Hibridinių metalo-formiato perovskitų tyrimai elektronų paramagnetinio rezonanso spektroskopija

Electron paramagnetic resonance spectroscopy of hybrid metal-formate perovskites

Mantas Šimėnas[1], Monika Gusowska[2], Miroslaw Maczka[2], Georg Völkel[3], Andreas Pöppl[3], Jūras Banys[1]
[1]Vilniaus universitetas, Fizikos fakultetas, Saulėtekio al. 3, LT-10257 Vilnius, Lithuania
[2]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, PL-50-950 Wroclaw 2, Poland
[3]Faculty of Physics and Earth Sciences, Universität Leipzig, Linnestrasse 5, D-04103 Leipzig, Germany
mantas.simenas@ff.vu.lt

Lately, novel hybrid materials called metal-organic frameworks (MOFs) emerged and immediately attracted attention of the scientific community. These crystalline compounds are unique due to the high degree of porosity which can be utilized for gas adsorption related applications. Additionally, many MOFs containing paramagnetic transition-metal ions exhibit peculiar magnetic properties. The organic part in several of such compounds consists of polar molecules which below a certain phase transition temperature order into a ferroelectric-type phase, making these materials single-phase hybrid multiferroics [1].

The most interesting class of MOFs that exhibit ferroelectric-like properties is metal-formate frameworks $[A][Zn(HCOO)_3]$, where A^+ is a molecular cations such as dimethylammonium $(CH_3)_2NH_2^+$. These compounds consists of metal-oxygen octahedra that are linked by the formate anions into cuboid cavities. Each cavity contains a single A^+ cation which forms H-bonds with the framework (Fig. 1). Usually, these materials exhibit structural phase transitions that involve ordering of these cations.

We use EPR, ENDOR and dielectric spectroscopic techniques to investigate and characterize the ferroelectric-like phase transitions in manganese and copper doped $[A][Zn(HCOO)_3]$ metal-formates based on the perovskite architecture (Fig. 1). Here A^+ is $NH_2NH_2CH_3^+$ or $(CH_3)_2NH_2^+$ molecular cations. The temperature dependent continuous-wave EPR spectra reveal that the local paramagnetic ion-probes are indeed sensitive to the local structural changes occurring at the phase transitions. Spectral simulations are used to obtain the ***g***, hyperfine ***A*** and fine structure ***D*** tensors at different temperatures. This allows us to probe the temperature dependence of the local order parameter and to characterize the observed phase transitions [2,3]. Pulse EPR and ENDOR measurements are performed to study structure of the framework, lattice dynamics and motion of the molecular cations in the low temperature phases. The magnetic resonance methods are complemented by the dielectric spectroscopy of MOF single crystal samples providing information about the nature of the phase transitions and dynamics of the molecular cations.

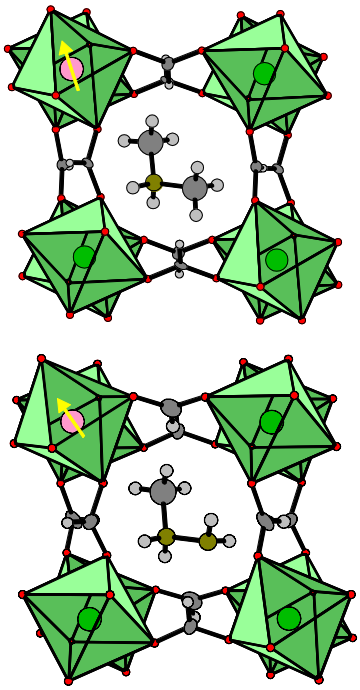

Fig. 1 Structural motifs of dimethylammonium and methylhydrazinium zinc-formate frameworks.

Reikšminiai žodžiai: elektronų paramagnetinis rezonansas, hibridiniai perovskitai, faziniai virsmai.

Literatūra

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