

Modification of dielectric properties in selected inorganic-organic hybrid compounds under high-pressure conditions

mgr inż. Andrzej Kamil Nowok

The thesis is devoted to investigation of hybrid inorganic-organic compounds. The studies are conducted in the three areas. The first one, and very interesting, deals with the aspects related to the influence of pressure on phase transition, i.e., its mechanism, phase transition temperature. In this regard, this dissertation aims primarily to obtain pressure-temperature phase diagrams of the studied hybrid inorganic-organic compounds. The second field of study is to investigate the influence of pressure on dielectric relaxation processes and related molecular dynamics of A-site organic cations in the crystal lattice. The third field concentrates on the influence of pressure on the dielectric switching process in switchable hybrid inorganic-organic dielectrics.

The first part of thesis is preface. Second part is devoted to dielectrics, ferroelectrics, antiferroelectrics, multiferroics and relaxors. It is very short overview of such materials. Section 2.2 is devoted to experimental methods – x-ray diffraction, DSC, broadband dielectric spectroscopy, different relaxational models – debye, Cole – Cole, Havriliak Negami etc. 2.4 section is devoted to the materials – MOFs and halides.

Section 3 is devoted to the General aims and research questions. The doctoral dissertation concentrates on three main research topics related to the high-pressure effects. The first one concerns the utility of broadband dielectric spectroscopy in phase transition detection. The second topic of this dissertation is the analysis of dielectric relaxation processes in hybrid inorganic-organic compounds. These processes are connected with the local motion of relaxing units (e.g., organic cations) in the crystal lattice. The third topic of this dissertation is the analysis of the dielectric switching between the low (OFF) and high (ON) dielectric states in switchable inorganic-organic hybrid dielectrics. The phenomenon of OFF/ON switching has only been achieved by temperature modulation so far. However, this method is extremely slow, especially if the switchable material is characterized by a significant temperature hysteresis between the heating and cooling cycles. Hence, the aim of this dissertation was to show the usefulness of external pressure changes (and thus mechanical stresses) in triggering the dielectric switching process and thus reducing its time.

In the section 4 five hybrid inorganic-organic compounds: formamidinium manganese(II) formate (FMDMn), acetamidinium manganese(II) formate (AceMn), 1,4-diaminobutane zinc formate (DABZn), bis(methylhydrazinium) lead tetrabromide (MHyPb), and bispyrrolidinium potassium hexacyanidocobaltate(III) (PyrKCo) are presented. I must mark that these compounds have never been investigated dielectrically under high-pressure conditions.

Section 5 is devoted to experimental part. Broadband dielectric spectroscopy under ambient-pressure conditions and broadband dielectric spectroscopy under high-pressure conditions are explained. X-ray diffraction studies, Scanning Electron Microscopy and Differential Scanning Calorimetry are explained.

Section 6 explains synthesis, preparation and characterization of the studied materials. In this section not only synthesis, but also x-ray characterization of obtained samples are presented.

Section 7 is devoted to the experimental results. Formamidinium manganese (II) formate was subjected to dielectric studies over wide temperature and pressure ranges. The comparative measurements of the single-crystal and pelletized forms of FMDMn revealed: (i) a dielectric anomaly at 336 K, connected with the phase transition, and (ii) a single relaxation process. The temperature dependencies of its relaxation times are linear in both samples, characterized by the same activation energy value, 0.46 eV. Hence, the origin of the relaxation remains the same in both studied materials: the reorientation motions of polar FMD⁺ cations in the crystal lattice. Nonetheless, under isothermal conditions, the relaxation times are slightly different for the single-crystal and pelletized samples of FMDMn. Considering the crystallographic directions averaging for the pellet, anisotropic features of FMDMn cannot be excluded. FMDMn is stable under high-pressure conditions, at least up to 600 MPa. This is reflected in the reversibility of all pressure-induced changes in its dielectric properties, namely, stepwise reduction in the relaxation peak amplitude and its gradual shifting towards lower frequencies. The latter effect is weak. In this respect, temperature decrease by only 9 K moves the relaxation peak as much as pressure elevation up to 600 MPa. It indicates that the manganese(II)-formate framework is rigid. Consequently, mechanical stress, represented by external hydrostatic pressure, exerts a small effect on the FMD⁺ cations dynamics in the LT phase. Their motions become slower only by about 0.25 of a decade after compression up to 600 MPa. The activation energy does not change with pressure. On the other hand, pressure increase triggers a significant ordering of the relaxing units in the crystal lattice, which is a much more pronounced effect than the one induced by lowering the temperature. Finally, the activation volume parameter was determined based on the high-pressure dielectric studies under isothermal conditions. Its values in-between 2.77-2.89 cm³ mol⁻¹ point out that the volume requirements for FMD⁺ motion are small. On the other hand, they confirm the high rigidity of the metal-formate framework.

Acetamidinium manganese(II) formate, the perovskite-like hybrid compound occurring in the low-temperature P21/c phase below 302 K and the high-temperature R $\bar{3}m:H$ one, was subjected to dielectric studies over wide temperature and pressure ranges. In these studies, particular emphasis was put on the dynamics of the disordered polar acetamidinium cations in the crystal lattice, reflected in the form of a relaxation process in dielectric spectra. As a result, their fundamentally different dynamic behavior in the LT and HT phases was observed under ambient-pressure conditions. Firstly, the energy barrier for their reorientation motions is about 7% higher in the HT phase, reaching 0.58 \pm 0.01 eV. For comparison, the activation energy in the LT phase is 0.54 \pm 0.01 eV. Secondly, a partial ordering of the Ace⁺ cations while lowering the temperature, reflected as diminishing the relaxation peak amplitude and decreasing $\Delta\epsilon$ values, was observed only in the LT phase.

Another thermodynamic variable applicable to control the disorder in the crystal lattice of AceMn, is pressure. Declining relaxation peak amplitude during compression showed that also pressure increase triggers a significant ordering of the relaxing units in the crystal lattice. However, this effect occurs in both HT and LT phases. Consequently, temperature and pressure increase cannot be treated as only opposite thermodynamics variables in controlling the Ace⁺ cations behavior.

Apart from the ordering effect, pressure and temperature play an important role in regulating the dynamics of relaxing units. Lowering the temperature by 37 K increases the relaxation time of Ace⁺ as much as pressure elevation by 1000 MPa. It means that external pressure has only a small impact on the molecular dynamics of the relaxing units due to a shielding effect of the relatively rigid manganese(II)-formate skeleton. The determined low value of the activation volume parameter (6.8 \pm 0.1 cm³ mol⁻¹) may confirm this statement. On the other hand, it points out that the volume requirements for Ace⁺ motion are relatively small.

Several pressure-induced effects were also observed. Firstly, the energy requirements for the Ace⁺ units' local motion (represented by activation energy, E_a , parameter) increase under mechanical stress for both LT and HT phases. This phenomenon demonstrates the ongoing crystal lattice distortions after compression. The pressure impact is more pronounced in the LT phase so that the differences in E_a between both phases eventually diminish. In the LT phase, compression up to 750 MPa leads to an increase in activation energy by 13% from 0.54 to 0.61 eV. Compression to the same pressure in the HT phase results in the growth of E_a by only 7% from 0.58 to 0.62 eV in the HT phase. Secondly, a linear increase in the phase transition temperature with dT_0/dp equal 85 ± 1 K GPa⁻¹ was detected.

Although FMDMn and AceMn crystallize in the LT phase with a monoclinic symmetry, there are significant differences between them. Firstly, both compounds differ in terms of the mechanism of local motion of the relaxing A-site units. While Ace⁺ cations become disordered around a single four-fold axis, FMD⁺ ions reorient themselves in a complex manner, which involves simultaneous motion around three two-fold symmetry axes. Secondly, the manganese(II)-formate framework is less rigid in AceMn. This is reflected in pressure-induced activation energy changes for the reorientation of relaxing A-site cations (not observed in FMDMn), more remarkable changes in their relaxation times upon compression, and higher activation volume value. The differences in activation volume between AceMn and FMDMn cannot be simply explained by various volume requirements for the motion of the A-site Ace⁺ and FMD⁺ cations, caused by their different size. Therefore, the activation volume parameter delivers complex information in hybrid inorganic-organic compounds, reflecting both the stiffness of the metal-organic framework and the volume requirements of the relaxing units. The changes in E_a under pressure are governed by the stiffness of the metal-organic framework.

The single crystal of 1,4-diaminobutane zinc formate, the niccolite-like inorganic-organic hybrid compound occurring at the low-temperature rhombohedral $R\bar{3}c$ and the high-temperature trigonal $P\bar{3}1/c$ phases, was subjected to dielectric studies along [100] and [001] directions under ambient- and high-pressure conditions. As a result, anisotropic features were observed, reflected in different ϵ' values and differentiated relaxation times of DAB2⁺ cations under isothermal conditions. Consequently, particular emphasis was put on the analysis, whether pressure affects the dynamics of DAB2⁺ to the same extent along [100] and [001] directions.

It was shown that the pressure impact is direction-dependent. While the energy barrier for the local motion of DAB2⁺ is the same for both directions at ambient pressure, it becomes diversified under 1700 MPa, being equal to 0.51 ± 0.01 eV and 0.47 ± 0.01 eV along [100] and [001] directions, respectively. Moreover, along [100] direction, the relaxation times of DAB2⁺ increase by about 57% after isothermal compression up to 1700 MPa. At the same time, the elevation of pressure from 0.1 to 1700 MPa makes DAB2⁺ relax by only 32% longer along [001]. Consequently, the performed high-pressure dielectric measurements show that mechanical stresses are transmitted anisotropically through the zinc-formate skeleton. Moreover, they indicate a tight relationship between the DAB2⁺ and the inorganic-organic framework.

Bis(methylhydrazinium) lead tetrabromide (MHyPb) occurs in three phases: the low-temperature (LT) ferroelectric $Pmn2_1$, the intermediate one with modulated structure, and the high-temperature (HT) paraelectric phase of $Pmnm$ symmetry. The phase transitions between them take place at roughly at 350 and 370 K at ambient pressure, and are reflected dielectrically as a discontinuity in the dielectric permittivity dependencies. MHyPb is characterized by a 2D layered structure, in which the MHy⁺ cations play the role of spacers. They interact with the inorganic counterions via weak N-H...Br. Consequently, the crystal structure is highly flexible. This is manifested as a high dT_0/dp

parameter value for the upper phase transition (170 K GPa^{-1}), which is much higher compared to its perovskite-like hybrid halide analogue with cage-like architecture.

Bispyrrolidinium potassium hexacyanidocobaltate(III) belongs to the group of switchable hybrid dielectrics, characterized by constant ϵ' values at the low OFF and high ON dielectric states, no relaxation process, and good resistance to fatigue. Therefore, this compound in the thesis was used as a model compound to study the utility of pressure to control the dielectric switching process. In PyrKCo, the mechanism of this process lies in a change in the crystal lattice disorder at the phase transition temperature, which is reflected as a step-like change in the ϵ' value. The transformation between low (OFF) and high (ON) dielectric states has been achieved only by temperature changes so far in the literature. However, the performed calorimetric measurements show that the temperature-controlled dielectric switching is slow due to the nonlinearly increasing temperature hysteresis between heating and cooling cycles with temperature variation rate. As revealed by the dielectric measurements carried out under various pressure-temperature conditions, this inconvenience can be solved using a second variable - pressure. In PyrKCo, the transformation from a high to a low dielectric state under isothermal conditions can be achieved by a stepwise pressure increase. In this respect, isothermal compression and isobaric cooling exert the same effect, that is switching downwards to the OFF state. The ϵ' values of the high and low dielectric states (equal to 14.8 and 11, respectively) do not change under pressure, at least up to 250 MPa. It means that the mechanism of dielectric switching remains the same also under high-pressure conditions, i.e., the ordering of pyrrolidinium cations at the phase transition.

Despite the differences, the reversibility and stability of the switchable properties in PyrKCo, as well as good endurance to numerous switching cycles, are preserved under both ambient and high pressure. Therefore, the performed high-pressure dielectric studies indicate the utility of pressure as another thermodynamic variable to control and accelerate the dielectric switching process.

Also it is my duty to say some drawbacks. The frequency range is quite narrow - it would be interesting to have data at lower frequencies for impedance spectroscopy and higher frequencies (higher than 1 MHz) and temperatures for the dielectric spectroscopy. Also I suggest as future work – to perform ultrasonic spectroscopy.

Thesis are written very well – easy to read and gives for the new reader valuable information.

All these remarks do not influence the overall rating of the work. Thesis are written clearly, huge work has been done, results are published in 4 papers in international journals. Due to that thesis are very good and author definitely deserves PhD title.

Prof. Juras Banys

