

Negative thermal expansion, thermodynamic properties and temperature dependent Raman scattering of a new metal-organic perovskite framework [C(NH₂)₃][Ca(HCOO)₃]

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Metal-organic frameworks consist of transition metals that are connected via organic ligands. Together they form frameworks which cavities can contain guest molecules. The incorporation of guest molecules allows to build MOFs with tailored and also multiple interesting properties by exchanging transition metals, organic ligands or guest molecules. Metal-guanidinium formate (MGuFo), [C(NH₂)₃][M²⁺(HCOO)₃], belongs to the perovskite-type MOFs with the general formula ABX₃, where B = M²⁺ is a metal cation which is octahedrally coordinated by formate ions (X = HCOO⁻, abbreviated as Fo⁻) [1]. The metal and formate ions form M–Fo–M chains and build up a tridimensional framework with cuboid cavities, which are occupied by the small organic guanidinium cations (A = [C(NH₂)₃]⁺).

We will present the synthesis, crystal structure, thermal expansion, Raman spectra and heat capacity of Ca-guanidinium formate ([C(NH₂)₃][Ca(HCOO)₃]), a new member of the family of metal-organic perovskites which is isostructural to CdGuFo [2]. CaGuFo shows an extraordinary strong negative thermal expansion between 100 K and 400 K in the crystallographic **a**₁ – **a**₂ plane which exceeds the corresponding coefficients of CdGuFo by a factor of about two. Perpendicular to this plane, along **a**₃, the crystal structure of [C(NH₂)₃][Ca(HCOO)₃] expands with increasing temperature very strongly and surmounts the corresponding value of CdGuFo as a reference by about 45 %. This behaviour is due to a reduction of the framework distortion on temperature. From temperature-dependent Raman spectroscopic measurements we observed three soft Raman modes. From heat capacity measurements we derived the Debye-temperature $\theta_{\text{D}} = 217$ K.

- [1] Hu K-L, Kurmoo M, Wang Z, Gao S. Metal-Organic Perovskites: Synthesis, Structures, and Magnetic Properties of [C(NH₂)₃][M^{II}(HCOO)₃] (M=Mn, Fe, Co, Ni, Cu, Zn; C(NH₂)₃ = Guanidinium). Chem. Eur. J. 15, 12050 (2009)
- [2] Collings I E, Hill J A, Cairns A B, Cooper R I, Thompson A L, Parker J E, Tang C C, Goodwin A L. Compositional dependence of anomalous thermal expansion in perovskite-like ABX₃ formates. Dalton Trans. 45, 4169 (2016)

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