PEROVSKITE-LIKE MODIFICATION OF $Cs_3Sb_2I_9$
AS A MEMBER OF THE *OD* FAMILY $A_3B_2X_9$

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The structure of the trigonal modification of $Cs_3Sb_2I_9$ was refined by XRD methods (Syntex $P\bar{1}$ diffractometer, λMoK_α) at T = 285 K. The structure is of perovskite type $A_3B_{3-x}X_9$ with ordered vacancies in the B-sublattice. The unit cell with pseudo-R-centering has the following parameters: a = 8.435(7), c = 10.390(7) Å, V = 151.8 Å³, Z = 1; d_x = 4.67 g/cm³. The centrosymmetric space group $P\bar{3}m1$ was chosen based on the laser radiation second harmonic generation test. The parameters of the pseudo-rhombohedron corresponding to the perovskite cell are a' = 5.976 Å, α = 89.78°. The R-lattice of a perovskite structure is disturbed by ordered Sb vacancies in one of the three I_6 octahedra. The structural modifications of the compounds $A_3B_2X_9$ are analyzed in terms of Dornberger-Schiff's OD theory as the members of the family formed by the two-dimensional periodic fragments of perovskite type structures.

INTRODUCTION

The compound $Cs_3Sb_2I_9$ belongs to the family $A_3B_2X_9$, where A = Cs, Rb, K, Tl (NH_4); B = Bi, Sb, W, Mo, Fe, V, Ti, Cr; X = Cl, Br, I [1]. In the crystal structures of the compounds of this family, the A and X atoms form close-packed layers AX_3, lying one under another subject to cubic or hexagonal closest packing laws [1]. Two thirds of the total number of closest-packed X_6 octahedra are occupied by the B atoms. Most structures are hexagonal with the hexagonal and trigonal polytypic modifications in accordance with the packing of AX_3 layers (Fig. 1*a* and *b*) [1-3].

Isostructural compounds $Cs_3Sb_2I_9$ and $Cs_3Bi_2I_9$ were investigated in [1] by single crystal X-ray diffraction analysis. The compounds crystallize as the hexagonal polytypic modification (space group $P6_3/mmc$), in which the AX_3 layers form an *hcc* type hexagonal packing (Fig. 1*a*). For $Cs_3Sb_2I_9$, the trigonal modification with AX_3 layers forming cubic closest packing was found in [4] (space group $P\bar{3}m1$) (Fig. 1*b*). The trigonal structure of $Cs_3Sb_2I_9$ was refined in [4] by full-profile analysis of the X-ray diffraction spectrum to R = 0.14. Thus for $Cs_3Sb_2I_9$, the hexagonal and trigonal polytypic modifications were established.

The physical properties of $Cs_3Sb_2I_9$ crystals were investigated in [5]; two low-temperature phase transitions were found: one at 85.3 and another at 72.6 K. Previously, a low-temperature phase transition (at 220 K) was detected for the hexagonal modification of $Cs_3Bi_2I_9$ [6]. Based on the analogous variation of the physical properties and NQR spectra near the phase transition temperatures, for $Cs_3Sb_2I_9$ and $Cs_3Bi_2I_9$ it was concluded [5] that the two compounds are isostructural and belong to the hexagonal polytypic modification studied in [1]. The preliminary X-ray diffraction data which we obtained on powder samples indicate that the $Cs_3Sb_2I_9$ crystals studied in [5] belong to the trigonal modification.

The absence of exact structural data for the trigonal modification of $Cs_3Sb_2I_9$ at room temperature in connection with the low-temperature transitions found for this modification stimulated a single crystal structure analysis. The second part of this work considers the structural types in the $A_3B_2X_9$ group as members of the same structural family using group analysis of Dornberger-Schiff's *OD* theory [7].
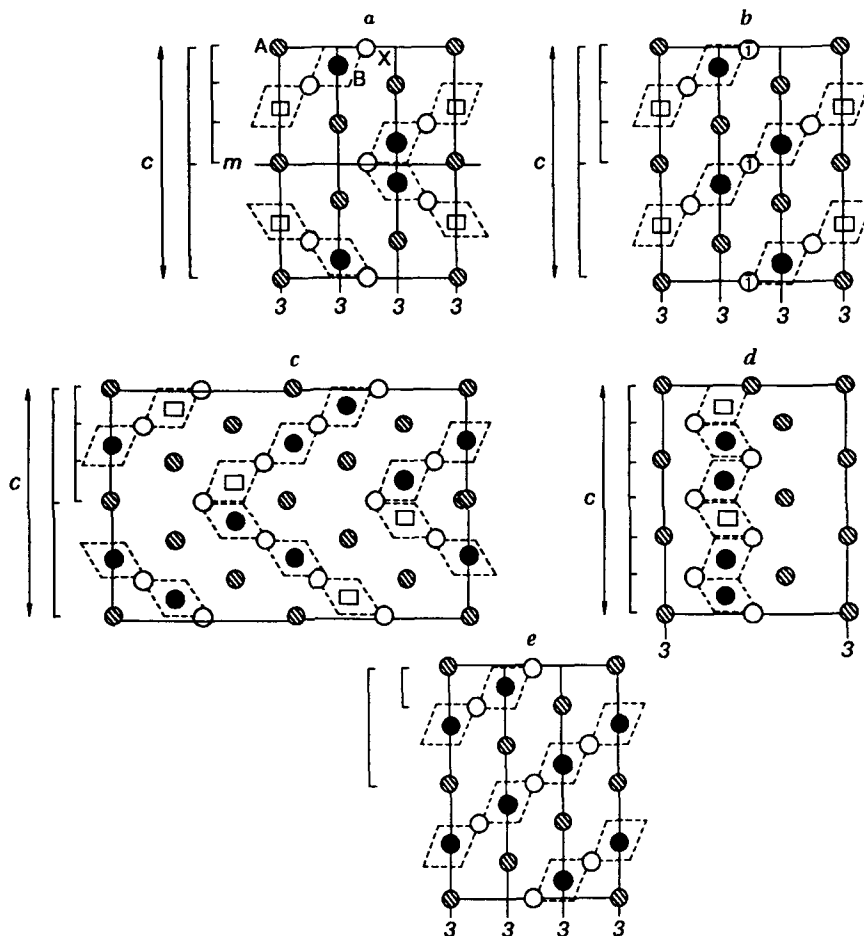
Fig. 1. Structural types of $A_3B_2X_9$ family and perovskite structure. Analogous cross sections along the 3 axis of the closest packing are presented. The small and large square brackets denote the minimal (single) and triple perovskite fragments, respectively. The arrows indicate the lattice parameters along the c direction: a) (110) cross section of the hexagonal modifications with (hcc) type of packing of AX_3 layers; the σPO sequences are (m,1,1,...) and (m,...) for the single and triple fragments, respectively; b) (110) cross section of the trigonal perovskite modifications with a (c,...) type packing of AX_3 layers; the σPO sequence is (1,...) for the triple fragments; c) (130) cross section of the orthorhombic modification with an (h, c, c,...) type of packing of AX_3 layers; the triple fragments are related by the n plane in the c direction; d) (100) cross section of the hexagonal modification with an (h,...) type of packing of AX_3 layers; the σPO sequence is (m,...) for the single fragments; e) cross section along the 3 axis of a cubic perovskite structure; the σPO sequence is (m,...) for both the single and the triple fragments.

EXPERIMENTAL

The procedure for the preparation of the single crystals under study is described in [5]. For crystal structure refinement of the trigonal modification of $Cs_3Sb_2I_9$, a flat sample was cut out from a single crystal plate ~ 0.5 cm in diameter and ~ 1 mm in thickness immediately after the plate was cooled in liquid nitrogen. The shape of the crystal, subsequently used for an absorption correction, is defined by the following faces and distances from them to the center of the crystal: for (100), (-100), (010), and (0$-$10), 0.085 mm; for (001) and (00$-$1), 0.01 mm. The crystals are ductile and easily deformable and retain these properties after cooling with liquid nitrogen.

The X-ray diffraction experiments were performed at $T = 283$ K on a Syntex $P\bar{1}$ diffractometer (λMoK_α, graphite monochromator, $2\theta/\theta$ scan mode). The structure computations were carried out with AREN software [8]. An absorption correction ($\mu = 173$ cm^{-1}) was applied by the numerical integration method for a crystal of given form and further refined with the DIFABS program [9]. The basic experimental set of integrated intensities was obtained for a

hemisphere of reciprocal space ($\sin\theta/\lambda < 0.89$ Å^{-1}) and involved 1241 reflections exceeding $3\sigma(I)$. After reflections with an asymmetric profile had been discarded (block structure and deformation of crystals) and the equivalent reflections had been averaged, the refinement was performed for 246 unique reflections. After the averaging of F_{hkl} of equivalent reflections, the residuals were 0.14 and 0.077 before and after the application of the correction, respectively. The hexagonal unit cell parameters were refined using 15 reflections: $a = 8.435(7)$, $c = 10.390(7)$ Å. The intensities of $-h + k + l = 3n$ (n is integer) type reflections were much higher than those of the other reflections, indicating pseudo-R-centering of the hexagonal cell.

The initial values of atomic coordinates for structure refinement were taken from [4] for centrosymmetric space group $P\bar{3}m1$. In this group, each of the Cs and I atoms occupies two crystallographically independent positions, one of which is at the inversion center for each kind of atom. The Sb atoms correspond to one independent position. The large values of the isotropic thermal parameters of the Cs atoms, along with the high residual ($R = 0.14$), were initially a reason for a transition to the acentric space group $P3m1$.

Refinement in the acentric space group $P3m1$ reduced the residual from 0.14 to 0.08 owing to the replacement of the cesium atom by 0.21 Å from the inversion pseudocenter along the 3 axis. The isotropic thermal parameter of this atom decreased from 6.1 to 5.6 Å^2. Table 1 lists the atomic coordinates obtained after full structure refinement to $R = 0.053$ in the anisotropic approximation of their thermal vibrations in space group $P3m1$. As follows from the coordinates, the other independent atoms retained their centrosymmetric arrangement.

To verify the acentricity of the model, we carried out a test for generation of the second harmonic of laser radiation (YAG:NB pulsed laser, reflection scheme, temperature of experiment $T = 290$-273 K; run by S. Yu. Stefanovich). The absence of the second harmonic indicated that the crystal is centrosymmetric at 0.98 probability; therefore, we returned to the centrosymmetric space group $P\bar{3}m1$.

Refinement in the centrosymmetric variant including the anisotropy of thermal vibrations lowered the residual to 0.085. The good cleavage along the (001) plane and plate ductility indicated that the crystal contains disoriented blocks (the maximal width of reflections in ω is 2.0-2.5° for $2\theta = $ const) and their deformation (the maximal width of reflections in 2θ is 3.0-4.5° for $\omega = $ const). The anisotropic factors of reduction to a single scale ($K11 = 1.05$, $K22 = 1.02$, $K33 = 0.53$, $K12 = 0.48$, $K13 = -0.03$, $K23 = 0.05$) and the isotropic extinction parameter ($E = 0.0000012$) were refined with allowance for this property of the crystal. At this stage, the residual was 0.062. Using the DIFABS program to refine the absorption correction with further re-refinement of the structure in an anisotropic approximation of

TABLE 1. Coordinates and Thermal Parameters (Å^2) of Atoms in the Acentric Variant of Structure for Cs$_3$Sb$_2$I$_9$ (space group $P3m1$)

Atom	x/a	y/b	z/c	B_{iso}	B_{eq}
Cs(1)	0	0	0.0201(8)	5.6(3)	5.9(5)
Cs(2)	1/3	2/3	0.6715(9)	6.3(4)	5.9(6)
Cs(3)	2/3	1/3	0.3280(9)	6.0(3)	5.6(5)
Sb(1)	1/3	2/3	0.1932(8)	3.4(2)	2.7(4)
Sb(2)	2/3	1/3	0.8126(8)	2.4(2)	2.5(4)
I(1)	0.8327(4)	0.6654(6)	0.6615(4)	4.09(2)	5.9(4)
I(2)	0.664(1)	0.8320(7)	0.3383(5)	5.04(2)	5.7(4)
I(3)	0.002(2)	0.5009(9)	0	5.6(1)	6.1(4)

TABLE 2. Coordinates and Thermal Parameters (Å^2) of Atoms in the Centrosymmetric Variant of Structure for Cs$_3$Sb$_2$I$_9$ (space group $P3m1$)

Atom	x/a	y/b	z/c	B_{iso}
Cs(1)	0	0	0	6.1(1)
Cs(2)	2/3	1/3	0.3257(7)	4.8(3)
Sb	2/3	1/3	0.8096(3)	2.8(2)
I(1)	0	1/2	0	4.7(2)
I(2)	0.6647(4)	0.8323(5)	0.3392(4)	4.5(2)

TABLE 3. Anisotropic Thermal Parameters of Atoms ($\times 10^3$) in the Structure of $Cs_3Sb_2I_9$ (centrosymmetric variant)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{eq}
Cs(1)	375	375	117	375	0	0	7.2(3)
Cs(2)	379	379	101	379	0	0	6.9(4)
Sb	236	236	20	236	0	0	3.7(2)
I(1)	423	423	106	532	58	−59	7.0(2)
I(2)	298	372	78	298	−106	−53	6.1(2)

TABLE 4. Interatomic Distances (Å) in Polyhedra in the Structure of $Cs_3Sb_2I_9$ (centrosymmetric variant)

Cs cuboctahedra	
Cs(1)–I(1) 4.228(2)×6 –I(2) 4.285(2)×6 ⟨4.256⟩	Cs(2)–I(1) 4.162(3)×3 –I(2) 4.230(1)×6 –I(2) 4.233(4)×3 ⟨4.214⟩

Sb octahedron

Sb–I(2) 2.874(3)×3
–I(1) 3.137(3)×3

thermal vibrations of atoms yielded $R_F = 0.059$ ($R_w = 0.054$, weighting scheme $w = 1/\sigma_F^2$). The final atomic coordinates, anisotropic thermal factors, and interatomic distances corresponding to the centrosymmetric model are listed in Tables 2-4.

A comparison between the centrosymmetric and acentric variants of structure based on the residuals (0.059 and 0.053) does not allow one to decide between the two. As can be seen from a comparison between Tables 1-3, the relative coordinates of all atoms except Cs at the inversion center differ by less than 0.002; the high values of equivalent thermal parameters are smaller in the acentric variant. These data, along with the low quality of the crystal and the high thermal mobility of all atoms, also prevent one from drawing an unambiguous conclusion concerning the inversion center. A critical argument in favor of the centrosymmetric space group is the absence of generated second harmonic of laser radiation. The NQR spectra recorded in [5] also favor the centrosymmetric variant, indicating two independent positions of I atoms (there are three of them in the acentric variant, Tables 1 and 2).

TRIGONAL MODIFICATION OF THE DEFECTIVE PEROVSKITE STRUCTURE

The crystal structure of the trigonal modification projected along the a axis is shown in Fig. 2. The (110) cross section of the structure is schematically represented in Fig. 1b. As follows from a comparison of Figs. 1b and 1e, the structure is of perovskite type ABX_3, differs from it in the presence of ordered vacancies in the B-sublattice, and corresponds to the formula $AB_{2/3}X_3$, where A = Cs, B = Sb, X = I. In Fig. 3, the scheme of a fragment of the trigonal structure, which is a pseudocubic perovskite-like cell, is compared with the cubic cell of perovskite. The layers of empty and filled SbI_6 octahedra alternate along one of the four space diagonals of the pseudocubic subcell in a ratio of 1:2. Thus only one of the four diagonals is a 3 axis. The recalculated parameters of the pseudorhombohedron ($a' = 5.976$ Å, $\alpha = 89.78°$) show that it is close to the pseudocubic perovskite cell (Fig. 3).

As in perovskite, c.n. = 12 for all A(Cs) atoms and 6 for B(Sb). The cuboctahedra of the Cs(1) atoms are slightly stretched along the 3 axis; the average distance Cs(1)–I ⟨4.256⟩ Å. In the other cuboctahedron, Cs(2) is shifted along the 3 axis toward I(1) to form three shorter distances Cs(2)–I(1) 4.162 Å (av. ⟨4.241⟩ Å). The Sb atoms are displaced from the centers of their octahedra by 0.216 Å, forming three short distances Sb–I(2) 2.874 Å and three long ones Sb–I(1) 3.137 Å (Table 4).

As opposed to the perovskite structure, in the structure under analysis the vertex-sharing SbI_6 octahedra constitute two-storied layers [Sb_2I_9], which are perpendicular to the 3 axis (Figs. 1b and 2), but not a framework. The Sb atoms are shifted from the centers of the octahedra toward the periphery of the layer, forming longer bonds with
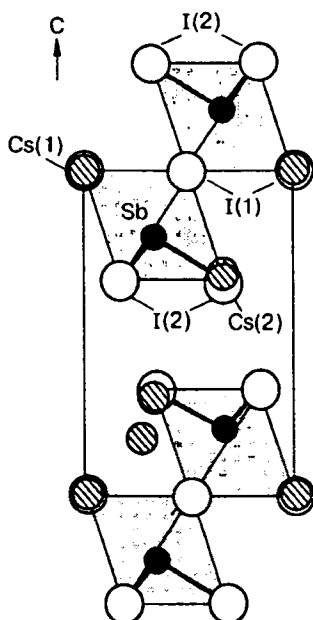
Fig. 2. Unit cell of the trigonal modification of $Cs_3Sb_2I_9$ projected along [100] according to the data obtained. The thick lines indicate shortened interatomic distances.
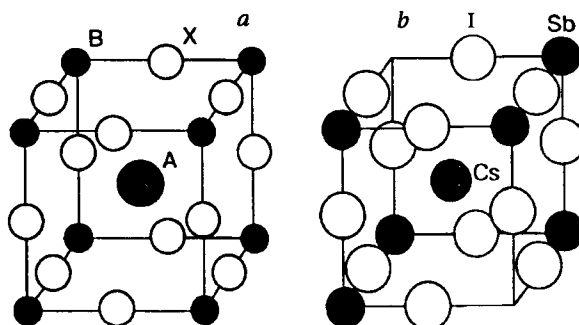

Fig. 3. Comparison of the cubic perovskite cell (a) with an idealized fragment of the trigonal perovskite-like structure with ordered vacancies in the B-sublattice (b). In the latter case, the cubic (rhombohedral) translations are broken for B atoms alone.

the bridging I(1) atoms and shorter ones with the terminal I(2) atoms. These octahedral layers, which may be regarded as relatively rigid structural fragments, are not involved in strong chemical interactions since the distances corresponding to such interactions are only those of SbI_6 octahedra (Table 4). The Cs–I distances vary within 4.162-4.285 Å (the sum of the ionic and atomic radii is 4.08 [10] and 4.00 Å [11], respectively) and, on the average, exceed the I–I distances (4.137-4.272 Å), indicating that the Cs and I atoms weakly interact with each other. These peculiarities of chemical interactions explain the high ductility of the crystals and the good cleavage along (001) coinciding with the plane of the structural layers.

The absence of strong chemical bonds is also confirmed by the high values of the thermal parameters of atoms, especially for Cs and I (Tables 2 and 3).

COMPARISON BETWEEN THE HEXAGONAL AND TRIGONAL POLYTYPES OF $Cs_3Sb_2I_9$

It is interesting to compare the structure of the trigonal perovskite-like modification investigated in this work with the structure of the hexagonal modification of $Cs_3Sb_2I_9$ studied in [1]. The schemes of the (110) cross section for

the two structures are shown in Figs. 1*b* and 1*a*, respectively. On the schemes, the Sb atoms lie at the centers of octahedra, whereas in real structures they are shifted to the terminal I atoms. The structures differ in the type of linking between SbI_6 octahedra. In the hexagonal modification, the face-sharing octahedra are linked into discrete pairs $[Sb_2I_9]$. In the trigonal modification, the octahedra are linked by their vertices to form two-dimensional periodic layers of the same composition. The relatively rigid elements of the former structure are isolated from each other, thus ensuring the isotropic character of chemical bonds; in [1], the ellipsoids of revolution with 0.19 and 0.128 mm axes were plotted for the hexagonal crystals by the revolution procedure. In the latter case, the layers are rigid elements in the structure. This leads to the anisotropy of chemical interactions and the aforementioned good cleavage in crystals. Three short contacts of Sb atoms with the terminal I atoms are observed in both modifications, their length being 2.87 Å. This suggests that the bonds are quite stable and invariant with respect to the polytypic modifications of the compound. The bonds between the Sb atoms and the bridging I atoms in the trigonal modification (3.137 Å) are markedly shorter than those in the hexagonal one (3.198 Å), the I–Sb–I angle being smaller in the latter case. This indicates a repulsion between the Sb atoms when the octahedra are linked by the common face. The above structural differences between the Sb octahedra arising from the different modes of linking lead to regular changes in the corresponding parameters of the hexagonal cells of the two modifications. The hexagonal polytype is characterized by a smaller a parameter and a larger c' parameter, whereas the corresponding unit cell parameters are close: $a_{hex} = 8.349$, $a_{trig} = 8.435$ Å; $c'_{hex} = c_{hex}/2 = 10.468$, $c_{trig} = 10.390$ Å; $V_{trig} = 151.8$, $V'_{hex} = V_{hex}/2 = 151.4$ Å^3.

In the trigonal modification, the first low-temperature phase transition is observed around 90 K [5]. For the hexagonal modification, no literature data are available on the low-temperature transformations; for the isostructural compound $Cs_3Bi_2I_9$, such transformations are observed at a higher temperature, 220 K [6]. It is suggested that for $Cs_3Sb_2I_9$ the hexagonal modification will also have a phase transition at a higher temperature compared to the trigonal one, since its discrete groups are likely to be more mobile than the rigid two-dimensional periodic modules in the trigonal phase.

OD FAMILIES $A_3B_2X_9$

The comparison of the above two polytypic modifications of $Cs_3Sb_2I_9$ with other structures of the $A_3B_2X_9$ family given in [1] shows that all structures are built up of two-dimensional periodic structural modules, which are layered fragments of the perovskite structure bounded along the 3 axis by close-packed AX_3 layers (Fig. 1). The minimal (unit) fragment consists of two such layers with B atoms lying between them in the X_6 octahedra (Fig. 1*e*). In all the structures of the family, 1/3 of the total number of X_6 octahedra are vacant, but the ordering of the vacancies differs between the structures (Fig. 1*a-d*). Any two neighboring perovskite fragments are separated by a common boundary AX_3 layer. If the ordering of vacancies in the X_6 octahedra is not taken into consideration, one can say that the neighboring perovskite fragments are related by one of the two local symmetry elements, namely, by the mirror plane *m* which is perpendicular to the axis of fragment alternation or by the inversion center lying in the plane of the boundary AX_3 layer (Fig. 1). Using the sequence of alternation of these local symmetry elements relating single perovskite fragments, one can describe all possible modifications (including the hypothetical ones). These structural families are conveniently considered using *OD* theory developed by Dornberger-Schiff [7] and elaborated in many later works (e.g., [12-14]). (*OD* is abbreviated from order–disorder to reflect a unified description of the periodic and aperiodic structures of definite types.) According to this theory, the structures formed from identical (zero-, one-, or two-dimensional) periodic structural modules are defined using the *OD* groupoid.

For structures formed from two-dimensional periodic modules, the *OD* groupoid consists of two group designations: the first corresponds to the symmetry of the layer (λ operations), with the direction of layer alternation (or the direction of disturbed periodicity according to [7, 12]) indicated in parentheses; the second describes all possible symmetry operations (σ operations) relating any two neighboring layers in the direction of their alternation. The local or partial symmetry operations (*PO* according to [7, 12]) relating the layer modules are not necessarily the elements of the whole structure. In contrast to the space group, the groupoid defines the structural diversity in a group rather than a separate structure by indicating the rule of formation of its members, each of which is characterized by its own sequence of alternation of σ operations (*σPO*). If a *σPO* sequence is periodic, the corresponding structure is ordered, i.e., is periodic in the direction of layer alternation. Otherwise, the structure is disordered in this direction. According

to [12], the structures of the family that are characterized by the σPO sequence consisting of only one operation are called *MDO* structures. For example, if the neighboring layers in the *OD* family are related to each other by one of two operations, namely, by the 2 axis or the m plane (two σ operations), then the two structures corresponding to the sequences σPO (2,...) and (m,...) are structures with the maximal order of alternation of σ operations and are designated as MDO_1 and MDO_2. The number of *MDO* type structures in the *OD* family equals the number of σ operations. As noted in [12], any family has structures with the same combinations in the *PO* sequence which correspond to doubled, tripled, etc. layers. In other words, in the *OD* family one can isolate a subset of structures for which the element multiplied by the σPO operations is a doubled (tripled, etc.) but not a single layer. In these subfamilies, one can also consider *MDO* structures.

In the family under analysis, if the ordering of vacancies in X_6 octahedra is neglected, then the above-described single perovskite fragments with $P\bar{3}m1$ symmetry are related to each other by the m plane or by the inversion center. The *OD* groupoid of this family is

$$\frac{P(3)m1}{\{(\bar{1}/m)11\}}. \tag{1}$$

This *OD* groupoid, multiplying a single perovskite fragment, actually defines the diversity of hexagonal structures (perovskite derivatives) which either have no vacancies at all or have them distributed statistically in any sublattice. In this case, the generated structural types fully reflect only variations of the closest packings of AX_3 layers. The σPO alternation sequences relating the double-layer perovskite fragments are analogous to the sequences of alternation of hexagonal and cubic layers in the structure. This follows from the fact that a c type AX_3 layer contains an inversion center relating two adjacent layers, and an h type AX_3 layer is a local symmetry plane for the neighboring layers. For example, an $(h,c,c,...)$ type closest packing in $Cs_3Bi_2Cl_9$ and in the hexagonal modifications of 17 compounds [1] corresponds to the sequence σPO (m,1,1,...) (Fig. 1a, c). An $(h,...)$ type packing in $Cs_3Tl_2Cl_9$ corresponds to the sequence σPO (m,...) (Fig. 1d); a $(c,...)$ cubic packing in the trigonal modification of $Cs_3Sb_2I_9$ (and three more compounds [1]), to the sequence σPO ($\bar{1}$,...) (Fig. 1b). In addition to the three known variants of the closest packings of AX_3 layers given in Fig. 1, any other variants are theoretically possible. Perovskite type structures (Fig. 1b, e) are MDO_1 structures, since they correspond to the sequence σPO ($\bar{1}$,...), and $Cs_3Tl_2Cl_9$ (Fig. 1d) is an MDO_2 structure.

The diversity of structural types in the $A_3B_2X_9$ family is determined not only by the variations of the closest packings of AX_3 layers but also by the ordered distribution of B atoms in 2/3 of the total number of X_6 octahedra. The known compounds from this family (according to [1]) mostly refer to the hexagonal and trigonal modifications described above for $Cs_3Sb_2I_9$. In these modifications one can isolate larger fragments of perovskite structure with ordered and identical arrangements of vacancies in the B positions. Each fragment consists of three single layers related by the limited sequence σPO ($\bar{1}$,1); two single fragments with fully occupied BX_6 octahedra are separated by a fragment with absolutely vacant $\Box X_6$ octahedra (Fig. 1a, b). Each of the tripled perovskite fragments contains four close-packed AX_3 layers and is three times as thick as a single double-layer fragment (Fig. 1e). In the hexagonal modification, they are related by the m plane; in the trigonal modification, by the inversion center (Fig. 1a, b).

Since the symmetry of the single and triple layers is the same, *OD* groupoid (1) may also be used to generate structural types based on the latter.

In this case, the trigonal perovskite-like modifications (Fig. 1b) are defined by the sequence σPO ($\bar{1}$,...); they correspond to the cubic packing of AX_3 layers and the parameter of the hexagonal cell $c = 3c'$ (c' is the thickness of a single perovskite fragment). The hexagonal modifications (Fig. 1a) are defined by the sequence σPO (m,...); the AX_3 layers form an hcc closest packing; the parameter is $c = 6c'$. Since the triple fragments described above form the most widespread modifications in the $A_3B_2X_9$ family, one can assume that there are structures with alternative periodic sequences σPO relating these fragments, for example, ($\bar{1}$,m,...) or ($\bar{1}$,m,m,...) and also with a lacking spacing in the σPO sequence. The latter variant is to be expected for crystals formed in conditions that are far from equilibrium.

The above variant of the ordered arrangement of B atoms in the X_6 octahedra of the triple perovskite fragment is not the only possible variant. In the orthorhombic modification of $Cs_3Bi_2Cl_9$, the ordering of $BiCl_6$ octahedra obeys the orthorhombic space group $Pmcn$ ($a_{orth} = a_{hex}$, $b_{orth} = a_{hex}\sqrt{3}$, $c_{orth} = c_{hex}$) [1] with λ operations of the triple perovskite layer $Pmc(1)$ (Fig. 1c). In this structure, the two neighboring fragments are related by the n plane along the alternation axis, with the ordering of B atoms taken into consideration. The absence of other known modifications constructed of the same perovskite fragments does not allow an adequate description of the possible *OD* family.

In the perovskite derivatives belonging to the $A_3B_2X_9$ family with different types of closest packings of AX_3 layers, other variants of ordering of B atoms are possible.

CONCLUSIONS

The structure refinement of the trigonal modification of $Cs_3Sb_2I_9$ showed that this form is of perovskite structural type with ordered vacancies in the B-sublattice and crystallizes in space group $P\bar{3}m1$ with unit cell parameters $a = 8.435(7)$, $c = 10.390(7)$ Å.

The Cs(1) atoms lying at the inversion center possess high thermal mobility.

The structure is characterized by relatively rigid layers of structural modules $[Sb_2I_9]$ consisting of vertex-sharing SbI_6 octahedra. The absence of strong interactions between the layers and between the Cs and I atoms and the high thermal mobility of all atoms in the structure result in the low-temperature phase transitions found in [5].

The known structural types in the $A_3B_2X_9$ group are considered using Dornberger-Schiff's theory of OD structures [7] as consisting of two-dimensional periodic perovskite fragments related to each other in the third direction by the inversion center or by the m plane. Possible OD families of structures from this group are described using OD groupoid.

The diversity of structures in the families is the result of two possible types of link between the perovskite-like fragments and variations of ordered distribution of B atoms in them.

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