



Własności optyczne, termiczne i transportowe przewodników
protonowych z dynamiczną, helikoidalną siecią wiązań wodorowych
utworzoną przez sole imidazoliowe
aromatycznych kwasów karboksylowych

mgr inż. Sylwia Zięba

Rozprawa doktorska

wykonana pod kierunkiem

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Abstract

The dissertation presents the results of a new group of compounds obtained based on heterocyclic molecules and aromatic carboxylic acids. The obtained imidazolium salts are characterized by a helicoidal network formed by anions and cations connected by $N^+-H\cdots O^-$ hydrogen bonds, which is rarely observed. The thesis discusses the thermal, transport, and spectroscopic properties of the studied group of compounds. Particular attention was paid to the effect of the helical network on the physical properties of imidazolium salts. Analysis of the temperature evolution of their spectroscopic properties allowed to clarify the nature of the observed phenomena, such as anomalous temperature expansion, proton transport in imidazolium salts, and dynamic structural disorder of the imidazolium ion in imidazolium hemimelitate salt (**ImiHem**·**H₂O**).

The main objective of the dissertation was to find a correlation between the structure of the helicoidal hydrogen bonding network, in the obtained compounds and its physical properties (thermal, transport and spectroscopic). An additional goal of the dissertation was to elucidate the nature of temperature-induced physical transformations in the studied group of imidazolium salts, and to build a new experimental bench that would enable the measurement of Raman spectra as a function of pressure.

The physical properties were analyzed based on studies performed by experimental and theoretical methods of solid state physics. The crystal structure and interactions in the crystal were analyzed using X-ray. Based on the obtained crystal structure, hydrogen bonding analysis was carried out by methods of the quantum theory of atoms in molecules, Hirshfeld Surface, and graph theory. Thermal properties were analyzed by DSC, TGA and DTG. Impedance spectroscopy, high-resolution NMR, and potential energy calculations (PES) were used to analyze transport properties. The variation of physical properties with temperature was explained based on the evolution of oscillatory spectra.

As part of the research conducted in the dissertation, a new bench was prepared for measuring oscillatory spectra as a function of pressure. A cryostat chamber was designed and modified, adapting it to the dimensions of a diamond anvil. The new test stand allowed the recording of Raman spectra as a function of temperature and pressure and made it possible to analyze the studied salts for the effect of pressure on their spectroscopic properties.

The mechanism of the phenomena of anomalous temperature expansion observed in three imidazolium salts: imidazolium terephthalate (**TerImi**), imidazolium salicylate (**SalImi**), and imidazolium benzoate (**BenImi**) is explained. **TerImi** shows a combination of

negative, near-zero, and positive temperature expansions. The nature of the phenomenon of anomalous temperature expansion is described by a scissor or folding lattice mechanism. Negative thermal expansion is observed in **Sallmi** and **BenImi**. The nature of anomalous thermal expansion can be described by the mechanism of folding or unfolding of the herringbone structure. In addition, a stretched helix mechanism is distinguished in each of the salts discussed. The change in helix parameters, such as the helix pitch, and the value of the major, and minor half-axis, depend on how the $\text{N}^+-\text{H}\cdots\text{O}^-$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds are arranged in the crystal lattice. Negative temperature expansion is observed in the direction of $\text{N}^+-\text{H}\cdots\text{O}^-$ hydrogen bonds, and positive temperature expansion is observed in the direction of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. Changes in the third direction are the result of positive and negative temperature expansion.

A Grotthuss mechanism was proposed to describe the transport properties of the studied imidazolium salts. In order to confirm the occurrence of the Grotthuss mechanism, high-resolution NMR studies were carried out as a function of temperature. Both one-dimensional spectra for ^{13}C carbon atoms and ^1H protons and two-dimensional $^1\text{H}-^{13}\text{C}$ correlation spectra were recorded. Due to the high symmetry of the imidazolium cation in the crystal structure of the studied salts, the one-dimensional spectra did not give a clear answer as to whether an ion rotation process occurs in a given temperature range. However, based on the spectra of two-dimensional correlation spectroscopy, it was possible to observe the changes within the hydrogen bonds and the regions in the structure of the studied salts where these bonds occurred.

Analysis of the temperature evolution of the spectroscopic spectrum showed that **TerImi**, **Sallmi**, and **BenImi** salts exhibit anomalous temperature expansion, which can be explained at the atomic level by the "bond rotation effect." In addition, analysis of the temperature evolution of the IR spectrum of imidazolium orthophthalate indicates that this salt is characterized by anomalous temperature expansion, which can also be explained at the atomic level by the "bond rotation effect." The anomalous temperature expansion in the group of imidazolium salts studied is related to the helical network formed by carboxylate anions and imidazolium cations connected by $\text{N}^+-\text{H}\cdots\text{O}^-$ hydrogen bonds. As the temperature increases, the distances between the donor and proton acceptor atoms decrease.

At high temperatures, the dynamic disorder was observed in **ImiHem·H₂O**. Above 300 K, the dynamic disorder of imidazolium ions occurs in this salt. As the temperature is lowered below 300 K, the cations become ordered in the crystal structure. At 130 K,

it was possible to determine a crystal structure with an ordered position of the cations based on the recorded X-ray diffraction image.