# The Crystal Structure of Ba₂Bi

By M. Martinez-Ripoll, A. Haase and G. Brauer

*Chemisches Laboratorium der Universität Freiburg, 78 Freiburg (Breisgau), Albertstrasse 21, Germany (BRD)*

Ba₂Bi crystallizes in the tetragonal system, space group *I4/mmm*, with 4 formula units in the cell; $a = 5.263$ (3), $c = 18.700$ (8) Å. The calculated density is $6.200$ g cm$^{-3}$. These data compare with the results of Brauer & Müller [*Angew. Chem.* (1961). **73**, 169]: $5.28$, $18.75$ Å and macroscopic density $6.04$ g cm$^{-3}$. This compound is isomorphous with Sr₂Sb.

## Introduction

Single crystals of Ba₂Bi can be prepared by cooling a melt of stoichiometry 3Ba + 2Bi with a small excess of barium from 1350°C to room temperature in argon atmosphere (Müller, 1960). Isolated single crystals can be obtained by subsequent leaching of the alloy with anhydrous ammonia. Because of their extreme instability in air they had to be kept under argon atmosphere.

Intensity data from seven reciprocal layers perpendicular to the *b* axis were obtained from a prismatic single crystal with nearly circular cross section (0.14 mm diameter) mounted on a single-crystal Huber diffractometer (RHD 402) on-line to a PDP-8 computer. Graphite-monochromated Mo *Kα* radiation was used in conjunction with a scintillation detector and pulse-height discrimination. 464 independent reflexions were collected. Of this total, 414 reflexions were considered 'observed' according to the criterion $I > 2 \cdot \sigma(I)$ and used in the calculations. Absorption corrections ($\mu R = 3.32$) were made assuming cylindrical crystal shape. The structure amplitudes were obtained after the usual Lorentz and polarization reduction.

Atomic coordinates and isotropic temperature factors taken from the isomorphous compound Sr₂Sb (Martinez-Ripoll, Haase & Brauer, 1973) were refined by the least-squares procedure using the program *CRYLSQ* written by F.A. Kundell and assuming unit weights. Scattering factors used were those for neutral atoms (Hanson, Herman, Lea & Skillman, 1964). The anomalous dispersion corrections $\Delta f' = -0.5$ and $\Delta f'' = 2.8$ for Ba, and $\Delta f' = -4.7$ and $\Delta f'' = 11.7$ for Bi are listed in *International Tables for X-ray Crystallography* (1962). The final residual $R = \sum \lVert F_o \rvert - \lvert F_c \rVert / \sum \lvert F_o \rvert = 0.071$ is based on the parameters given in Table 1. A table listing the observed and calculated structure factors is available.* The programs used in this determination were those of the X-RAY 70 System (Stew-

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30444 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

art, Kundell & Baldwin, 1970) running on the 1108 UNIVAC computer of the University of Freiburg, Germany.

### Table 1. *Positional and thermal parameters*

Standard deviations are given in parentheses.

| | x/a | y/b | z/c | B |
|---|---|---|---|---|
| Ba(1) | 0 | ½ | 0 | 1.58 (3) Å² |
| Ba(2) | 0 | 0 | 0.32679 (15) | 2.05 (4) |
| Bi | 0 | 0 | 0.13661 (8) | 1.41 (2) |

## Discussion

Calorimetric measurements undertaken by Kubaschewski & Villa (1949) on the binary system Ba–Bi indicated the existence of a compound with stoichiometry Ba₃Bi₂ which was later prepared by Shchukarev, Morozova, Kan Kho-in & Sharov (1957). Through the measurement of enthalpy of formation, these authors also assumed the existence of another compound BaBi, in the system. Later, Zhuravlev & Melik-Adamyan (1961) identified the compound BaBi₃ with tetragonal symmetry ($a = 5.188$, $c = 5.157$ Å), isomorphous with SrPb₃. Finally, an intermediate phase of approximate stoichiometry Ba₂.₂₋₂.₄Bi was identified by Brauer & Müller (1961) as tetragonal with $a = 5.28$ and $c = 18.75$ Å. As part of a programme of investigation of intermetallic compounds, the present paper reports the crystal structure of the latter compound, whose formula Ba₂Bi was deduced from this study. The different stoichiometry suggested by Brauer & Müller (1961) is perhaps caused by residual contamination with barium amide which had not been perfectly extracted by the liquid ammonia used in the preparation.

Ba₂Bi is isomorphous with Sr₂Sb (Martinez-Ripoll, Haase & Brauer, 1973). Its crystal structure can be visualized as being built up from atomic layers perpendicular to the **c** direction. The *A* layers (see Martinez-Ripoll *et al.*, 1973, Fig. 1) contain the Ba(1) atoms, occupying special positions corresponding to the point symmetry *mmm*, all exactly coplanar. The *B* layers contain Ba(2) and Bi atoms forming, to a

first approximation, a closest-packed sheet. The sequence of layers is $ABBA\cdots$, but one of the two neighbouring $B$ layers is translated by a vector $(a/2 + b/2)$ with respect to the other, in such a way that each Ba(2) atom has a Bi atom as nearest neighbour on the adjacent layer of the same kind. The atoms of these $B$ layers are not exactly coplanar. Each Ba(2) atom is shifted 0·68 Å from the plane built up by the Bi atoms in the direction of the adjacent $B$ layer.

The Ba(1) atoms have 12 neighbours, 4Bi, 4Ba(1) and 4Ba(2) atoms at distances of 3·668, 3·722 and 4·173 Å, respectively. The Ba(2) atoms have nine neighbours, 1Bi, 4Bi and 4Ba(1) atoms at distances of 3·556, 3·784 and 4·173 Å, respectively. Additionally there are 4Ba(2) atoms of the adjacent $B$ layer at distances appreciably greater (4·701 Å) which probably contribute to a smaller extent to the bonding. Each Bi atom is surrounded by nine barium atoms forming the unit $BiBa_9$ similar to the $SbSr_9$ units found in the isomorphous compound $Sr_2Sb$. The average of the Bi–Ba distances is 3·707 Å.

The Ba(1)–Ba(1) distances of 3·722 Å mentioned above are appreciably shorter than the minimum distance of 4·34 Å in metallic barium and probably indicate some ionic character of bonds.

A list of interatomic distances is given in Table 2.

Table 2. *Interatomic distances*

Estimated standard deviation ±0·008 Å.

| Around Ba(1) | | Around Ba(2) | |
|---|---|---|---|
| Ba(1)–Bi | 3·668 Å (×4) | Ba(2)–Bi | 3·556 Å (×1) |
| Ba(1)–Ba(1) | 3·722 (×4) | Ba(2)–Bi | 3·784 (×4) |
| Ba(1)–Ba(2) | 4·173 (×4) | Ba(2)–Ba(1) | 4·173 (×4) |
| | | Ba(2)–Ba(2) | 4·701 (×4) |
| Around Bi | | Averages | |
| Bi–Ba(2) | 3·556 Å (×1) | Ba(1)–Bi | 3·668 Å |
| Bi–Ba(1) | 3·668 (×4) | Ba(1)–Ba | 3·948 |
| Bi–Ba(2) | 3·784 (×4) | Ba(2)–Bi | 3·738 |
| | | Ba(2)–Ba | 4·173 |
| | | Bi––Ba | 3·707 |

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# The Crystal Structure of $Ca_5Bi_3$

BY M. MARTINEZ-RIPOLL, A. HAASE & G. BRAUER

*Chemisches Laboratorium der Universität Freiburg, 78 Freiburg (Breisgau), Albertstrasse 21, Germany (BRD)*

$Ca_5Bi_3$ crystallizes in the orthorhombic system, space group *Pnma*, with 4 formula units in a cell of size $a = 12\cdot722$ (8), $b = 9\cdot666$ (6), $c = 8\cdot432$ (6) Å. The calculated density is 5·298 g cm$^{-3}$. These data compare with those given by Brauer & Müller [*Angew. Chem.* (1961). **73**, 169]: 12·74, 9·69, 8·46 Å and macroscopic density 5·21 g cm$^{-3}$. $Ca_5Bi_3$ is isomorphous with $Ca_5Sb_3$.

## Introduction

Single crystals of $Ca_5Bi_3$ can be prepared by a method similar to that described in the case of $Ca_5Sb_3$ (Martinez-Ripoll & Brauer, 1974). The crystals are black and have nearly prismatic shape, the $a$ axis being parallel to the needle axis. Because of their extreme instability in air they had to be kept under argon atmosphere.

A prismatic single crystal with nearly circular cross section (0·16 mm diameter) was used mounted on a

Huber diffractometer (RHD 402) on-line to a PDP-8 computer. The intensity data from 16 reciprocal layers perpendicular to the $a$ axis were obtained by using graphite-monochromated Mo $K\alpha$ radiation in connexion with a scintillation detector and pulse-height discrimination. 1378 reflexions were collected. Of this total, 1070 reflexions were considered 'observed' according to the criterion $I > 2\sigma(I)$ and used in the refinement. Absorption corrections ($\mu R = 4\cdot04$) were made assuming cylindrical crystal shape. The intensities were