

The InSnCl₃-Type Arrangement

II. High Pressure Synthesis of TIPbCl₃ and of Solid Solutions Containing Rb or Br

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We report on the synthesis and crystal structure of TIPbCl₃ which can only be prepared by a high pressure synthesis. In similar experiments solid solutions of the type Tl_{1-x}Rb_xPbCl₃ (0 < x < 0.25) and TIPbCl_{3-x}Br_x (0 < x < 2.5) were prepared. The structural parameters are given. All compounds are isotypic with InSnCl₃. The stability of such compounds and crystal chemical features are discussed. © 1999 Academic Press

INTRODUCTION

In a preceding paper (1) we have reported on the synthesis and crystal structure of ternary indium tin halides with the general formula ABX_3 . In these compounds the size relations of the ions do not allow a perovskite-type arrangement; the high coordination numbers of the large cations lead to a new structure where the coordination polyhedra share many corners, edges, and even faces. Their centers are therefore quite close, and such arrangements seem only possible when they are stabilized by the special effects of ns^2 cations which are evidently a prerequisite for such structures (2). However, InSnCl₃ and InSnBr₃ seem to be destabilized to a certain extent. The latter is only stable in a narrow range of higher temperatures and the experiences during the refinement of both structures from single crystal data show that these crystals are evidently disordered in polydomain configurations due to specific distortions brought about by the ns^2 configuration of the cations. In order to study such effects in more detail we have tried to synthesize isotypic compounds with the higher homologous elements. The quasi-binary systems TlCl–PbCl₂ and TlBr–PbBr₂ were most recently investigated by Keller (3, 4). According to his results 1:1 compounds do not exist under normal conditions. We have therefore varied the procedures of synthesis hoping to get such compounds at least as metastable phases. In this paper we report on the synthesis of TIPbCl_{3-x}Br_x and Tl_{1-x}Rb_xPbCl₃ compounds by high pressure experiments.

EXPERIMENTAL

High pressure experiments were undertaken with a belt-type apparatus using BN containers and pyrophyllite as pressure transmitting media. Stoichiometric mixtures of TlX and PbX₂ (X = Cl, Br) were held at 25 kb and 1000°C for 2 min. The temperature was then quickly lowered and kept at 500°C or below (see below). The pressure was released after quenching to room temperature. To avoid unwanted side reactions all substances were handled in inert atmospheres (Ar) in a glove box.

For X-ray investigations, the substances were sealed in glass capillaries under argon. Powder diagrams were taken with a diffractometer in transmission geometry with CuK α_1 radiation using a position sensitive detector. The structures were refined by a Rietveld procedure (5) (see Table 1). A comparison of a calculated and an experimental diagram for the refinement of TIPbBr_{1.5}Cl_{1.5} is given in Fig. 1 as an example.

RESULTS AND DISCUSSION

TIPbCl₃, not existent at ambient pressure, can indeed be prepared under high pressure conditions (2.5 GPa and 500°C). The same is true for solid solutions of the type TIPbCl_{3-x}Br_x with 0 < x < 2.5. The lattice parameters of this series are given in Table 2. They fit nicely on a Vegard line. In the case of compounds with 1 < x < 2 the temperature of synthesis could even be lowered to 300°C (see below). The ternary thallium lead bromide itself could not be prepared under such conditions.

A substitution of the A cation Tl by Rb as an example of a ns^0 -type cation of comparable size is possible, but only up to 25%. In experiments with higher Rb contents the alkaline cation segregates into a second phase with the composition Rb₆Pb₅Cl₁₆. (We have reported the structure of this compound recently (6)). RbPbCl₃ itself is only stable above 305°C at ambient pressure. It melts at 441°C and has a perovskite-type structure because of the slightly larger A/X size

TABLE 1
Details of the Data Collection and Refinement Procedures

	TlPbCl ₃	TlPbCl _{1.5} Br _{1.5}	Rb _{0.25} Tl _{0.75} PbCl ₃
Range of data collected in steps of 0.02°	20–87	18–87	18–87
Wavelength [pm]		154.056	
Temperature factor	4.15 (8)	5.69 (6)	3.87 (5)
Line width parameters ^a			
<i>U</i>	0 (fixed) ^b	0.003 (fixed) ^b	0 (fixed) ^b
<i>V</i>	0.027 (3)	0.024 (1)	0.008 (1)
<i>W</i>	−0.002 (1)	0 (fixed)	0.016 (1)
Pearson VII exponent	0.865 (3)	1.43 (1)	0.865 (3)
<i>R</i> _{Bragg} (%)	10.34	13.04	10.44
<i>R</i> / <i>R</i> _w (%)	3.8/5.3	2.5/3.5	4.4/5.8

^a Pertaining to the formula $H_W^2 = U \cdot \tan^2 \Theta + V \cdot \tan \Theta + W$ used in the Rietveld refinement (5).

^b Attempts to refine these parameters resulted in instabilities of the procedure.

relation. Our investigations on the phase diagram of the quasi-binary system RbCl–PbCl₂ will be reported elsewhere (7).

A substitution of Pb by Sr was not possible. Such experiments always gave two phased products, a InSnCl₃-type phase—having virtually the same lattice parameters as TIPbCl₃—and TlSr₂Cl₅. This substitution is evidently impossible; the alkaline earth ion segregates into the well-known AB₂X₅ compound (8).

The Structure

All compounds are isotypic crystallizing in the InSnCl₃-type arrangement. Figure 2 gives an overall view of this

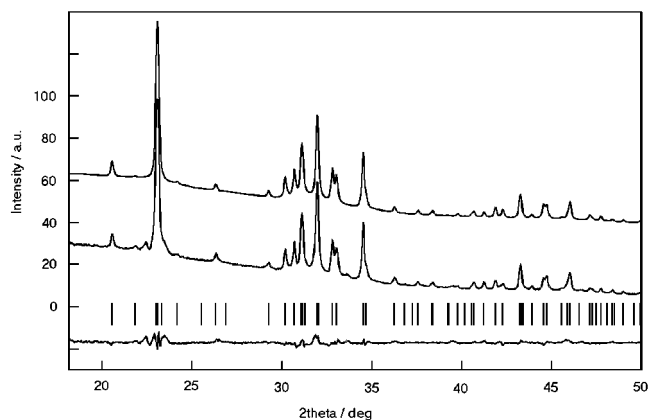


FIG. 1. Calculated and measured intensities, theoretical line positions, and difference plot (from top to bottom) for TIPbBr_{1.5}Cl_{1.5} as an example for the quality of the Rietveld refinements.

TABLE 2
Lattice Parameters of InSnCl₃-Type Compounds in pm

Compound	<i>a</i>	<i>c</i>
InSnCl ₃	1200.9(3)	1594.4(4)
InSnBr ₃	1249.7(2)	1641.1(3)
TlPbCl ₃	1190.2(1)	1580.5(1)
TlPbCl _{2.5} Br _{0.5}	1193.8(5)	1594.1(5)
TlPbCl ₂ Br	1209.1(1)	1602.8(1)
TlPbCl _{1.5} Br _{1.5}	1217.7(1)	1622.6(5)
TlPbClBr ₂	1221.5(1)	1629.4(1)
TlPbCl _{0.5} Br _{2.5}	1234.6(4)	1635.0(7)
Rb _{0.25} Tl _{0.75} Br _{2.5}	1191.8(1)	1594.9(4)

Note. The standard deviations given in brackets refer to the last digit.

structure. Since single crystals could not be grown their positional parameters have been derived from Rietveld refinements of powder data. A selection of such parameters is given in Table 3. Since the electron density of In and Sn and of Tl and Pb is virtually the same the assignment to different crystallographic sites by X-ray experiments is not possible. The cation positions are therefore not distinguished in the tables giving the positional parameters. Crystal chemical considerations, however, will allow an assignment where the 8*h* and the 4*a* positions are chosen for Pb and the 4*c*

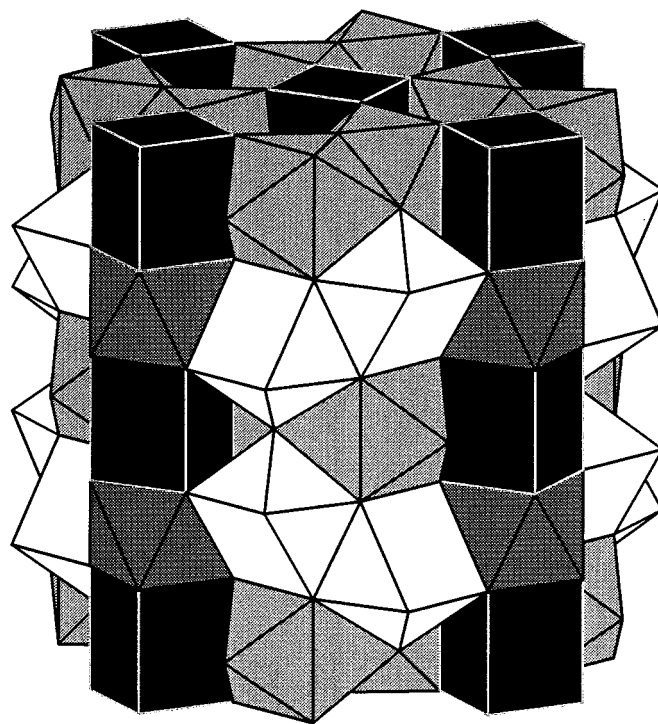


FIG. 2. The InSnCl₃-type arrangement (the intensity of shading of the cation polyhedra increases in the sequence M(1), M(2), M(3), M(4) (see Table 3)).

TABLE 3
Structural Parameters for TIPbCl₃ and Its Substitution Variants Derived from Rietveld Refinements of Powder Data
(Space Group *I4/mcm*; *Z* = 16)

Compound	Wyckoff position	TIPbCl ₃				TIPbCl _{1.5} Br _{1.5}					Rb _{0.25} Tl _{0.75} PbCl ₃			
		x	y	z	sof	x	y	z	sof	[sof]	x	y	z	sof
M1	16l	0.1657(3)	0.6657(4)	0.1842(3)	0.5	0.1626(2)	0.6626(2)	0.1838(2)	0.5	—	0.1640(2)	0.6640(2)	0.1792(3)	0.5
M2	8h	0.6392(5)	0.1392(5)	0	0.25	0.6362(3)	0.1362(3)	0	0.25	—	0.6384(4)	0.1384(4)	0	0.25
M3	4a	0	0	0.25	0.125	0	0	0.25	0.125	—	0	0	0.25	0.125
M4	4c	0	0	0	0.125	0	0	0	0.125	—	0	0	0	0.125
Cl(1)	32m	0.071(1)	0.193(1)	0.138(1)	1.0	0.0738(6)	0.1968(5)	0.1401(4)	0.27(1)	0.73(1)	0.076(1)	0.219(1)	0.141(1)	1.0
[Br(1)]														
Cl(2)	8h	0.152(4)	0.653(4)	0	0.25	0.171(1)	0.671(1)	0	0.16(1)	0.09(1)	0.150(4)	0.650(4)	0	0.25
[Br(2)]														
Cl(3)	8g	0	0.5	0.121(2)	0.25	0	0.5	0.132(2)	0.22(1)	0.03(1)	0	0.5	0.148(1)	0.25
[Br(3)]														

Note. Site occupancy factors (sof and [sof]) of corresponding atoms add up to the symmetry defined multiplicity factors.

The second number pertains to the substituting atom. The positional parameters of substituting atoms could not be refined separately.

position for Tl, whereas the 16l position contains Tl and Pb statistically distributed in a 3:1 ratio. (A detailed discussion of the structure and the reasons for such an assignment are given in (1).)

Effects of Substitution

In order to understand the substitution scheme of the anions we have calculated their effective coordination numbers (ECON) and values for the mean fictive ionic radii (MEFIR) (9). Without going into the details of these numbers we may state that these values are quite different for the three anion sites. They are especially large for the *X*(1) anions at the Wyckoff site 32m. When placing Cl as well as Br on the same positions and refining occupational parameters for TIPbCl₂Br, TIPbCl_{1.5}Br_{1.5}, TIPbClBr₂, and TIPbCl_{0.5}Br_{2.5} this position clearly showed the highest Br content. The phases richest in Br were found to have all 32m positions substituted by Br. From such refinements the 8h position of *X*(2) seemed to have a slightly higher Br content too; however, we are not sure whether the small difference in the occupancy by Cl or Br is significant on the basis of these powder data, especially since such a result would contradict the development of the MEFIR values in the series of the anions. The preference of Br for the *X*(1) position is, however, clearly proven. This would show that the mechanism of anion substitution is mainly governed by size effects.

A second feature of interest is the effect of substitution by *ns*⁰ ions in the cation sublattice. To exclude the effect of size we have chosen Rb as a substitute for Tl since the radii of these two ions are believed to be equal within 1–2 pm. We find the monovalent ions in the 4c position in fairly close contact with Pb in 4a. These atoms are aligned in a string

along [001]. It may be assumed that the repulsive interaction by electrostatic charges is screened to a certain extent by shielding via the *ns*² electrons (2) and that this effect ensures the existence of compounds having such a structure. Another sore point in the structure is the 16l position which is mostly occupied by the monovalent ion (see above). Two cations in this position are in close contact too because their coordination polyhedra share a common rectangular face. The same arguments therefore hold for this part of the cation sublattice.

As stated above Tl can be substituted up to 25% by Rb. The cell volume increases only by 1.2%; however, there is a considerable anisotropy in the expansion. The *c* axis increases by 14 pm and the others by 1.6 pm. We attribute this deformation mainly to the decrease of the shielding effect in the chains made up by the 4a and 4c positions. In addition we observe an increase in the distance between two adjacent 16l positions by about 5 pm, and this may also be explained by the same arguments since this is more than would be expected from a comparison of the tabulated ionic radii of Rb (161 pm) and Tl (159 pm) and in view of the fact that only a smaller part of the Tl atoms has been substituted. It may be assumed that the limitation of the substitution is due to electrostatic reasons, viz. the decrease of shielding by *ns*² electrons.

Effects of High Pressure

In view of the discussion given in the preceding paragraphs it seems surprising, if not paradoxical, that high pressure conditions should favor the existence of these compounds. Remember that InSnCl₃ exists at ambient temperatures and remains stable up to its melting point. The higher

homolog InSnBr_3 is stable only above 206°C , and it decomposes in a peritectic reaction at 223°C . To replace A - and B -type cations by the higher homologous elements we need elevated pressures.

At first glance, this finding contrasts with the pressure homology rule which states that at higher pressures compounds with lower homologous elements may adopt the structures of those made up of higher homologous elements; e.g., TlPbCl_3 may exist at ambient pressures with such a structure and InSnCl_3 could possibly be synthesized or converted to such a structure under high pressure. The contrary seems to be true, since TlPbCl_3 itself could only be prepared under high pressure conditions.

We can, however, put up a temperature homology rule which explains how compounds or structures where we have heavier elements can exist at higher temperatures just as their lower homologs will be stable at ambient temperatures already. In the cases discussed here very high temperatures seem to be needed to stabilize such compounds with elements from the highest period of the periodic system, and these temperatures are evidently beyond a fictive melting point. Pressure now has another effect. It increases the melting point of the compounds considerably so that they can now be synthesized in solid state reactions without melting or peritectic decomposition. Retaining the compounds as solids at higher temperatures by higher pressures will also give entropy effects a chance to stabilize the system. To synthesize TlPbCl_3 under high pressure, temperatures of at least 500°C are needed. Possibly TlPbBr_3 could be prepared at even higher temperatures and pressures. The fact that the mixed crystals $\text{TlPbCl}_{3-x}\text{Br}_x$ could even be prepared at lower temperatures clearly supports the assumption that configurational entropy plays an important role in the delicate equilibrium between stabilizing and destabilizing effects.

CONCLUSION

The InSnCl_3 structure is a new structure type which will only be encountered for larger cations A and B having a ns^2 electron configuration. This electron configuration is essential for the stability and structure of all these compounds. The compounds crystallizing in such a structure all show a disorder of A and B cations on some of the crystallographically different cation sites. The most stable of all ABX_3 compounds described here with respect to the temperature range of existence and the melting characteristics is InSnCl_3 . Compounds where A , B , and X are replaced by higher homologous elements are only stable at higher temperatures—one may define a temperature homology rule—which would sometimes be beyond a melting or decomposition point. The application of pressure may then help in retaining a solid phase. Partial substitutions in the anion sublattice may sometimes stabilize the phases to lower temperatures by an entropy effect. A substitution of the ns^2 cations by others having a rare gas electron configuration will immediately destabilize the structure or even be impossible.

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