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Crystalline and Glassy Phases in the Ternary System Tl/Bi/Cl: Synthesis and Crystal Structures of the Thallium(I) Chloridobismutates(III) Tl_3BiCl_6 and $TlBi_2Cl_7$

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Dedicated to Professor Rüdiger Kniep on the Occasion of His 65th Birthday

Keywords: Thallium; Chloridobismutates; Lone pair effect; NMR spectroscopy; X-ray absorption spectroscopy; Glass formation

Abstract. Slow cooling of melts composed of TlCl and $BiCl_3$ allows for the isolation of the compounds Tl_3BiCl_6 (**1**) and $TlBi_2Cl_7$ (**2**). Compound **1** is formed by sublimation at 480 °C from the black melt of 3 TlCl + 1 $BiCl_3$ as colourless crystals. The crystal structure determination (tetragonal, $P4_2/m$) consists of nearly regular octahedral $[BiCl_6]^{3-}$ anions and two independent Tl^+ cations, which have coordination number 8 in form of a slightly distorted cube and 10 in form of an *Edshamar* polyhedron, respectively. The structure is not isotypic with the recently reported naturally occurring form of Tl_3BiCl_6, the mineral steropesite. Compound **2** is obtained from a dark red melt of composition TlCl + 2 $BiCl_3$. On rapid cooling, this melt solidifies to a metastable dark red glass which at ambient temperature crystallises to a light amber crystalline powder within some weeks. The structure of **2** was determined by powder diffraction (triclinic, $P\bar{1}$). A distinct lone pair effect is present causing an irregular coordination on the two independent bismuth atoms. Taking Bi–Cl bonds up to 3.5 Å into account, both bismuth atoms gain coordination number seven. ^{203}Tl and ^{205}Tl solid state NMR and XANES spectra on the Bi and Tl-L_{III} edges of both glassy and crystalline $TlBi_2Cl_7$ show that a close structural similarity exists between both forms. In contrast, the Raman spectra show distinct differences in the bands of the Bi–Cl vibrations region.

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Introduction

The crystal chemistry of the halides of trivalent bismuth is strongly influenced by the stereochemical activity of the lone electron pair on Bi^{3+}. Its structural influence is generally strong among the fluorides, but decreases with the heavier halogens. In the structure of BiF_3, the Bi^{3+} ion has a distorted square-antiprismatic coordination [1]. In $BiCl_3$, a strongly distorted 3+3 octahedral coordination with three short and three long Bi–Cl bonds is present [2], whereas for BiI_3 an almost undistorted octahedral coordination environment was found [3]. During the last two decades, a number of alkali halogenidobismutates have been characterised, which show a large structural variability, mainly caused by the absence or presence of the lone-pair effect of the trivalent bismuth atoms. Examples are $CsBi_2F_7$ [4] containing a Bi/F framework, in which the bismuth atoms have a strongly distorted six to eight fold coordination by fluoride anions. On the other hand, the structure of Cs_3BiCl_6 [5] contains discrete $BiCl_6$ units in which the Bi–Cl coordination is nearly ideally octahedral.

This structural variability can be further expanded by the substitution of alkali ions by such ions which themselves have a potentially steric active lone-pair. Looking for substances with nonlinear optical properties, *Hagemann* and *Weber* prepared crystals of the compounds $Tl_7Bi_3I_{16}$ and Tl_3BiI_6. The crystal structures, however, could not be determined due to twinning problems [6]. Later, *Ruck* and co-workers were able to characterise structurally the phases $Tl_7Bi_3I_{16}$, Tl_3BiI_6 [7], and $Tl_3Bi_2I_9$ [8] by X-ray diffraction. All three iodidobismutates have bismuth in sixfold coordination. The BiI_6 coordination octahedra are distorted, which is assigned to the effect of the lone pair.

Only one compound in the ternary system Tl/Bi/Cl was described so far. The mineral steropesite of the approximated formula Tl_3BiCl_6 was recently found in volcanic high-temperature fumaroles [9]. The lack of knowledge on this ternary system led us to explore the formation and structures of phases among the thallium chloridobismutates.

Experimental Section

Starting Materials

$BiCl_3$ was obtained by chlorination of bismuth at 400 °C followed by several cycles of sublimation in vacuo. TlCl was precipitated from an aqueous solution of $TlNO_3$ with hydrochloric acid, washed with water and dried in dynamic vacuum for several days. Glass ampoules of 10 cm length and 1.5 cm diameter were used as reaction vessels. All manipulations with the hygroscopic $BiCl_3$ including charging and opening of the reaction ampoules were performed in an argon filled glove box.

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Synthesis of Tl_3BiCl_6

Tl_3BiCl_6 was synthesised by heating a melt of TlCl and $BiCl_3$ in 3:1 molar ratio to 480 °C for ten hours in evacuated glass ampoules and slow cooling (5 °C·h^{-1}) the black-brown melt to ambient temperature. In a typical experiment, an ampoule of 12 cm length and 1.5 cm diameter was loaded with the TlCl/$BiCl_3$ mixture (700 mg). Besides a black amorphous residue, colourless crystals of high refractivity deposited at the inner walls of the ampoule in the cooler region above the melt.

Synthesis of $TlBi_2Cl_7$

Polycrystalline samples of $TlBi_2Cl_7$ were prepared by heating a mixture of TlCl and $BiCl_3$ in the molar ratio 1:2 to 250 °C in evacuated glass ampoules and slowly cooling (10 °C·h^{-1}) the dark red melt to ambient temperature. Trying to obtain single crystals by sublimation of the product only lead to sublimation of $BiCl_3$ leaving behind the less volatile TlCl.

Analytical Methods

Raman spectra were recorded using a BRUKER FT Raman spectrometer RFS100 in backscattering geometry, a Nd:YAG laser (λ = 1036 nm) and a resolution of 4 cm^{-1}. The laser power was adjusted between 30 and 300 mW. Measurements were done on powdered samples enclosed in sealed glass capillaries of 1 mm diameter. X-ray absorption spectra were measured at the synchrotron light source ANKA of the Forschungszentrum Karlsruhe, Germany. Solid state NMR spectra were recorded with a VARIAN Infinity Plus spectrometer applying the MAS technique. Samples were packed in a rotor of 4 mm diameter and a rotation frequency of 12 kHz was applied. The spectrum was calibrated against a solution of $TlNO_3$ with a concentration of 0.1 mol·L^{-1}. The resonance frequencies were 229.36 MHz for ^{203}Tl and 231.62 MHz for ^{205}Tl. Differential scanning calorimetry mesurements were carried out with a DSC 204 Phoenix instrument (Netzsch Inc.) in closed aluminium crucibles with samples of about 15 mg.

Crystal Structure Determination of Tl_3BiCl_6

The crystals of Tl_3BiCl_6, deposited from the gas phase as described above, were notoriously multiple twinned with diffraction patterns that could not be indexed and it took several attempts until a suitable single crystal specimen was found. Diffraction data were recorded at ambient temperature using a Bruker Nonius Kappa-CCD diffractometer with Mo-K_α radiation. The tetragonal symmetry and the systematic absences led to the space group $P4_2/m$. An empirical absorption correction was applied to the data set [10]. The structure model was obtained by direct methods and refined based on F^2 with anisotropic displacement parameters for all atoms [11]. The crystallographic data and details of data collection are summarised in Table 1, atomic coordinates in Table 2. The powder diffractograms of bulk samples can, however, be completely indexed and simulated on the basis of the tetragonal unit cell and the positional parameters obtained by the single crystal structure analysis. No reflections of additional phases are present indicating that under the applied reaction conditions only one single phase is formed.

Table 1. Crystallographic data and details of the structure determination for Tl_3BiCl_6 and $TlBi_2Cl_7$.

Compound	Tl_3BiCl_6	$TlBi_2Cl_7$
Formula	$BiCl_6Tl_3$	Bi_2Cl_7Tl
Crystal system, space group	tetragonal, $P4_2/m$	triclinic, $P\bar{1}$
Number of formula units, Z	2	2
a /Å	8.9690(2)	8.8832(1)
b /Å		10.7632(1)
c /Å	7.4876(2)	6.9329(1)
α /°		107.523(1)
β /°		107.334(1)
γ /°		75.684(1)
V /Å^3	602.32(2)	594.30(1)
Density (calcd.) /g·cm^{-3}	5.706	4.86
Absorption coefficient μ /mm^{-1}	55.84 (Mo-K_α)	96.89 (Cu-K_α)
Diffractometer type	Bruker-Nonius κ-CCD	Bruker D8 Advance
Radiation, wavelength /Å	Mo-K_α, 0.7107	Cu-$K_{\alpha1}$, 1.540598
Temperature /K	293	293
$2\theta_{max}$ /°	54.94°	4° < 2θ < 81°
hkl range	h±11, k±8, l±9	$0 \le h \le 7$, $-8 \le k \le 9$, $-5 \le l \le 5$
Absorption correction	empirical [9]	cylinder correction
T_{min}/T_{max}	0.005/0065	0.060/0.107
Reflections collected	1356	1484
Independent reflections, R_{merg}	730, 0.027	
No. of data and parameters	730 and 31	1480 and 41
Goodness-of-fit on F^2	1.066	1.55
$wR(F^2)$	0.070	0.043
$R(\|F\|)$ for [n] $F_o > 4\sigma(F_o)$	0.028 [682]	
$R(\|F\|)$ for all data	0.031	
$R_{Profiles}$		0.031
$wR_{Profiles}$		0.043
$wR(F^2)$		0.079
Largest difference peak and hole /e·Å^{-3}	+1.30 and –1.57	+1.88 and –1.61

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Table 2. Positional coordinates and equivalent isotropic displacement parameters U_{eq} /Å^2 for the atoms in the structure of Tl_3BiCl_6. Standard deviations refer to the last significant digit.

Atom	*x*	*y*	*z*	U_{eq}
Tl(1)	0.07685(7)	0.26533(6)	0	0.0540(3)
Tl(2)	0.5	0.5	0	0.0373(3)
Bi	0	0.5	0.5	0.0221(2)
Cl(1)	0.2037(2)	0.5612(3)	0.2463(3)	0.0382(5)
Cl(2)	0.0644(4)	0.2068(4)	0.5	0.059(1)

Crystal Structure Determination of $TlBi_2Cl_7$

To protect the slightly hygroscopic powder of $TlBi_2Cl_7$ from moisture, samples were filled in glass capillaries with a diameter of 0.2 mm after thoroughly grinding with an equal amount of glass powder. Data were collected at ambient temperature using a Bruker-D8 Advance powder diffractometer with Cu-K_α radiation. 10482 data points were recorded in the 2θ range 4 to 81° with increments of 0.00735°. Indexing of the diffractogram and determination of the lattice parameters were performed using the program WinXPow [12]. The diffraction pattern could be indexed by a triclinic cell. A first kind Chebyshev background function with 30 terms was applied as implemented in the GSAS program system [13]. A Pseudovoigt function with 18 terms was used to fit the reflection profiles for all 1480 identified reflections. Structure models were obtained with the aid of the program Endeavour [14]. Due to the closely similar atom scattering factors of bismuth and thallium, it turned out to be advantageous to assume both kinds of atoms as occupied by Pb in the structure solution process and in the early stages of refinement. Out of the suggested structure models those were chosen fulfilling the restraints d_{min}(Pb–Pb) = 3,5 Å, d_{min}(Pb–Cl) = 2.5 Å, d_{min}(Cl–Cl) = 3.0 Å. Eliminating all models with high coordination numbers of cations by cations or anions by anions, one centrosymmetric model was left, which was refined by the Rietveld method using the program GSAS [12]. Finally, an assignment of the different thallium and bismuth positions could be made unequivocally based on the respective cation–Cl bond lengths. Isotropic displacement parameters for all atoms were chosen and refined as free parameters. Table 1 contains the crystallographic data and details of the refinement, Table 3 the positional parameters of the atoms. Figure 1 shows the observed the calculated powder diffractogram.

Table 3. Positional coordinates and isotropic displacement parameters U_{iso} /Å^2 for the atoms in the structure of $TlBi_2Cl_7$. Standard deviations refer to the last significant digit.

Atom	*x*	*y*	*z*	U_{iso}
Tl	0.6739(2)	0.1409(2)	0.9225(3)	0.0437(7)
Bi(1)	–0.2437(2)	0.5188(2)	0.5569(3)	0.0156(5)
Bi(2)	0.1380(2)	0.1583(2)	0.6966(2)	0.0209(6)
Cl(1)	–0.158(1)	0.3547(9)	0.795(1)	0.030(3)
Cl(2)	0.000(1)	0.0194(8)	0.262(1)	0.023(3)
Cl(3)	0.352(1)	0.318(1)	0.705(2)	0.053(4)
Cl(4)	0.256(1)	0.1904(9)	1.094(1)	0.032(3)
Cl(5)	0.370(1)	–0.0332(8)	0.647(1)	0.024(3)
Cl(6)	0.053(1)	0.6431(8)	0.648(1)	0.027(3)
Cl(7)	–0.445(1)	0.3869(9)	0.311(1)	0.028(3)

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-421317 for Tl_3BiCl_6 and CSD-421318 for $TlBi_2Cl_7$ [15]. The graphical representations were drawn with the use of the programs DIAMOND [16] and POV-RAY [17].

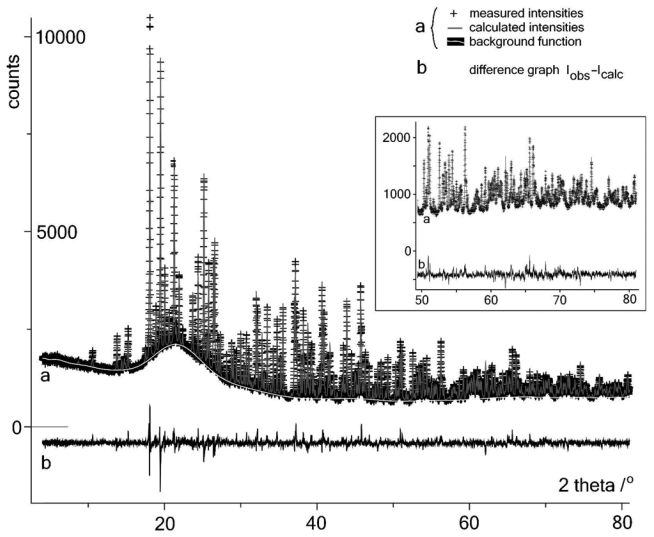

Figure 1. Powder diffractogram of $TlBi_2Cl_7$. Shown are the measured intensities, the calculated intensities, the background function, and the difference curve I_{obs}–I_{calcd}. The inset shows an enlarged view of the high angle region of the diffractogram.

Results and Discussion

Synthesis of Thallium(I) Chloridobismutates

In a series of experiments, the formation of discrete phases in the ternary system Tl/Bi/Cl was investigated by reactions of TlCl and $BiCl_3$ in different molar ratios from 3:1 to 1:3. With intermediate compositions no formation of compounds was observed. Powder diffractograms of solidified melts of compositions between 2:1 and 1:1 showed beside reflections of new phases reflections of the starting materials TlCl and $BiCl_3$. Another common feature is the widespread formation of dark coloured glassy solids on solidification of the melts. The formation of ternary compounds was only observed on the border areas of the investigated compositions, in the thallium rich and the bismuth rich region. Two different thallium(I) chloridobismutates, Tl_3BiCl_6 and $TlBi_2Cl_7$, composed of TlCl and $BiCl_3$ in the stoichiometric amounts 3:1 and 1:2, could be synthesised and isolated as discrete phases. With both compositions as a typical feature dark coloured melts are formed. In the case of the 3:1 mixture, the deposition of crystals of Tl_3BiCl_6 from the gas phase above the melt in a small temperature gradient during the slow cooling process from 480 °C to ambient temperature could be achieved. The deposited colourless crystals of Tl_3BiCl_6 are strongly light refracting. The analogous experiments with melts of the composition 1 TlCl:2 $BiCl_3$ gave melts of dark-red colour. In contrast to the TlCl rich melts, no deposition of crystalline material was observed from the gas phase above the melts of this composition. Slow cooling of such a melt from 250 °C to ambient temperature gives an amber coloured microcrystalline solid. By rapid quenching the melt from

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250 °C to –38 °C, performed by immersing the hot reaction ampoule into chilled liquid mercury, an amorphous, glassy, transparent, dark-red product was isolated (Figure 2a). Grinding of the red glass gives a light red to rose powder. The non-crystallinity was verified by X-ray powder diffraction. Leaving this glassy material at room temperature under protection from moist air causes the slow conversion into the light amber coloured crystalline phase (Figure 2b).

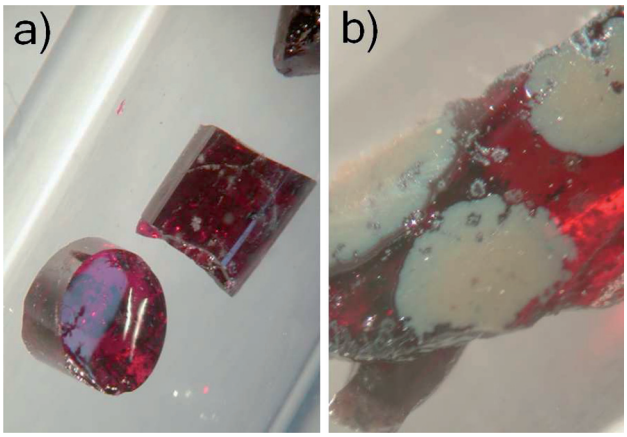

Figure 2. Photographs of pieces of the rapidly cooled melt of $TlBi_2Cl_7$, forming a dark red, transparent glass (a), and this glass after two weeks at room temperature with emerging amber coloured crystalline segregations (b).

Crystal Structure of Tl_3BiCl_6

The tetragonal unit cell of Tl_3BiCl_6 contains two formula units (Figure 3). Two bismuth atoms occupying the site symmetry 2/*m* are almost regular octahedrally coordinated by six chlorine atoms. The two independent Bi–Cl distances are equal within standard deviations and amount 2.692(2) and 2.693(3) Å (Table 4). The angular distortions within the $BiCl_6$ octahedra are small. A significant deviation from rectangularity is observed for the plane containing the bismuth atoms and the four Cl(1) atoms, which is inclined by 3° to the Cl(2)–Bi–Cl(2^{II}) axis. An almost regular shape of $BiCl_6$ octahedra in the structures of chloridobismutates(III) is not unusual and found e.g. in the structure of $(NH_4)_3[BiCl_6]$ (Bi–Cl 2.682 to 2.753 Å, angle deviations from 90° less than 6°) [18].

The tetragonal unit cell of Tl_3BiCl_6 contains two independent thallium atoms. The coordination sphere around the Tl(1) atoms, located on the *Wykoff* site 4*j* in the mirror plane may be described best by a distorted *Edshamar* polyhedron with coordination number of 10 and Tl–Cl distances in the region between 3.117(3) to 3.802(3) Å, formally built by half a cube and half an icosahedron. Tl(2) atoms with site symmetry 2/*m* are surrounded by eight chlorine atoms in shape of a cube. The actual reduction of the ideal cubic symmetry to 2/*m* allows for distortions which find their expressions in two different Tl–Cl distances of 3.281(3) and 3.312(3) Å. The cuboidal $Tl(2)Cl_8$ polyhedra are condensed to linear strands along the crystallographic *c* axis with the thallium ions being half the length of

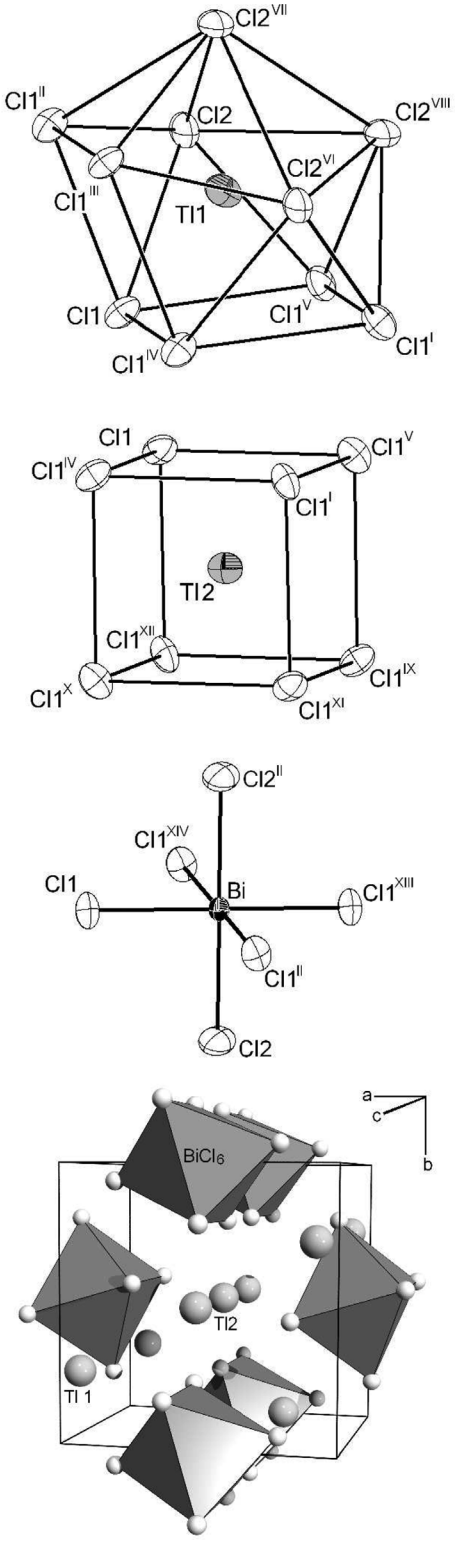

Figure 3. Details of the crystal structure of Tl_3BiCl_6 (from top to bottom): The coordination polyhedra of the two independent Tl^+ ions Tl(1) and Tl(2), the octahedral $[BiCl_6]^{3-}$ anion, and a view of the unit cell along the crystallographic *c* axis. Thermal ellipsoids are drawn to include a probability density of 50 %. Symmetry operations: I: 1 –*y*, *x*, –0.5+*z*; II: –*x*, 1 –*y*, *z*; III: –*x*, 1 –*y*, –*z*; IV: *x*, *y*, –*z*; V: 1 –*y*, *x*, 0.5–*z*; VI: *x*, *y*, –1+*z*; VII: –*y*, *x*, –0.5+*z*; VIII: *y*, –*x*, –0.5+*z*; IX: 1 –*x*, 1 –*y*, *z*; X: *y*, 1 –*x*, –0.5+*z*; XI: 1 –*x*, 1 –*y*, –*z*; XII: *y*, 1 –*x*, 0.5–*z*; XIII: –*x*, 1 –*y*, 1 –*z*; XIV: *x*, *y*, 1 –*z*.

Table 4. Selected bond lengths /Å in the structures of Tl_3BiCl_6 and $TlBi_2Cl_7$. For symmetry operations see legends of Figure 1 and Figure 2.

Tl_3BiCl_6		$TlBi_2Cl_7$	
Bi–Cl(1), Cl(1^{II}), Cl(1^{XIII}), Cl(1^{XIV})	2.692(2)	Bi(1)–Cl(1)	2.603(9)
Bi–Cl(2), Cl(2^{II})	2.693(3)	Bi(1)–Cl(3^{II})	2.705(9)
Tl(1)–Cl(1), Cl(1^{IV})	3.426(3)	Bi(1)–Cl(4^{I})	3.331(9)
Tl(1)–Cl(1^{II}), Cl(1^{III})	3.486(3)	Bi(1)–Cl(6)	3.059(9)
Tl(1)–Cl(1^{I}), Cl(1^{V})	3.802(3)	Bi(1)–Cl(6^{II})	2.533(9)
Tl(2)–Cl(1), Cl(1^{IV}), Cl(1^{IX}), Cl(1^{XI})	3.281(3)	Bi(1)–Cl(7)	2.470(9)
Tl(2)–Cl(1^{I}), Cl(1^{V}), Cl(1^{X}), Cl(1^{XII})	3.312(3)	Bi(1)–Cl(7^{III})	3.010(9)
		Bi(2)–Cl(1)	3.048(10)
		Bi(2)–Cl(2)	2.967(8)
		Bi(2)–Cl(2^{IV})	2.636(8)
		Bi(2)–Cl(3)	2.845(10)
		Bi(2)–Cl(4)	2.584(9)
		Bi(2)–Cl(5)	2.551(8)
		Bi(2)–Cl(6^{II})	3.467(9)
		Tl–Cl	3.374(9) to 4.087(9)

the *c* axis (3.744 Å) apart. The $Tl(1)Cl_{10}$ polyhedra share two of their square faces and four edges with the $Tl(2)Cl_8$ polyhedra resulting in a three-dimensional network (Figure 3).

Since Tl_3BiCl_6 is of the basic formula type A_3BX_6, for which numerous representatives are known, we attempted to contribute its structure to a known structure type. The actual release of the ICSD database [19] contains 479 known crystal structures of this formula type. Using the subroutine CMPZ of the program KPLOT [20] a similarity search was performed. The tolerances were set to high values: for all lattice constants a tolerance of ±15 %, for deviation of angles ±5 %, the inclusion spheres for atom positions were enlarged to 1.0 Å. Surprisingly and despite the wide tolerances, no coincidence with any of the deposited structures of the A_3BX_6 formula type compounds was found. The arrangement of the Tl^+ ions in rows along one crystallographic axis with the remarkably short $Tl^+\cdots Tl^+$ distances is unusual and causes the uniqueness of Tl_3BiCl_6 within the structures of this formula type.

The recently described mineral steropesite was discovered as yellow crystals of the formula Tl_3BiCl_6 [9]. The structure was solved on a crystal containing 10 % bromine on the chlorine positions. It crystallises in the monoclinic system with a very large unit cell having a volume of almost 5000 $Å^3$. Its crystal structure consists of discrete and slightly distorted octahedral $[BiCl_6]^{3-}$ anions and Tl^+ cations with coordination numbers between six and eight. The reported structure can be considered as a distorted variant of the structure of Cs_3BiCl_6, but besides the presence of the analogous building units there is no direct relation to the tetragonal form of Tl_3BiCl_6 reported here.

High Temperature Phase of Tl_3BiCl_6

The thermal behaviour of Tl_3BiCl_6 was investigated in the temperature region between ambient temperature and 400 °C by differential scanning calorimetry at a heating rate of 10 °C·min^{-1}. Two reproducible, endothermic effects could be detected, a solid state phase transition at 189.1 °C (0.93 kJ·mol^{-1}), and the melting at 378.4 °C (3.4 kJ·mol^{-1}). To test for a transition into a high temperature form, crystals of the low temperature form were grinded to a powder, filled into a glass capillary, which was sealed, and investigated by X-ray powder diffractometry. Above 230 °C the diffraction pattern changed completely and the reflections of the room temperature phase disappeared. Lowering the temperature again to 180 °C caused only an incomplete reconversion since the diffractogram of the room temperature phase appeared again but the strongest reflections of the high temperature diffractogram remained. The powder diffractogram at high temperature shows a significant higher number of reflections. This behaviour may indicate a transition to a high temperature phase with a structure of lower symmetry. On looking for a structure model for the assumed high temperature phase, we found that the calculated powder diffractogram of monoclinic Cs_3BiCl_6, after substitution of caesium against thallium, shows a striking similarity to the diffractogram of HT-Tl_3BiCl_6. The complete indexing of the diffractogram was not successful and a refinement of the structure model was not possible on basis of the observed diffraction data. We cannot, however, rule out the possibility of a partial decomposition of the sample.

Crystal Structure of $TlBi_2Cl_7$

The triclinic unit cell of $TlBi_2Cl_7$ contains two formula units with all atoms occupying general positions. The coordination of the two independent bismuth atoms and the thallium atom by surrounding Cl atoms is much more irregular in comparison to the structure of Tl_3BiCl_6. In Figure 4 the distribution of these distances is depicted in the form of histograms. For all three independent cations present in the crystal structure, a distinct gap is observed which allows for the definition of coordination polyhedra. The two bismuth atoms both gain coordination number seven with all Bi–Cl distances up to 3.34 Å for Bi(1) and 3.47 Å for Bi(2) taken into account. In each of the two $BiCl_7$ polyhedra one Cl atom achieves a long distance which is typical for a pronounced lone pair effect of the three-valent bismuth atom. The $BiCl_7$ polyhedra are connected by common corners and edges to a three dimensional net, in

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which the Tl^+ ions are embedded. Thallium gains the coordination number eleven if all Tl–Cl distances up to 4.09 Å are considered (Figure 4).

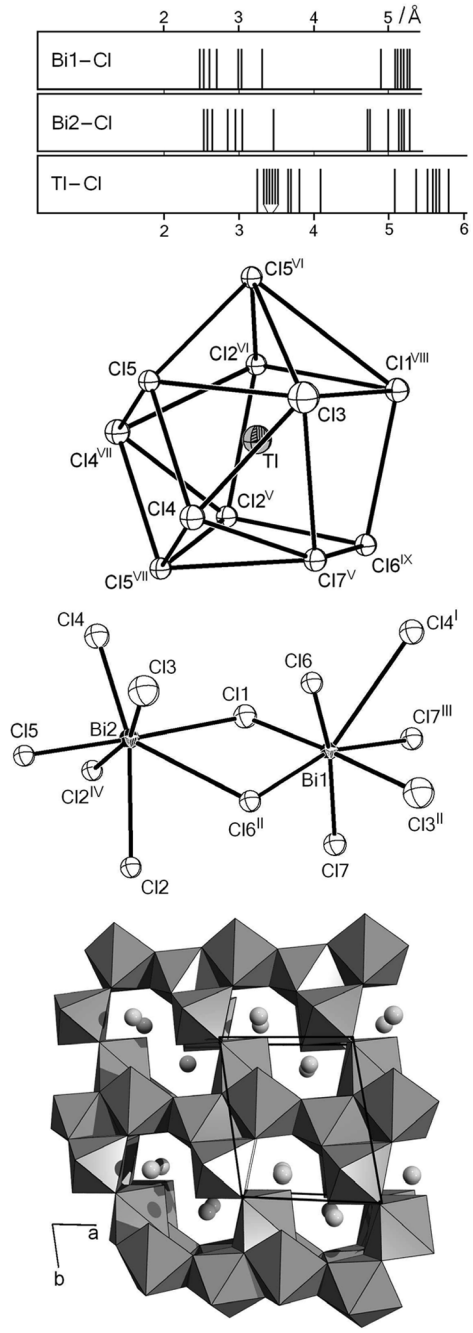

Figure 4. Details of the crystal structure of $TlBi_2Cl_7$ (from top to bottom): The Bi–Cl and Tl–Cl distances in the form of histograms, the coordination polyhedron of the Tl^+ ion, the coordination of the two independent bismuth atoms Bi(1) and Bi(2), and a view of the unit cell along the crystallographic *c* axis. In the two detailed representations, atoms are drawn as spheres with radii corresponding to 50 % of the probability density of the thermal vibration. Symmetry operations: I: –*x*, 1 –*y*, 2 –*z*; II: –*x*, 1 –*y*, 1 –*z*; III: – 1 –*x*, 1 –*y*, 1 –*z*; IV: –*x*, –*y*, 1 –*z*; V: 1+*x*, *y*, 1+*z*; VI: 1 –*x*, –*y*, 1 –*z*; VII: 1 –*x*, –*y*, 2 –*z*; VIII: 1+*x*, *y*, *z*; IX: 1 –*x*, 1 –*y*, 2 –*z*.

Vibrational Spectra

Of both compounds, Tl_3BiCl_6 and $TlBi_2Cl_7$, Raman spectra were recorded. As expected, the spectrum of Tl_3BiCl_6 shows only a low number of bands due to the high local symmetry of the vibrational active $BiCl_6$ group. Three broad bands at 261 (vs), 218 (s), and 117 (vs) cm^{-1} were observed. These bands are identical with those of Cs_3BiCl_6 within the resolution limit and can be attributed to the fundamental Raman active vibrations A_{1g}, E_g, T_{2g} of the $BiCl_6$ octahedron. In the region between 300 and 100 cm^{-1} the Raman spectrum of $TlBi_2Cl_7$ shows 10 bands (104(s), 116(m), 121(m), 132(s), 144(w), 172(s), 186(s), 247(s), 269(s), 290(s) cm^{-1}). Due to the irregular, low symmetric coordination of the cation in this structure, a definite attribution of these bands cannot be made.

Structural Investigations of Glassy $TlBi_2Cl_7$

The thermal behaviour of glassy $TlBi_2Cl_7$ was measured in the temperature region between –20 and 230 °C, the respective differential scanning calorimetry (DSC) function, obtained at a heating rate of 10 °C·min^{-1} is given in Figure 5. The endothermic effect at 41.3 °C (point *a* in Figure 5, 2.9 kJ·mol^{-1}) is attributed to the glass transition. The two following exothermic effects at 59.3 (*b* and *c*, –6.0 kJ·mol^{-1}) are attributed to crystallisation processes. The small endothermic effect at 180 °C (*d*) was not observable in all measurements and is probably an artefact. At 189.5 °C melting occurs (*e*, 30.3 kJ·mol^{-1}). On cooling the samples after melting, a sharp exothermic signal at 109 °C appears (*f*, –22.1 kJ·mol^{-1}) originating from crystallisation of the melt. If the measurement is carried out with a lower heating rate of 1 °C·min^{-1}, the glass transition shifts to 35.2 °C. According to the empirical relation $T_g = A + B \log\beta$ with T_g = observed glass transition temperature, A = true glass transition temperature, B = empirical factor depending on the preparation of the glass, β = heating rate, the transition temperature at 32.5 °C is identical with the true transition temperature [21]. The relation of the absolute glass transition temperature to the melting temperature allows within limits for information on the structural properties of amorphous networks. For highly symmetric polymers made up from small monomeric units, T_g/T_m is generally 0.5 or lower, for the broad majority of polymers, however, this relation amounts 2/3 [22]. For the amorphous $TlBi_2Cl_7$ phase T_g/T_m is 308 K/463 K = 0.66. The observed thermal effects do thus not allow for detailed conclusions on the structural properties of the glass.

^{205}Tl and ^{203}Tl MAS solid state NMR spectra were recorded in order to find further insight into the structure of the red glassy form of $TlBi_2Cl_7$. The MAS spectra of both, the glassy and the crystalline $TlBi_2Cl_7$ do not show differences. Only one broad signal centred at 47.7 ppm relative to the standard was observed (Figure 6). This is in line with the crystallographic cell, which contains only one symmetry-independent thallium atom. The similarity of the spectra suggests that the chemical environment of the thallium atoms in both phases does not show large differences.

The vibrational spectrum of the amorphous $TlBi_2Cl_7$ phase shows, however, distinct differences to the spectrum of the

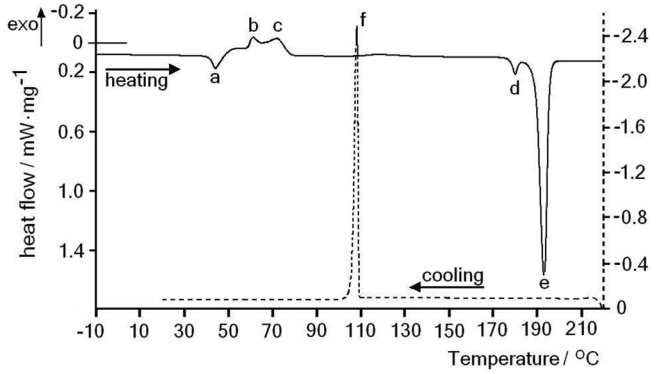

Figure 5. Differential scanning calorimetry function of $TlBi_2Cl_7$. The solid line represents the heating curve from –10 to 210 °C, the dotted line the cooling process back to ambient temperature. The observable thermal effects are indicated by letters a–f, see text. The temperature rate for heating and for cooling was 10 °C·min^{-1}.

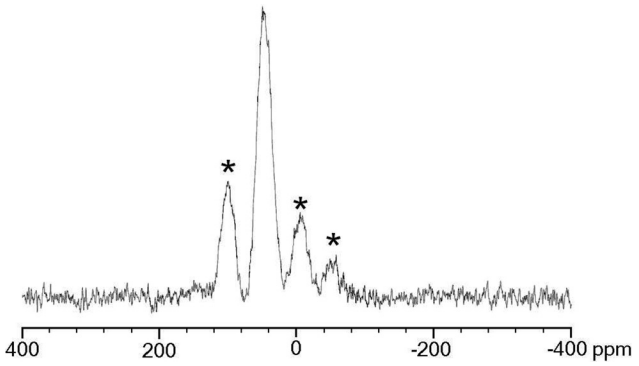

Figure 6. ^{205}Tl MAS-NMR spectrum of amorphous $TlBi_2Cl_7$ at 12 kHz spinning speed. Signals marked with an asterisk are rotational bands. The respective ^{203}Tl spectrum is of almost identical shape but shows lower signal intensity.

crystalline form. Eight bands (126(s), 142(m), 157(m), 178(s), 246(m), 268(w), 292(sh, s), 306(vs) cm^{-1}) are present, of which only three (142, 246, 268 cm^{-1}) are observed at the same frequencies as for the crystalline state. The spectrum of amorphous $TlBi_2Cl_7$ shows instead a close similarity to the spectrum of $BiCl_3$ (six bands at 280(vs), 262(m), 252(sh, w), 179(m), 141(m), 119(m)) in the frequency and intensity distribution. For $BiCl_3$ the bands at 280 (A_1) and 252 cm^{-1} (E) can be attributed to the C_{3v} symmetric molecules, which are present in the solid state. The vibrational spectra lead to the suggestion that amorphous $TlBi_2Cl_7$ contains $BiCl_3$ building units as present in the structure of crystalline $BiCl_3$.

Near edge X-ray absorption spectra (XANES) of Tl_3BiCl_6, and amorphous and crystalline $TlBi_2Cl_7$ were recorded on both the Tl-L_{III} and the Bi-L_{III} edges. Figure 7 shows the spectra on the Bi-L_{III} edges as a superposition for all three samples. A striking similarity is observed between the spectra of glassy and crystalline $TlBi_2Cl_7$, whereas the spectrum of Tl_3BiCl_6 is different throughout the entire energy interval. This observation is also valid for the spectra on the Tl-L_{III} edge. This result is in line with the solid state NMR spectra, indicating that $TlBi_2Cl_7$ in the glassy and the crystalline state both have closely related coordination environments around the thallium and bismuth atoms. On the other hand, the Raman spectra with their differing patterns of vibrational bands indicate a substantially altered local structure.

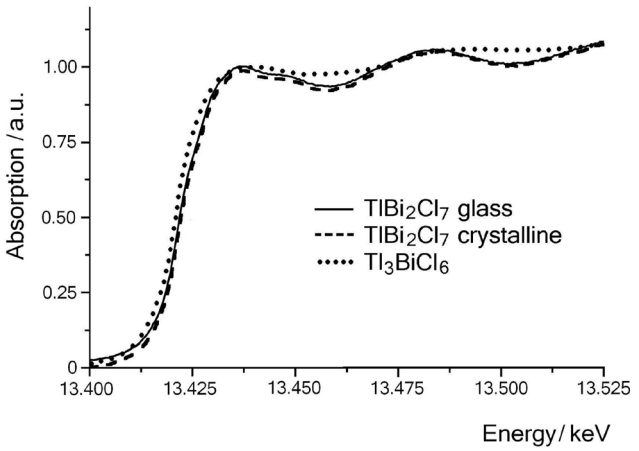

Figure 7. XANES spectrum on the Bi-L_{III} absorption edge of glassy and crystalline $TlBi_2Cl_7$, and of crystalline Tl_3BiCl_6.

Conclusions

Two discrete phases were prepared and characterised in the ternary system Tl/Bi/Cl, both showing structural pecularities. The TlCl rich compound Tl_3BiCl_6 is built of only slightly distorted $[BiCl_6]^{3-}$ octahedra, whereas the $BiCl_3$ rich phase $TlBi_2Cl_7$ is made of a complex network of connected, irregular $BiCl_7$ polyhedra. In both structures, the Tl^+ ions gain high coordination numbers between eight and eleven. A remarkable and yet not elucidated detail is the amorphous state of $TlBi_2Cl_7$, which forms a glass on rapid cooling of the melt. The metastable, transparent glass is of intensive dark-red colour, whereas the crystalline phase is almost colourless. No explanation for the colour of the glass could be found and the attempts to find structural relations between the glassy and the crystalline state by XANES, NMR and Raman spectra lead to contradictory results.

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