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Dielectric, pyroelectric and structural properties of rare-earth calcium oxoborates RCa_4

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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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Insertion/disinsertion of oxygen in $BaCoO_{2+x}$ ($0 \leq x \leq 1$)

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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 $\mu_{eff} = 3.87\mu_B$. 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....

