Trisodium dicalcium bismuth hexaoxide

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Single crystals of the title compound, Na$_3$Ca$_2$BiO$_6$, were grown from a high-temperature reactive flux solution of Na$_2$CO$_3$. Na$_3$Ca$_2$BiO$_6$ crystallizes as an ordered rock-salt structure (space group Fddd), in which the octahedral holes in the oxide array are filled by an ordered 3:2:1 arrangement of Na$^+$, Ca$^{2+}$ and Bi$^{5+}$ cations. All atoms except for one O atom lie on special positions; site symmetries are as follows: Bi 222, Ca 2, Na 222 and 2, O 2.

Comment

The most common bismuth oxidation state found in oxides is Bi$^{III}$ as, for example, in BiNbO$_4$ (Keve$^{\text{et al.}}$, 1973) and Bi$_2$MoO$_6$ (Teller$^{\text{et al.}}$, 1984). However, some oxides, including NaBiO$_3$ (Kumada$^{\text{et al.}}$, 2000), KBiO$_3$ (Nguyen$^{\text{et al.}}$, 1993), LiSr$_2$BiO$_6$, NaSr$_3$BiO$_6$, Li$_6$KBiO$_6$, Li$_6$RbBiO$_6$ and Li$_2$Ba$_5$Bi$_2$O$_{11}$ (Carlson$^{\text{et al.}}$, 1992) contain Bi(V) cations.

Compound (I) also possesses a fully ordered arrangement of Na$^+$, Ca$^{2+}$ and Bi$^{5+}$ cations (Fig. 1). The metal-oxygen bond distances (Table 1) are normal and the octahedra are close to

Figure 1

The asymmetric unit of (I), expanded to show the metal coordination polyhedra. Displacement ellipsoids are drawn at the 75% probability level. Colour key: Ca yellow, Bi blue, Na green and O red. [Symmetry codes: (i) $\frac{1}{4} - x, \frac{1}{4} - y, \frac{1}{4} + z$; (ii) $x, y - \frac{1}{4}, \frac{1}{4} + z$; (iii) $x - \frac{1}{4}, y, z + \frac{1}{4}$; (iv) $\frac{3}{4} - x, \frac{1}{4} - y, \frac{1}{4} + z$; (v) $\frac{1}{4} - x, y, \frac{1}{4} - z$; (vi) $x - \frac{1}{4}, y, \frac{1}{4} - z$; (vii) $\frac{1}{4} + x, y - \frac{1}{4}, \frac{1}{4} - z$; (viii) $-x, \frac{1}{4} - y, \frac{1}{4} - z$; (ix) $x + \frac{1}{4} + y, \frac{3}{4} - z$; (x) $\frac{3}{4} - x, -y, \frac{1}{4} - z$; (xi) $\frac{3}{4} - x, \frac{1}{4} + y, \frac{1}{4} + z$; (xii) $\frac{3}{4} - x, y - \frac{1}{4} + z$; (xiii) $\frac{3}{4} - x, -y, \frac{1}{4} - z$; (xiv) $\frac{1}{4} - x, -y, \frac{1}{4} - z$.]

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regular. The rock-salt-type structure contains edge- and corner-sharing NaO$_6$, CaO$_6$ and BiO$_6$ octahedra (Fig. 2), ordered so that the calcium and bismuth octahedra share an edge.

**Experimental**

Bi$_2$O$_3$ (Alfa Aesar, 99.975%, 2.0 mmol) and CaCO$_3$ (Alfa Aesar, 99.95%, 1.0 mmol) were ground under acetone in an agate mortar until dry. The mixture, along with excess Na$_2$CO$_3$ (Fisher, ACS reagent, 12.5 g), was loaded into an alumina crucible, covered with an alumina lid, and placed into a programmable tube furnace. The system was heated to 1323 K at a rate of 873 K h$^{-1}$ and held at the target temperature for 24 h. It was then cooled slowly to 1073 K at a rate of 15 K h$^{-1}$ and held at that temperature for 1 h, at which point the furnace was shut off and the reaction allowed to cool to room temperature. The excess flux was dissolved in water and yellow transparent crystals of (I) were isolated using sonication and vacuum filtration.

**Crystal data**

Na$_3$Ca$_2$Bi$_2$O$_6$  
$M_r$ = 454.11  
Orthorhombic, Fdd2  
$a$ = 6.7039 (8) Å  
b = 9.6251 (11) Å  
c = 19.947 (2) Å

V = 1287.1 (3) Å$^3$  
$Z$ = 8  
Mo $K\alpha$ radiation  
$\mu$ = 29.17 mm$^{-1}$  
$T$ = 294 (2) K  
D$_\text{calc}$ = 4.05 g cm$^{-3}$

**Data collection**

Bruker SMART APEX CCD diffractometer  
Absorption correction: multi-scan (SADABS, Bruker, 2003)  
$T_{\text{min}}$ = 0.778, $T_{\text{max}}$ = 1.000  
(expected range = 0.324-0.417)  
5827 measured reflections  
499 independent reflections  
$R_{	ext{int}}$ = 0.047

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.013$  
w$R(F^2) = 0.032$  
$S = 1.08$  
499 reflections  
32 parameters  
$\Delta$,$\rho_{\text{max}}$ = 0.92 e Å$^{-3}$  
$\Delta$,$\rho_{\text{min}}$ = −0.65 e Å$^{-3}$

**Table 1**

Selected bond lengths (Å).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi1–O1$^i$</td>
<td>2.117 (3)</td>
</tr>
<tr>
<td>Bi1–O2$^i$</td>
<td>2.138 (2)</td>
</tr>
<tr>
<td>Ca1–O1$^{iii}$</td>
<td>2.340 (7)</td>
</tr>
<tr>
<td>Ca1–O2$^{ii}$</td>
<td>2.378 (3)</td>
</tr>
<tr>
<td>Na1–O2</td>
<td>2.398 (2)</td>
</tr>
</tbody>
</table>

Data collection: SMART-NT (Bruker, 2003); cell refinement: SAINT-Plus-NT (Bruker, 2003); data reduction: SAINT-Plus-NT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 2001); software used to prepare material for publication: SHELXTL.

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**References**