

Study on A_4BX_6 Compounds. III [1]

ns^2 Cations as a Prerequisite for a Structure Type and their Interaction in Ternary Halides with the Formula Type A_4BX_6 (A: In, Tl; B: Cd, Pb, Ge; X: Cl, Br, I)

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Abstract. We discuss the interaction of ns^2 -type cations in ternary halides of the formula type A_4BX_6 (A: In, Tl; B: Cd, Pb, Ge; X: Cl, Br, I) crystallizing in a Tl_4HgBr_6 -type arrangement. We report on high pressure experiments on such A_4BX_6 compounds and on x-ray studies and structure refinements of mixed crystals of the type $A'_x A_{4-x} BX_6$, where cations A' with a closed shell configuration partly substitute for the ns^2 -type A ions. The results of our experiments show, that ns^2 -type cations stabilize this unusual structure type by polarization effects and by their higher electronegativity as compared with alkali ions of comparable size.

Untersuchungen an A_4BX_6 -Verbindungen. III. ns^2 -Kationen als Bedingung für einen Strukturtyp und ihre Wechselwirkung in ternären Halogeniden vom Typ A_4BX_6 (A: In, Tl; B: Cd, Pb, Ge; X: Cl, Br, I)

Inhaltsübersicht. Wir diskutieren die Art der Wechselwirkung von Kationen mit ns^2 -Konfiguration in ternären Halogeniden des Formeltyps A_4BX_6 (A: In, Tl; B: Cd, Pb, Ge; X: Cl, Br, I), die im Tl_4HgBr_6 -Typ kristallisieren. Wir berichten über Hochdruckexperimente an solchen A_4BX_6 -Verbindungen und über röntgenographische Untersuchungen und Kristallstrukturverfeinerungen an Mischkristallen des Typs $A'_x A_{4-x} BX_6$, in denen die ns^2 -Kationen teilweise durch solche mit Edelgaskonfiguration substituiert sind. Die Ergebnisse unserer Experimente zeigen, daß die ns^2 -Kationen diesen ungewöhnlichen Strukturtyp durch Polarisierungseffekte stabilisieren und durch ihre größere Elektronegativität im Vergleich zu der von Alkaliionen von ähnlicher Größe.

Introduction

In the first papers of this series [1, 2] we have described in detail the structure types, which are found for ternary halides with the general formula type A_4BX_6 and having fairly large A ions, i. e. the rhombohedral K_4CdCl_6 -type [3], the tetragonal Tl_4HgBr_6 -type [4] and the orthorhombic Tl_4PbI_6 -type [5]. The first two structure types could be separated in a structure field diagram on the basis of the size relations A/X and B/X . It seemed, that for small B/X ratios the size of the

A type ion alone would determine the structure, larger A ions giving the rhombohedral one, in which they are incorporated into the eutactic arrangement of the X ions. Increasing the B/X ratio expands the framework of the X ions in the tetragonal structure, so that larger A ions can now fill characteristic voids in this arrangement. We find them in doubly capped trigonal prismatic coordination polyhedra of X ions. Two such prisms share the noncapped rectangular face. The two A ions within such a A_2X_{12} double prism are therefore in quite close contact, one being the third cap on the trigonal prism of X ions surrounding the other, an electrostatically extremely unfavourable arrangement.

A closer inspection of the structure field diagram reveals, that this tetragonal structure is virtually restricted to A_4BX_6 compounds having a cation with ns^2 electron configuration in the A position, and this may well explain the unusual structural features. In the structure type series $K_4CdCl_6 - Tl_4HgBr_6 - Tl_4PbI_6$ we find an increasing number of short contacts between A type ions. They are completely isolated in the first structure, they form the pairs just described in the second and four membered chains in the last one. However it was not clear, whether the short distance between them may be taken as a proof for attractive forces. On the contrary, the A cations are displaced from the centers of the trigonal prisms, thereby increasing the distance between them, as would be expected according to Pauling's rules for structures of ionic compounds. It is the aim of the investigations presented here to elucidate the nature of the interaction of the ns^2 cations in this tetragonal structure by proving or disproving statements commonly used in discussions of the crystal chemistry of such ions.

On the Stereochemical Activity of the Lone Pairs

Distortions from a possible higher symmetric arrangement are often attributed to some stereochemical activity of lone electron pairs, and the tetragonal Tl_4HgBr_6 structure is indeed a slightly deformed variant of another structure with higher symmetry, which is found for double borides $M'M_2B_2$ with M' , $M = Mo, Ti, Al$ etc. In this arrangement having the space group $P4/mbm$ there are $4.3^2.4.3$ nets of M atoms stacked coincidingly along $[001]$ with 4 atoms per unit area. Between these nets we find a layer having the composition $B_4M'_2$, where M' atoms center the cubes and B atoms center the trigonal prisms formed by the atoms in the nets just described. Doubling the c axis in a „klassengleich“ step leads to the space group of the Tl_4HgBr_6 arrangement ($P4/mnc$), where $Br(2)$ corresponds to M, $Br(1)$ to M' and B to Tl. Since Hg is additionally incorporated into octahedral voids, this structure can be classified as a stuffed variant of the double boride structure. Here successive $4.3^2.4.3$ nets are slightly displaced against each other in the projection along $[001]$. This leads to two characteristic polyhedra, first a deformed cube with top and bottom square of unequal size, which is centered by another halogen X, and second a A_2X_{12} double prism, which seems twisted in the rectangular face common to both prisms (Fig. 1). (For a more detailed description of the structure see [1].) At first sight the symmetry reduction and the “twisting” may be attributed to the stereochemical activity of the two ns^2 -type cations within these double prisms, which could be repelled by the interelectronic repulsion. However, the geometrical peculiarities can be explained even better by other interactions in the structure. The additional incorporation of bivalent cations into every second square of the $4.3^2.4.3$ net of anions leads to a contraction of these squares due to covalent and electrostatic interactions and therefore to the characteristic picture of deformed cubes and tilted double prisms mentioned above. By this tilting the edges of the prisms along $[001]$ become

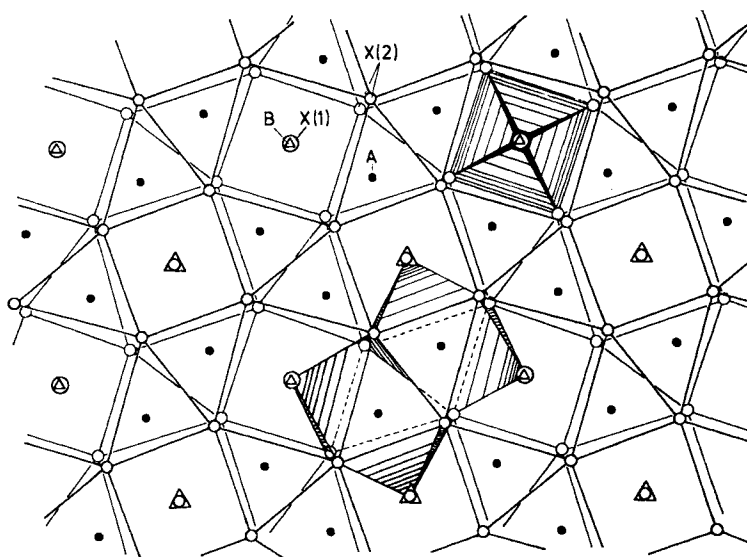


Fig. 1 The Tl_4HgBr_6 structure in a projection along $[001]$. (Open circles: Br, solid circles: Tl, open triangles: Hg, representatives for the $HgBr_6^-$ and the Tl_2Br_{12} -polyhedra are outlined)

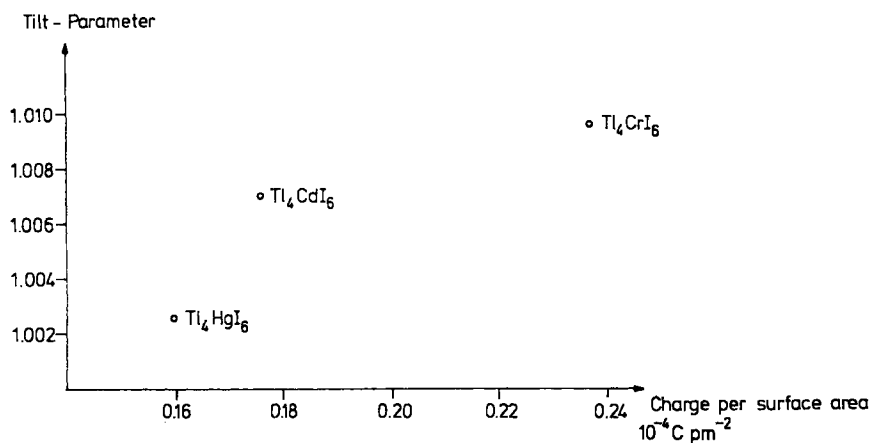


Fig. 2 Tilt-parameter (ratio of the prism edge length along c in the real structure over that in the undistorted one) vs. hardness parameter (charge per surface area) of the B-cations for three tetragonal Tl_4BI_6 compounds.

longer, and this elongation may be taken as a quantitative measure for the distortion. Fig. 2 gives a plot of this "tilt parameter" vs. a hardness parameter of the B ions in different Tl_4BI_6 compounds, where hardness is calculated as charge per surface area of the B ions differing in size. This correlation shows, that the "distortion" seen in this structure type is not to be attributed to lone pair effects, but to B—X interactions.

On Bonding between ns^2 -Type Cations

In the introduction we have pointed out, that the tetragonal Tl_4HgBr_6 -type structure is restricted to compounds having a ns^2 type majority cation. The close contact between the two ns^2 cations within the A_2X_{12} double prisms puts up the question, whether an attractive interaction between these ions stabilizes the unusual arrangement. Inquiring on the nature of such interactions we have followed two routes. We have tried to simulate an internal cohesion due to attractive interactions of the ns^2 ions by applying high pressure conditions, and we have synthesized mixed crystals $A'_x A_{4-x} BX_6$, where alkali ions of comparable size substitute for the lone pair cations.

High Pressure Experiments

Since the space filling is slightly better in the tetragonal Tl_4HgBr_6 -type structure than in the rhombohedral arrangement, high pressures should favour the former structure. We have done such experiments on K_4CdCl_6 , which is close to Tl_4HgBr_6 itself in the structure field diagram of A_4BX_6 compounds, on Cs_4PbBr_6 , because Rb_4PbBr_6 was reported to crystallize in the tetragonal system [6] in contradiction to our own findings, on Tl_4CdI_6 , which crystallizes in the tetragonal Tl_4HgBr_6 type (but it could perhaps be transformed into a Tl_4PbI_6 -type arrangement with an even more pronounced aggregation of ns^2 -type cations (see Introduction)) and on a 4:1 stoichiometric mixture of KI and CdI_2 , because the compound K_4CdI_6 could well exist, if size relations between the ions were decisive.

Table 1 High pressure experiments, compounds and conditions

Substance	Pressure (kb)	Temperature (°C)	Time (h)
K_4CdCl_6	40	160	24
Tl_4CdI_6	40	300	48
Cs_4PbBr_6	40	400	72
KI/ CdI_2 (4:1)	30	550	24

The experiments were done in an internally heated belt-type apparatus in boron nitride containers. All handling of the substances for preparation, during the high pressure experiments and for the x-ray investigations proceeded under Ar atmosphere. After the high pressure treatment (see Table 1) the pressure was released after quenching the specimens to ambient temperatures. For the x-ray investigations the substances were sealed in glass capillaries and diffraction diagrams were taken with the Simon-Guinier technique [7] using Si as internal standard.

Results

The experiments with K_4CdCl_6 and Tl_4CdI_6 gave no high pressure phase under the conditions described in Table 1. It seems unlikely, that unquenchable transformations took place, the powder diagrams of the high pressure products show

no line broadening or changes in the relation of intensities. The high pressure treatment of the KI/CdI₂ mixture did not yield an A_4BX_6 compound. X-ray powder diagrams showed KI and lines of a neighbouring phase in the KI—CdI₂ system.

Cs_4PbBr_6 did not transform to the expected tetragonal structure. This compound decomposes under high pressures according to the equation



In an earlier paper [8] we have summarized the crystal chemistry of ternary halides with the general formula AB_2X_5 , where we find two structures, the monoclinic $NH_4Pb_2Cl_5$ type and the tetragonal $NH_4Pb_2Br_5$ type. The first arrangement shows no unusual structural features, the B-type cations are well separated in the structure. The $NH_4Pb_2Br_5$ type, however, is closely related to the tetragonal Tl_4HgBr_6 type discussed in this paper. We find the same arrangement of A_2X_{12} double prisms built up by adjacent $4.3^2.4.3$ nets of anions. These double prisms are now centered by the divalent B-type cations, which again must have a ns^2 configuration.

The result of the high pressure experiment on Cs_4PbBr_6 is insofar interesting as it proves, that the majority cation with a closed shell configuration cannot be forced to enter into the peculiar biprismatic coordination with close contacts between such ions. Reducing the volume by high pressures "expels" these cations by decomposition, and the structure formed for the remaining AB_2X_5 compound is again the one, which is found only, when the majority cation B — now Pb — has an ns^2 electron configuration.

It is interesting to note, that among such AB_2X_5 compounds there are some, which can be transformed under pressure into the structure built up of A_2X_{12} double prisms (e. g. KPb_2Br_5 , $TlPb_2Br_5$), whereas others decompose into the binary halides (e. g. $InSn_2Cl_5$ and $TlPb_2Br_5$ (at higher pressures)). We may therefore conclude, that beyond certain pressure conditions the biprismatic arrangement is always unstable. Pressure will never enhance an attractive interaction between the ns^2 cations therein. We tend to believe, that there is no such attractive interaction.

Preparation of Mixed Crystals

Since it turned out to be impossible to incorporate two closed shell cations into the biprismatic structural unit, we have tried to substitute them only partly for the ns^2 type ions. We have synthesized mixed crystals $A'_x A_{4-x} BX_6$ by melting and subsequently equilibrating the corresponding mixtures of the binary compounds in the systems $Tl_x In_{4-x} CdI_6$, $Rb_x Tl_{4-x} CdI_6$, $K_x Tl_{4-x} CdI_6$, $Cs_x Tl_{4-x} CdI_6$ and $Rb_x Tl_{4-x} GeI_6$. In the first of these examples an ns^2 cation substitutes for another one, the only difference being the size of the cations. This system should give information on the influence of radii of A ions in the tetragonal structure. The other systems should show the influence of both electron configuration and geometric criteria simultaneously. Tables 2 gives the compositions and the lattice constants of the mixed crystals prepared during this study, and Table 3 gives the conditions and the results of structure refinements using single crystal data of $Tl_{1.5} In_{2.5} CdI_6$ and $Rb_{0.2} Tl_{3.8} CdI_6$.

Table 2 Composition, lattice constants and cell volumes of the mixed crystals $A'_x A_{4-x} BX_6$ and the related $A_4 BX_6$ compounds

Compound	Lattice constants (pm)	Cell volume (10^3 pm^3)
In_4CdI_6	$a = 906.0(2), c = 975.4(4)$	8.007 ^{a)}
$\text{Tl}_{1.0}\text{In}_{3.0}\text{CdI}_6$	$a = 911.6(6), c = 972.4(12)$	8.081 ^{b)}
$\text{Tl}_{1.5}\text{In}_{2.5}\text{CdI}_6$	$a = 913.2(3), c = 971.3(4)$	8.100 ^{a)}
Tl_4CdI_6	$a = 922.2(4), c = 960.3(4)$	8.167 ^{a)}
$\text{Rb}_{0.2}\text{Tl}_{3.8}\text{CdI}_6$	$a = 924.6(3), c = 959.4(5)$	8.202 ^{a)}
$\text{Rb}_{0.5}\text{Tl}_{3.5}\text{CdI}_6$	$a = 927.8(9), c = 960.3(9)$	8.266 ^{b)}
$\text{Rb}_{1.0}\text{Tl}_{3.0}\text{CdI}_6$	$a = 932.7(6), c = 961.0(12)$	8.360 ^{b)}
$\text{K}_{0.5}\text{Tl}_{3.5}\text{CdI}_6$	$a = 926.8(6), c = 959.8(9)$	8.244 ^{b)}
$\text{K}_{1.0}\text{Tl}_{3.0}\text{CdI}_6$	$a = 930.4(9), c = 958.7(9)$	8.299 ^{b)}
Tl_4GeI_6	$a = 908.5(6), c = 994.5(9)$	8.208 ^{b)}
$\text{Rb}_{0.5}\text{Tl}_{3.5}\text{GeI}_6$	$a = 913.0(9), c = 996.5(15)$	8.307 ^{b)}

^{a)} indicates data from single crystals^{b)} indicates data from polycrystalline material

Results

The changes of the lattice constants and of the cell volumes are summarized in Fig. 3 for the systems $\text{Tl}_x\text{In}_{4-x}\text{CdI}_6$ and $\text{Rb}_x\text{Tl}_{4-x}\text{CdI}_6$. In the first x can range from 0 to 4. Here substitution of Tl^+ for the smaller In^+ leads to a slight increase of the cell volume as would be expected. Surprisingly this volume change is accompanied by a marked change of the c/a ratio.

ZANDBERGEN [10] has given a convincing explanation for this effect when comparing the lattice parameters of a series of such compounds. The size of the A cation determines the distance between the BX_6 octahedra in the a_1, a_2 -plane. When these octahedra come closer, they "pile up" thereby leading to a dilatation on the c direction. Evidently this distortion of the structure has nothing to do with lone pair interactions.

In the system $\text{Rb}_x\text{Tl}_{4-x}\text{CdI}_6$ the substitution of the closed shell cation for Tl^+ cannot proceed beyond $x \cong 1.2$, even though these ions are comparable in size. X-ray diagrams of the corresponding products clearly showed the presence of the unreacted binary compounds. Furthermore the change of the c/a ratio and the marked increase in cell volume are now solely effected by a strong expansion in the a_1, a_2 -plane, in which the A—A contacts are closest. In the structure refinements with single crystal data of the mixed crystals $\text{Tl}_{1.5}\text{In}_{2.5}\text{CdI}_6$ and $\text{Rb}_{0.2}\text{Tl}_{3.8}\text{CdI}_6$ we were able to refine the positions of the two different A-type cations independently. In the first compound the positional parameters of Tl^+

Table 3 Structural parameters and data pertaining to the refinement procedures for mixed crystals $A'_x A_{4-x} BX_6$ and related $A_4 BX_6$ compounds

Compound	In_4CdI_6	$In_2.5Tl_{1.5}CdI_6$	Tl_4CdI_6	$Rb_{0.3}Tl_{3.8}CdI_6$
Lattice parameters	$a = 906.0(2)$ pm, $c = 975.4(4)$ pm	$a = 913.2(3)$ pm, $c = 971.3(4)$ pm	$a = 922.2(4)$ pm, $c = 960.3(4)$ pm	$a = 924.6(3)$ pm, $c = 959.4(5)$ pm
Space group	$P4/mnc$	$P4/mnc$	$P4/mnc$	$P4/mnc$
Atomic positions	In in 8(g) .35829(8) .85829(8) .25	In in 8(g), 62.5% .3610(21) .8610(21) .25 Tl in 8(g), 37.5% .3534(18) .8534(18) .25	Tl in 8(g) .3534(1) .8534(1) .25 Cd in 2(a) 0 0 0	Rb in 8(g), 5% .356(12) .856(12) .25 Tl in 8(g), 95% .3528(3) .8528(3) .25 Cd in 2(a) 0 0 0
Measured sections in reciprocal space	$h\ k\ l, \bar{h}\ \bar{k}\ \bar{l}$	$h\ k\ l, \bar{h}\ \bar{k}\ \bar{l}, \bar{h}\ \bar{k}\ \bar{l}, h\ \bar{k}\ \bar{l}$	$h\ k\ l, \bar{h}\ \bar{k}\ \bar{l}$	whole sphere
Theta-range ($AgK\alpha$ radiation)	$3^\circ \leq \Theta \leq 25^\circ$	$2^\circ \leq \Theta \leq 16^\circ$	$3^\circ \leq \Theta \leq 18^\circ$	$2^\circ \leq \Theta \leq 16^\circ$
Number of unique reflections	770	533	315	405
R_w -value	0.0451	0.0380	0.0653	0.0433
Absorption coefficient	96.6 cm^{-1}	157.8 cm^{-1}	280.6 cm^{-1}	258.8 cm^{-1}
Calculated density	5.54 $g\ cm^{-3}$	6.05 $g\ cm^{-3}$	6.88 $g\ cm^{-3}$	6.80 $g\ cm^{-3}$

The lattice parameters were refined using the program GIVER [9] from 25 reflections in the range $12^\circ < \Theta < 20^\circ$ measured with the diffractometer. The Rb atom could be refined only isotropically.

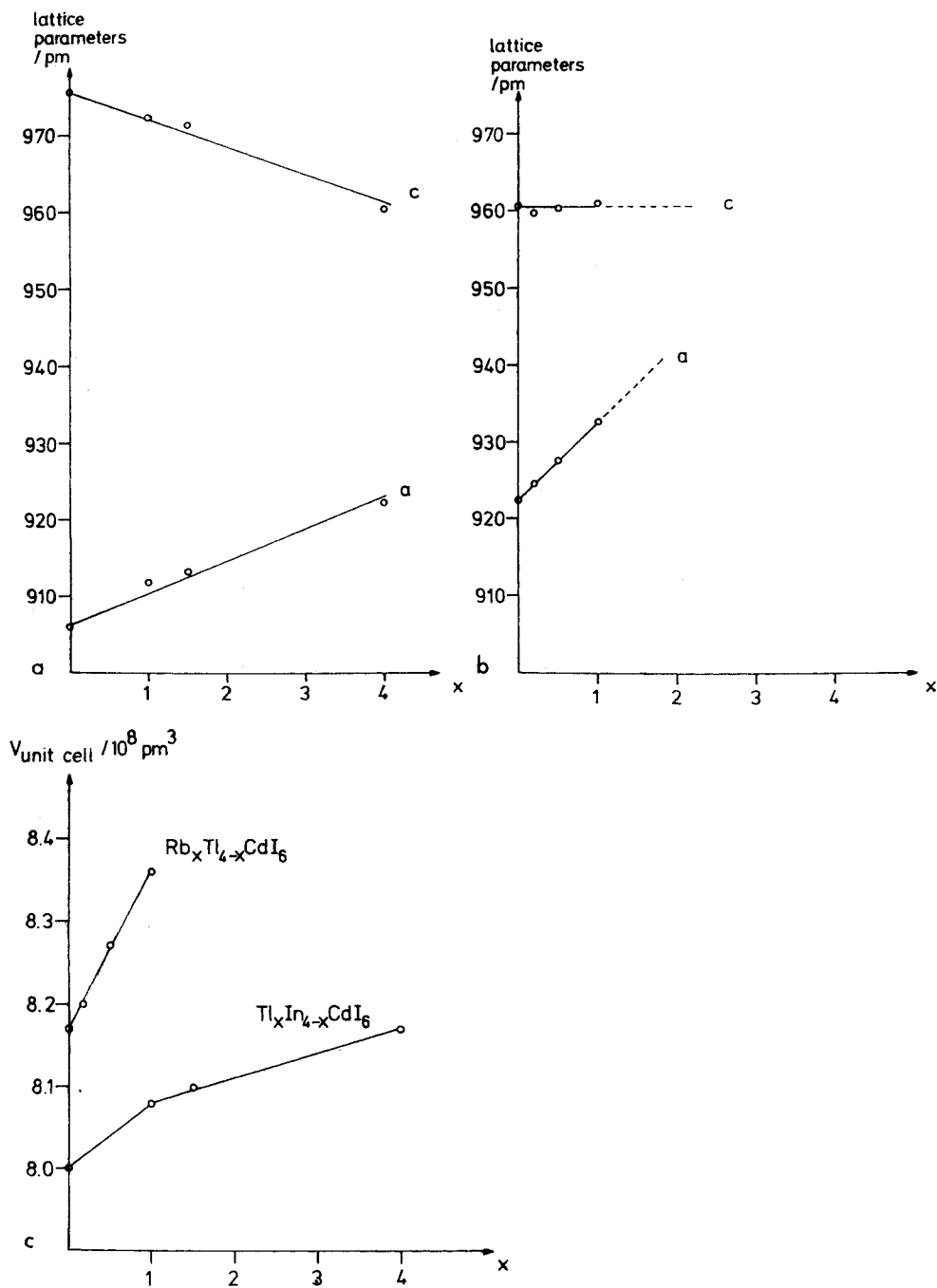


Fig. 3 Lattice constants of $\text{Tl}_x\text{In}_{4-x}\text{CdI}_6$ (a) and $\text{Rb}_x\text{Tl}_{4-x}\text{CdI}_6$ (b) as a function of increasing Tl- and Rb content x , resp.; (c) Unit cell volumes of $\text{Rb}_x\text{Tl}_{4-x}\text{CdI}_6$ and $\text{Tl}_x\text{In}_{4-x}\text{CdI}_6$ vs. increasing Rb- and Tl content x , resp.

and In^+ both give shorter $A-A$ contacts than in the pure ternary compounds Tl_4CdI_6 or In_4CdI_6 . For Tl^+ this may be explained by the fact, that the dimensions of the matrix are still governed by the smaller In^+ ions, which outweigh the Tl^+ ions at this composition. This leads to a compression of the $Tl-Tl$ distance. On the other hand the substituting Tl^+ ions have expanded the Iodide matrix enough to allow a movement of the In^+ ions in their trigonal prismatic coordination, and the direction of this movement is evidently determined by the displacements of iodine ions forced by the incorporation of larger A ions in neighbouring A_2X_{12} double prisms. For ns^2 cations repulsive forces within the different combinations of $A-A$ pairs are small enough to allow such adjustments throughout the whole series of mixed crystals, and this result compares well with the results of our high pressure experiments.

In $Rb_{0.2}Tl_{3.8}CdI_6$ the distance between the A ions within a A_2X_{12} double prism increases markedly, even though only 5% of the ns^2 cations have been replaced by closed shell cations, and this clearly shows the effect of strong repulsive forces.

Conclusions

Our study on A_4BX_6 compounds has shown, that the tetragonal Tl_4HgBr_6 -type arrangement is stabilized by A cations with an ns^2 -type electron configuration. This structure type can be classified as a stuffed and distorted variant of the so called double boride structure. A detailed crystal chemical analysis proves, that the distortion from a possible higher symmetry is not due to repulsive interactions of the lone pairs on the A -type ions. The structural peculiarities may be explained by strong covalent interactions in the $B-X$ sublattice. On the other hand there is no evidence for attractive interactions between the ns^2 type cations. High pressure conditions simulating such attractive interactions cannot substitute for the effect of the ns^2 configuration. Again the tetragonal structure is found as a high pressure modification only for those compounds with an ns^2 -type A cation. We have even observed a decomposition of such A_4BX_6 compounds under pressure.

The incorporation of A ions with a closed shell configuration in mixed crystals $A'_x A_{4-x} BX_6$ destabilizes the tetragonal structure. In such mixed crystals the $A-A$ distance and the cell volume increases much more than could be accounted for by the size relation A'/A .

We therefore conclude, that the Tl_4HgBr_6 type is an electrostatically unfavourable arrangement, which will only be stable in systems with low ionicity. Taking a mean electronegativity (χ) of the cations in relation to that of the anion ($(4\chi(A) + \chi(B))/5\chi(X)$) as a measure for ionicity we find markedly lower values, i. e. higher ionicities, for the substances, which crystallize with the K_4CdCl_6 -type arrangement (0.3–0.4) compared with those having the Tl_4HgBr_6 -type structure (0.6–0.7).

In addition to the lower ionicity the high polarizability of the ns^2 -type cations may play an important part in stabilizing this structure. A simple electrostatic calculation shows, that localization of the lone pair electrons between the two cations within the A_2X_{12} double prisms is an energetically favourable state. We believe, that such a localization occurs and that the positive charges are thereby shielded against each other, and we are convinced, that this is the cause for the existence of these unusual structure types. This hypothesis is supported by the findings of other authors. BRODERSEN et al. [4] claim, that $(NH_4)_4HgBr_6$ containing the highly polarizable NH_4^+ ion crystallizes with the Tl_4HgBr_6 -type arrangement, and BLACHNIK et al. [11] have established the existence of compounds such as Tl_6Cl_4S or Tl_6Br_4Se , which crystallize in an antitype structure, where the highly polarizable anions S or Se play the part of the ns^2 -type cations in the ternary halides A_4BX_6 described in this paper.

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