

The Crystal Structures of BaSe₂ and BaSe₃

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BaSe₂ crystallizes with a monoclinic cell, $a = 9.820(5)$, $b = 4.929(3)$, $c = 9.335(5)$ Å, $\beta = 118.48(5)^\circ$; $Z = 4$, space group C 2/c. BaSe₃ is tetragonal, $a = 7.2802(5)$, $c = 4.2495(4)$ Å; $Z = 2$, space group P $\bar{4}2_1m$. Both polyselenides are isotopic with the corresponding polysulfides.

In the system Ba–S three polysulfides are known and structurally characterized: tetragonal Ba₂S₃ [1], monoclinic BaS₂ [2, 3] and tetragonal BaS₃ [2]. We tried to synthesize the corresponding selenides by reacting the constituent elements in the appropriate ratios in closed silica tubes at temperatures between 500 and 700 °C. BaSe₃ was obtained as a brown-red powder while in the case of BaSe₂ red transparent single crystals grew occasionally. Both compounds are fairly stable in dry air. X-ray patterns immediately suggested isomorphism with the sulfides. We used Guinier patterns, taken with copper radiation and silicon as internal standard, for the determination of the lattice parameters. For BaSe₃ we tried to derive the positional parameters from diffractometer intensity measurements. Unfortunately the BaSe₃ powder was not so well crystallized so that we were able to determine the intensities of only 25 independent reflections. With isotropic refinement we arrived at a reliability factor $R = 0.092$. Thus, although the resulting interatomic distances are less accurate than we would wish, there is no doubt that BaSe₃ crystallizes in the same structure as the corresponding polysulfide.

The single-crystal measurements on BaSe₂ were carried out on an automatic four-circle diffractometer SYNTEX P2₁ with monochromatic Mo K α radiation. Up to $2\vartheta_{\max} = 50.3^\circ$ (corresponding to $\sin\vartheta/\lambda = 0.6$) we collected 789 independent reflexions of which 364 had an intensity $> 3\sigma$. The absorption corrections of the intensities were somewhat hampered by the very unfavorable plate-like shape of the crystal. The refinement led to a final R value of 0.13.

Table I. Crystallographic data for BaSe₃. BaS₃ type, space group P $\bar{4}2_1m$ (Nr. 113).

$a = 7.2802(5)$, $c = 4.2495(4)$ Å; $Z = 2$.

Ba in 2(a):

0, 0, 0; 1/2, 1/2, 0.

Se(1) in 2(c):

0, 1/2, z ; 1/2, 0, \bar{z} with $z = 0.175(15)$.

Se(2) in 4(e): x , 1/2 + x , z ; \bar{x} , 1/2 – x , z ; 1/2 + x , \bar{x} , \bar{z} ; 1/2 – x , x , \bar{z} with $x = 0.189(3)$, $z = 0.485(20)$.

Interatomic distances

Ba – 4 Se(2) at 3.36(6) Å
4 Se(2) at 3.44(6) Å
4 Se(1) at 3.72(1) Å
2 Ba at $c = 4.25(1)$ Å

Se(1) – 2 Se(2) at 2.35(6) Å
2 Se(2) at 3.52(9), 3.54(7) Å
4 Ba at 3.72(1) Å

Se(2) – 1 Se(1) at 2.35(6) Å
2 Ba at 3.35(5) Å
2 Ba at 3.44(5) Å
2 Se(1) at 3.51(3), 3.54(7) Å

The structural data for BaSe₃ and BaSe₂ are collected in Table I and Table II, respectively. Both compounds are nonmetallic polyselenides. Thus, they are Mooser–Pearson phases [4] and therefore can formally be described by ionic formulae Ba⁺²Se₂^{–1} and Ba⁺²Se⁰Se₂^{–1}. From their color we deduce an energy gap of roughly 2 eV, somewhat larger in the diselenide than in the triselenide.

In the ThC₂-type structure of BaSe₂ the anions form pairs with an Se–Se separation of 2.40 Å. This distance lies well within the range observed in other nonmetallic polyselenides (in pyrite-type MnSe₂: 2.38 Å [5], in orthorhombic PdSe₂: 2.36 Å [6], in the pyrite derivative Rh₃Se₈: 2.415 and 2.416 Å [7] and in marcasite-type FeSe₂: 2.535 Å [8]). The less accurate Se–Se distances in BaSe₃, 2.35 Å, appear to be at the lower limit. In the alkali triselenides which

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Table II. Crystallographic data for BaSe₂. Monoclinic ThC₂ type, space group C 2/c (Nr. 15) $a = 9.820(5)$, $b = 4.929(3)$, $c = 9.335(5)$ Å, $\beta = 118.48(5)^\circ$; $Z = 4$. $(0, 0, 0; 1/2, 1/2, 0) +$ Ba in 4(e): $\pm (0, y, 1/4)$; Se in 8(f): $\pm (x, y, z; x, \bar{y}, 1/2 + z)$.

	x	y	z	$10^4 \times$ U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba		0.131(1)		52	83	61	0	27	0
Se	0.1600(5)	0.634(1)	0.5248(5)	44	130	110	3	52	-8

Interatomic distances

Ba - 2 Se at 3.28(2) Å	Se - 1 Se at 2.40(1) Å
2 Se at 3.34(2) Å	4 Ba at 3.28(2), 3.34(2), 3.35(2) and 3.36(2) Å
2 Se at 3.35(2) Å	
2 Se at 3.36 Å	1 Se at 3.16(1) Å

contain very similar polyanions, the Se-Se distances and the Se-Se-Se angles are as follows: K₂Se₃ 2.382(2) Å, 102.5(1)°; Rb₂Se₃ 2.383(7) Å, 103.1(3)°; Cs₂Se₃ 2.358(1) Å, 103.6(5)° [9]. Shorter distances were found in orthorhombic Rb₂Se₅ [10] which contains 5-membered Se chains: I-II = 2.31(2) Å, II-III = 2.36(1) Å, III-IV = 2.37(2) Å, IV-V = 2.33(1) Å, and angles of 109.1(5)°, 104.5(6)° and 108.0(5)°. In the infinite chains of grey selenium the distance is 2.373(5) Å and the angle is 103.1(2)° [10]. Shorter Se-Se distances are observed in metal-organic compounds such as Fe₂(CO)₆(μ -Se₂): 2.293(2) Å [11].

The bonding Ba-Se distances range from 3.28 to 3.36 Å in BaSe₂ and from 3.36 to 3.45 Å in BaSe₃. They may be compared with the separation Ba-Se = $a/2 = 3.30$ Å in rocksalt-type BaSe, where however, both Ba and Se are six-coordinated. The ThC₂-type structure of BaSe₂ can formally also be derived from the rocksalt structure by replacing one kind of atoms by anion pairs. The different orientations of the anion pairs are responsible for the various degrees of distortions of the originally cubic cell in cubic pyrite, tetragonal CaC₂ and monoclinic ThC₂. Whereas in pyrite the cation coordination number

remains six (while the coordination number of the anion is reduced to four) it is increased to eight in the ThC₂ structure while the anion coordination number is five. Whereas the non-bonding Ba-Se distances are at least as large as the sum of the Van-der-Waals radii in BaSe₂, four additional Se atoms surround the cation in BaSe₃ at a distance which is only ~0.3 Å larger than the bond distance.

It may be noteworthy that the structure of Yb⁺²S₂ [12] is not of a new type but belongs also to the ThC₂ family. Since the size of the Sr ion is between those of Ba and Yb²⁺, but SrS₂ crystallizes in the CuAl₂ type [2], either the reported structure of YbS₂ or that of SrS₂ does not correspond to the normal-pressure room-temperature modification. Moreover, CaS₂ might also exist in a ThC₂ modification although we failed to synthesize this phase.

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