$Rb_4CuSb_2Br_{12}$: A new vacancy-ordered quadruple perovskite

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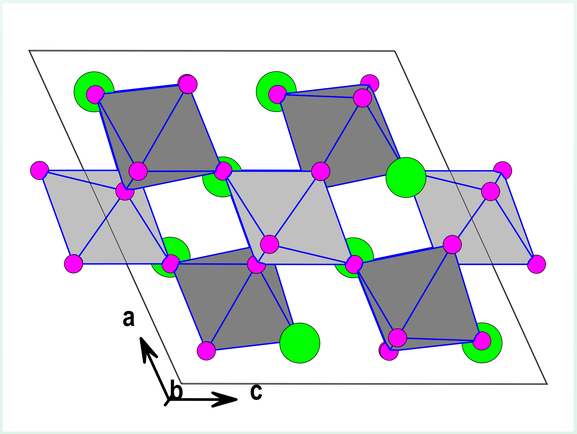
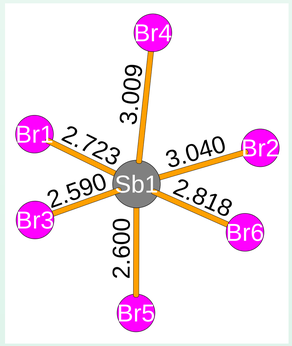
Introduction: The introduction of $MAPbI_3$ as a new absorber material for solar cells [1] resulted in an enormous boost in research on metal halide perovskites and related compounds. Such compounds include divalent halides ABX_3, double perovskites $A_2BB'X_6$ with mono and trivalent cations, or similar representatives with only trivalent ($A_3M_2X_9$) or even tetravalent (A_2MX_6) cations. A relatively new contender, in this context, is the class of so-called vacancy-ordered quadruple perovskites, with the general formula $A_4B\square B'_2X_{12}$ [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 $Cs_4BB'_2Cl_{12}$ (B=Cd, Mn; B'=Sb, Bi) [3] and $K_4Fe_3F_{12}$ [4], which can be described in the rhombohedral space group $R\bar{3}m$, also $Cs_4CuSb_2Cl_{12}$, [5] which takes on a lower symmetry ($C2/m$), was found some time ago. During our systematic investigations, we were able to isolate $Rb_4CuSb_2Br_{12}$ ($P2_1/c$, a=13.656(3), b=7.4280(16), c=13.633(3) Å and β=114.604(3)°) as black polyhedral crystals. The lower symmetry, compared to the other representatives of this class, results from the fact that Cu^{2+}, as a d^9 system, typically prefers a 4+2 (Jahn–Teller effect) coordination. The smaller Rb^+ cations of $Rb_4CuSb_2Br_{12}$, in contrast to $Cs_4CuSb_2Cl_{12}$, favor, in combination with the larger $CuSb_2X_{12}$-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, is shown via group-subgroup relations using the Bärnighausen formalism.

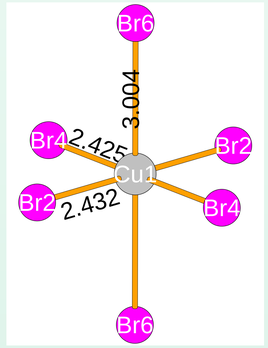
Crystal Structure



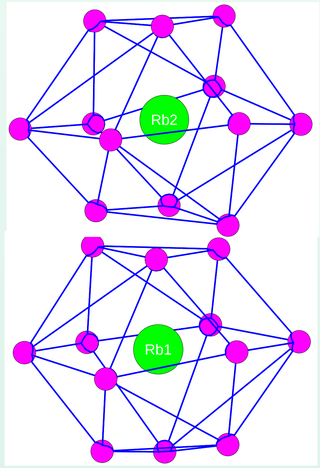
Unit Cell of $Rb_4CuSb_2Br_{12}$.



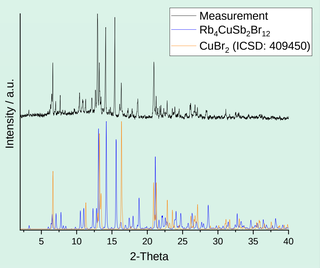
CN = 2+2+2



CN = 4+6
Jahn-Teller

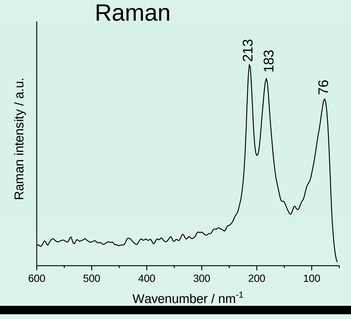


Synthesis: The evaporation of a solution of Sb_2O_3, CuO and RbBr in concentrated aqueous hydrobromic acid yielded beside $CuBr_2$, black polyhedral crystals of $Rb_4CuSb_2Br_{12}$. For spectroscopic investigations, crystals of $Rb_4CuSb_2Br_{12}$ were separated from $CuBr_2$ using a microscope.

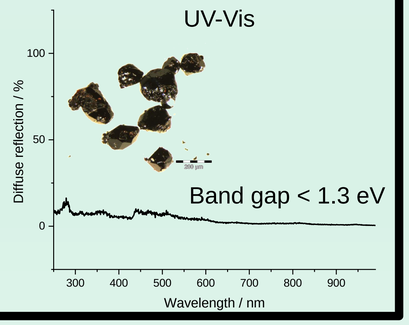


Spectroscopic Investigations

Raman



UV-Vis



References: [1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka Organometal *J. Am. Chem. Soc.* **2009**, *131*, 6050. [2] M. B. Gray, J. D. Majher, N. P. Holzapfel, P. M. *Chem. Mater.* **2021**, *6*, 2165. [3] B. Vargas, R. Torres-Cadena, D. T. Reyes-Castillo, J. Rodríguez-Hernández, M. Gembicky, E. Menéndez-Proupin, D. Solis-Ibarra *Chem. Mater.* **2020**, *32*, 424. [4] S. W. Kim, R. Zhang, P. S. Halasyamani, M. A. Hayward *Inorg. Chem.* **2015**, *54*, 6647–6652. [5] B. Vargas, E. Ramos, E. Pérez-Gutiérrez, J. C. Alonso, D. Solis-Ibarra J. Am. Chem. Soc. **2017**, *139*, 9116.

Group-Subgroup Relations

No. 221
$P\frac{4}{m}\bar{3}\frac{2}{m}$
$CsPbBr_3$

k2
2a, 2b, 2c

Cs	1b	Pb	1a	Cl	3d
$m\bar{3}m$		$m\bar{3}m$		$\frac{4}{m}m.m$	
½		0		½	
½		0		0	
½		0		0	

$\frac{1}{2}x,\frac{1}{2}y,\frac{1}{2}z;\ +(\frac{1}{2},0,0)$

No. 225
$F\frac{4}{m}\bar{3}\frac{2}{m}$
$CsAgBiBr_6$

Cs	8c	Ag	4a	Bi	4b	Br	24e
$\bar{4}3m$		$m\bar{3}m$		$m\bar{3}m$		4m.m	
¼		0		½		0.250	
¼		0		0		0	
¼		0		0		0	

t4
$-\frac{1}{2}a+\frac{1}{2}b, -\frac{1}{2}b+\frac{1}{2}c, a+b+c$

$\frac{2}{3}(-2x+y+z),\frac{2}{3}(-x-y+2z),\frac{1}{3}(x+y+z)$

Nr. 166
$R\bar{3}\frac{2}{m}$

k2
−b, a+b, 2c

$-x,-y,\frac{1}{2}z+\frac{1}{4};\ +(0,0,\frac{1}{2})$

No. 166
$R\bar{3}\frac{2}{m}$
$Cs_4CdBi_2Cl_{12}$

Cs	6c	Cs	6c	⌂	3a	Cd	3b	Bi	6c	Cl	18h	Cl	18h
3m		3m		$\bar{3}m$		$\bar{3}m$		3m		.m		.m	
0		⅔		0		0		⅔		0.509		0.840	
0		⅓		0		0		⅓		0.492		0.160	
0.623		0.460		0		½		0.587		0.629		0.539	

t3
$-a, a+b, \frac{1}{3}a-\frac{1}{3}b-\frac{1}{3}c$

$\frac{1}{2}(-x+y), -z, \frac{1}{2}(x+y), -3z$

No. 12
$C\,1\frac{2}{m}1$
$Cs_4CuSb_2Cl_{12}$

Cs	4i	Cs	4i	⌂	2a	Cu	2d	Sb	4i	Cl	8j	Cl	4i	Cl	8j	Cl	4i
m		m		$\bar{3}m$		$\bar{3}m$		3m		.m		.m		m		m	
0.624		0.374		0		½		0.252		0.612		0.375		0.370		0.134	
0		0.500		0		0		0		0.222		0		0.238		0	
0.870		0.620		0		½		0.759		0.611		0.635		0.874		0.878	

k2
c, b, a

z, y, x

Nr. 14
$P\,1\frac{2_1}{c}1$
$Rb_4CuSb_2Br_{12}$

Rb	4e	Rb	4e	⌂	2a	Cu	2d	Sb	4e	Br	4e	Br	4e	Br	4e	Br	4e	Br	4e	Br	4e
1		1		$\bar{1}$		$\bar{1}$		1		1		1		1		1		1		1	
0.876		0.621		0		½		0.759		0.640		0.579		0.360		0.902		0.860		0.869	
0.013		0.516		0		0		0		0.163		0.782		0		0.293		0.792		0	
0.626		0.372		0		½		0.253		0.646		0.586		0.621		0.891		0.852		0.126	

Total index = 96