

Investigating the Role of the Alkali Metals in the Structure Type $K_{14}Cd_9Tl_{21}$



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During the last decade, exploration of systems between group 13 elements and alkali metals has uncovered a very interesting field of solid state chemistry with a rich novelty regarding the anionic substructure.¹ In these systems, the electronegative elements are able to adapt their bonding and coordination to fit a wide range of electron counts. Due to their electron poor character and the position at the frontier between metallic and salt-like materials makes alkali metal thallides are very interesting concerning their structural chemistry as they allow to investigate the limits of the *Zintl-Klemm* formalism.^{2,3} Alkali metal thallides can form three-dimensional networks, two-dimensional layers as well as isolated clusters.⁴ In this context the phase $A_{15}Tl_{27}$ ($A=K, Rb, Cs$)^{5,6} is quite interesting, as it combines isolated hypoelectronic $[Tl_{11}]^{7-}$ -clusters with two-dimensional $[Tl_{16}]^{8-}$ -layers. The porous two-dimensional $[Tl_{16}]^{8-}$ -layers contain large alkali metals as it was shown by Corbett for the ternary compound $CsRb_{14}Tl_{27}$.

The $K_{14}Cd_9Tl_{21}$ structure type, which was first reported in 1997 by *Tillard-Charbonnel et al.*, is related to the $A_{15}Tl_{27}$ phase.⁷ Here, one symmetry inequivalent thallium atom in the two-dimensional layer is substituted by a cadmium atom. Further, the large alkali metal, that resides in the pore of this layer (Wyckoff position 1b), is also replaced by a triangle of cadmium atoms (Wyckoff position 3g). That leads to a chemical composition of $[Cd_9Tl_{10}]^{9-}$ instead of $[Tl_{16}]^{8-}$ for the two-dimensional layer, what corresponds to a formal oxidation. Our investigations on the role of the different alkali metals on the structure type $K_{14}Cd_9Tl_{21}$ revealed new ternary and quaternary compounds of this structure type.⁸ It turned out that the alkali metals influence the composition of the two-dimensional layer whereas the isolated clusters stay unchanged.

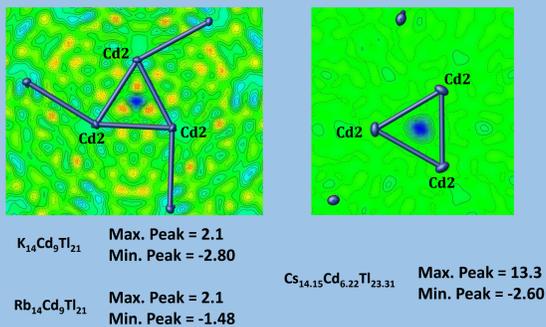
Ternary compounds of the $K_{14}Cd_9Tl_{21}$ structure type

Chemical formula	$K_{14}Cd_9Tl_{21}$	$Rb_{14}Cd_9Tl_{21}$	$Cs_{14.15}Cd_{6.22}Tl_{23.31}$
Formula weight	5850.77	6499.95	7343.67
Temperature [°C]	-150	-150	-150
Crystal system	hexagonal	hexagonal	hexagonal
Space group	P-62m	P-62m	P-62m
a = b [Å]	9.8623(4)	10.0131(4)	10.2145(3)
c [Å]	17.0878(8)	17.7296(7)	18.3007(6)
Volume [Å ³]	1439.37(13)	1539.45(14)	1653.61(11)
Z	1	1	1
ρ_{calc} [g/cm ³]	6.75	7.011	7.372
μ [mm ⁻¹]	33.853	37.071	35.619
F(000)	2399	2651	2925.0
Crystal size [mm ³]	0.05 × 0.02 × 0.02	0.05 × 0.03 × 0.02	0.04 × 0.03 × 0.02
Radiation [Å]	Ag K α ($\lambda = 0.56087$)	Ag K α ($\lambda = 0.56087$)	Ag K α ($\lambda = 0.56087$)
2 θ range [°]	5.322 to 55.672	5.186 to 55.716	5.054 to 61.306
Index ranges	-16 ≤ h ≤ 11, -12 ≤ k ≤ 11, -28 ≤ l ≤ 16	-15 ≤ h ≤ 16, -16 ≤ k ≤ 16, -23 ≤ l ≤ 29	-18 ≤ h ≤ 18, -16 ≤ k ≤ 18, -33 ≤ l ≤ 26
Reflections collected	10969	13903	18597
Independent reflections	2559	2642	3800
R_{int}	0.0391	0.0333	0.0307
Data/restraints/parameters	2559/0/47	2642/0/47	3800/1/51
Goof	1.048	1.032	1.103
Final R-values [$I > 2\sigma(I)$]	$R_1 = 0.0223$, $wR_2 = 0.0360$	$R_1 = 0.0200$, $wR_2 = 0.0348$	$R_1 = 0.0230$, $wR_2 = 0.0475$
Final R-values [all data]	$R_1 = 0.0258$, $wR_2 = 0.0367$	$R_1 = 0.0216$, $wR_2 = 0.0352$	$R_1 = 0.0253$, $wR_2 = 0.0482$
$\Delta\rho_{max}/\Delta\rho_{min}$ [eÅ ⁻³]	2.13/-2.80	2.33/-1.48	2.51/-1.68
Flack Parameter	-0.002(7)	0.029(7)	-0.009(5)

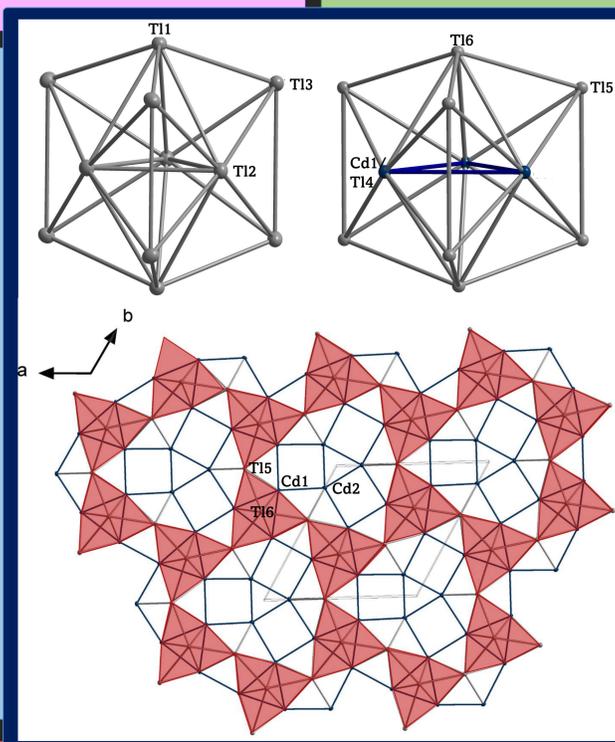
Quaternary compounds of the $K_{14}Cd_9Tl_{21}$ structure type

Chemical formula	$Rb_{1.78}K_{12.22}Cd_8Tl_{21}$	$Cs_{1.34}K_{12.73}Cd_{8.42}Tl_{21.39}$	$Cs_{2.06}Rb_{12.04}Cd_{8.12}Tl_{21.58}$
Formula weight	5933.31	5993.72	6625.85
Temperature [°C]	-150	-150	-150
Crystal system	hexagonal	hexagonal	hexagonal
Space group	P-62m	P-62m	P-62m
a = b [Å]	9.8793(2)	9.9334(4)	10.0773(3)
c [Å]	17.1230(2)	17.0628(7)	17.7629(5)
Volume [Å ³]	1447.31(7)	1458.06(13)	1562.19(10)
Z	1	1	1
ρ_{calc} [g/cm ³]	6.807	6.826	7.043
μ [mm ⁻¹]	34.400	34.278	36.991
F(000)	2431	2452	2697.0
Crystal size [mm ³]	0.04 × 0.03 × 0.03	0.034 × 0.024 × 0.019	0.059 × 0.036 × 0.024
Radiation	Ag K α ($\lambda = 0.56087$)	Ag K α ($\lambda = 0.56087$)	Ag K α ($\lambda = 0.56087$)
2 θ range	4.2 to 61.31	5.306 to 55.714	5.164 to 61.31
Index ranges	-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -31 ≤ l ≤ 31	-16 ≤ h ≤ 16, -16 ≤ k ≤ 15, -24 ≤ l ≤ 28	-18 ≤ h ≤ 17, -15 ≤ k ≤ 18, -31 ≤ l ≤ 32
Reflections collected	40460	19700	32478
Independent reflections	3333	2616	3597
R_{int}	0.0353	0.0575	0.0397
Data/restraints/parameters	3333/0/49	2616/6/57	3597/0/53
Goof	1.129	1.162	1.104
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0142$, $wR_2 = 0.0313$	$R_1 = 0.0335$, $wR_2 = 0.0583$	$R_1 = 0.0229$, $wR_2 = 0.0530$
Final R indexes [all data]	$R_1 = 0.0150$, $wR_2 = 0.0314$	$R_1 = 0.0365$, $wR_2 = 0.0590$	$R_1 = 0.0241$, $wR_2 = 0.0534$
$\Delta\rho_{max}/\Delta\rho_{min}$ [eÅ ⁻³]	1.68/-1.40	3.40/-2.62	3.81/-2.30
Flack parameter	0.002(3)	-0.019(9)	0.045(5)

What is going on in the pore?

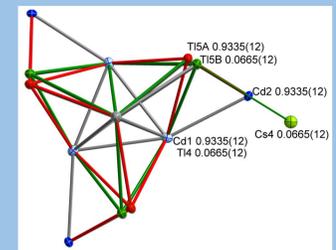


	$Cs_{1.34}K_{12.73}Cd_{8.42}Tl_{21.39}$	$Cs_{2.27}K_{12.73}Tl_{27}$	$Cs_{2.06}Rb_{12.04}Cd_{8.12}Tl_{21.58}$	$Cs_{2.11}Rb_{12.83}Tl_{27.2}$
Cs4-Tl4 [Å]	4.1063(6)	4.1476(4)	4.1625(7)	4.1931(3)
Cs4-Tl5(B) [Å]	4.0076(62)	4.2584(5)	4.4106(4)	4.2811(11)
Cs4-A3 [Å]	4.0060(24)	4.2196(29)	4.1427(10)	4.3065(8)
Tl4-Tl4 bzw. Cd1-Cd1 [Å]	2.9682(17)	3.0606(9)	2.9839(14)	3.0807(14)
Tl7-Tl4 bzw. Cd2-Cd1 [Å]	3.1027(13)	3.2665(8)	3.1639(12)	3.2833(12)
Tl7/Cd2-Tl5 [Å]	3.0121(9)	/	3.0551(9)	3.0124(53)
Tl7/Cd2-A3 [Å]	2.9680(10)	/	2.9821(9)	3.0705(18)
Tl7-Tl7 bzw. Cd2-Cd2 [Å]	3.8203(22)	/	3.9579(9)	4.0921(12)
	2.8319(20)	/	2.8797(18)	3.0765(12)



Role of the Alkali Metals

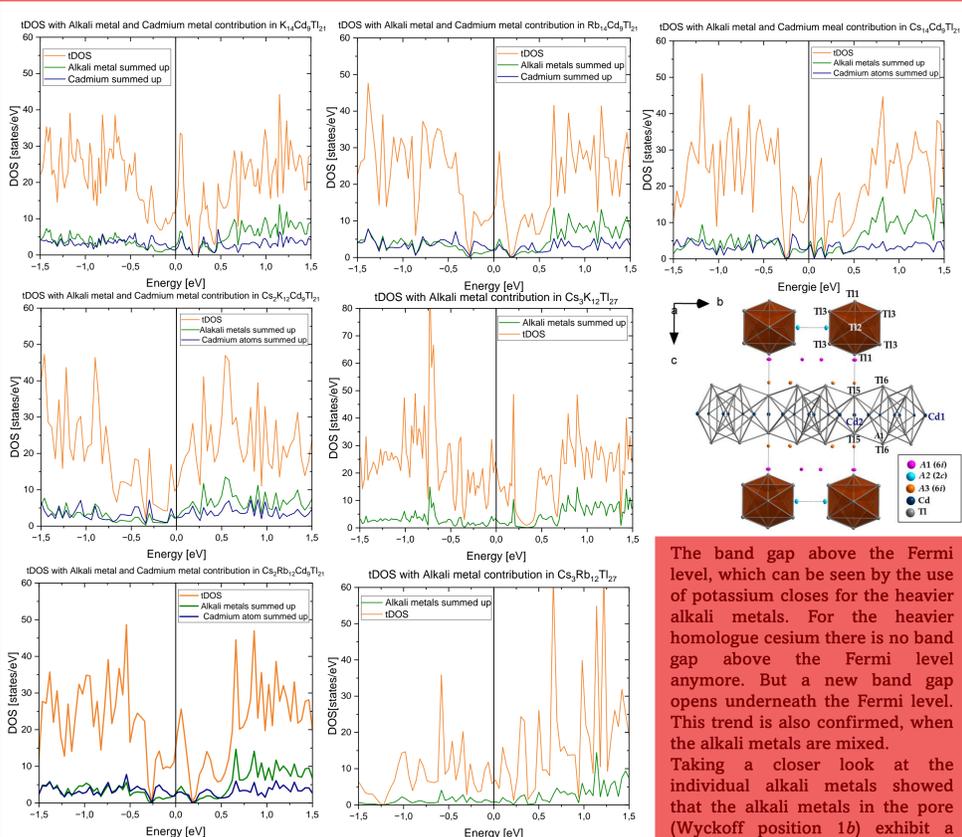
Apparently cesium expands the unit cell and elongates the Cd2-Cd2 distances (3g), which then rather fit Tl7-Tl7 distances (3g). This leads to an additional Tl incorporation in the pore of the two-dimensional layer on Wyckoff position 3g for the ternary compound $Cs_{14.15}Cd_{6.22}Tl_{23.31}$. The Tl5-Tl5-distances are compressed with the growing size of the alkali metal. Hence, this shows the more space demanding effect of the heavier alkali metal cesium compared to potassium or rubidium. With this compression there is less space available in the pore of the layer and therefore the single alkali metal (1b) is observed next to the more space demanding Cd-triangle (3g). This is the involvement of the $A_{15}Tl_{27}$ phase, which is always present if cesium is used. In the quaternary approaches, where the lighter alkali metals are present next to cesium the expansion is not that big. Thus, only the ternary compound shows an involvement of the binary $Cs_{14.52}Tl_{28.4}$.



The replacement of the Cs4 (1b) by a Cd2 (3g) leads to unusually short Cd2-Tl5 distances. Hence the Tl5 atom splits into Tl5A, which has the same s.o.f. as the Cd atom and Tl5B, which can be found in presence of the Cs4 atom. This model yields a reasonable Tl5A-Cd2 distance.

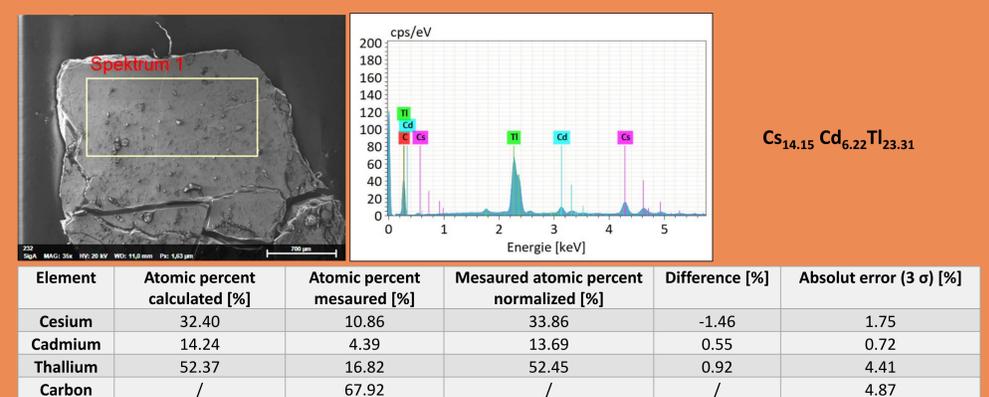
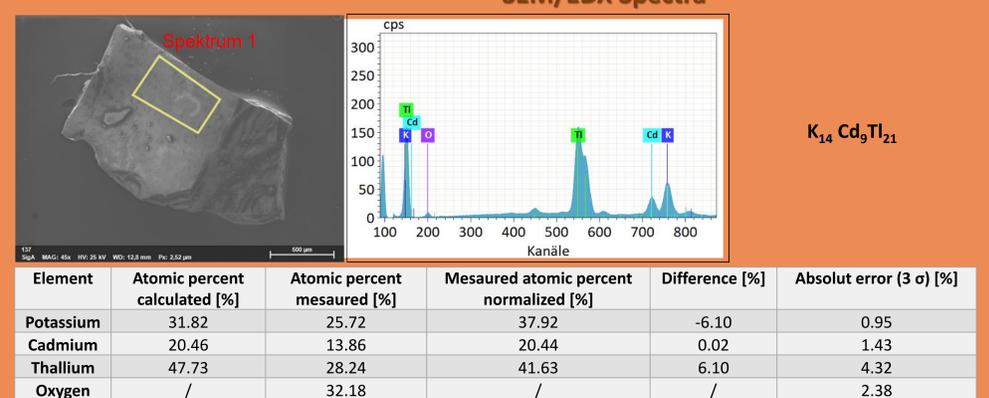
Density of States

Program: FPLO21, full-potential non orthogonal local orbital minimum-basis within the generalized approximation (GGA) for a full relativistic mode; exchange correlation: PBA



Also here it was tried to calculate the band structure and DOS for the hypothetically $K_{14}Cd_9Tl_{27}$, which only shows a Cd-triangle in the pore, but no substitution of the capping Tl4 atom by a cadmium atom. However, the calculations never converged.

SEM/EDX Spectra



Conclusion

While potassium and rubidium form a solid solution, the use of cesium always results in an involvement of the $A_{15}Tl_{27}$ phase next to the $K_{14}Cd_9Tl_{21}$ structure type. At the first glance it seemed to be only a size effect of the growing atomic radii of cesium compared to potassium and rubidium. Theoretical DFT calculation gave insight in the electronic properties of the compounds and suggested, that the different alkali metals might vary in their electronic effects. This seems to be a second explanation of the involvement of the $A_{15}Tl_{27}$ phase, if the heavy cesium is present. More sophisticated theoretical studies are planned.

Further investigations are focusing on the solid solution of rubidium and potassium in $A_{14}Cd_9Tl_{21}$. The use of the lighter homologue sodium never resulted in a compound of the desired structure type.

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