

Synthesis and Crystal Structure of $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$

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Dedicated to Professor Hartmut Bärnighausen on the Occasion of his 65th Birthday

Abstract. The synthesis of a hitherto unknown 6:5 phase in the quasi-binary system $\text{RbCl}/\text{PbCl}_2$ and its structure determination is reported. The compound $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$ crystallizes in the tetragonal space group $P4/\text{mbm}$ with a large variety of different coordination polyhedra for the cations. Special feature of the structure is a statistical distribution of Rb and Pb

at one of the cation sites with a ratio of 1:3 as defined by electroneutrality. There is no evidence for symmetry reduction by ordering.

Keywords: Ternary halide; lone pair cation; high coordination

Synthese und Kristallstruktur von $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$

Inhaltsübersicht. Im quasi-binären System $\text{RbCl}/\text{PbCl}_2$ wurde eine bislang unbekannte 6:5 Phase synthetisiert und deren Struktur bestimmt. Die Verbindung $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$ kristallisiert in der tetragonalen Raumgruppe $P4/\text{mbm}$ und weist eine Vielzahl unterschiedlichster Koordinationspolyeder für

die Kationen auf. Eine Besonderheit der Struktur ist die statistische Besetzung nur einer Kationenlage durch Rb und Pb im Verhältnis 1:3, was sich aus der Elektroneutralitätsbedingung ergibt. Es gibt keine Hinweise auf eine Symmetrierniedrigung durch Ordnungsvorgänge.

Introduction

In the course of our studies on the crystal chemistry of cations with ns^2 configuration we have examined a variety of binary and ternary halides containing such species. We have found many new compounds of this type by establishing phase diagrams of quasi-binary

systems by thermoanalysis [1–7]. The structures of these compounds show some peculiar features which can be attributed to geometrical and electronic effects of the ns^2 cations. Such cations are a prerequisite for specific structures [8], and in these their substitution by cations with a noble gas configuration (ns^0) will always lead to a destabilization. The compound will then either not exist or adopt a different structure.

The results reported here stem from our investigations of the quasi-binary system $\text{RbCl}-\text{PbCl}_2$. We were especially interested in a 1:1 phase which seemed to exist in two polymorph modifications according to an early paper [9]. However, our thermoanalytical investigations show that such a phase is stable only in the temperature range between 353 and 441 °C, it melts

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congruently at the latter temperature. The reaction of 1:1 mixtures of RbCl and PbCl₂ as well as annealing the 1:1 phase below 353 °C always gives a mixture of RbPb₂Cl₅ and a hitherto unknown Rb-rich phase. (The complete phase diagram will be reported in a forthcoming paper [10]). This report deals with the synthesis and structure determination of the new phase, which turns out to have the formula Rb₆Pb₅Cl₁₆. We will furthermore discuss specific problems of the structure determination and structural details in view of the influence of the ns² cations.

Experimental

RbCl (Merck p. a. grade) was dried under vacuum at temperatures up to 250 °C. PbCl₂ was first precipitated from a lead nitrate solution by aqueous hydrochloric acid and then purified by sublimation under vacuum in a glass tube. These educts and the product were later on stored in Schlenk tubes to prevent any reaction with moisture. They are however fairly stable in air, especially when kept at temperatures above 100 °C. The educts were characterized by x-ray powder diagrams which showed no foreign phases.

Appropriate amounts of the starting materials were sealed in a silica tube and melted above 500 °C for half an hour. After rapid quenching the mixture was kept at 335 °C for several weeks and then quenched again.

Since single crystals could not be grown by this procedure we were forced to solve and refine the structure from powder diffraction data. The powder pattern (measured on a conventional Siemens D5000 diffractometer) could be indexed on the basis of a tetragonal cell with fairly large lattice parameters. A structure solution could only be expected using very good data with sharp reflections to reduce the heavy overlap. Such data were available using the synchrotron facility at Brookhaven National Laboratory.

For these experiments the thoroughly ground sample was loaded in a flat plate low background quartz single crystal sample holder with a diameter of 19 mm by side-loading technique. High resolution powder diffraction data were collected at the SUNY X3B1 beamline at the National Synchrotron Light Source. X-rays of wavelength 115.040(2) pm were selected by a double Si(111) monochromator. The wavelength and zero point error were calibrated using 8 precisely measured peaks of the NBS1976 flat plate Alumina standard.

The diffracted beam was analyzed with a Ge(111) crystal and detected with a Na(Tl)I scintillation counter with a pulse height discriminator in the counting chain. The incoming beam was monitored by an ion-chamber for normalization of the decay of the primary beam. In this parallel beam configuration the resolution is determined by the analyzer crystal instead of by slits. Data were taken at room temperature for 2.2 seconds at each 2θ position in steps of 0.003° in the range from 5° to 20.0° and for 4.2 seconds at each 2θ position in steps of 0.003° from 20.0° to 69.62°.

Using a parallel beam height of 2 mm the sample will be completely illuminated at approx. 12° 2θ. Below that critical angle the intensities are altered by the overspill effect. No corrections have been applied for that data range since they are mostly semiempirical and only few peaks of lower intensity are affected.

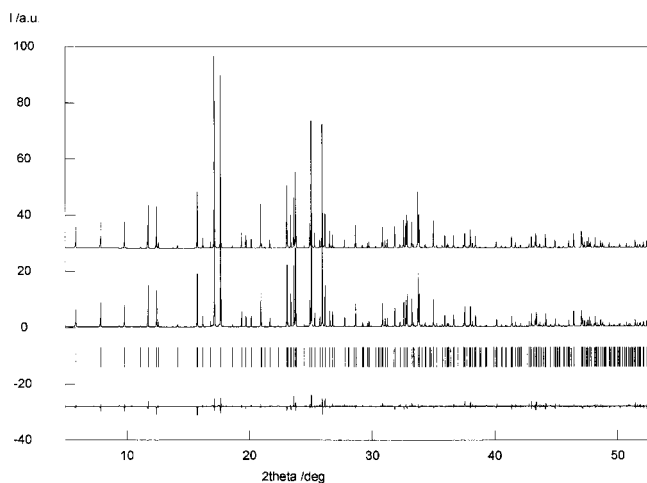


Fig. 1 Results of the Rietveld refinement (from top to bottom: calculated diagram; diagram taken at $\lambda = 115.040$ pm; position of Bragg reflections; difference pattern)

Despite the very fine grained nature of the powder θ -scans did show some crystallite size effects. The sample was therefore rocked around θ for 3° during measurement for better statistics. Low angle diffraction peaks had a FWHM of 0.018° in 2θ , not significantly broader than the resolution of the spectrometer.

Indexing this data set with the Ito method [11] confirmed the same tetragonal lattice as before. The space group P4/mbm was chosen from those allowed according to the extinction rules. (Others gave no reasonable results in direct method runs.) The number of formula units per unit cell was derived by estimation of volumes. A Le-Bail fit [12] worked well to extract about 400 integrated intensities up to 65° in 2θ compared with about 100 in conventional diffraction experiments. These were used as input for the direct methods program SIRPOW92 [13]. The complete structure could be found in a default run. Later refinements confirmed the chosen space group.

The program package GSAS [14] was used for the final Rietveld refinements [15]. The quality of the refinement may be evaluated from the diagram given in Fig. 1. The peak profile function was modeled using a multiterm Simpson's rule integration of the pseudo-Voigt function [16]. The strong asymmetry in the low angle region was modeled by a lately implemented function [17] which accounts for the asymmetry due to axial divergence. This gives a strongly improved fit and therefore better profile R-factors. A manually defined background was used in combination with a refinable 4-term cosine-series to give some flexibility back to the program. Traces of an unknown second phase are visible in the scan, but these reflections could clearly be distinguished from those of the main phase by their different FWHM, and their intensities were all below 1% of the maximum intensity of the pattern.

Refined Procedures and Results

The first model derived from the data was unreasonable since it resulted in a formula "Rb₅Pb₆Cl₁₆" – writing it according to the different sites in the whole cell this would be "Rb₄Rb₄Rb₂Pb₄Pb₈Cl₃₂" – and re-

fined to reduced occupancy factors for the two proposed Pb positions. The only sensible approach was to assume that the Pb sites were partially substituted by Rb and/or only partially occupied. Looking at the mean cation-anion distances, substitution is probable only for the 8k site, a general formula would now be $\text{Rb}^1_4\text{Rb}^2_4\text{Rb}^3_2(\text{Pb}^1_{4-x}\square_x)(\text{Pb}_{8-y}\text{Rb}_y)\text{Cl}_{32}$. Electroneutrality conditions will give the relations $y = 2 - 2x$ and $0 \leq x \leq 1$, however, the thermoanalytical investigations clearly point to a composition “ $\text{Rb}_{12}\text{Pb}_{10}\text{Cl}_{32}$ ”, i.e. $x = 0/y = 2$. The compound is evidently a line phase since other preparations with compositions slightly off the 6:5 ratio showed no different intensity pattern (besides the expected foreign phases).

Refinements of the unconstrained occupancy factors showed strong correlations and did not converge. A constrained refinement with the condition that the sum of the Rb and Pb atoms at the 8k site has to be 8 refined clearly to an occupancy of 75(1)% Pb and 25(1)% Rb, confirming the hypothesis given above (Reliability factors: $R_p = 8.1\%$, $R_{wp} = 11.4\%$, $R_{Bragg} = 7.2\%$). In order to verify the result obtained by an unbiased approach the use of anomalous dispersion was considered.

Two additional scans near the Pb– $L_{3\text{-edge}}$ were performed in order to get different contrast in scattering power between Rb and Pb. (This edge was chosen because it shows the strongest contrast and because the Rb–K- and the Pb– $L_{2\text{-edges}}$ coincide.) The sample was loaded in a flat plate Aluminium sample holder the same way as described before. After scanning the Pb– $L_{3\text{-edge}}$ in fluorescence mode to verify the precise location of the edge and to estimate the chemical shift two room temperature scans were taken. The first at wavelength ($\lambda = 95.357(2)$ pm) for 3.3 seconds at each 2θ position in steps of 0.003° from 4 to 47.07 and the second at wavelength $\lambda = 94.500(2)$ pm for 4.2 seconds at each 2θ position in steps of 0.003° from 3° to 57° . All three data sets could be refined simultaneously using the program system GSAS [14]. The values for the anomalous dispersion corrections of Pb have been taken from the KEK [18] table and have not been refined (at $\lambda = 94.500$ pm: $f' = -12.794$, $f'' = 10.021$; at $\lambda = 95.357$ pm: $f' = -14.625$, $f'' = 3.955$ and at $\lambda = 115.040$ pm: $f' = -6.461$, $f'' = 5.349$).

In contrast with the single data set refinement the unconstrained refinement of the occupancy of the Pb and Rb positions converged although with a high statistical uncertainty of the “true” value. The positions of Pb and Rb at this site, which were refined individually, were virtually the same within the standard deviations. (Reliability factors averaged for the three data sets taken at the wavelengths given above: $R_p = 11.9\%$, $R_{wp} = 8.8\%$, $R_{Bragg} = 11.7\%$). The quality of the refinement may be evaluated from the diagram in Fig. 1. The metric and positional parameters together with the isotropic temperature factors are given in Table 1. A selection of bond lengths is given in Table 2.

Table 1 Structural parameters for $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$ (Standard deviations given refer to the last digit)

Lattice parameters : $a = 1185.519(2)$ pm; $c = 1123.711(2)$ pm, Space Group: P4/mbm

| Atom | site | x | y | z | U_{iso} |
|-------|------|-------------|-------------|-------------|------------|
| Rb1 | 4h | 0.63800(8) | 0.13800(8) | 1/2 | 0.0406(6) |
| Rb2 | 4g | 0.62346(8) | 0.12346(8) | 0 | 0.0290(6) |
| Rb3 | 2a | 0 | 0 | 0 | 0.0621(9) |
| Pb1 | 4e | 0 | 0 | 0.34176(6) | 0.0330(3) |
| Pb/Rb | 8k | 0.17388(3) | 0.67388(3) | 0.25934(5) | 0.0384(3) |
| Cl1 | 16l | 0.06600(13) | 0.20477(13) | 0.21025(12) | 0.0350(7) |
| Cl2 | 8j | 0.20229(19) | 0.09008(18) | 1/2 | 0.0281(9) |
| Cl3 | 4g | 0.15882(19) | 0.65882(19) | 0 | 0.0353(13) |
| Cl4 | 4f | 0 | 1/2 | 0.28287(27) | 0.0400(14) |

Table 2 Interatomic distances in the coordination spheres and mean values in pm (Standard deviations given apply to the last digit)

| Central atom | ligand | distance | number | mean cation-anion distance |
|--------------|--------|----------|--------|--|
| Rb(1) | Cl(2) | 3.298(4) | 2× | 3.534 (shortest distance to another cation) |
| | Cl(2) | 3.314(4) | 2× | |
| | Cl(4) | 3.354(4) | 2× | |
| | Cl(1) | 3.852(3) | 4× | |
| | Pb/Rb | 4.150(3) | 2× | |
| Rb(2) | Cl(1) | 3.200(3) | 4× | 3.424 (shortest distance to another cation) |
| | Cl(3) | 3.391(5) | 2× | |
| | Cl(3) | 3.628(5) | 1× | |
| | Cl(4) | 3.802(4) | 2× | |
| | Rb(2) | 4.130(3) | 1× | |
| Rb(3) | Cl(1) | 3.469(3) | 8× | 3.469 (shortest distance to another cation) |
| | Pb(1) | 3.839(2) | 2× | |
| Pb(1) | Cl(1) | 2.938(3) | 4× | 3.056 (shortest distance to another cation) |
| | Cl(2) | 3.173(3) | 4× | |
| | Pb(1) | 3.560(2) | 1× | |
| Pb/Rb | Cl(4) | 2.927(2) | 1× | 3.183 (shortest distance to another cation) |
| | Cl(3) | 2.930(2) | 1× | |
| | Cl(1) | 3.151(3) | 2× | |
| | Cl(2) | 3.227(3) | 2× | |
| | Cl(1) | 3.245(3) | 2× | |
| | Rb(1) | 4.150(3) | 1× | |

Discussion

The Structure

Despite its high symmetry the structure of $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$ is quite complex. There are three different coordination polyhedra for the Rb- and two for Pb-atoms. The unusual polyhedron around Rb(1) may be described by an arrangement of 6 chlorine atoms in a six-membered ring in boat form with pairs of chlorine atoms above and below this ring in an orthogonal arrangement. (In another description the polyhedra may also be classified as a distorted 1:5:4 polyhedron accord-

ing to a widely used nomenclature [19] where ligands are assumed to lie on a sphere and may be grouped in several planes.) Fig. 2 a gives a view along [001] onto a slice of the structure where only these polyhedra and their connections are shown though others exist as well in this part of the structure (see below). We find them arranged in pairs via a common edge made up of one pair of atoms mentioned above, and such double polyhedra are linked together by corners to form a two-dimensional net.

The polyhedra around Rb(2) (see Fig. 2 b) are also arranged in pairs consisting of tricapped trigonal prisms sharing a common prism edge and two capping atoms. Such pairs are connected via these capping atoms to non-shared capping atoms of adjacent double polyhedra. Within this network we also find the polyhedra around Rb(3) in the form of an elongated cube. They share their edges parallel [001] with the prisms around Rb(2). Fig. 2 c gives a detailed view of the linking between a double prism (Rb(2)) and the elongated cubes (Rb(3)). In this view one sees that

the triangular top and bottom faces of the prisms are not parallel, so the polyhedra may also be described as capped quadratic antiprisms sharing the uncapped quadratic face.

Layers with Rb(2) and Rb(3) polyhedra alternate with the ones containing Rb(1) polyhedra as shown in Fig. 2 a. Within this latter layer – but pointing out a little above and below – we find additionally the polyhedra around Pb(1) and Pb/Rb in a double-layer like arrangement. Fig. 2 d shows a side-view along [210] of this double layer. (For the sake of clarity we have now shown only the polyhedra around these latter atoms. The voids between them are filled by the Rb(1) polyhedra.) Pb(1) has a quadratic antiprismatic coordination and two such polyhedra share a quadratic face. Pb/Rb, the site partly substituted by Rb, is surrounded by 8 chlorine atoms in an arrangement which we call a distorted “1:5:2 polyhedron” according to the nomenclature mentioned above. Here we see the anion neighbours in a five membered almost plane (“distorted”) ring and in addition one above and two be-

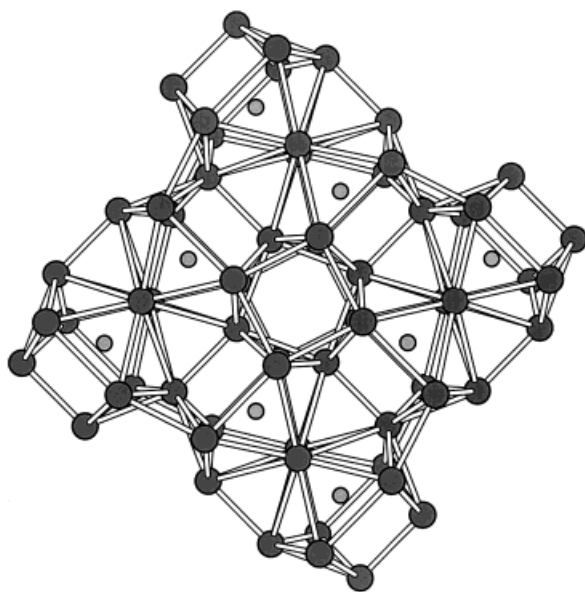


Fig. 2 a Polyhedra around Rb(1) and their connections (small circles Rb, large circles Cl)

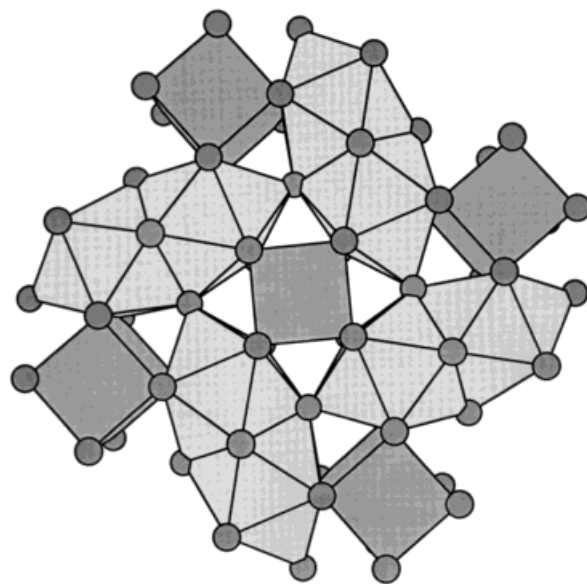


Fig. 2 b Polyhedra around Rb(2) and their connections

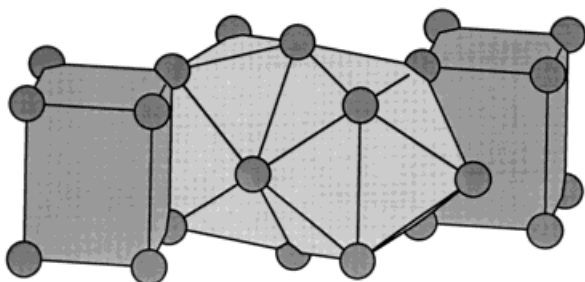


Fig. 2 c The linking of Rb(2)- (lighter shade) and Rb(3)-polyhedra (darker shade)

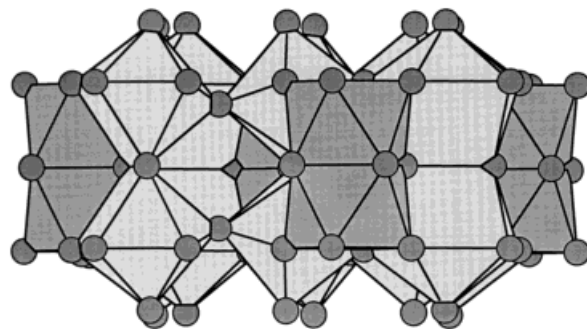


Fig. 2 d Linking of polyhedra around Pb(1) (darker shade) and Pb/Rb (lighter shade)

low this ring. Within (001) planes such polyhedra are connected by sharing atoms in the five membered ring. Along [001] they are connected by alternately sharing the single atoms on one side of the ring or the other two on the other side.

Fig. 3 assembles all the details mentioned before to a view of the complete structure where the *c* axis lies vertically. Slices containing the polyhedra around Rb(1), Pb(1) and Pb/Rb alternate with slices containing the Rb(2) and Rb(3) polyhedra. The packing is very dense, the connectivity is high.

Some features of the structure may be emphasized because we find them in several other structures of ternary halides containing large cations and cations with ns^2 configuration. The first is a columnar “backbone” made up by distorted cubes and tetragonal antiprisms in a 1:2 ratio and sharing the quadratic faces. The InSnCl_3 structure type contains such columns in a 1:1 ratio of the corresponding polyhedra, and the same is true for the tetragonal $\text{NH}_4\text{Pb}_2\text{Br}_5$ type [2]. The other polyhedra sort of fill out the space between these columns and catenate according to their shape and size. The second specific feature is the way by which these polyhedra in between are connected to the columns. The large polyhedra around Rb(1) have common triangular faces with two adjacent quadratic antiprisms in such a way that four of them are arranged in a cross-like manner around the columns mentioned before (see Fig. 2 a). Along *c* this arrangement alternates with a so-called “windmill” arrangement of Rb(2) double-prisms around the cube-like Rb(3) polyhedra with which they have rectangular faces in common (see Fig. 2 b). Such windmill arrange-

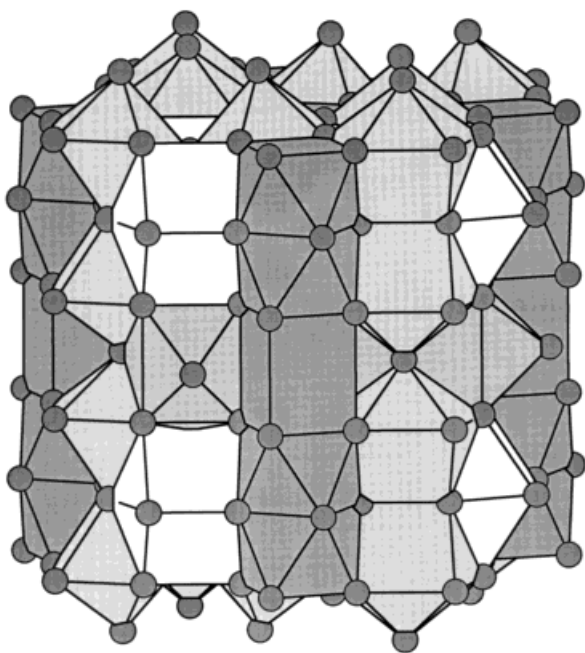


Fig. 3 Overall view of the structure of $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$ (*c* axis points vertically)

ments are found in several structure types such as the InSnCl_3 - [20], $\text{NH}_4\text{Pb}_2\text{Br}_5$ - [2] and In_3SnI_5 -type [21]. For a detailed discussion of this topology we refer to [2].

Another feature which we generally encounter in such structures is the short distance between some of the cations (see Table 2). In this compound they are found between Rb(1) and Pb/Rb, Rb(2) and Rb(2), Rb(3) and Pb(1), and there is an especially short distance between Pb(1) and Pb(1). High coordination numbers will of course lead to a strong linking of the coordination polyhedra via corner-, edge- or even face-sharing, and thereby to short cation-cation distances. According to Pauling’s rules this will destabilize compounds with a high ionicity. In the structure described here, as well as in the others mentioned above, mechanisms are evidently at work which will reduce electrostatic repulsion. One may conjecture that the electrons left with the ns^2 configured cations exercise a shielding effect and reduce the repulsion (see [8]), and this is especially effective in the case of the very close Pb(1)–Pb(1)-contact. The structure of the compound described here again manifests this specific effect of lone-pair cations.

The composition

Looking at the mean cation-anion distances (Table 2) it becomes evident that the substitution of Pb by Rb has taken place at the 8k site (Pb/Rb). A second argument comes from the shape of the polyhedron. We have found such 1:5:2 polyhedra only in structures which are isotypic with InSnCl_3 [10] where they always contain cations with a ns^2 configuration. The InSnCl_3 structure contains pairs of such polyhedra sharing a common rectangular face, the cations therein get fairly close. As mentioned before ns^2 cations are a prerequisite for such a structural constellation. A substitution by ns^0 cations will destabilize the structure. In the case of $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$ we find a different connection between the 1:5:2 polyhedra, i.e. they share only edges and corners. The central cations lie slightly off the centre of gravity of the surrounding anions due to the effect of the lone pair, and their distance is fairly large. Therefore the partial substitution by the ns^0 cation Rb will not destabilize the structure as much. The amount of substitution is restricted mainly by size effects in a densely packed surrounding with a high connectivity of all points in the three-dimensional network.

As mentioned above the degree of substitution is evidently fixed to a definite value by electroneutrality. A deviation from the 3:1 ratio is only possible when either vacancies or interstitial cations are incorporated into the structure. The latter seems highly impossible in view of the dense packing of the structure, and the thermal parameters on the other hand give no definite

clue to partial occupancy of cation sites. The mechanisms governing the structure of this compound remain unclarified as long as ordered substitution in a superstructural arrangement cannot be established. One may speculate about possible ordering schemes. The powder method used here is certainly sensitive enough to rule out any ordering pattern which would lead to a larger unit cell, i. e. symmetry reductions in so-called "klassengleich"-steps [22]. The "translationengleiche" tetragonal space groups with the same extinction rules as P4/mbm offer no appropriate splitting of the Pb/Rb site in a 3:1 ratio. Even if there were a reduction of symmetry to one of the "translationengleiche" orthorhombic space groups (and the corresponding subgroups) the metrics still turn out to be strictly (pseudo-) tetragonal since the very sharp lines of the patterns taken with synchrotron radiation show neither splitting nor even shoulders. In the course of such an ordering process one would also expect a polydomain structure by twinning because of the symmetry reduction in t2 steps. A merohedral twinning situation will always result in a diffraction pattern with complete overlap of symmetrically inequivalent reflections and an appropriate mathematical treatment of the data is difficult.

In conclusion one might say that the structure is certainly well defined and proven according to the state of the art. However, the result keeps us a little puzzled since a fixed substitution ratio as in this case should result in a specific ordering scheme, and this would lead to a symmetry reduction and/or a superstructure. We have no clues to that but we cannot exclude this possibility.

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