Struktūriniai faziniai virsmai ir dinaminiai efektai hibridinėse medžiagose

Structural phase transitions and dynamic effects in hybrid materials

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Recently, hybrid organic-inorganic materials attracted exceptional attention due to their remarkable gas sorption, optoelectronic, multiferroic, barocaloric and other functional properties originating from a tight interplay between the organic and inorganic motifs.

A highly promising class of such materials is AMX_3 hybrid perovskites, where A is an organic molecular cation, M is a metal ion, and X represents an organic or inorganic anionic linker. Among hybrid perovskites, metal formate frameworks $[A][M(HCOO)_3]$ and lead halides $APbX_3$ (X = Cl, Br, I) (see Fig. 1) are the most promising families due to their multiferroic and photovoltaic properties, respectively. The majority of these compounds exhibit structural phase transitions followed by the molecular cation ordering and framework deformation [1].

Another class of interesting hybrid materials is metal-organic frameworks (MOFs), which exhibit remarkable porosity utilizable for gas absorption, catalysis and chemical sensing. The organic linkers in MOFs are embedded in a porous crystalline lattice providing a handle to tune their dynamic behaviour, which in turn can affect the chemical and physical properties of these compounds [1].

Here, we use a multitechnique experimental and theoretical approach to study the aforementioned phenomena in hybrid perovskites and MOFs. The EPR and dielectric spectroscopies are used to elucidate the cation dynamics, phase transition mechanism, lattice distortion and possible ferroelectric nature of metal formate frameworks. In addition, we show that EPR spectroscopy can be used to excite and read the methyl group tunnel coherence in this class of compounds [2]. We also use the broadband dielectric, ultrasonic and vibrational spectroscopies to probe frustration of electric dipoles and determine phase diagrams of mixed-cation lead halide perovskites revealing signatures of a peculiar dipolar glass phase [3,4]. Finally, we also show how dielectric spectroscopy can help to elucidate emergence of the coupled rotor dynamics upon tuning of the steric linker interactions in MIL-53 MOF [5].

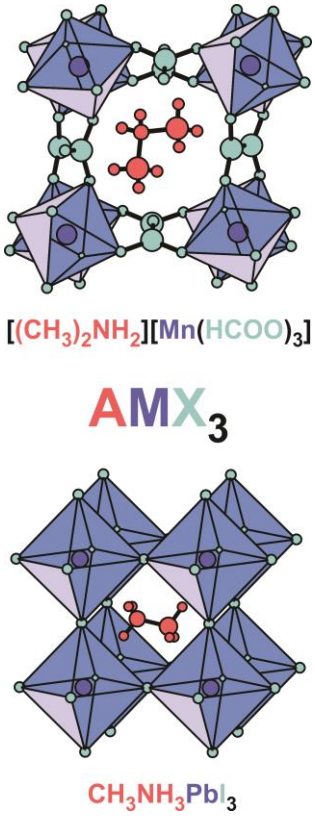

Fig. 1. Representatives of formate (top) and lead halide (bottom) hybrid perovskites investigated in this work.

Keywords: hybrid material, MOF, phase transition, dynamics, EPR, dielectric spectroscopy

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