

# Single crystal X-ray structure analyses of thallides: halide incorporation and mixed alkali sites in $A_8Tl_{11}X$ (A=K, Rb, Cs; X=Cl, Br)

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The largest (empty) thallide cluster is represented by the  $Tl_{11}^{7-}$  cluster which is present in the binary materials  $A_8Tl_{11}^{[1,2]}$  and  $A_{15}Tl_{27}^{[3]}$  (A=K, Rb, Cs). The  $A_8Tl_{11}$  structure type was first described in 1991 for the lighter homologue indium in  $K_8In_{11}^{[4]}$  of which the crystal structure proved the presence of a naked, pentacapped trigonal prismatic shaped  $In_{11}$  cluster, which was assigned a charge of  $-7$ . Additionally, one extra-electron per formula unit is present, being responsible for the metallic character. The additional electron, referred to the charge of  $-7$  of the cluster anion, is not necessary for the stability of the clusters<sup>[5]</sup> and can be replaced by halide atoms, which are located at a void position (Wyckoff position 6b) at the origin of the

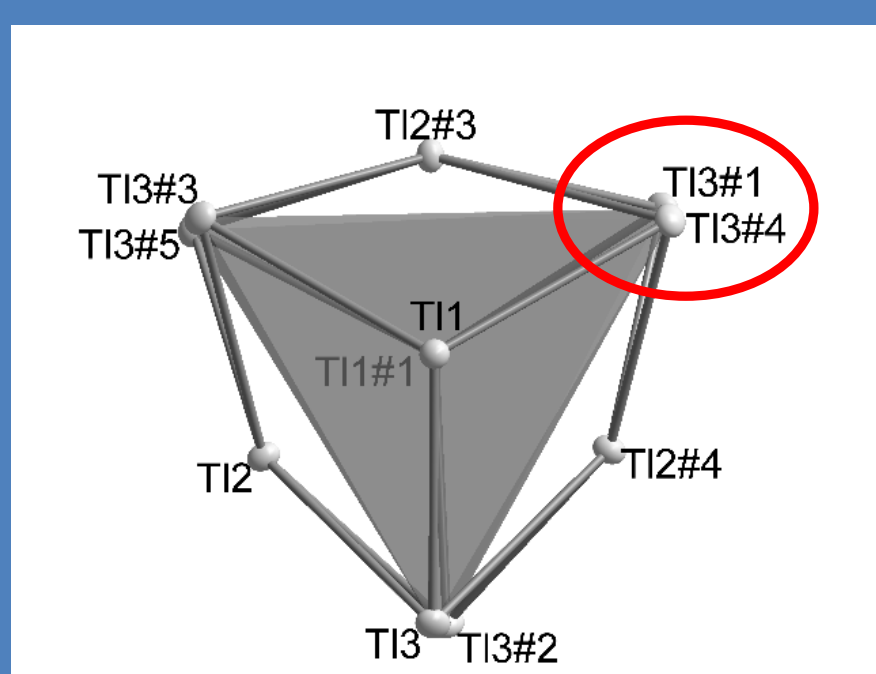
unit cell. Halide incorporation was proven for the lighter homologue of the group,  $Cs_8Ga_{11}Cl$  by X-Ray single crystal structure analysis.<sup>[6]</sup> Powder diffraction experiments suggested the formation of the heavier homologues  $Rb_8Ga_{11}Cl$ ,  $Cs_8Ga_{11}X$  (X=Br, I),  $Rb_8In_{11}Cl$ ,  $Cs_8In_{11}Cl$ ,  $Cs_8Tl_{11}X$  (X=Cl, Br, I). The formation of  $Rb_8Tl_{11}Cl$  was termed as doubtful due to the lack of a significant change in the lattice constants compared to  $Rb_8Tl_{11}$ .

The questions we wanted to answer were: 1.) How does the geometry of the thallide cluster change on halide incorporation; 2.) Is there a  $Rb_8Tl_{11}Cl$ ? ; 3) How do mixed cation sites affect the amount of halide incorporation?

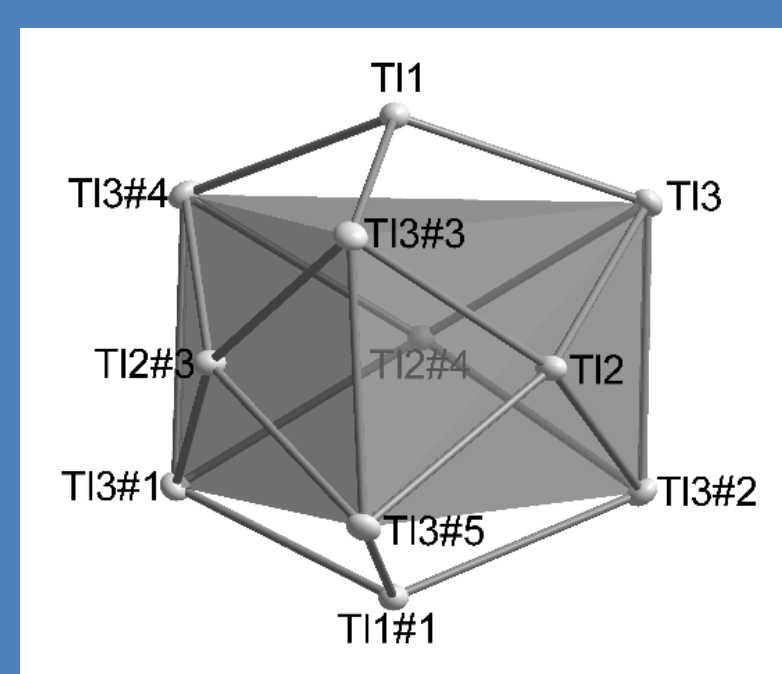
Chemical formula	$Cs_8Tl_{11}Cl_{0.8}$	$Cs_8Tl_{11}Br_{0.9}$	$Cs_5Rb_3Tl_{11}Cl_{0.50(4)}$	$Cs_{5.7}K_{2.3}Tl_{11}Cl_7$
$a$ [Å]	10.4697(4)	10.5608(3)	10.3791(5)	10.3291(9)
$c$ [Å]	53.297(3)	53.401(2)	52.437(3)	51.909(5)
$\alpha$ [°]	90	90	90	90
$\beta$ [°]	90	90	90	90
$\gamma$ [°]	120	120	120	120
$V$ [Å <sup>3</sup> ]	5058.8(5)	5157.9(4)	4892.0(5)	4796.3(9)
$\mu$ [mm <sup>-1</sup> ]	60.902	60.745	64.052	61.908
$R$ indices (all data)	$R1 = 0.0309$ $wR2 = 0.0629$	$R1 = 0.0280$ $wR2 = 0.0541$	$R1 = 0.0466$ $wR2 = 0.0970$	$R1 = 0.0566$ $wR2 = 0.1034$
$R_{int}$	0.0497	0.0385	0.0446	0.0449
Largest diff. peak/hole [ $e \cdot \text{Å}^{-3}$ ]	2.6/-1.7	1.83/-3.38	4.82/-2.29	3.62/-2.21

All compounds crystallize in a variant of the  $K_8In_{11}$  structure type (rhombohedral, spacegroup  $R\bar{3}c$ ) and especially for the mixed alkali metal compounds many of the crystals happened to form typical "multicrystals". Due to the presence of reverse/obverse twinning a  $R$ (obv) filter was applied during data reduction. The materials naturally possess very high absorption coefficients ( $m > 60 \text{ mm}^{-1}$ ), therefore small single crystals have been chosen for the X-ray analyses. However, the data sets still suffer from severe absorption effects which could be reduced by carefully applying numerical absorption correction.

## 1.) How does the geometry of the thallide cluster change on halide incorporation?



Distortion of the trigonal prism results in  $D_3$  instead of  $D_{3h}$  symmetry of the  $Tl_{11}$  cluster in  $A_8Tl_{11}(R\bar{3}c)$



The distortion is reflected in the distances of the atoms, which cap the rectangular faces (TI2) to the atoms, which build the trigonal prism (TI3). For a simple estimation of the degree of distortion solely from the capping distances ( $cd=d(TI2-TI3)$ ;  $cd_{av}$  = average capping distance) we introduce a  $cdd/cd_{av}$  ratio (1).

$$\frac{cdd}{cd_{av}} = \frac{|cd_2 - cd_1|}{\left(\frac{cd_2 + cd_1}{2}\right)} \text{ with } cd_1 \leq cd_2 \quad (1)$$

		$K_8Tl_{11}^*$	$Rb_8Tl_{11}^*$	$Cs_8Tl_{11}Cl_{0.8}$	$Cs_8Tl_{11}Br_{0.9}$	$Cs_5Rb_3Tl_{11}Cl_{0.5}$	$Cs_{5.7}K_{2.3}Tl_{11}Cl_7$
TI2	TI3	3.0476(4)	3.060	3.0656(4)	3.0743(2)	3.0605(6)	3.0554(7)
TI2	TI3 <sup>3</sup>	3.1396(4)	3.157	3.0632(4)	3.0766(2)	3.0896(6)	3.0656(4)
TI1	TI3 <sup>1</sup>	3.1304(4)	3.147	3.0894(4)	3.1006(2)	3.1049(7)	3.0884(8)
TI3	TI3 <sup>3</sup>	3.2054(7)	3.219	3.2019(11)	3.2102(4)	3.2025(11)	3.1873(11)
	Tilt	4.69(2)°	4.90°	0.12(2)	0.069(7)	0.94(2)	0.34(5)
	<b>cdd/cd<sub>av</sub> [%]</b>	<b>3.0</b>	<b>3.1</b>	<b>0.1</b>	<b>0.1</b>	<b>0.9</b>	<b>0.4</b>

\*values taken from [1,2]

Without halide

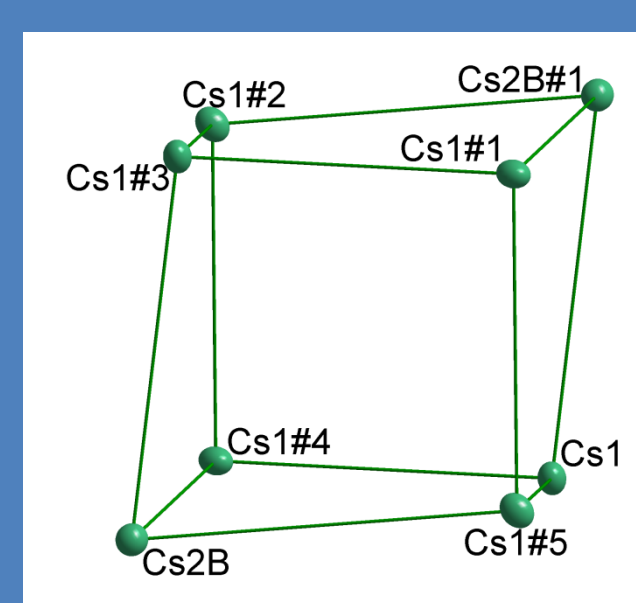
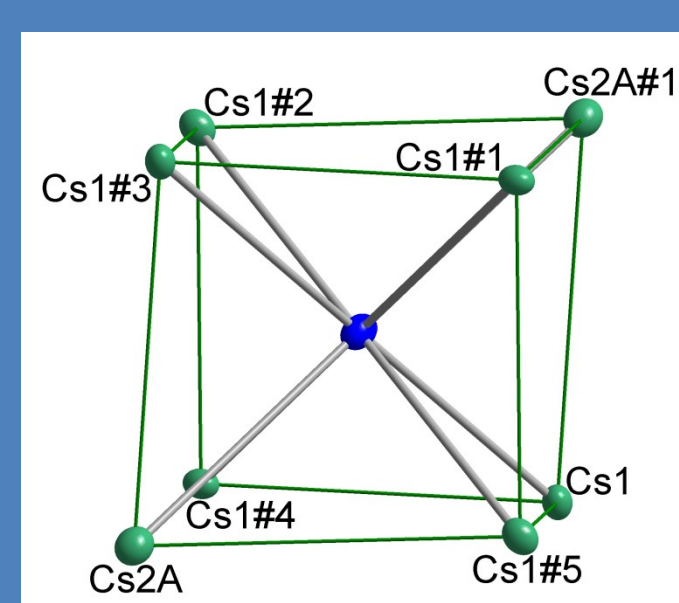
Containing halide

## 2.) Is there a $Rb_8Tl_{11}Cl$ ?

Despite numerous efforts we did not succeed in synthesizing  $Rb_8Tl_{11}Cl$  and the analogous reaction approaches only yielded crystals of  $Rb_8Tl_{11}$  of bad quality. The incorporation of halide cannot be completely ruled out as there is some residual electron density at Wyckoff position 6b according to the position of the halide atom in the previously discussed compounds. However, the  $cdd/cd_{av}$  ratio of 2.4% compared to 3.0% ( $K_8Tl_{11}$ ) and 3.1% ( $Rb_8Tl_{11}$ ) and a tilt angle of 2.4° ( $K_8Tl_{11}$ : 4.7°,  $Rb_8Tl_{11}$ : 4.9°) suggest a minimal involvement of chloride; the s.o.f. for chlorine at this position refined to a value of 10%, but the resolution of the data set does not allow for a distinct statement.

## 3) How do mixed cation sites affect the amount of halide incorporation?

	$Cs_8Tl_{11}Br_{0.9}$	$Cs_8Tl_{11}Cl_{0.8}$
Cs2A - X1	3.990(2)	3.991(9)
Cs2B - void	4.388	4.354
Cs1-X1/void	3.6705(4)	3.5876(7)
s.o.f.(X/Cs2A)	0.924(6)	0.76(2)



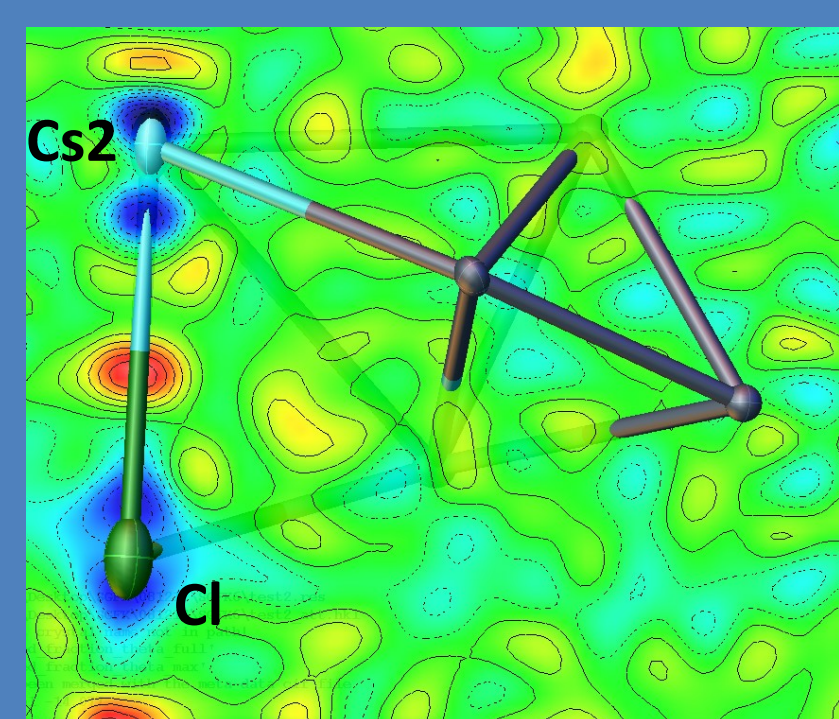
Containing halide Without halide

For  $Cs_8Tl_{11}X$  (X=Cl, Br) well resolved data sets could be obtained which showed a split position for Cs2 (Wyckoff 12c), where the position closer to the halide X1 shows the same s.o.f. as the halide position.

	$Cs_5Rb_3Tl_{11}Cl_{0.5}$	$Cs_{5.7}K_{2.3}Tl_{11}Cl_7$
Cs2 - X1/void	4.099(2)	4.007(2)
A1-X1/void	3.6160(13)	3.5492(2)
s.o.f. (A1=Cs)	0.521(12)	0.612(9)
s.o.f.(X)	0.50(4)	0.60(4)

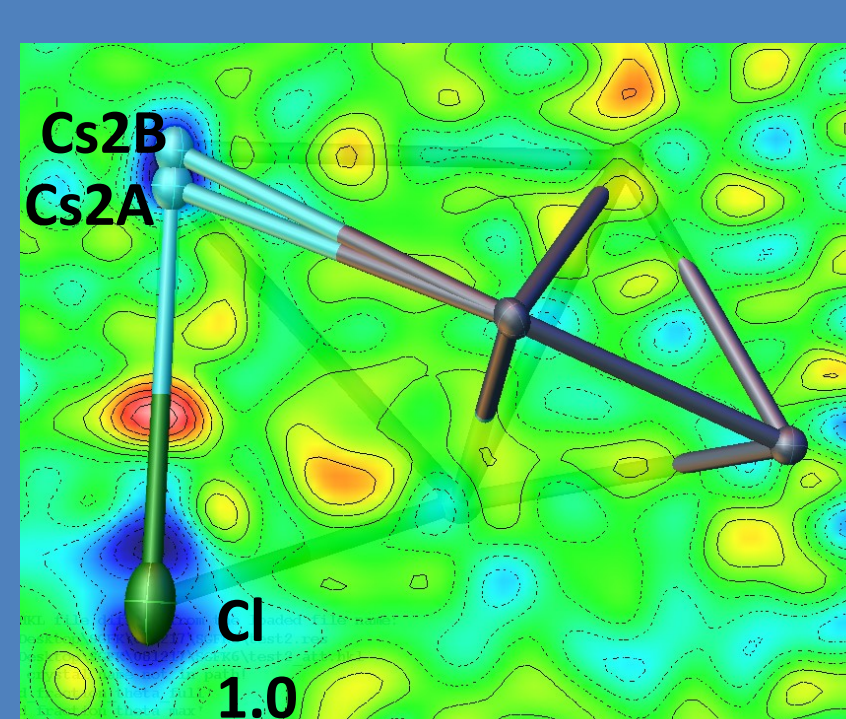
Less cesium → less halide

Introduction of a split position and free s.o.f. for chlorine in  $Cs_8Tl_{11}Cl_{0.8}$  results in an improved model.



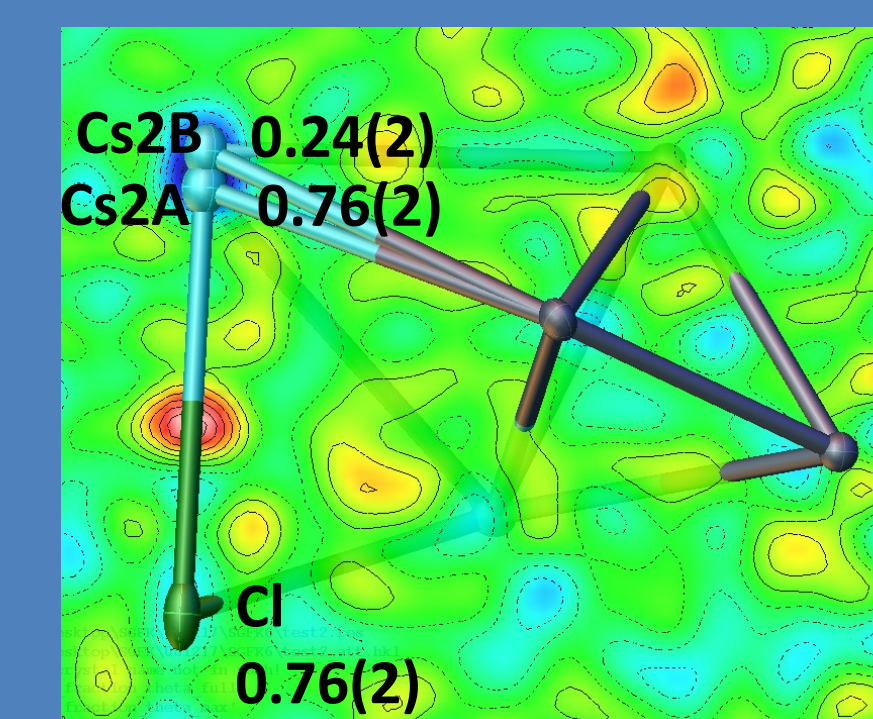
R1: 2.73%, max Peak 2.8, min peak -2.8

Split position for Cs2



R1: 2.68% max Peak 2.6 min peak -1.8

Split position for Cs2 and free s.o.f. for Cl



R1: 2.65%, max Peak 2.6, min peak -1.7

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