2-28-2007

Trisodium Dicalcium Bismuth Hexaoxide

Irina V. Puzdrjakova
University of South Carolina - Columbia

Rene B. Macquart
University of South Carolina - Columbia

Mark D. Smith
University of South Carolina - Columbia, mdsmith3@mailbox.sc.edu

Hans-Conrad zur Loye
University of South Carolina - Columbia, zurloye@mailbox.sc.edu

Publication Info

Published in *Acta Crystallographica Section E*, Volume 63, Issue 3, 2007, pages i95-i96.

electronic reprint

Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368
Editors: **W. Clegg and D. G. Watson**

Trisodium dicalcium bismuth hexaoxide

Irina V. Puzdrjakova, René B. Macquart, Mark D. Smith and Hans-Conrad zur Loye

Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Trisodium dicalcium bismuth hexaoxide

Irina V. Puzdrjakova, René B. Macquart, Mark D. Smith and Hans-Conrad zur Loye*

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, USA

Correspondence e-mail: zurloye@sc.edu

Received 13 February 2007
Accepted 21 February 2007

Single crystals of the title compound, $Na_3Ca_2BiO_6$, were grown from a high-temperature reactive flux solution of Na_2CO_3. $Na_3Ca_2BiO_6$ 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.

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(i–O) = 0.002 Å
R factor = 0.013
wR factor = 0.032
Data-to-parameter ratio = 15.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The most common bismuth oxidation state found in oxides is Bi^{III} as, for example, in $BiNbO_4$ (Keve *et al.*, 1973) and Bi_2MoO_6 (Teller *et al.*, 1984). However, some oxides, including $NaBiO_3$ (Kumada *et al.*, 2000), $KBiO_3$ (Nguyen *et al.*, 1993), $LiSr_3BiO_6$, $NaSr_3BiO_6$, Li_6KBiO_6, Li_6RbBiO_6 and $Li_2Ba_5Bi_2O_{11}$ (Carlson *et al.*, 1992) contain Bi(V) cations.

The title compound, (I), crystallizes as an ordered rock-salt structure. Use of a reactive sodium carbonate flux allowed for the stabilization of the Bi cation in the unusual +V oxidation state. The syntheses and characterization of $Li_3M_2XO_6$ (*M* = Mg, Co, Ni; *X* = Nb, Ta; Mather *et al.*, 1993), as well as $Na_3Ca_2TaO_6$ (Yamane *et al.*, 2000), have been reported previously. These oxides are isostructural with (I). In the lithium phases, the cations show partial ordering over the octahedral sites. $Na_3Ca_2TaO_6$ is the first compound reported to have a fully ordered cation arrangement of Na^+, Ca^{2+} and Ta^{5+} 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

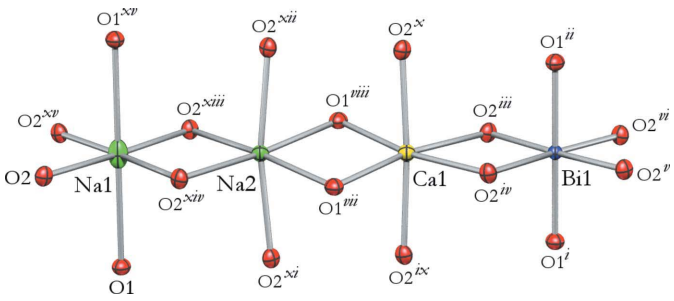

Figure 1
The asymmetric unit of (I), expanded to show the metal coordination polyhedra. Displacement ellipsoids are drawn at the 75% probability level. Colour key: Ca yellow, Bi blue, Na green and O red. [Symmetry codes: (i) $\frac{1}{4}-x,\frac{3}{4}-y,\frac{1}{2}+z$; (ii) $x,y-\frac{1}{2},\frac{1}{2}+z$; (iii) $x-\frac{1}{2},y,z+\frac{1}{2}$; (iv) $\frac{3}{4}-x,\frac{1}{4}-y,\frac{1}{2}+z$; (v) $\frac{3}{4}-x,y,\frac{3}{4}-z$; (vi) $x-\frac{1}{2},\frac{1}{4}-y,\frac{3}{4}-z$; (vii) $\frac{1}{4}+x,y-\frac{1}{4},\frac{1}{2}-z$; (viii) $-x,\frac{1}{2}-y,\frac{1}{2}-z$; (ix) $x-\frac{1}{4},\frac{1}{4}+y,\frac{1}{2}-z$; (x) $\frac{1}{2}-x,-y,\frac{1}{2}-z$; (xi) $x-\frac{1}{4},\frac{1}{2}-y,\frac{1}{4}+z$; (xii) $\frac{1}{2}-x,y-\frac{1}{4},\frac{1}{4}+z$; (xiii) $\frac{1}{4}-x,y,\frac{1}{4}-z$; (xiv) $x,\frac{1}{4}-y,\frac{1}{4}-z$; (xv) $\frac{1}{4}-x,\frac{1}{4}-y,z$.

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_2O_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_2CO_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

$Na_3Ca_2BiO_6$
M_r = 454.11
Orthorhombic, *Fddd*
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
μ = 29.17 mm^{-1}
T = 294 (2) K
0.05 × 0.04 × 0.03 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.778, T_{max} = 1.000
(expected range = 0.324–0.417)
5827 measured reflections
499 independent reflections
414 reflections with $I > 2\sigma(I)$
R_{int} = 0.047

Refinement

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

Table 1
Selected bond lengths (Å).

Bi1—O1^{i}	2.117 (3)	Na1—O1	2.696 (3)
Bi1—O2^{ii}	2.138 (2)	Na2—O1^{iii}	2.4305 (13)
Ca1—O1^{iii}	2.3404 (7)	Na2—O2^{v}	2.458 (3)
Ca1—O2^{iv}	2.378 (3)	Na2—O2^{vi}	2.533 (3)
Na1—O2	2.398 (2)		

Symmetry codes: (i) $-x+\frac{1}{4}, -y+\frac{3}{4}, z+\frac{1}{2}$; (ii) $-x+\frac{3}{4}, y, -z+\frac{3}{4}$; (iii) $-x, -y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, -y, -z+\frac{1}{2}$; (v) $x-\frac{1}{4}, -y+\frac{1}{2}, z+\frac{1}{4}$; (vi) $-x+\frac{1}{4}, y, -z+\frac{1}{4}$.

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*.

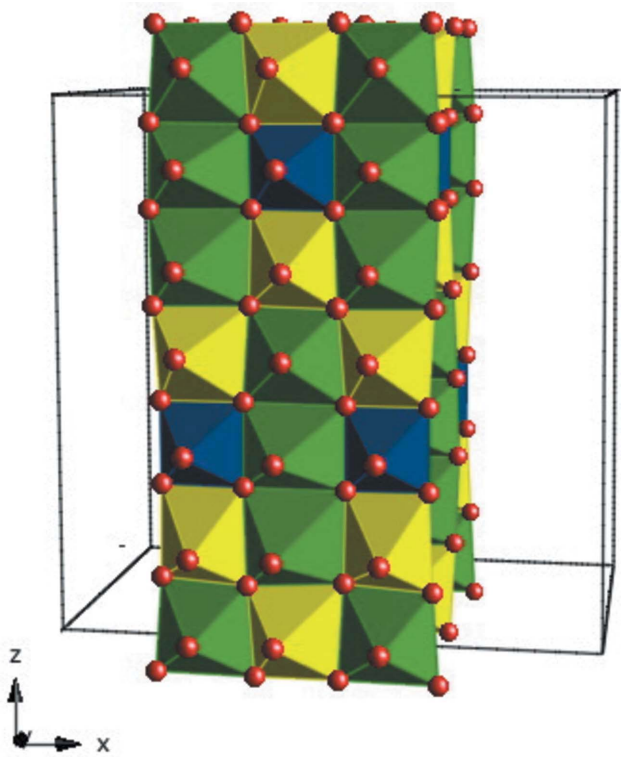

Figure 2
Polyhedral view of (I), showing the ordering of cations. NaO_6 octahedra are shown in green, CaO_6 octahedra in yellow and BiO_6 octahedra in blue.

This work was supported by the Department of Energy through grant DE-FG02–04ER46122 and the National Science Foundation through grant DMR:0450103.

References

Bruker (2003). *SMART-NT* (Version 5.630), *SAINT-Plus-NT* (Version 6.45) and *SADABS* (Version 2.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Carlson, V. A. & Stacy, A. M. (1992). *J. Solid State Chem.* **96**, 332–343.
Keve, E. T. & Skapski, A. C. (1973). *J. Solid State Chem.* **8**, 159–165.
Kumada, N., Kinomura, N. & Sleight, A. W. (2000). *Mater. Res. Bull.* **35**, 2397–2402.
Mather, G. C., Smith, R. I., Skakle, J. M. S., Fletcher, J. G., Castellanos, M. A. R., Gutierrez, M. P. & West, A. R. (1993). *J. Mater. Chem.* **3**, 1177–1182.
Nguyen, T. N., Giaquinta, D. M., Davis, W. M. & zur Loye, H.-C. (1993). *Chem. Mater.* **5**, 1273–1276.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Gõttingen, Germany.
Sheldrick, G. M. (2001). *SHELXTL*. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
Teller, R. G., Brazdil, J. F., Grasselli, R. K. & Jorgensen, J. D. (1984). *Acta Cryst.* C**40**, 2001–2005.
Yamane, H., Takahashi, H., Kajiwara, T. & Shimada, M. (2000). *Acta Cryst.* C**56**, 1177–1178.