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Two Hydrous Divalent-Metal Diarsenates

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Abstract

Two new hydrous diarsenates, $Mg_2As_2O_7.2H_2O$ (dimagnesium diarsenic heptaoxide dihydrate) and $Zn_2As_2O_7.2H_2O$ (dizinc diarsenic heptaoxide dihydrate), have been synthesized. The two compounds are isotypic. Their frameworks are characterized by zigzag infinite chains of edge-sharing MO_6 octahedra linked by As_2O_7 groups to form a three-dimensional architecture with intersecting tunnels. Water O atoms are tightly bound to the Mg or Zn atoms with the H atoms directed into the tunnels. Both the MO_6 octahedra and the AsO_4 tetrahedra are more distorted in the zinc compound than in the magnesium compound.

Comment

Two new hydrous divalent-metal diarsenates, $Mg_2As_2O_7.2H_2O$ and $Zn_2As_2O_7.2H_2O$, have been synthesized as part of a continuing effort to explore the hydrothermal synthesis and properties of new compounds in the *A*–*M*–As–O system, where *A* includes alkali metal and alkaline earth metal cations, and *M* includes transition metals (Horng & Wang, 1994; Wang & Lee, 1994; Wang, Wu & Liu, 1994; Wang, Hsu & Nieh, 1991). To our knowledge, only a few structurally well characterized metal diarsenates have been reported, among which most are anhydrous diarsenates. Compounds in which water and diarsenate groups co-exist are rare. $Co_2As_2O_7.2H_2O$ and $Ni_2As_2O_7.2H_2O$ (Wang, Horng & Lee, 1994) were the first examples of hydrous divalent transition metal diarsenates. The present two compounds are isostructural with the cobalt and nickel compounds.

As in the cobalt and nickel compounds, there are two unique MO_6 octahedra alternating in the infinite chains. The octahedral distortion (Shannon, 1976) in $M(2)O_6$, which shares skew edges with two $M(1)O_6$ octahedra, is much more pronounced than that in $M(1)O_6$, which shares *trans* edges with two $M(2)O_6$ octahedra. The $M(2)O_6$ octahedra are even more distorted in the magnesium and zinc compounds than in the cobalt and nickel compounds. The distortions $\{\Delta \times 10^4$, where $\Delta = \frac{1}{6}\Sigma[(R_i - \bar{R})/\bar{R}]^2$, R_i is an individual bond length and $\bar{R}$ is the average bond length$\}$ in $M(2)O_6$ calculated for the magnesium, cobalt, nickel and zinc compounds are 11.04, 3.85, 4.01 and 16.71, respectively. The distortions in the $M(1)O_6$ octahedra are much smaller ($\Delta \times 10^4 < 1$) for all four compounds.

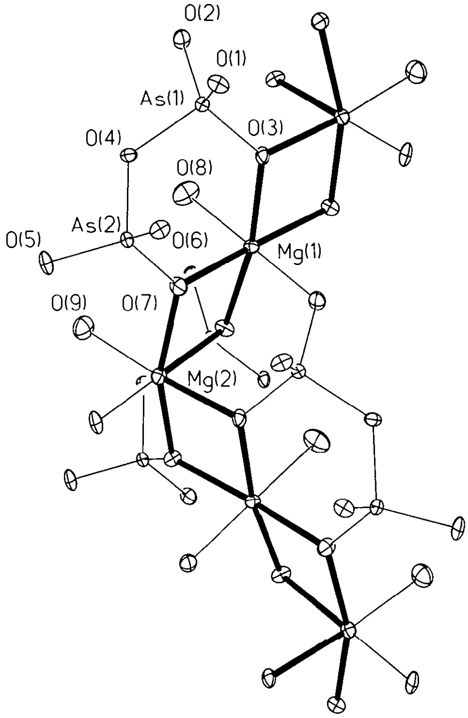

Fig. 1. Section of an infinite chain in $Mg_2As_2O_7.2H_2O$. Displacement ellipsoids are drawn at the 60% probability level.

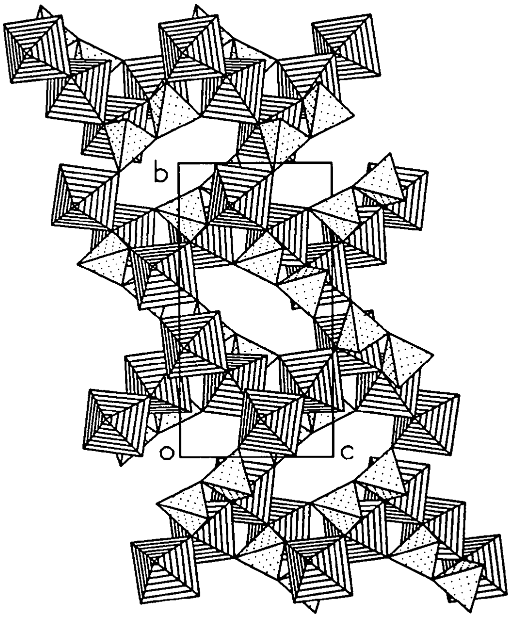

Fig. 2. Perspective view of the $Mg_2As_2O_7.2H_2O$ structure along the [100] direction.

The two AsO_4 tetrahedra in the diarsenate group are in a nearly eclipsed configuration with As—O—As 120.5° for the magnesium compound and 121.8° for the zinc compound. The torsion angles between the two tetrahedra in the As_2O_7 group are 12.7, 11.0, 10.5 and 10.6° for the magnesium, cobalt, nickel and zinc compounds, respectively.

Water molecules are tightly bound to the divalent metal cations. The magnesium compound lost water at *ca* 713 K in thermogravimetric analysis. A powder X-ray diffraction measurement indicated that the dehydrated product contained pure $Mg_2As_2O_7$ (Calvo & Neelakantan, 1970). No pure sample of the zinc compound for thermogravimetric analysis could be obtained.

Experimental

Crystals of $Mg_2As_2O_7.2H_2O$ were obtained by heating a mixture of $Mg(OH)_2$ (0.5475 g), 80% H_3AsO_4 (1.666 g) and water (11.2 cm^3) in a Teflon-lined autoclave (23 cm^3) at 603 K for 4 d followed by slow cooling to room temperature at 5 K h^{-1}. Crystals of $Zn_2As_2O_7.2H_2O$, obtained from a reaction mixture of ZnO (0.2 g), $Ba(OH)_2.8H_2O$ (0.70 g), KCl (0.12 g), 80% H_3AsO_4 (1 cm^3) and water (11.0 cm^3), proceeded under the same hydrothermal conditions as those in the preparation of the magnesium compound. Energy-dispersive X-ray fluorescence analysis on the crystal subsequently used for indexing and intensity-data collection showed that no barium was present in the zinc compound.

$Mg_2As_2O_7.2H_2O$

Crystal data

$Mg_2As_2O_7.2H_2O$
M_r = 346.5
Monoclinic
$P2_1/n$
a = 6.499 (1) Å
b = 14.191 (4) Å
c = 7.607 (2) Å
β = 93.95 (2)°
V = 699.9 (8) Å^3
Z = 4
D_x = 3.288 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 16 reflections
θ = 6.6–14.4°
μ = 9.75 mm^{-1}
T = 296 K
Rod
0.23 × 0.14 × 0.13 mm
Colorless

Data collection

Siemens *R*3*m*/*V* diffractometer
2θ–θ scans
Absorption correction: empirical *via* ψ scans (*SHELXTL-Plus*; Sheldrick, 1991)
$T_{\min}$ = 0.418, $T_{\max}$ = 0.754
1816 measured reflections
1605 independent reflections

1333 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.0232
$\theta_{\max}$ = 27.5°
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 9$
3 standard reflections monitored every 50 reflections intensity decay: none

Refinement

Refinement on F
R = 0.0253
wR = 0.0278
S = 0.997
1333 reflections
119 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0009F^2]$
$(\Delta/\sigma)_{\max}$ = 0.001

$\Delta\rho_{\max}$ = 0.77 e Å^{-3}
$\Delta\rho_{\min}$ = −0.80 e Å^{-3}
Extinction correction: $F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$
Extinction coefficient: χ = 0.0021 (2)
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Mg_2As_2O_7$.-$2H_2O$*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mg(1)	−0.0441 (2)	0.2486 (1)	0.6374 (2)	0.008 (1)
Mg(2)	−0.2632 (2)	0.3846 (1)	0.9126 (2)	0.008 (1)
As(1)	0.4429 (1)	0.3144 (1)	0.5539 (1)	0.006 (1)
As(2)	0.2378 (1)	0.4193 (1)	0.8452 (1)	0.006 (1)
O(1)	0.6545 (4)	0.2901 (2)	0.6837 (4)	0.009 (1)
O(2)	0.4816 (4)	0.3435 (2)	0.3489 (4)	0.010 (1)
O(3)	0.2627 (4)	0.2314 (2)	0.5752 (4)	0.009 (1)
O(4)	0.3364 (4)	0.4179 (2)	0.6356 (4)	0.009 (1)
O(5)	0.1878 (4)	0.5312 (2)	0.8798 (4)	0.011 (1)
O(6)	0.4281 (4)	0.3695 (2)	0.9731 (4)	0.009 (1)
O(7)	0.0254 (4)	0.3521 (2)	0.8307 (4)	0.010 (1)
O(8)	−0.0594 (5)	0.3453 (2)	0.4258 (4)	0.020 (1)
O(9)	−0.2634 (5)	0.4972 (2)	0.7419 (4)	0.017 (1)

Table 2. *Selected geometric parameters (Å, °) for $Mg_2As_2O_7.2H_2O$*

Mg(1)—O(3)	2.095 (3)	Mg(2)—O(5^{iv})	2.014 (3)
Mg(1)—O(7)	2.105 (3)	Mg(2)—O(6^{i})	2.100 (3)
Mg(1)—O(8)	2.112 (4)	As(1)—O(1)	1.673 (3)
Mg(1)—O(1^{i})	2.098 (3)	As(1)—O(2)	1.649 (3)
Mg(1)—O(2^{ii})	2.070 (3)	As(1)—O(3)	1.676 (3)
Mg(1)—O(6^{iii})	2.091 (3)	As(1)—O(4)	1.756 (3)
Mg(2)—O(7)	2.069 (3)	As(2)—O(4)	1.759 (3)
Mg(2)—O(9)	2.058 (3)	As(2)—O(5)	1.645 (3)
Mg(2)—O(1^{i})	2.234 (3)	As(2)—O(6)	1.676 (3)
Mg(2)—O(3^{ii})	2.060 (3)	As(2)—O(7)	1.675 (3)
O(3)—Mg(1)—O(7)	94.4 (1)	O(1^{i})—Mg(2)—O(3^{ii})	89.6 (1)
O(3)—Mg(1)—O(8)	84.2 (1)	O(7)—Mg(2)—O(5^{iv})	101.1 (1)
O(7)—Mg(1)—O(8)	94.3 (1)	O(9)—Mg(2)—O(5^{iv})	91.4 (1)
O(3)—Mg(1)—O(1^{i})	169.9 (1)	O(1^{i})—Mg(2)—O(5^{iv})	179.4 (1)
O(7)—Mg(1)—O(1^{i})	81.1 (1)	O(3^{ii})—Mg(2)—O(5^{iv})	89.9 (1)
O(8)—Mg(1)—O(1^{i})	87.1 (1)	O(7)—Mg(2)—O(6^{i})	160.5 (1)
O(3)—Mg(1)—O(2^{ii})	94.3 (1)	O(9)—Mg(2)—O(6^{i})	105.0 (1)
O(7)—Mg(1)—O(2^{ii})	84.0 (1)	O(1^{i})—Mg(2)—O(6^{i})	85.9 (1)
O(8)—Mg(1)—O(2^{ii})	177.7 (1)	O(3^{ii})—Mg(2)—O(6^{i})	80.0 (1)
O(1^{i})—Mg(1)—O(2^{ii})	94.2 (1)	O(5^{iv})—Mg(2)—O(6^{i})	94.2 (1)
O(3)—Mg(1)—O(6^{iii})	79.4 (1)	O(1)—As(1)—O(2)	115.9 (1)
O(7)—Mg(1)—O(6^{iii})	169.2 (1)	O(1)—As(1)—O(3)	110.5 (1)
O(8)—Mg(1)—O(6^{iii})	93.9 (1)	O(2)—As(1)—O(3)	114.9 (1)
O(1^{i})—Mg(1)—O(6^{iii})	106.4 (1)	O(1)—As(1)—O(4)	106.9 (1)
O(2^{ii})—Mg(1)—O(6^{iii})	87.6 (1)	O(2)—As(1)—O(4)	102.4 (1)
Mg(1)—Mg(2)—O(7)	39.3 (1)	O(3)—As(1)—O(4)	105.0 (1)
Mg(1)—Mg(2)—O(9)	92.1 (1)	O(4)—As(2)—O(5)	104.2 (1)
O(7)—Mg(2)—O(9)	86.8 (1)	O(4)—As(2)—O(6)	102.8 (1)
O(7)—Mg(2)—O(1^{i})	78.7 (1)	O(5)—As(2)—O(6)	117.4 (1)
O(9)—Mg(2)—O(1^{i})	89.1 (1)	O(4)—As(2)—O(7)	106.5 (1)
O(7)—Mg(2)—O(3^{ii})	88.0 (1)	O(5)—As(2)—O(7)	112.9 (1)
O(9)—Mg(2)—O(3^{ii})	174.7 (1)	O(6)—As(2)—O(7)	111.7 (1)

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

$Zn_2As_2O_7.2H_2O$

Crystal data

$Zn_2As_2O_7.2H_2O$
$M_r = 428.6$
Monoclinic
$P2_1/n$
$a = 6.496\ (21)$ Å
$b = 14.211\ (6)$ Å
$c = 7.628\ (4)$ Å
$\beta = 93.91\ (4)°$
$V = 702.3\ (10)$ Å^3
$Z = 4$
$D_x = 4.025$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 4.2–14.5°$
$\mu = 16.21$ mm^{-1}
$T = 296$ K
Rod
0.40 × 0.08 × 0.06 mm
Colorless

Data collection

Siemens *R3m/V* diffractometer
$2\theta–\theta$ scans
Absorption correction: empirical *via* ψ scans (*SHELXTL-Plus*; Sheldrick, 1991)
$T_{\min} = 0.647$, $T_{\max} = 0.792$
1725 measured reflections
1412 independent reflections

1096 observed reflections $[I > 3\sigma(I)]$
$R_{\text{int}} = 0.011$
$\theta_{\max} = 25.0°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 9$
3 standard reflections monitored every 50 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.059$
$wR = 0.0616$
$S = 0.76$
1096 reflections
94 parameters
H atoms not located
$w = 1/[\sigma^2(F) + 0.0043F^2]$
$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 3.37$ e Å^{-3}
$\Delta\rho_{\min} = -2.46$ e Å^{-3}
Extinction correction: $F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$
Extinction coefficient: $\chi = 0.0012\ (5)$
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)

Table 3. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for* $Zn_2As_2O_7.2H_2O$

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
Zn(1)	−0.0456 (3)	0.2477 (1)	0.6381 (2)	0.022 (1)
Zn(2)	−0.2617 (3)	0.3867 (1)	0.9155 (2)	0.017 (1)
As(1)	0.4436 (2)	0.3139 (1)	0.5532 (1)	0.003 (1)
As(2)	0.2390 (2)	0.4189 (1)	0.8449 (1)	0.002 (1)
O(1)†	0.6547 (14)	0.2880 (6)	0.6840 (10)	0.008 (2)
O(2)†	0.4838 (13)	0.3453 (6)	0.3500 (10)	0.006 (1)
O(3)†	0.2660 (13)	0.2314 (6)	0.5751 (9)	0.005 (1)
O(4)	0.3357 (14)	0.4172 (5)	0.6399 (10)	0.006 (2)
O(5)	0.1835 (14)	0.5319 (5)	0.8723 (10)	0.006 (2)
O(6)†	0.4311 (13)	0.3721 (5)	0.9739 (10)	0.006 (1)
O(7)†	0.0282 (13)	0.3512 (5)	0.8346 (9)	0.004 (1)
O(8)	−0.0571 (17)	0.3444 (7)	0.4253 (12)	0.019 (3)
O(9)	−0.2565 (16)	0.4960 (7)	0.7390 (13)	0.016 (3)

† U_{iso}.

Table 4. *Selected geometric parameters (Å, °) for* $Zn_2As_2O_7.2H_2O$

Zn(1)—O(3)	2.124 (9)	Zn(2)—O(5$^{\text{iv}}$)	2.026 (8)
Zn(1)—O(7)	2.131 (8)	Zn(2)—O(6$^{\text{i}}$)	2.085 (9)
Zn(1)—O(8)	2.124 (10)	As(1)—O(1)	1.681 (8)
Zn(1)—O(1$^{\text{i}}$)	2.082 (9)	As(1)—O(2)	1.651 (8)
Zn(1)—O(2$^{\text{ii}}$)	2.086 (8)	As(1)—O(3)	1.661 (8)
Zn(1)—O(6$^{\text{iii}}$)	2.112 (8)	As(1)—O(4)	1.774 (8)
Zn(2)—O(7)	2.083 (8)	As(2)—O(4)	1.725 (8)
Zn(2)—O(9)	2.057 (10)	As(2)—O(5)	1.662 (7)
Zn(2)—O(1$^{\text{i}}$)	2.291 (8)	As(2)—O(6)	1.673 (8)
Zn(2)—O(3$^{\text{ii}}$)	2.074 (8)	As(2)—O(7)	1.672 (8)
O(1)—As(1)—O(2)	116.2 (4)	O(1$^{\text{i}}$)—Zn(1)—O(2$^{\text{ii}}$)	94.7 (3)
O(1)—As(1)—O(3)	109.2 (4)	O(3)—Zn(1)—O(6$^{\text{iii}}$)	79.0 (3)
O(2)—As(1)—O(3)	116.1 (4)	O(7)—Zn(1)—O(6$^{\text{iii}}$)	167.6 (3)
O(1)—As(1)—O(4)	106.7 (4)	O(8)—Zn(1)—O(6$^{\text{iii}}$)	94.1 (3)
O(2)—As(1)—O(4)	102.6 (4)	O(1$^{\text{i}}$)—Zn(1)—O(6$^{\text{iii}}$)	106.9 (3)
O(3)—As(1)—O(4)	104.6 (4)	O(2$^{\text{ii}}$)—Zn(1)—O(6$^{\text{iii}}$)	87.0 (3)
O(4)—As(2)—O(5)	102.9 (4)	O(7)—Zn(2)—O(9)	86.2 (4)
O(4)—As(2)—O(6)	103.0 (4)	O(7)—Zn(2)—O(1$^{\text{i}}$)	78.2 (3)
O(5)—As(2)—O(6)	118.0 (4)	O(9)—Zn(2)—O(1$^{\text{i}}$)	88.4 (3)
O(4)—As(2)—O(7)	107.3 (4)	O(7)—Zn(2)—O(3$^{\text{ii}}$)	86.2 (3)
O(5)—As(2)—O(7)	112.2 (4)	O(9)—Zn(2)—O(3$^{\text{ii}}$)	172.1 (4)
O(6)—As(2)—O(7)	112.0 (4)	O(1$^{\text{i}}$)—Zn(2)—O(3$^{\text{ii}}$)	87.9 (3)
O(3)—Zn(1)—O(7)	93.6 (3)	O(7)—Zn(2)—O(5$^{\text{iv}}$)	101.1 (3)
O(3)—Zn(1)—O(8)	83.2 (4)	O(9)—Zn(2)—O(5$^{\text{iv}}$)	94.4 (3)
O(7)—Zn(1)—O(8)	94.9 (3)	O(1$^{\text{i}}$)—Zn(2)—O(5$^{\text{iv}}$)	177.1 (3)
O(3)—Zn(1)—O(1$^{\text{i}}$)	169.8 (3)	O(3$^{\text{ii}}$)—Zn(2)—O(5$^{\text{iv}}$)	89.2 (3)
O(7)—Zn(1)—O(1$^{\text{i}}$)	81.9 (3)	O(7)—Zn(2)—O(6$^{\text{i}}$)	159.5 (3)
O(8)—Zn(1)—O(1$^{\text{i}}$)	88.0 (4)	O(9)—Zn(2)—O(6$^{\text{i}}$)	105.9 (4)
O(3)—Zn(1)—O(2$^{\text{ii}}$)	93.9 (3)	O(1$^{\text{i}}$)—Zn(2)—O(6$^{\text{i}}$)	85.6 (3)
O(7)—Zn(1)—O(2$^{\text{ii}}$)	83.6 (3)	O(3$^{\text{ii}}$)—Zn(2)—O(6$^{\text{i}}$)	80.8 (3)
O(8)—Zn(1)—O(2$^{\text{ii}}$)	176.7 (4)	O(5$^{\text{iv}}$)—Zn(2)—O(6$^{\text{i}}$)	94.4 (3)

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

During the diffraction measurements it was found that the crystal quality of the zinc compound was rather poor. The crystal used for indexing and intensity-data collection showed slight twinning in the ω-scan profile analysis. Therefore, five O atoms, O(1), O(2), O(3), O(6), and O(7), could not be anisotropically refined and the final agreement factors as well as e.s.d.'s in bond lengths and angles were somewhat higher than for the magnesium compound. The maximum and minimum peaks in the final difference Fourier map were near As(1). All four water H atoms in the structure of $Mg_2As_2O_7.2H_2O$ were located on a difference Fourier map. Their positions were fixed in the subsequent refinement and final structure-factor calculations. No water H atoms could be found for the zinc structure.

All calculations were performed using *SHELXTL-Plus* (Sheldrick, 1991).

We are grateful to the National Science Council for their support of this study.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Yttrium and Titanium Bismuthates with Structures Related to β-Bi$_2$O$_3$

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Abstract

Y and Ti atoms in Bi$_{7.5}$Y$_{0.5}$O$_{12}$ and Bi$_{7.68}$Ti$_{0.32}$O$_{12.16}$ replace Bi atoms in the structure of β-Bi$_2$O$_3$ with additional O atoms completing their coordination polyhedra. Anti-glass disorder is indicated by neutron diffraction and EXAFS.

Comment

Metastable β-Bi$_2$O$_3$ (Sillén, 1937; Levin & Roth, 1964; Aurivillius & Malmros, 1972) is stabilized by various oxides. Such nonstoichiometric phases are known as β^*-Bi$_2$O$_3$ (Gattow & Schröder, 1962) or β^* bismuthates. Our aim was to locate the Y and Ti atoms and characterize their local environments in the structure of β-Bi$_2$O$_3$ by neutron powder diffraction. Many bismuthates show anti-glass disorder (Burckhardt & Trömel, 1983; Trömel, 1988), the characteristics of which are: (i) a nonstoichiometric composition, (ii) a high concentration of anion defects, (iii) large irregular atomic displacements, *i.e.* three-dimensional positional disorder and (iv) static disorder. In the case of β^* bismuthates, of which more than 50 are known (Ducke, 1993; Delicat, 1993), the presence of this kind of disorder cannot be proved by vibrational spectroscopy. For this reason, we studied the disorder by neutron diffraction and EXAFS, with which it is possible to investigate separately the environments of atoms which share the same crystallographic positions.

β-Bi$_2$O$_3$ has a fluorite-type superstructure, space group $P\bar{4}2_1c$, with $a = 7.739$, $c = 5.636$ Å, $Z = 4$, Bi in position (8*e*) and O in positions (8*e*) and (4*d*) according to X-ray single crystal and neutron powder diffraction (Aurivillius & Malmros, 1972; Blower & Greaves, 1988). BiO$_4E$ trigonal bipyramids (E = equatorial lone pair) form a network with empty channels along [00*z*] and $[\frac{1}{2}\frac{1}{2}z]$. Two more O atoms with Bi—O distances of about 2.7 Å are considered as neighbours of Bi (Fig. 1) according to the geometrical definition of coordination (Alig & Trömel, 1992), the definition of Frank & Kasper (1958) or the '*Wirkungsbereich*' (Niggli, 1927).

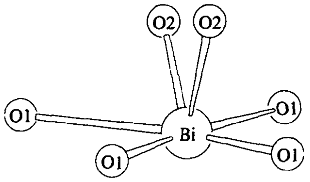

Fig. 1. Bi–O coordination in β-Bi$_2$O$_3$.

In the neutron powder patterns of Bi$_{7.5}$Y$_{0.5}$O$_{12}$, (I), and Bi$_{7.68}$Ti$_{0.32}$O$_{12.16}$, (II), the space groups $P\bar{4}2_1c$ and $P4_2/nmc$ cannot be distinguished by systematic absences. All calculations were performed assuming $P4_2/nmc$.† Satisfactory agreement was obtained assuming the Y and Ti atoms to be statistically distributed over the Bi positions. The agreement improved further when partial occupancy of additional O-atom positions was taken into account. In Bi$_{7.5}$Y$_{0.5}$O$_{12}$, O with an occupancy factor of 0.22 was found in (2*a*). The number of O3 atoms, 0.44 per cell, corresponds roughly to the number of Y atoms (0.5 per cell) and we assume that the additional O atoms are coordinated to Y. Thus, from the irregular sixfold coordination of Bi, an also irregular sevenfold coordination polyhedron results (Fig. 2). The presence of additional O atoms in (2*a*) is compensated for by 0.16 vacancies per cell in the O1 position (8*e*) and 0.28 vacancies per cell in the O2 position (4*d*), which implies that Bi, Y or both are not uniformly coordinated.

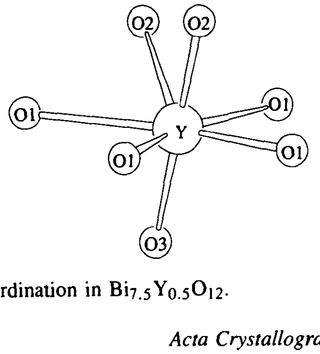

Fig. 2. Y–O coordination in Bi$_{7.5}$Y$_{0.5}$O$_{12}$.

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† Refinements in space group $P\bar{4}2_1c$ resulted in somewhat lower R values, presumably due to the greater number of free parameters. For these parameters see Ducke *et al.* (1996). The space group $P\bar{4}2_1c$ for β-Bi$_2$O$_3$ itself is not in doubt (Blower & Greaves, 1988).