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BiSeI crystals obtained by a chemical-transport reaction are orthorhombic (space group *Pnma*) with a = 8.6967 (17) Å, b = 4.2205 (8) Å and c = 10.574 (2) Å. It could be confimed that BiSeI crystallizes in the centrosymmetric SbSI structure type.

Comment

The chalcogenide halides of antimony and bismuth have been known for a long time. Dönges studied crystals of the thiohalides (Dönges, 1950*a*) and selenohalides (Dönges, 1950*b*), and found that SbSBr, SbSI, BiSCl, BiSBr, BiSI, BiSeBr and BiSeI all crystallize in the same structure type. He was able to solve the structure of SbSI and determined the lattice spacings of the remaining members of that family.

After it was discovered that SbSI is both a photoconductor (Nitsche & Merz, 1960) and, at temperatures below 295 K, a ferroelectric (Fatuzzo *et al.*, 1962), these compounds have been studied in great detail (for a review see, for example, Fenner *et al.*, 1980). It is somewhat surprising that there are no single-crystal structure determinations that prove that SbSeBr, BiSeBr and BiSeI actually adopt the SbSI structure type. Since the other members of that series show some variablity in the exact positions of the atoms, it is worthwhile verifying that these phases are indeed isostructural.

According to our findings this is the case for bismuth selenide iodide.

Experimental

A mixture of Bi, Se, P and I was sealed in an evacuated quartz ampoule and heated in a box furnace. The temperature was slowly raised to a nominal temperature of 600°C and kept constant for one week. The sample was then cooled within one day and black needle-like crystals could be collected from the top of the quartz ampoule. Since it has been shown that BiSeI melts incongruently at about 535°C (Belotskii *et al.*, 1970), we suppose that the actual temperature at the top of the ampoule did not exceed that value. The crystals grown by this chemical-transport reaction were suitable for a single-crystal X-ray structure determination.

Crystal data

BiSeI
M_r = 414.84
Orthorhombic, *Pnma*
a = 8.6967 (17) Å
b = 4.2205 (8) Å
c = 10.574 (2) Å
V = 388.11 (13) Å^3
Z = 4
D_x = 7.100 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 443 reflections
θ = 3.03–27.43°
μ = 62.497 mm^{-1}
T = 293 (2) K
Needle, metallic silver
0.22 × 0.03 × 0.02 mm

Data collection

CCD area-detector diffractometer
ω scans
Absorption correction: by integration (Busing amp; Levy, 1957; Sheldrick, 1998)
$T_{\min}$ = 0.063, $T_{\max}$ = 0.299
3812 measured reflections
457 independent reflections
443 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.073
$\theta_{\max}$ = 27.43°
$h = -4 \rightarrow 11$
$k = -5 \rightarrow 4$
$l = -12 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.123
S = 1.198
457 reflections
20 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 36.9940P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 2.31 e Å^{-3}
$\Delta\rho_{\min}$ = −2.90 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0048 (8)

Several single crystals were broken off the quartz wall of the reaction container. The crystal quality was determined by collecting rotation frames on a Bruker CCD system. A suitable crystal with indexable faces was chosen for the data collection. An initial matrix was determined from 28 reflections from an initial measurement to compare the cell constants with previously published data (Fenner *et al.*, 1980).

A full hemisphere was collected and the data have been integrated with a refined cell, assuming orthorhombic symmetry. Application of a numerical absorption correction [face indexing: Gaussian integration method (Busing & Levy, 1957), optimized by Sheldrick, 1998] resulted in a substantial improvement of $R_{\rm int}$ from 0.193 for the raw data to 0.0734 for the corrected data set.

The two space groups *Pnma* (centrosymmetric) and $Pna2_1$ (non-centrosymmetric) were consistent with the observed systematic absences. The refinement is possible in both space groups, leading to R values that were larger (by 0.032 for wR_2) in the non-centrosymmetric case. The difference electron density was also slightly higher than for the refinement in *Pnma*. Most importantly, only one 'free' positional parameter in $Pna2_1$ deviated by more than 3σ from the fixed value for the centrosymmetric case (considering the unconventional setting and the necessary origin shift).

Deepest hole −2.90 e Å^{-3} at (0.8122, 0.0463, 0.3720) (1.00 Å from Bi1); highest peak 2.31 e Å^{-3} at (0.6587, 0.2500, 0.6864) (1.52 Å from I1).

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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