# Crystal structures of tetrastrontium dibismuthide oxide, $Sr_4Bi_2O$, and tetrabarium dibismuthide oxide, $Ba_4Bi_2O$

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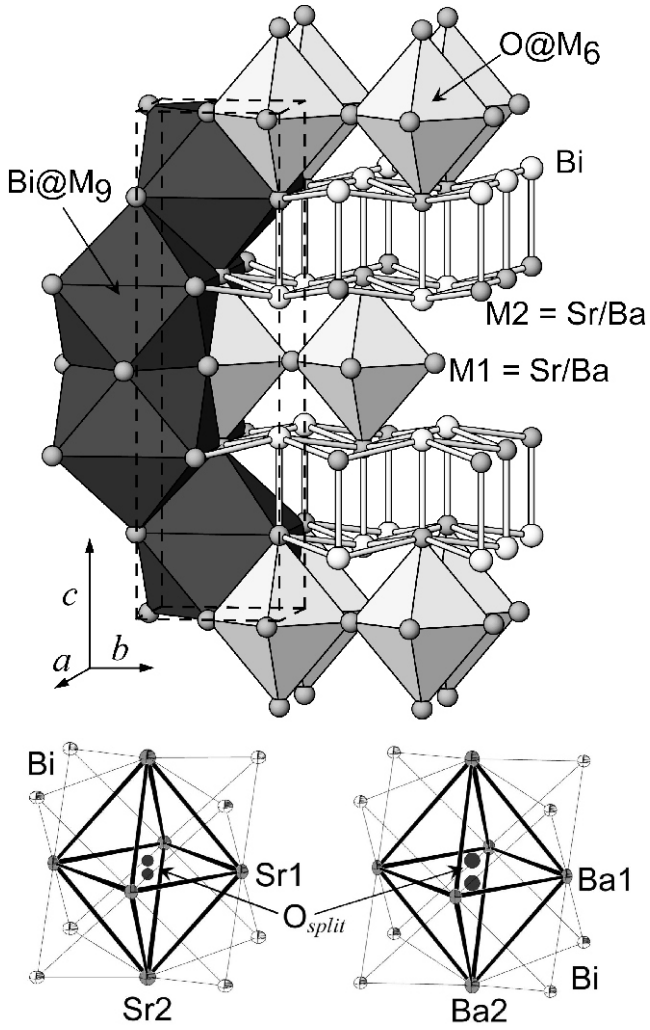


**Abstract**

$Bi_2OSr_4$, tetragonal, *I*4/*mmm* (no. 139), $a$ = 4.9948(7) Å, $c$ = 17.548(4) Å, $V$ = 437.8 Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.075, $wR_{ref}(F^2)$ = 0.196, $T$ = 298 K.

$Ba_4Bi_2O$, tetragonal, *I*4/*mmm* (no. 139), $a$ = 5.2662(7) Å, $c$ = 18.625(4) Å, $V$ = 516.5 Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.109, $T$ = 298 K.

**Source of material**

$Sr_4Bi_2O$ and $Ba_4Bi_2O$ were synthesized from stoichiometric amounts of alkaline-earth metals (Sr, Ba), Bi and $Bi_2O_3$ (ratio 12:4:1) in sealed niobium ampoules (≈ 2 g), using argon as inert gas, and a quartz glass jacket. The following temperature profiles were applied: 298 K → 1150 K (40 Kh$^{-1}$, subsequent annealing for 72 h) → 298 K (25 Kh$^{-1}$) for $Sr_4Bi_2O$; and 298 K → 1270 K (50 Kh$^{-1}$, subsequent annealing for 36 h) → 298 K (30 Kh$^{-1}$) for $Ba_4Bi_2O$, respectively.

**Experimental details**

The oxygen atom was refined isotropically on the 4*e* position (0 0 $z$, SOF = 0.5) showing reasonable displacement coefficients, instead of 2*a* (0 0 0, SOF = 1), because of the unusually large ratios of the maximum ($U_{33}$) and minimum ($U_{11}$) libration amplitudes about a factor of 12 ($Sr_4Bi_2O$) and 25 ($Ba_4Bi_2O$), if refined anisotropically on the initial 2*a* position.

The relatively large residuals of electron densities, found during structure refinement of $Sr_4Bi_2O$, are all very close to the Bi-position, and caused by absorption effects, notice the exceptionally high absorption coefficient of 642 cm$^{-1}$ for this compound.

**Discussion**

$Sr_4Bi_2O$ and $Ba_4Bi_2O$ are isopointal with the $K_2NiF_4$ type of structure (*tI*14). Both also represent a filled up variant of the $La_2Sb$ structure type (*tI*12) with oxygen localized in the octahedral cavities formed by the alkaline earth metals; this is in similarity with compounds like $Yb_4As_2O$ [1], $Eu_4Sb_2O$ [2] or $Eu_4Bi_2O$ [3]. All of them have originally been misunderstood as binary phases $M_2X$: $Sr_2Bi$ ($a$ = 5.01(2) Å, $c$ = 17.68(3) Å) [4], $Ba_2Bi$ ($a$ = 5.263(3) Å, $c$ = 18.700(8) Å) [5]. The formation of distinguished O@$M_6$ octahedra leads to pronounced changes of the $c/a$ ratio (3.513 for $Sr_4Bi_2O$ and 3.536 for $Ba_4Bi_2O$ with $c/a \approx 3.414 = 2+2^{½}$) in contrast to oxygen free compounds with $La_2Sb$ type of structure and $c/a >> 3.414$: $c/a$ = 3.936 ($Ce_2Sb$ [6]) or 3.896 ($Nd_2Sb$ [7]). It can also be demonstrated, that formerly reported $Sr_2Bi$ [4] and $Ba_2Bi$ [5] must contain oxygen, just by analysing their $c/a$ ratios [8].

The structures are built up by mono-capped square antiprims Bi@$M_9$ (M = Sr, Ba) which are condensed via the square basal plane, yielding [Bi@$M_5M_{4/2}$]$_2$. Such units extend along [110] via triangular faces, whereby the oxygen atoms occupy the octahedral voids. Along [001], the thus formed double layers [Bi@$M_1M_{4/4}M_{4/4}$]$_2$ are linked by common edges resulting in a 3D arrangement [Bi@$M_{4/5}M_{4/5}M_{4/4}$]. Five pnictide atoms are arranged around the M2 atoms at the corners of a square pyramid, forming NaCl type fragments, which are also a distinct feature of $Sc_2Sb$ [9] and related structures [10-12]. A remarkable feature is the pronounced anisotropy of the atomic displacement of the O atoms. This indicates that the oxygen atoms prefer the coordination number 5 instead of 6, which was taken into account by using a split-position. A comparable, but well ordered, square pyramidal coordination of oxygen is known from other oxygen containing pnictides of the formula $M_9Sb_5O_5$ (M = rare earth element) [13-15].

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## 1. Tetrastrontium dibismuthide oxide, $Sr_4Bi_2O$

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | metallic dark-black block, size 0.06 × 0.07 × 0.07 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 641.56 $cm^{-1}$ |
| Diffractometer, scan mode: | STOE STADI4, $\omega$ |
| $2\theta_{max}$: | 79.94° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 1550, 449 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 352 |
| $N(param)_{refined}$: | 12 |
| Programs: | SHELXS-97, SHELXL-97 [16], ATOMS [17] |

**Table 2.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | Occ. | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|---|
| O | 4*e* | 0.50 | 0 | 0 | 0.010(2) | 0.010(6) |

**Table 3.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Bi | 4*e* | 0 | 0 | 0.36169(6) | 0.0163(4) | $U_{11}$ | 0.0115(3) | 0 | 0 | 0 |
| Sr(1) | 4*c* | 0 | ½ | 0 | 0.013(1) | 0.011(1) | 0.0162(8) | 0 | 0 | 0 |
| Sr(2) | 4*e* | 0 | 0 | 0.1689(2) | 0.0190(8) | $U_{11}$ | 0.019(1) | 0 | 0 | 0 |

## 2. Tetrabarium dibismuthide oxide, $Ba_4Bi_2O$

**Table 4.** Data collection and handling.

| | |
|---|---|
| Crystal: | metallic dark-black block, size 0.06 × 0.08 × 0.08 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 488.78 $cm^{-1}$ |
| Diffractometer, scan mode: | STOE STADI4, $\omega$ |
| $2\theta_{max}$: | 99° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 2661, 835 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 621 |
| $N(param)_{refined}$: | 13 |
| Programs: | SHELXS-97, SHELXL-97 [16] ATOMS [17] |

**Table 5.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | Occ. | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|---|
| O | 4*e* | 0.50 | 0.0 | 0.0 | 0.017(1) | 0.019(3) |

**Table 6.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Bi | 4*e* | 0 | 0 | 0.36259(3) | 0.0134(1) | $U_{11}$ | 0.0115(1) | 0 | 0 | 0 |
| Ba(1) | 4*c* | 0 | ½ | 0 | 0.0114(2) | 0.0083(2) | 0.0183(2) | 0 | 0 | 0 |
| Ba(2) | 4*e* | 0 | 0 | 0.17127(5) | 0.0164(2) | $U_{11}$ | 0.0217(3) | 0 | 0 | 0 |

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