

## Rb<sub>4</sub>CuSb<sub>2</sub>Br<sub>12</sub>: A new vacancy-ordered quadruple perovskite

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The introduction of MAPbI<sub>3</sub> as a new absorber material for solar cells [1] resulted in an enormous boost in research on metal halide perovskites and related compounds. Such compounds include divalent halides ABX<sub>3</sub>, double perovskites A<sub>2</sub>BB'X<sub>6</sub> with mono and trivalent cations, or similar representatives with only trivalent (A<sub>3</sub>M<sub>2</sub>X<sub>9</sub>) or even tetravalent (A<sub>2</sub>MX<sub>6</sub>) cations. A relatively new contender, in this context, is the class of so-called vacancy-ordered quadruple perovskites, with the general formula A<sub>4</sub>B□B'<sub>2</sub>X<sub>12</sub> [2], containing one divalent cation, two trivalent cations and one vacancy. The crystal structure can be seen as an alternating order of the B/B' cations and the vacancies, forming layers that are perpendicular to the direction (111), with respect to the cubic (double) perovskite structure. Besides Cs<sub>4</sub>BB'<sub>2</sub>Cl<sub>12</sub> (B=Cd, Mn; B'=Sb, Bi) [3] and K<sub>4</sub>Fe<sub>3</sub>F<sub>12</sub> [4], which can be described in the rhombohedral space group *R-3m*, also Cs<sub>4</sub>CuSb<sub>2</sub>Cl<sub>12</sub>, [5] which takes on a lower symmetry (*C2/m*), was found some time ago.

During our systematic investigations, we were able to isolate Rb<sub>4</sub>CuSb<sub>2</sub>Br<sub>12</sub> (*P2<sub>1</sub>/c*, a=13.656(3), b=7.4280(16), c=13.633(3) Å and β=114.604(3)°) as black polyhedral crystals from Sb<sub>2</sub>O<sub>3</sub>, CuO and RbBr in concentrated aqueous hydrobromic acid. The lower symmetry, compared to the other representatives of this class, results from the fact that Cu<sup>2+</sup>, as a d<sup>9</sup> system, typically prefers a 4+2 (Jahn-Teller effect) coordination. The smaller Rb<sup>+</sup> cations of Rb<sub>4</sub>CuSb<sub>2</sub>Br<sub>12</sub>, in contrast to Cs<sub>4</sub>CuSb<sub>2</sub>Cl<sub>12</sub>, favor, in combination with the larger CuSb<sub>2</sub>X<sub>12</sub>-Framework, an additional rotation of the octahedra along one direction, which further decreases symmetry. The relationship between the different representatives of these kinds of “cation-deficient Perovskites”, as well as to the cubic (double) perovskites, will be shown via group-subgroup relations using the Bärnighausen formalism.

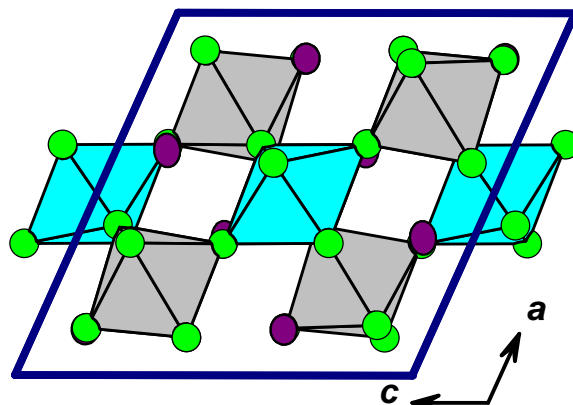


Figure 1 Crystal structure of Rb<sub>4</sub>CuSb<sub>2</sub>Br<sub>12</sub>. Color code: Rb = violet, Cu = turquoise, Sb = grey, Br = green.

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