanisms of structural phase transitions of metal-formate frameworks with selected ammonium cations.

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The hybrid metal- organic frameworks (MOF) are currently intensively explored by the scientific community. These materials enjoy broad attention by virtue of their unique properties that are appealing from the fundamental science point of view. They may also constitute the basis for the preparation of functional materials, drawing from their multiferroic properties and phase transition behaviour, particularly of order-disorder nature. Generally, these compounds are constructed from metal ion (clusters) coordinated by organic ligands. The characteristic feature of such networks is the presence of organic cations occupying the large voids.

The dissertation is about hybrid materials and the role of hydrogen bonds in metal-organic compounds of the formate family. The aim of this work was to determine and describe mechanisms of phase transitions of the studied compounds. It includes a broad analysis of the physical and chemical properties of compounds with various ammonium cations using methods of thermal, dielectric and optical (Raman and IR) spectroscopies.

The first part presents the result of measurements on the dimethylammonium zinc formate, which composition was modified by doped copper ions, replacing the hydrogen atom with deuterium in a metal-formate framework and by the synthesis with applied external electric field. The influence of the strength of hydrogen bonds on the temperature of phase transition has been demonstrated. The possibilities of controlling the physical and chemical properties were discussed. Additionally, it has been proven that contrary to universal belief, the organic cation does not freeze below the temperature of phase transition.

The second part of the dissertation characterizes the physical and chemical properties of the ammonium copper-formate framework, showing the isostructural phase transition presence which has not been reported so far. Additionally, the influence of Jahn-Teller's effect on the mechanism of phase transition has been shown.

The last part of the thesis characterizes a new hybrid metal-formate framework of the niccolite-like structure i.e. bis(3-ammoniumpropyl)ammonium manganesium formate, in which the ordering of the cation is comprised of various rotor modes. On the basis of the obtained results, it has been shown that contrary to popular belief, there is no direct relationship between the number of accepted protons in polyammoniums and the activation energy in metal-formate framework.

Metal-formate frameworks may exhibit interesting physical and chemical properties, e.g. ferroelectricity, dielectric or magnetic properties. For many years, scientists have been looking for new, functional materials that would combine these properties in the same phase. The presented dissertation is a contribution to the fundamental research, the main purpose of which is to understand the mechanisms of the temperature-induced phase transitions. This type of research is necessary to synthesize future structures with desired physical and chemical properties.