$Ag_{1+x}TIO_2$ (0.03 $\leq x \leq$ 0.18), Novel Adaptations of the Delafossite Structure Type Featuring Subvalent Silver

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Dedicated to Professor C. N. R. Rao on the Occasion of His 80th Birthday

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Abstract. A family of novel variations of the delafossite type of structure, Ag_{1+x}TlO₂, was synthesized and characterized. For three members the crystal structures were solved and refined on single crystal data: Ag_{1+a}TlO₂ [a = 0.18, $P\bar{3}m1$, Z = 1, a = 3.40427(9), c = 6.1296(1) Å, $R_1 = 0.033$, 126 independent reflections]; Ag_{1+ β}TlO₂ [$\beta = 0.09$, $R\bar{3}m$, Z = 6, a = 3.40685(8), c = 37.5953(9) Å, $R_1 = 0.039$, 214 independent reflections]; Ag_{1+ $\beta}TlO₂$ [$\gamma = 0.03$, $R\bar{3}m$, Z = 9, a = 3.40685(8), c = 37.5953(9) Å, $R_1 = 0.039$, 214 independent reflections]; Ag_{1+ $\gamma}TlO₂$ [$\gamma = 0.03$, $R\bar{3}m$, Z = 9, a = 3.40685(8), c = 37.5953(9) Å, $R_1 = 0.039$, 214 independent reflections]; Ag_{1+ $\gamma}TlO₂$ [$\gamma = 0.03$, $R\bar{3}m$, Z = 9, a = 3.40685(8), c = 37.5953(9) Å, $R_1 = 0.039$, 214 independent reflections]; Ag_{1+ $\gamma}TlO₂$ [$\gamma = 0.03$, $R\bar{3}m$, Z = 9, a = 3.40685(8) ($R_1 = 0.039$, $R\bar{3}m$, Z = 9, R = 0.039, $R\bar{3}m$, Z = 0.039, $R\bar{3}</sub></sub></sub></sub>$

Introduction

The $A^{I}M^{III}O_2$ delafossite type of structure^[1] can be realized virtually for any main group or transition metal *M* in the oxidation state +3 that tolerates octahedral coordination by oxygen, and the coinage metals *A* (Cu or Ag) in their monovalent states. Oxides featuring this structure continue to attract significant interest, among others as catalysts,^[2–6] inorganic phosphors,^[7,8] battery materials,^[9] transparent semiconductors,^[10–12] or in general for special properties.^[13,14] The basic structural variation encountered so far is related to the stacking sequences characterizing the trigonal structure, and is resulting in the formation of 2*H* and 3*R* polymorphs.^[15] Only recently variants of this apparently quite robust structure type have been reported. Among them are the first examples of quaternary delafossites Ag₃LiM₂O₆ (*M* = Rh, Ir),^[16] and Ag₃Ni₂O₄ as a new stage-2 intercalation compound of 2*H* AgNiO₂.^[17]

Quite a number of conventional 2*H* and 3*R* silver delafossites $AgMO_2$ (*M* = Al, Co, Cr, Fe, Ga, In, Lu, Ni, Rh, Sc, Tm, Yb) have been reported.^[18–25]

AgTlO₂ was first mentioned by *Geßner* in 1970 to adopt the 3*R* delafossite structure.^[26] In 1971 *Shannon* et al. published a hydrothermal synthesis of 3*R* AgTlO₂,^[19] starting from Ag₂O and Tl₂O₃, in aqueous sodium hydroxide (50%) at 500 °C. However, except for the lattice parameters no further crystallographic details were given. The reported lattice constant a = 3.568(2) Å is significantly larger than expected and

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does not follow the otherwise generally valid linear increase with increasing cation (3+) radius. *Sheets* et al. published an alternative hydrothermal synthesis route in 2006,^[27] reacting Ag₂O with Tl_2O_3 in an aqueous solution of 2.5 M NaOH at 210 °C. The yield of AgTIO₂ was about 50% and the sample contained unreacted Tl_2O_3 and elemental silver.

3.403(2), c = 56.67(3) Å, $R_1 = 0.038$, 397 independent reflections].

Different from the conventional delafossite structure, part of the silver

layers accommodate an excess of ca. 0.18 silver atoms per layer, thus

generating a subvalent bonding state of silver. In accordance with the

structural findings, the new silver oxthallates(III) are metallic conduc-

tors, and show reduced binding energies for the silver $3d_{5/2}$ states,

Herein we report on new silver delafossites $Ag_{1+x}TIO_2$, systematically accommodating an excess of silver.

Experimental Section

compared to silver(I) oxide.

Syntheses: $Ag_{1+\beta}TIO_2$ and $Ag_{1+\gamma}TIO_2$ can be synthesized from Ag_2O and TI_2O_3 (both freshly precipitated), adding an aqueous solution of 1 M KOH.

Phase pure $Ag_{1+\beta}TIO_2$ was obtained by reacting Ag_2O (266 mg, 1.15 mmol) and TI_2O_3 (457 mg, 1 mmol) in stainless steel autoclaves at elevated oxygen pressure and temperature.^[28] The intimately mixed starting materials were placed in gold tubes and reacted at $p(O_2) =$ 48 MPa and T = 400 °C, for 200 h. Addition of small amounts (0.2 mL) of an aqueous 1 M KOH solution resulted in enlarged crystallite sizes. Alternatively $Ag_{1+\beta}TIO_2$ was synthesized by ion exchange reaction in nitrate melts. Therefore a mixture of β -NaTIO₂^[29] and an excess of AgNO₃ and KNO₃ (ratio 2:1) were heated in sealed glass ampoules in an argon atmosphere for 50 h at 280 °C.

For $Ag_{1+y}TIO_2$, in a typical experiment Ag_2O (255 mg, 1.1 mmol), TI_2O_3 (457 mg, 1 mmol) and KOH (1 M, 15 mL) were combined and reacted for 14 d at 200 °C in a steel autoclave. The yield after filtration and elution with water and alcohol was 100% referred to the starting amount of thallium.

Pure samples of $Ag_{1+a}TIO_2$ were obtained from solid state reactions of mixtures of Ag_2O (freshly precipitated) and TINO₃ (Sigma-Aldrich, > 99.9%) in stainless steel autoclaves at elevated oxygen pressures and temperatures. The starting materials with a silver to thallium ratio of 1.4 were intimately mixed and placed into gold tubes, which were sealed from one side and mechanically closed from the other side. In a typical experiment phase pure samples of black, polycrystalline Ag_{1+a}TIO₂ were obtained by reacting Ag₂O (325 mg, 1.4 mmol) and TINO₃ (532 mg, 1 mmol) at the $p(O_2)$ and *T* conditions of 135 MPa and 420 °C, respectively.

All silver thallates are black crystalline solids with hexagonal platelike morphology. They are stable towards air and water.

X-ray Investigations: X-ray investigations on powder samples were performed using high-resolution X-ray powder diffraction data (D8,

Bruker, Cu- $K_{\alpha 1}$ radiation from primary Ge(111) Johannson-type monochromator), recorded at room temperature. The powder diffraction data were collected in the range of 5 to 100 degrees in 2θ . For refinement of the powder pattern, the program TOPAS was used.^[30]

The single crystal diffraction data were collected with a Bruker AXS Smart-CCD diffractometer (Mo- K_{α} radiation, graphite monochromator). Data reductions, including corrections for the Lorentz and polarization effect as well as absorption, were carried out.^[31,32] The structures were solved with direct methods and refined by using full-matrix least-squares techniques using the program package SHELXTL.^[33] For the technical details of data acquisition and selected crystallographic data, see Table 1 and Table 2.

Table 1. Crystal data	, data collection,	and refinement	details for	$Ag_{1+a}TlO_2$, Ag _{1+β} TlO	P_2 , and Ag_{1+}	$_{\gamma}$ TlO ₂ at 25	°C
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	$Ag_{1+a}TlO_2$	$Ag_{1+\beta}TlO_2$	$Ag_{1+\gamma}TlO_2$
Formula unit	Ag _{1.18} TlO ₂	Ag _{1.09} TlO ₂	Ag _{1.03} TlO ₂
Formula weight	363.66	351.97	347.84
Space group (no.), Z	$P\bar{3}m1$ (164), 1	$R\bar{3}m$ (166), 6	$R\bar{3}m$ (166), 9
Lattice constants			
a /Å	3.430(1)	3.4007(5)	3.4037(5)
	3.40427(9) ^{a)}	3.40685(8) ^{a)}	3.403(2) ^{a)}
c /Å	6.153(4)	37.52(2)	56.734(9)
	6.1296(1) ^{a)}	37.5953(9) ^{a)}	56.67(3) ^{a)}
V/Å ³	62.70(4)	375.8(1)	569.2(2)
$\rho_{\rm xray}$ /g·cm ⁻³	9.631	9.332	9.132
Crystal size /mm ³	$0.12 \times 0.10 \times 0.08$	$0.08 \times 0.06 \times 0.04$	$0.08 \times 0.06 \times 0.04$
Diffractometer		SMART APEX I, Bruker AXS	
X-ray radiation, $\lambda / \text{Å}$		Mo- K_{α} , 0.71073	
Absorption correction		Multi-scan, SADABS ^[32]	
2θ range /°	$6.62 \le 2\theta \le 68.14$	$9.72 \le 2\theta \le 64.60$	$2.16 \le 2\theta \le 69.56$
Index range	$-5 \le h \le 5$	$-5 \le h \le 5$	$-5 \le h \le 5$
	$-5 \le k \le 5$	$-4 \le k \le 5$	$-5 \le k \le 5$
	$-9 \le l \le 9$	$-54 \le l \le 54$	$-90 \le l \le 90$
Reflection collected	874	3001	2848
Data, <i>R</i> _{int}	126, 0.062	214, 0.061	397, 0.038
No. of parameters	11	18	23
Transmission: t_{max} , t_{min}	0.068, 0.041	0.160, 0.069	0.163, 0.070
$R_1 [F^2 > 2\sigma(F^2)]$	0.033	0.039	0.038
$wR(F^2)$	0.077	0.084	0.092
Extinction coefficient	_	0.0012(3)	_
CSD no.	427302	427303	427304

a) Lattice constants calculated from powder data by LeBail-fits.^[30]

Table 2. Ato	mic coordinates,	occupation	factors, a	nd displ	acement	parameters	$U_{ij} / 10^{-1}$	$^{-4} \cdot A^2$	at 25	°C.
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Atom	Site	x	у	z	Occ.	U_{11}	U ₂₂	U ₃₃	U_{12}	U ₁₃	U ₂₃	$U_{\rm eq}$
$Ag_{1+a}TlO_2$												
TI	1a	0	0	0	1	75(3)	U_{11}	372(6)	$U_{11}/2$	0	0	174(3)
Ag	3f	1/2	0	1/2	0.393(8)	1321(53)	4236(193)	832(39)	$U_{22}/2$	861(37)	1722(75)	1806(71)
õ	2d	1/3	2/3	0.809(2)	1	141(35)	U_{11}	194(55)	$U_{11}/2$	0	0	158(24)
$Ag_{1+\beta}TlO_2$												
TI	6 <i>c</i>	0	0	0.08194(2)	1	82(4)	U_{11}	144(5)	$U_{11}/2$	0	0	103(4)
Ag1	3 <i>b</i>	0	0	1/2	1	283(9)	U_{11}	84(10)	$U_{11}/2$	0	0	217(6)
Ag2	9e	1/2	0	0	0.390(11)	1214(60)	3543(206)	364(32)	$U_{22}/2$	-496(29)	-992(57)	1448(72)
01	6 <i>c</i>	0	0	0.4449(5)	1	123(46)	U_{11}	105(69)	$U_{11}/2$	0	0	117(31)
O2	6 <i>c</i>	0	0	0.7169(5)	1	131(48)	U_{11}	119(72)	$U_{11}/2$	0	0	127(32)
$Ag_{1+\nu}TlO_2$												
Tl1	3a	0	0	0	1	134(3)	U_{11}	178(4)	$U_{11}/2$	0	0	149(2)
T12	6 <i>c</i>	0	0	0.44471(1)	1	128(2)	U_{11}	187(3)	$U_{11}/2$	0	0	148(2)
Ag1	6 <i>c</i>	0	0	0.27707(3)	1	312(6)	U_{11}	126(6)	$U_{11}/2$	0	0	250(4)
Ag2	9 <i>d</i>	1/2	0	1/2	0.367(6)	1194(48)	3359(164)	393(24)	$U_{22}/2$	504(24)	1007(48)	1407(57)
01	6 <i>c</i>	0	0	0.2404(2)	1	161(38)	U_{11}	105(48)	$U_{11}/2$	0	0	142(25)
O2	6 <i>c</i>	0	0	0.3135(2)	1	147(38)	U_{11}	141(54)	$U_{11}/2$	0	0	145(25)
03	6 <i>c</i>	0	0	0.1333(2)	1	192(42)	U_{11}^{11}	135(52)	$U_{11}^{11}/2$	0	0	173(27)



Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository number CSD-427302 (Ag_{1+a}TIO₂), CSD-427303 (Ag_{1+b}TIO₂) and CSD-427304 (Ag_{1+y}TIO₂).

Energy Dispersive X-ray Spectoscropy: EDX analyses were carried out on single crystals of different samples, with a Philips XL 30 TMP, equipped with an energy dispersive unit for microanalysis (Phönix, EDAX).

Conductivity Measurements: Measurements of the electrical conductivity were performed by the four-point-probe method (Van-der-Pauw) on pressed pellets (diameter: 6 mm, thickness: 1 mm).

X-ray Photoelectron Spectroscopy: XPS measurements were performed on powder samples, with an Axis ULTRA spectrometer (Al- K_{α} radiation: $h \times v = 1486.58$ eV, resolution ca. 0.1 eV). As an external standard, the binding energy of the C-1*s*- band was used.

Thermal Analysis: The thermal behavior was measured with the DTA/TGA equipment STA 409, Netzsch, Selb, coupled with a quadrupole mass spectrometer. The samples were heated in a corundum crucible with a rate of 10 °C·min⁻¹ in a flow of dry argon.

Results and Discussion

Syntheses

The title compounds of general composition $Ag_{1+x}TIO_2$ embody novel adaptations of the delafossite structure type. For their syntheses, diverse combinations of starting materials may be applied, which are subjected to respective specific modes of processing. The most obvious approach is to start from the binary oxides, Ag₂O and Tl₂O₃. Ion exchange of Ag⁺ for Na⁺ in NaTlO₂, and reacting Ag₂O and TlNO₃ work as well. In each case a ratio 1.0 < Ag/Tl < 1.4, elevated oxygen pressure and hydrothermal conditions with degrees of filling ranging from 1 to 5% of the autoclave volume was applied, with reaction temperatures ranging from 200 to 420 °C. At any of those conditions members of the new family of silver thallates form reproducibly. However, it has proven difficult to achieve fully targeted preparation of individual members of the family consisting of Ag_{1+a}TlO₂ ($a \approx 0.18$), Ag_{1+b}TlO₂ ($\beta \approx 0.09$), and Ag_{1+ γ}TlO₂ ($\gamma \approx 0.03$), which in a wider sense represent polytypes.



Figure 1. Structural building units encountered in $Ag_{1+x}TIO_2$ delafossites with O–Ag–O dumbbells oriented parallel (a) and inclined (b) to the *c* axis. Color code: TI = green, Ag = white/black, O = red.

Crystal Structures

For the three cases mentioned, single crystals were grown and the crystal structures were solved and refined on single crystal data. All structures are constructed of the same building units, which are combined in different ratios and stacking sequences. The anionic partial structure $(TlO_2)^-$ is the same in all three cases, the very common slab of edge sharing $[TIO_6]$ octahedra. It is representing a cut out of the rock salt structure, and is found e.g. in the α -NaFeO₂,^[34] CuFeO₂ (delafossite),^[1] and β -RbScO₂ types of structure.^[35,36] Usually, these 2D polyanions are arranged on trigonal lattices, stacking along the respective c directions. The spacings in between are occupied by the monovalent cations in octahedral, trigonal or linear surroundings. The group 11 elements, Cu and Ag, always adopt a linear coordination. Within the resulting 3R and 2H delafossites the O– A^+ –O dumbbells are oriented parallel to the *c* axis, while they are inclined to the c axis direction in the related Ag₅Pb₂O₆ structure family.^[37,38] In the new silver thallates these building units (see Figure 1) are combined to form different stacking variants, see Figure 2. We had to refine average structures with respect to the silver atoms located within the



Figure 2. Crystal structures of $Ag_{1+a}TIO_2$ (a), $Ag_{1+\beta}TIO_2$ (b), and $Ag_{1+\gamma}TIO_2$ (c). The viewing direction is [010], with red spheres (oxygen), green (thallium), white (ordered silver atoms), black (disordered silver positions), blue polyhedra represent the TIO₆ octahedra.

tilted dumbbells (see Figure 3), while all remaining parts of the structures appear to be fully ordered. Applying split atom models have resulted in rather good figures of merit for the refinements. The site occupation factors for the split silver positions, which should amount to 1/3 for the ideal composition AgTlO₂, converged to significantly higher values ranging from 0.367 to 0.393 (see Table 2). This is indicating significant excess of silver to be present, which was confirmed by independent analyses. The compositions can be narrowed down to 1.17 silver atoms per disordered layer. Taking into account the stacking sequences the deviations from an ideal composition amount to a = 0.18, $\beta = 0.09$, and $\gamma = 0.03$ within the respective stacking variants given in Figure 2.



Figure 3. Positions of the silver atoms, ideal delafossite (open circles, cf. Figure 1a), and disordered layers (black circles, cf. Figure 1b).

The quite sizeable non-stoichiometry as found for the otherwise rather robust delafossite structure type comes as a surprise, on a first glance. However, in the light of findings during the recent past the observations appear reasonable. In the wake of having acquired the capability to react Ag₂O virtually with any other binary oxide in a solid state reaction, silver-rich multinary oxides have become generally accessible.[28,39] Many of these compounds show as a common feature clusterlike arrangements of silver(I) cations, displaying Ag-Ag separations partly as short as 2.80 Å, which is substantially below the sum of the van der Waals radii. This general feature has encouraged us to suggest some kind of bonding to be active between the equally charged silver atoms,^[39,40] and to predict that silver should be able to exist in a subvalent state, i.e. in an oxidation state smaller than 1+.[41] Indeed, several such examples of "metallic" oxides have been discovered, meanwhile. Among them are exotic representatives like Ag₅GeO₄,^[42-44] Ag₂NiO₂,^[45,46] and Ag₁₃OsO₆.^[47] Against this background, the results presented herein can be well explained: the length of the *a* axis of delafossites is determined by the size of the M^{3+} cation, accordingly Tl³⁺ features the longest *a* lattice constant (3.4 Å) for any delafossite known. As a consequence, the silver spacings on this lattice are much larger than the shortest Ag^+-Ag^+ distances known (about 2.8 Å), even wider than the sum of the van der Waals radii. Depending on the Ag^+-Ag^+ distances assumed, the space available would allow to accommodate by a factor of 1.2–1.4 more silver atoms per layer than required for the ideal composition. Noteworthy, in all three cases the parameters of thermal motion show considerable anisotropies in the displacements of the silver atoms at the split positions indicating that these are smeared out within the *ab* plane.

The refinements of the average structures leave some unresolved crystallographic implications behind. While the lengths of the c axes have been unambiguously determined from the diffraction patterns, and comply well with the respective stacking sequences found, within the h,k-space no superstructure reflections were visible. Thus, based on the structural models suggested several different real structures may be discussed.

Starting from the split atom model as refined, one might derive various ordering patterns. Two are displayed in Figure 4, whereby both require to shift the silver atoms within the ellipsoids of displacement from the refined split position and to delete some of them. However, the resulting models show too short Ag–Ag separations of only 2.45–2.65 Å, and a too high silver content. It appears much more reasonable to assume a composite crystal, where the periodicities of the $[TIO_2]^-$ and silver substructures within the *ab* plane do not comply. So far, we do not have any evidence that the two substructures mentioned are commensurate.



Figure 4. Possible ordering patterns of silver layers, (a) corresponds to a silver layer with Ag–Ag distances of ca. 2.65 Å and a composition of Ag_{1.25}TlO₂. In (b) the composition is Ag_{1.50}TlO₂ with Ag–Ag distances of ca. 2.45 Å. The ellipses are projections of the displacement parameters of Ag onto the *ab* plane (50% probability level), and each corner of the grey squares represents an accessible silver position.

Analyses and Physical Properties

The results of the crystal structure refinements, indicating the presence of an excess of silver and thus a subvalence in silver character for all of the new silver thallates presented, were corroborated by EDX analyses, electronic conductivity measurements, and XPS. EDX analyses on single crystals are in fair agreement with the results of the refinements of the site occupation factors.

Figure 5 shows the electrical resistance of Ag_{1+γ}TIO₂, which like Ag_{1+a}TIO₂ and Ag_{1+β}TIO₂, is a metallic conductor. The specific resistivities at room temperature are $2.21 \times 10^{-5} \,\Omega \cdot \text{cm}^{-1}$ (Ag_{1+a}TIO₂), $6.74 \times 10^{-5} \,\Omega \cdot \text{cm}^{-1}$ (Ag_{1+β}TIO₂), and $1.03 \times 10^{-4} \,\Omega \cdot \text{cm}^{-1}$ (Ag_{1+γ}TIO₂), respectively. Thus, the resistance increases with the number of ordered silver layers, confirming the subvalent character of silver in the more crowded disordered layers.



Figure 5. Temperature dependence of the electrical resistivity (*R*) of $Ag_{1+y}TIO_2$.

The 3d binding energies of the title compounds along with suitable references were monitored by X-ray photoelectron spectroscopy (see Figure 6). The energies of the Ag-3d states for Ag_{1+a}TlO₂, Ag_{1+β}TlO₂, and Ag_{1+γ}TlO₂ are between those of elemental silver and Ag₂O. With the number of overcrowded (subvalent) silver layers growing, the binding energies approach those of elemental silver. The Ag-3d_{5/2} band for Ag_{1+γ}TlO₂ at 367.9 eV is close in energy to 3d_{5/2} for Ag₂O (367.8 eV), whereas for Ag_{1+a}TlO₂ (368.2 eV) virtually the same binding energies for Ag_{1+a}TlO₂ (368.1 eV) were found to be between Ag_{1+a}TlO₂ and Ag_{1+γ}TlO₂.

In 1 atm argon atmosphere, $Ag_{1+a}TIO_2$ starts decomposing at 350 °C. The onset of thermal decomposition of $Ag_{1+\beta}TIO_2$ is at 390 °C, the highest decomposition rate is observed at 480 °C with a final weight loss of 2.4% at 510 °C. For $Ag_{1+\gamma}TIO_2$ the thermal decomposition starts at 370 °C with the highest degradation rate at 450 °C and a final mass loss of 2.2% at 490 °C. In all three compounds the decomposition is caused by the reduction of Ag^{+1} to elemental silver, leaving



Figure 6. XPS-spectra of Ag₂O (black), Ag_{1+a}TIO₂ (red), Ag_{1+ β}TIO₂ (blue), Ag_{1+ γ}TIO₂ (purple) and Ag (turquoise).

Ag and Tl_2O_3 as solid residues behind, which were identified by means of X-ray powder diffraction.

Conclusions

We report on the synthesis and characterization of a new family of silver oxothallates(III), Ag_{1+x}TlO₂, which represent novel variants of the delafossite type of structure. In contrast to the conventional 2H and 3R delafossites, silver forms two distinct kinds of layers on the basic trigonal lattice. One type (A) features 2D close packed layers of silver fully adapted to the ab lattice spacings, realizing a Ag/Tl ratio of 1, and with the resulting O-Ag-O dumbbells aligned parallel to the c axis. This is the situation commonly encountered in delafossites. The second type (B) of 2D layers of silver is accommodating additional silver atoms, with the linear units O-Ag-O inclined against the c axis. Apparently, the $[TIO_2]^-$ slabs can be intercalated by the two different kinds of silver layers in any sequence. There are two obvious factors of influence that favor, or admit, to accommodate additional silver atoms in the structure. One degree of freedom results from the large ab lattice spacing (3.4 Å), the second from the capability of silver to adopt subvalent (< 1+) bonding states. It is known from cluster-like arrangements of Ag⁺ that the respective homo-ionic separations can be as small as 2.8 Å, in respective systems containing subvalent silver even values of 2.7 Å have been observed. Given these numbers, the *ab* lattice base would have room for about 1.4 silver atoms per thallium atom. While the possible stacking sequences of A and B can be easily enumerated, and thus the possible structures be predicted, the silver content within the B layers may vary from slightly above 1 to about 1.4. For three individual members of the family, $Ag_{1+x}TIO_2$ (x = a = 0.18, β = 0.09, γ = 0.03), the crystal structures were solved and refined applying a split atom model to the B silver layers, from single crystal data. The physical properties as determined thus far corroborate the subvalent (electron rich) character of the Ag_{1+x}TlO₂ family, displaying metallic conductivity, and reduced 3d_{5/2} binding energies ranging between elemental silver and silver(I) oxide. In order to reveal the real structure further studies, including HRTM, are required.

ARTICLE

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