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 $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$**

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Dynamic Disorder of Bi_8^{2+} Clusters in the Plastic Phase $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$

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Dedicated to Professor Gerd Meyer on the Occation of his 60th birthday.

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Abstract

Black, air-insensitive crystals of the bismuth-rich tetraiodido-indate(III) $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ have been prepared from melts of the contributing elements. X-ray diffraction on a single crystal at 293 K and 220 K revealed a cubic structure with $[\text{InI}_4]^-$ tetrahedra, isolated Bi^{3+} cations and rotationally disordered Bi_8^{2+} square antiprisms (space group $Fm\bar{3}c$; $a = 20.162(2)$ Å at $T = 293(1)$). The principal arrangement of the complex ions corresponds to the AuCu_3 type. The small bulk modulus $B_0 = 12(1)$ GPa and its large pressure derivative $B_0' = 11(1)$ as well as the low Debye temperature $\theta_D = 52$ K are in accordance with a plastic behavior. Cooling below 148(1) K induces the first order transition into an ordered phase with 0.43 % higher density but much larger unit cell and lower crystallographic point group. The transition enthalpy $\Delta H \approx 3.8$ kJ·mol⁻¹ and transition entropy $\Delta S \approx 3$ R were determined from specific heat data. A similar reversible phase transition into a lower symmetric structure is observed at a pressure of approximately 5 GPa. $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ is a diamagnetic semiconductor.

Keywords: Bismuth; Cluster compounds; Order disorder transition; Plastic phase; Polycations

Introduction

The stabilization of polycations of group 15 or 16 in the solid necessitates weak Lewis bases, like $[\text{AsF}_6]^-$, $[\text{WOCl}_4]^-$, $[\text{WCl}_6]^-$, $[\text{NbCl}_6]^{2-}$ or $[\text{Al}_2\text{Cl}_7]^-$ [1 – 5], which do not undergo redox reactions. In the case of the bismuth polycations Bi_5^{3+} and Bi_8^{2+} the tetrahedral species $[\text{AlCl}_4]^-$, $[\text{GaCl}_4]^-$ and $[\text{GaBr}_4]^-$ proved to be suitable counter anions [6 – 8]. Recently, we reported on the first tetrabromido- and tetraiodido-aluminates(III) of bismuth [9]. The orthorhombic structure of $\text{Bi}_5[\text{AlI}_4]_3$ is an ordered packing of Bi_5^{3+} trigonal bipyramids and $[\text{AlI}_4]^-$ tetrahedra that corresponds to the PuBr_3 structure type. On the contrary, the cubic room temperature structure of the $\text{Bi}_5[\text{AlBr}_4]_3$, which is related to the AuCu_3 type, shows a dynamic disorder of the Bi_5^{3+} polycations. Cooling below 260(2) K induces the transition into an ordered rhombohedral phase isostructural to $\text{Bi}_5[\text{AlCl}_4]_3$. In the course of our investigation of bismuth halogenido-indates(III), we discovered the bromides $(\text{Bi}_9)_3[\text{Bi}_3\text{Br}_{13}][\text{Bi}_7\text{Br}_{30}][\text{InBr}_5]$ [10] and $\text{Bi}_8[\text{InBr}_4]_2$, the later one being first published by *Popovkin* et al. [11], as well as the iodide $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$, on which we report here. Furthermore some properties of the isostructural compounds $(\text{Bi}_8)_3\text{Bi}[\text{InBr}_4]_9$ and $(\text{Bi}_8)_3\text{Bi}[\text{GaI}_4]_9$ are presented.

Experimental Section

Syntheses

All steps of the preparation were performed under inert atmosphere in an argon filled glove box (MBraun; H₂O, O₂ < 1 ppm). Bismuth (Chempur, 99.99999 %), indium (Chempur, 99.99999 %), and iodine (Alpha Aesar, 99.9985 %, resublimated) in the atomic ratio of 0.36 : 0.13 : 0.51 were sealed in silica ampoules, heated in a chamber furnace to 800 K, then cooled to 600 K with $\Delta T/t = 3$ K/h, and finally quenched in ice water.

An alternative way to isolate crystals of (Bi₈)₃Bi[InI₄]₉ is the centrifugation method [12]. The starting mixtures contained the elements in the atomic ratio Bi : In : I = 1 : 1 : 3. The annealing temperatures were varied in the range of 450 K to 600 K for several days, before the melt was centrifuged through a filter made of silica wool, where the crystals remained. Using bismuth and InBr₃ or GaI₃ resulted in the isostructural compounds (Bi₈)₃Bi[InBr₄]₉ and (Bi₈)₃Bi[GaI₄]₉.

The black crystals of (Bi₈)₃Bi[InI₄]₉ are stable in air for at least weeks and can easily be broken mechanically. (Bi₈)₃Bi[InBr₄]₉ and especially (Bi₈)₃Bi[GaI₄]₉ are sensitive to air and moisture and even react with the residual oxygen in the glove box atmosphere.

Density measurements

Density measurements at 300(1) K were performed with a helium pycnometer (AccuPyc 1330 V3.03) on a, according to X-ray powder diffractometry, pure sample of (Bi₈)₃Bi[InI₄]₉ in an argon filled glove box. The determined volume of 0.508(1) g

sample was $0.0848(4) \text{ cm}^3$, which results in a density $\rho = 5.99(1) \text{ g}\cdot\text{cm}^{-3}$. The positive difference compared with the calculated density from X-ray data ($\rho = 5.86 \text{ g}\cdot\text{cm}^{-3}$) might be due to some ($\sim 3 \%$) bismuth impurities ($\rho = 9.78 \text{ g}\cdot\text{cm}^{-3}$).

Crystal Structure Determination

Initial investigations of the reciprocal lattice of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ were performed on a Buerger precession camera equipped with an imaging plate using Zr-filtered Mo radiation. The symmetry of the diffraction pattern (Laue class $m\bar{3}m$) together with the reflection conditions lead to the cubic space groups $F\bar{4}3c$ or $Fm\bar{3}c$ with the lattice parameter $a = 20.162(2) \text{ \AA}$ (single crystal). A characteristic trait of the diffraction pattern was the rapid decrease of the scattering intensities with increasing diffraction angles. In high resolution powder diffraction patterns recorded with synchrotron radiation ($\lambda = 0.40119 \text{ \AA}$) neither splitting nor broadening of the reflections was observed (Fig. 2). The FWHM is close to the instrumental resolution of $\text{FWHM}(600) \approx 0.005^\circ$.

Intensity data of a single crystal of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ were collected at 293 K and 220 K (Table 1). The structure solution (space group $Fm\bar{3}c$, no. 226) with direct methods and subsequent Fourier syntheses yielded the positions of the indium and iodine atoms as well as a hollow sphere of electron density around Wyckoff position $8a$ and some significant electron density at Wyckoff position $8b$. The disorder model developed in the following is in accordance with the physical properties, which indicate a plastic phase above 148 K.

A section through the sphere of electron density around Wyckoff position $8a$ (Fig. 1) shows only weak maxima. Hence the assignment of electron density to atomic

split positions, which is necessary in a conventional structure determination, is somewhat arbitrary. Nevertheless, in a first step the procedure was used to roughly estimate the scattering power, which turned out to be equivalent to about 700 electrons per sphere. The diameter of the sphere is approximately 5 Å, matching the diagonal of a Bi_8^{2+} square antiprism (5.1 Å), while a Bi_9^{5+} capped prism would be too large (5.5 Å) and a Bi_6^{2+} octahedron too small (4.5 Å). For an advanced model the Bi_8^{2+} polyhedron was taken from the structure of $\text{Bi}_8[\text{AlCl}_4]_2$ [16] and introduced as a fragment (Bi1a to Bi1h) that is allowed to rotate around its center of gravity as well as to expand or shrink uniformly. Notwithstanding the 24 symmetry generated orientations of the Bi_8^{2+} polycation around the highly symmetric Wyckoff position 8a (site symmetry 4 3 2), it became necessary to introduce a second fundamental orientation for the Bi_8^{2+} polycation (Bi2a to Bi2h). The refinement, which comprised restrictions on the sum of occupancies, converged well. The residual electron density amounts to less than $\pm 2 \text{ e} \cdot \text{\AA}^{-3}$ indicating a good description of the electron density distribution.

The electron density around the Wyckoff position 8b was modeled by an isolated Bi^{3+} cation (Bi3) with a fixed occupation of 1/3 per cavity, i. e. 8/3 atoms per unit cell. The best position proved to be on the threefold axis, 0.54 Å away from the site 8b.

The structure model was refined on F^2 and anisotropic displacement parameters were applied to the indium and the iodine atoms. Final values of the positional and displacement parameters at 220 K are given in Table 2. Further data, in the form of a CIF, have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (E-mail address: crysdata@fiz-karlsruhe.de), as supplementary material no. CSD-420154 (293 K) and CSD-420155 (220 K), and can be

obtained by contacting the FIZ (quoting the article details and the corresponding CSD number). Graphics of the structure were prepared using the program Diamond [17].

At 130 K the diffraction pattern of the crystal of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ had changed radically, showing a non-indexable starfield of additional weak superstructure reflections, which indicate a dramatic decrease in point-group as well as translational symmetry accompanied by multiple twinning.

The room temperature diffraction patterns of $(\text{Bi}_8)_3\text{Bi}[\text{InBr}_4]_9$ ($a = 19.320(1) \text{ \AA}$) and $(\text{Bi}_8)_3\text{Bi}[\text{GaI}_4]_9$ ($a = 19.777(3) \text{ \AA}$) are very similar to $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$, suggesting the same type of disordered structure.

High-Resolution Powder Diffraction

High resolution powder diffraction data of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ were recorded at the ESRF beamline ID31 using a wavelength of $\lambda = 0.40119 \text{ \AA}$. The gently powdered sample was filled in a glass capillary with a diameter of 0.6 mm. At 293(1) K and 80(3) K, high-resolution data were recorded in the range of $0 < 2\theta \leq 35^\circ$ with acquisition times of about 90 minutes. During the one hour of cooling from ambient temperature to 80 K the metrical changes were followed by short measurements (2 minutes of acquisition time) in the range of $0 < 2\theta \leq 20^\circ$.

High-Pressure X-Ray Diffraction Experiments

In-situ high-pressure X-ray diffraction experiments were performed at the beamline ID09A at ESRF selecting a wavelength of $\lambda = 0.41254 \text{ \AA}$. Pressures up to about 15 GPa were generated with a diamond anvil cell employing a 4:1 methanol-ethanol mixture as transmitting medium and in-situ monitoring of pressure by means of the ruby scale [18].

To enhance orientational statistics the powder samples of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ were oscillated $\pm 3^\circ$ during the exposures. The exposure times were approximately 3 seconds. The two-dimensional scattering information was transformed into intensity vs. 2θ data [19]. The first 6 reflections were used to determine the cell parameters by means of a profile fit using the program Fullprof [20]. The pressure dependence of the cell parameters ($X = a, V$) was fitted with a least square procedure to a *Murnaghan* equation of state [21]:

$$\frac{X}{X_0} = \left(\frac{p \cdot B_0'}{B_0} + 1 \right)^{-\frac{1}{B_0'}}$$

Therein B is the bulk modulus and B' the bulk modulus pressure derivative. B_0 is the value of B when $p = 0$ (approximated by $p_0 = 10^5$ Pa).

Thermal analyses

The analyses of the thermal properties by DSC (Netsch DSC 404) were performed in the temperature range of 140 K to 770 K with heating rates of 10 K/min in sealed aluminum and gold crucibles. The ordering temperatures (onset, increasing temperature) were determined as 149(3) K for $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$, 215(3) K for $(\text{Bi}_8)_3\text{Bi}[\text{InBr}_4]_9$, and 269(3) K, for $(\text{Bi}_8)_3\text{Bi}[\text{GaI}_4]_9$.

The heat capacity $C_p(T)$ was determined by a relaxation method on a PPMS (Quantum Design) between 1.8 K and 300 K. Due to the flaked consistency of the sample piece ($m = 10.252$ mg) and the required larger amount of grease (Apiezon N, $m = 0.196$ mg) to attach the sample to the calorimeter platform, the data are only reliable to temperatures up to $T \approx 200$ K. The sharp first order transition of the compound was measured in more detail with small heat pulses. Approximate values for the transition enthalpy and entropy were calculated.

Measurement of Magnetization and Electrical Conductivity

The magnetization of a polycrystalline sample of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ was measured in the temperature range $1.8 \text{ K} \leq T \leq 400 \text{ K}$ and external fields $2 \text{ mT} \leq \mu_0 H \leq 7 \text{ T}$ using a SQUID magnetometer (MPMS XL-7, Quantum Design). The electrical resistivity was tested in a cryostat on a polycrystalline piece; however the electrical resistance was too high to be measured with the device ($R > 10 \text{ M}\Omega$ for $T = 320 \text{ K}$).

Results and Discussion

Black, air-insensitive crystals of tris(octabismuth(2+))-bismuth(III)-nonakis(tetraiodidoindate(III)), $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$, have been synthesized by melt reaction of the elements. At room temperature and down to 148 K the metal-rich compound has a cubic structure. The face-centered unit cell ($Fm\bar{3}c$; $a = 20.087(2) \text{ \AA}$ at 220 K; $Z = {}^{24}/_9 = {}^8/_3$) contains 24 isolated tetrahedral $[\text{InI}_4]^-$ anions, which surround two types of cavities (eight of each kind in the cell). The larger one, a truncated cube defined by 24 iodide vertices, contains a hollow sphere of electron density. This sphere can be modeled by a rotationally disordered Bi_8^{2+} square antiprism (Fig. 3). The presence of other Bi_n^{m+} polycations is unlikely, since they would have an improper size, shape or charge. The shape of the polycation was transferred from the structure of $\text{Bi}_8[\text{AlCl}_4]_2$, but its diameter was adapted in the course of the structure refinement procedure. The apparent expansion of about three percent ($3.11 \text{ \AA} \leq d(\text{Bi}-\text{Bi}) \leq 3.16 \text{ \AA}$) should be

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4 interpreted as a slight displacement of the center of gravity from the highly symmetric
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6 Wyckoff position $8a$. The probability for the 48 orientations is almost equal.
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9 In neither orientation the distance of a bismuth atom of the polycation to the
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11 nearest iodide ion is shorter than 3.34 Å. Although in $\text{Bi}_5[\text{AlI}_4]_3$ the shortest Bi...I
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13 distances is 3.59 Å, the model seems to be reasonable taking into account the
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15 approximations made. Furthermore, the large displacement ellipsoids of the indium and
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17 the iodine atoms, even at 220 K, indicate librations and small shifts of the $[\text{InI}_4]^-$
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19 tetrahedra ($d(\text{In-I}) = 2.703(2)$ Å), which allow a better accommodation of the
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21 antiprisms. Almost certainly this motion also facilitates the reorientation of the
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23 polycations. A cooperative effect is imaginable but can not be proven.
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28 The principal arrangement of Bi_8^{2+} polycations and $[\text{InI}_4]^-$ anions corresponds to
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30 the AuCu_3 structure type and leads to the formula $(\text{Bi}_8^{2+})[\text{InI}_4^-]_3$. To ensure the balance
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32 of charges, additional Bi^{3+} cations are included into smaller, cuboctahedral cavities (12
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34 iodide vertices). In statistical distribution one out of three cavities hosts a Bi^{3+} cation,
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36 which is located about 0.5 Å from the center of the coordination polyhedron (Wyckoff
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38 position $8b$) on one of the three-fold axes. The distance towards the nearest iodide ion is
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40 rather long (3.69 Å). Similar non-coordination bismuth cations have been identified in
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42 the cluster salt $\text{Bi}_{2/3}[\text{PtBi}_6\text{Cl}_{12}]$ [22].
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47 Physical characteristics of the plastic phase $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ are vanishing X-ray
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49 scattering at higher diffraction angles, the small bulk modulus of $B_0 = 12(1)$ GPa and its
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51 strong pressure dependence ($B_0' = 11(1)$) as well as the low Debye temperature of $\theta_D =$
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53 52 K. The compression behavior of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ is up to $p \approx 1$ GPa very similar as for
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55 elemental iodine [23] (Fig. 4). However it is much more compressible than elemental
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57 bismuth [24], indium [25] or the cluster compound $\text{Bi}_6\text{Br}_7 = (\text{Bi}_9)[\text{Bi}_5\text{Br}_{14}]$ [26].
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The temperature dependence of the molar heat capacity $C_p(T)$ of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ up to 200 K is plotted in Fig. 5. At low temperatures a very small temperature range is observed (up to 3 K) where *Debye's* T^3 -approximation is valid. The derived initial Debye temperature $\theta_D = 52$ K is accordingly extremely low (for comparison, lead has $\theta_D = 88$ K) and rises very fast with temperature. At 200 K the heat capacity attains a value of $C_p(T) = 1650 \text{ J mol}^{-1} \text{ K}^{-1} = 23.6 \text{ J mol}^{-1} \text{ atom}^{-1} \text{ K}^{-1}$, in agreement with the expectation that the Petit-Dulong value of $3Rn$ (with n the atoms in the formula unit) should be reached for $T \gg \theta_D$. These findings are the natural consequence of the loosely bonded, heavy clusters in the structure. The phase transition anomaly centered at 148.1(2) K has a transition enthalpy $\Delta H \approx 3.8 \text{ kJ mol}^{-1}$ and transition entropy $\Delta S \approx 3 R$. The comparatively small enthalpy and entropy change at the transition temperature might be explained by a creeping ordering process in the course of cooling and the coupled movements of the cluster atoms.

Low-temperature X-ray diffraction experiments on powder samples and single crystals revealed that the low-temperature structure of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ has a lower point-group symmetry and a much larger unit cell. The diffraction pattern below approximately 130 K (Fig. 6) hints to a rhombohedral sub-cell (hexagonal setting: $a \approx 14.075 \text{ \AA}$, $c \approx 34.727 \text{ \AA}$ at 80 K), which however does not allow the indexing of the additional weak super-structure reflections.

The a first order phase transition at 148 K is accompanied by a discontinuous change in the volume of about 0.43 % with respect to the rhombohedral sub-cell (Fig. 7). Since the ordered structure has a smaller unit cell, we followed the idea of pressure induced ordering. Unfortunately, the reflections are too broad to identify small derivations from the cubic metric. Only very pronounced variations of the structure

evidenced by a fully changing powder pattern were observed at $p > 5$ GPa. Owing to the huge number of overlapping reflections in the powder pattern of this phase, the high-pressure structure could not be determined. Surprisingly the X-ray powder pattern recovered at ambient pressure is the same than before the experiment except the significantly smaller cubic unit cell ($a = 19.80(2)$ Å; $\Delta a \approx 2\%$). This memory effect suggests that all pressure induced transformations are reversible and the rotation of the polycations is rather slow at room temperature.

The high-field magnetic susceptibility $\chi(T) = M/H$ of $(\text{Bi}_8)_3\text{Bi}[\text{InL}_4]_9$ is negative (diamagnetism) in the whole temperature range. After taking into account minor paramagnetic impurities by a Curie term, a value of $\chi_0 = -6.3 \cdot 10^{-3} \text{ emu mol}^{-1}$ is estimated. No anomaly is observed in the temperature range of the structural phase transition.

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Table 1 Crystallographic data and details of the structure determinations for $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$.

	293(1) K	220(2) K
Formula	$(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$	
Crystal system, space group	cubic, $Fm\bar{3}c$ (no. 226)	
Cell parameter	$a = 20.162(2) \text{ \AA}$	$a = 20.087(2) \text{ \AA}$
Formula units per cell	$Z = 8/3$	
Calculated density	$\rho = 5.86 \text{ g cm}^{-3}$	$\rho = 5.93 \text{ g cm}^{-3}$
Crystal dimensions	$0.03 \times 0.04 \times 0.08 \text{ mm}^3$	
Measurement device	imaging-plate diffractometer (Stoe IPDS-II)	
Radiation	graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$)	
Measurement limits	$4.0^\circ \leq 2\theta \leq 49.8^\circ$; $-23 \leq h, k, l \leq 23$	
Absorption correction	numerical [13], on the basis of a crystal description optimized using sets of equivalent reflections [14]	
Absorption coefficient	$\mu(\text{MoK}\alpha) = 46.3 \text{ mm}^{-1}$	$\mu(\text{MoK}\alpha) = 46.9 \text{ mm}^{-1}$
Transmission factors	0.06 to 0.33	0.04 to 0.39
Number of measured / independent reflections	13246 / 334	12948 / 330
Data averaging	$R_{\text{int}} = 0.098$, $R_\sigma = 0.020$	$R_{\text{int}} = 0.098$, $R_\sigma = 0.021$
Structure refinement	full-matrix least-squares on F_o^2 [15]; anisotropic displacement parameters	
Number of parameters	28	
Residual electron density	+1.3 to $-1.4 \text{ e}\cdot\text{\AA}^{-3}$	+1.8 to $-1.6 \text{ e}\cdot\text{\AA}^{-3}$
Figures of merit	R_1 (all F_o) = 0.097 R_1 ($268 F_o > 4\sigma(F_o)$) = 0.078 wR_2 (all F_o) = 0.08	R_1 (all F_o) = 0.095 R_1 ($294 F_o > 4\sigma(F_o)$) = 0.086 wR_2 (all F_o) = 0.077

Table 2 Wyckoff positions, coordinates, occupancies and (equivalent) isotropic displacement parameters for $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ at 220(2) K.

atom	W.p.	<i>x</i>	<i>y</i>	<i>z</i>	<i>sof</i>	$U_{\text{iso}}/U_{\text{eq}}^{[\text{a}]}$
Bi1a	192 <i>j</i>	0.2594(7)	0.1470(5)	0.1811(6)	0.022(1)	150(20)
Bi1b	192 <i>j</i>	0.1992(7)	0.1479(7)	0.3242(7)	<i>sof</i> (Bi1a)	<i>U</i> (Bi1a)
Bi1c	192 <i>j</i>	0.3504(6)	0.1792(8)	0.3051(6)	<i>sof</i> (Bi1a)	<i>U</i> (Bi1a)
Bi1d	192 <i>j</i>	0.2618(9)	0.276(1)	0.3881(5)	<i>sof</i> (Bi1a)	<i>U</i> (Bi1a)
Bi1e	192 <i>j</i>	0.3506(5)	0.2749(7)	0.1830(7)	<i>sof</i> (Bi1a)	<i>U</i> (Bi1a)
Bi1f	192 <i>j</i>	0.1967(6)	0.2858(6)	0.1533(5)	<i>sof</i> (Bi1a)	<i>U</i> (Bi1a)
Bi1g	192 <i>j</i>	0.1361(5)	0.2877(6)	0.2962(7)	<i>sof</i> (Bi1a)	<i>U</i> (Bi1a)
Bi1h	192 <i>j</i>	0.2631(6)	0.3723(5)	0.2664(9)	<i>sof</i> (Bi1a)	<i>U</i> (Bi1a)
Bi2a	192 <i>j</i>	0.256(1)	0.2949(8)	0.6303(5)	0.020(1)	<i>U</i> (Bi1a)
Bi2b	192 <i>j</i>	0.157(1)	0.330(1)	0.744(1)	<i>sof</i> (Bi2a)	<i>U</i> (Bi1a)
Bi2c	192 <i>j</i>	0.169(1)	0.182(1)	0.6972(8)	<i>sof</i> (Bi2a)	<i>U</i> (Bi1a)
Bi2d	192 <i>j</i>	0.1806(9)	0.216(1)	0.8483(7)	<i>sof</i> (Bi2a)	<i>U</i> (Bi1a)
Bi2e	192 <i>j</i>	0.323(1)	0.1634(5)	0.6842(9)	<i>sof</i> (Bi2a)	<i>U</i> (Bi1a)
Bi2f	192 <i>j</i>	0.3743(8)	0.3047(8)	0.730(1)	<i>sof</i> (Bi2a)	<i>U</i> (Bi1a)
Bi2g	192 <i>j</i>	0.276(2)	0.3397(6)	0.8444(6)	<i>sof</i> (Bi2a)	<i>U</i> (Bi1a)
Bi2h	192 <i>j</i>	0.3340(8)	0.1958(8)	0.836(1)	<i>sof</i> (Bi2a)	<i>U</i> (Bi1a)
Bi3	64 <i>g</i>	0.0157(4)	0.0157(4)	0.5157(4)	0.04167	260(90)
In	24 <i>c</i>	0	0	1/4	1	531(9)
I	96 <i>i</i>	0.11000(9)	0	0.32746(9)	1	714(6)

Figure 1 Section of a Fourier map (F_{obs}) around Wyckoff position $8a$ ($z = 0.25$) for $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ at 220 K.

Figure 2 X-ray diffraction pattern of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ at 293(1) K collected with synchrotron radiation ($\lambda = 0.40119 \text{ \AA}$). The dramatic decrease of the diffraction intensities towards higher diffraction angles is clearly visible.

Figure 3 One quarter ($0 \leq x, y \leq \frac{1}{2}$; $1 \leq z \leq 0$) of the cubic unit cell of the plastic phase $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ at 220 K. Two symmetry-independent orientations of the rotationally disordered Bi_8^{2+} square antiprism are highlighted (dark grey) within the multitude of 48 orientations (light grey). A possible distribution of the $\text{Bi}(3)$ atoms on the partially occupied positions is represented in the same way. The ellipsoids of the In and I atoms correspond to 90 % probability.

Figure 4 Compression behavior of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ (black line), elemental bismuth (solid grey line), indium (dashed grey line), iodine (dotted grey line), and Bi_6Br_7 (dashed black line). Measured points are indicated by open squares ($(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$) or open circles (Bi_6Br_7).

Figure 5 Heat capacity of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$.

Figure 6 Details of the high resolution synchrotron powder diffraction data of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ (normalized to $I_{\text{max}} = 100$; $\lambda = 0.40119 \text{ \AA}$) at 293 K (high temperature plastic phase; top) and at 80 K (low temperature phase; below). The tentative indexing of the 80 K pattern with a rhombohedral cell ($a = 14.075 \text{ \AA}$, $c = 34.727 \text{ \AA}$) models the splitting of main reflections but does not explain the additional weak reflections.

Figure 7 Temperature dependence of the unit-cell parameters of $(\text{Bi}_8)_3\text{Bi}[\text{InI}_4]_9$ with the cubic plastic phase above 148 K. The lattice parameters of the low temperature phase are based on a rhombohedral cell. Clearly visible is the accompanying volume drop of the first order transition.