

MS16-P12

Dielectric, pyroelectric and structural properties of rare-earth calcium oxoborates RCa_4 Erik Mehner¹, Hartmut Stöcker¹, Marie Münchhalfen², Christoph Reuther¹, Jens Götzke¹, Jürgen Schreuer², Dirk C. Meyer¹

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Although rare-earth oxoborates are known since 1991 [1], they have been studied mainly for their non-linear optical properties that are useful for Laser applications. Recently, these materials gathered interest due to their piezoelectric properties, which are not only stable up to high temperatures [2], but also unimpaired by phase transitions. Furthermore, the materials lend themselves to rare-earth substitution, thus, offering a systematic possibility to tweak their properties. However, the low symmetry of their monoclinic structure of space group Cm complicates characterisation. Here, we report on the dielectric and pyroelectric properties of some rare-earth calcium oxoborates and present high-temperature powder diffraction data giving insight into possible structural instabilities around temperatures of 1000 K.

Samples of rare-earth calcium oxoborates $RCa_2Ca_2O(BO_3)_3$ with $R = Gd, Y, Er, La$ were cut and polished from large Czochralski-grown single-crystals. The four components of the dielectric tensor were investigated at room temperature with the substitution method. Furthermore, the two components of the pyroelectric tensor were measured via the Sharp-Garn method from room temperature to 420 K. The stability of noble metal electrodes was investigated up to 1200 K.

High-temperature X-ray powder diffraction patterns obtained on samples milled from crystals exhibit a discontinuity in the expansion of the crystal lattice at elevated temperatures for $R = Gd, La, Y, Sm$. Comparing the initial and final diffraction patterns reveals changes in the cation ordering due to the thermal treatment.

References:

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Keywords: borate dielectric pyroelectric

MS16-P13

Insertion/disinsertion of oxygen in $BaCoO_{2+x}$ ($0 \leq x \leq 1$)Aliou Diatta¹, Pascale Armand¹, Jérôme Rouquette¹

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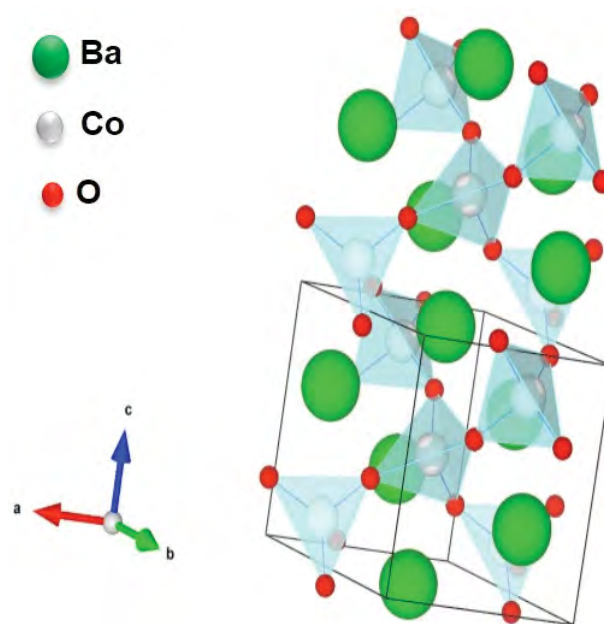
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The crystal structure of $BaCoO_2$ was determined for the first time by Spitsbergen [1] in 1960. Despite the absence of experimental structural data, it was reported to crystallize in the non-centrosymmetric $P3_121$ trigonal space group (no. 152), similar to that observed for SiO_2 quartz, which has potential piezoelectric properties. The screw axis of this trigonal unit cell is defined by the arrangement of corner-sharing CoO_4 tetrahedra around the barium atom, which is located in a distorted 8-fold ($4+2+2$) oxygen atoms coordination (fig).

The $3d^7$ electron configuration of the tetrahedral Co^{2+} ion exhibits a theoretical effective magnetic moment $\mu_{\text{eff}} = 3.87\mu_B$. The existence of this magnetic moment associated with the $P3_121$ space group permits potential piezo-magnetic coupling [2].

The $BaCoO_2$ phase was synthesized by the solid state reaction under secondary vacuum and its structural changes as a function of temperature were studied as the function of oxygen partial pressure. $BaCoO_2$ presents antiferromagnetic ordering at room temperature and crystallizes in the $P3_121$ space group which confirms potential piezo-magnetic coupling. In addition, oxygen insertion/disinsertion over an extended compositional range was characterized in $BaCoO_{2+x}$ ($0 \leq x \leq 1$) by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Raman spectroscopy.

Such properties could be of interest for catalysis applications, commercial air separation, solar water splitting, solar CO_2 splitting, chemical looping, oxy-combustion, [3], etc....



References:

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Keywords: Synthesis, Magnetism, Piezomagnetism

MS16-P14

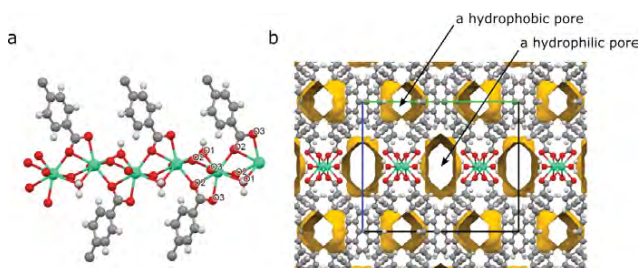
A bi-porous metal–organic framework with tuneable sorption performance facilitated by intrinsic flexibility

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Efficient CO₂/CH₄ separation has constantly been a challenge for natural gas processing, and in general, modern chemical industry.[1] While classical separation techniques including cryogenic distillation or low-temperature chemical absorption are widely in use, they are energetically costly, and present a considerable environmental issue.[2] Porous materials, constantly developed as alternative solutions to these techniques, are showing a great promise.[3] The purpose, however, is not only to design a material with maximum selectivity and working capacity, but also to rationally control and tune its performance. Herein we present the synthesis of a novel MOF based on Ca(II) and a tetracarboxylate ligand TBAPy⁴⁻ endowed with two chemically distinct types of pores: the hydrophobic and the hydrophilic one. Owing to judicious choice of conditions access is gained to two stages of activation, at which the material shows strikingly different gas sorption performances. The material's intrinsic flexibility helps it to adsorb a higher amount of gas molecules than is allowed by its unexpanded state. The observed preference of adsorbing CO₂ over CH₄ was further studied in fixed-bed breakthrough experiments imitating the real process in an industrial-scale installation. The difference of sorption behaviour on the material was supported by molecular simulations.



References:

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Keywords: metal–organic frameworks, gas adsorption, CO₂/CH₄ separation