

Elasticity of dense metal-organic framework compounds

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Metal-organic framework (MOF) compounds are a class of promising crystalline microporous materials containing metal ions coordinated by organic linkers. Among the various MOF structures, perovskite-like structured MOFs have attracted attention due to their chemical diversity and their potential for a number of applications, e.g. in photovoltaic energy generation [1].

In the present study, the elastic behavior of metal-guanidinium formates (MGF), where $M = \text{Cu, Zn, Mn, Co, Ca}$ and Cd has been investigated. This is of interest as these MOFs are known to undergo magnetic and/or structural phase transitions at low temperatures [3,4,5] and their elastic stiffness tensors may provide insight into the origin of their ferroic or multiferroic behavior.

MGFs are perovskite-like MOFs. Their general formula is ABX_3 , where A represents $\text{C}(\text{NH}_2)_3$, B is a divalent metal ion ($M = \text{Cu, Zn, Mn, Co, Ca}$ or Cd), and X is the polyatomic linker anion, formate = HCOO . The elastic properties of ZnGF, MnGF, CoGF and CuGF have been investigated by plane wave / parallel plate ultrasound spectroscopy, resonant ultrasound spectroscopy (RUS), Brillouin spectroscopy (BS), density functional theory, and the analysis of thermal diffuse scattering.

Fig. 1 shows a comparison of the experimental results to DFT-results for ZnGF. There generally is a good agreement between the different techniques and the theoretical data, if dispersion-corrected DFT calculations are employed. The MGFs crystallize in different structure types, where ZnGF, MnGF and CoGF are isostructural. The structure of CuGF only differs slightly from that of ZnGF [3], while CdGF and CaGF have distinct structures [4, 5]. Our results show a systematic variation of the bulk modulus as a function of the radius of the M -cation, which leads to the conclusion that at ambient conditions the elastic behavior is mainly due to the packing density and depends little on the bonding between the M -cation and the formate.

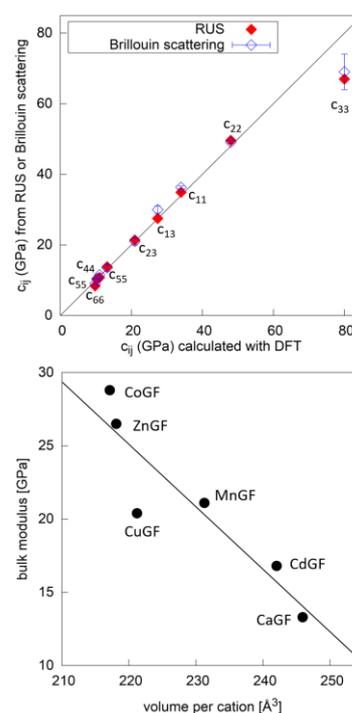


Fig.1 Top: c_{ij} for ZnGF obtained by DFT compared to those obtained by RUS and BS. Experimental values on the black line indicate perfect agreement with the results from DFT. Bottom: Bulk modulus of the MGF as a function of volume of their unit cells per cation.

[1] Kanemitsu Y, Handa T, Photophysics of metal halide perovskites: From materials to devices, *Jpn. J. Appl. Phys.* 57, 090101 (2018)

[3] Hu K-L, Kurmoo M, Wang Z, Gao S, Metal-organic perovskites: synthesis, structures, and magnetic properties of $[\text{C}(\text{NH}_2)_3][\text{M}^{\text{II}}(\text{HCOO})_3]$ ($M = \text{Mn, Fe, Co, Ni, Cu, Zn}$), *Chem. Eur. J.* 15, 12050 (2009)

[4] Gao H, Li C, Li L, Wei W, Tan Y, Tang Y, High pressure and elastic properties of a guanidinium-formate hybrid perovskite, *Dalton Trans.* 49, 7228 (2020)

[5] Haussühl E, Bayarjargal L, Winkler B, Luchitskaia R, Büscher J, Negative thermal expansion, thermodynamic properties and T-dependent Raman scattering of a new metal-organic perovskite framework, *submitted*

EH and JB are grateful for funding from the DFG (HA 5137-5) BW and LP thank the DFG for funding in Wi 1232. KB thanks the GSI (Darmstadt) for financial support. BW is grateful for support through the BIOVIA Science Ambassador program.