MS15-2-12 Ammonothermal synthesis of new cation-deficient antiperovskites
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Abstract
Inorganic antiperovskites with the formula X_3AN (X^{2+} = Ba, Sr, Ca, Mg; A^{3-} = As, Sb) have recently been reported to exhibit excellent optoelectronic properties like small carrier effective masses, suitable direct bandgaps, high optical absorption coefficients as well as allowed optical transitions at band edges. These properties can be tuned depending on the *X*- and *A*-site. Extending the composition to quaternary antiperovskites ($X_6AA'N_2$) enables enlarging the theoretical maximum solar cell efficiencies to above 29%.[1-2]
Here we report on the ammonothermal synthesis of $X_5Sb_2(NH)_2$ (*X* = Ca, Sr), starting from XH_2 (*X* = Ca, Sr) and Sb. The crystal structures of $X_5Sb_2(NH)_2$ were solved and refined by single-crystal X-ray diffraction (scXRD). $X_5Sb_2(NH)_2$ crystallizes in the orthorhombic space group *Pbam* ($Ca_5Sb_2(NH)_2$: *a* = 6.7980(16) Å, *b* = 13.327(4) Å, *c* = 4.9213(11) Å, *R*1 = 0.016, *wR*2 = 0.027; Sr5Sb2(NH)2: *a* = 7.2257(12) Å, *b* = 13.9816(4) Å, *c* = 5.2195(7) Å, *R*1 = 0.026, *wR*2 = 0.052). SEM-EDX (scanning transmission electron microscopy, energy dispersive X-ray spectroscopy) confirm the *X*/Sb-ratio obtained by scXRD. The obtained structures were further confirmed using powder X-ray diffraction and Raman spectroscopy.
The new compounds feature a square-pyramidal-like coordination geometry around the imide-group (X_5NH), forming ordered defects in the antiperovskite-derived structure. They crystallize as an inverse variant of $Ca_2Mn_2O_5$, where the effect of the oxygen vacancies and structural order have been correlated to their electrocatalytic properties.[3]

References
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Ca5Sb2NH2 crystal structure along [001]