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On the Rare Earth Metal Bismuthide Oxides RE_2BiO_2 (RE = Nd, Tb, Dy, Ho)

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Abstract. A series of new RE_2BiO_2 compounds (RE = Nd, Tb, Dy, Ho) has been synthesized from elemental bismuth, REBi, and RE_2O_3 in all-solid state reactions in sealed tantalum ampoules at 1770 K. The dark grey metallic compounds adopt the *anti*-$ThCr_2Si_2$ type of structure ($I4/mmm$, $tI10$), according to X-ray single crystal structure analysis. As a main structural feature, there are PbO analogous slabs, $[REO]^+$, and 4^4 nets of Bi^{2-} anions, alternately stacked along the c-axis.

Introduction

Rare earth metal pnictide oxides have attracted interest as potential thermoelectrics, in recent times.[1–3] On one hand, they contain some of the heaviest elements in the periodic table which reduces thermal lattice vibrations, on the other the combination with oxide may also minimize thermal conductivity, since the efficiency of phonon propagation is perturbed by structural complexity.[1,4]

The rare earth metal pnictide oxides, Ce_2SbO_2 and Ce_2BiO_2, were already reported by *Benz* in 1971,[5] the charge balance as adjusted by the presence of Ce^{3+} *and* Ce^{4+}, together with the formation of Pn^{3-} (Pn = Sb, Bi), was assumed to stabilize these compounds. Recent studies, including additional praseodymium representatives, have clearly shown that in all of these examples the rare earth metal is in the trivalent state, exclusively. This finding was evidenced by magnetic susceptibility measurements.[6] The electron count according to $[RE^{3+}]_2[Pn^{2-}][O^{2-}]_2$, in analogy to isoelectronic RE_2TeO_2,[7] seems to be valid for all of them. While semiconducting behavior is observed for the antimonides, due to Sb–Sb bond formation, the bismuthides display metallic conductivity. The latter appear to formally contain unusual Bi^{2-} anions, without any effective chemical bond between them.[2] Consequently, there is no need for the presence of Ce^{4+} or Pr^{4+}, and it should be possible to extend this class of materials including other rare earth metals.

The validity of this assumption was already affirmed by powder diffraction studies on RE_2BiO_2 representatives with RE = Nd, Sm, Gd, Ho, Er, and Y.[2] However, for understanding the properties of this class of materials, more accurate structure data are desirable. In particular, the localization of the oxygen atoms in such heavy-element structures, using powder methods, can be a rather difficult task.[8]

Herein we report on the synthesis and single crystal structure refinements of new RE_2BiO_2 representatives, with RE representing the trivalent rare earth metals neodymium, terbium, dysprosium, and holmium.

Results and Discussion

Starting from elemental bismuth, the bismuthides (REBi) and oxides (RE_2O_3), Nd_2BiO_2, Tb_2BiO_2, Dy_2BiO_2 and Ho_2BiO_2 have been synthesized by all-solid state reactions. When exposed to humid air, the dark grey metallic compounds slowly corrode, and may start smoldering after mechanical treatment.

The title compounds crystallize in the tetragonal space group $I4/mmm$ (no. 139) adopting a structure analogous to *anti*-$ThCr_2Si_2$ (Table 1, Table 2). The rare earth metal cations, which are occupying the Si positions, are surrounded by four oxygen and four bismuth atoms in the shape of square antiprisms (Figure 1). The oxygen atoms (Cr positions) are tetrahedrally coordinated by four rare earth metals forming PbO analogous slabs, and finally, the bismuth atoms are arranged in 4^4 nets, along (001), separating the REO slabs, whereby each bismuth atom is surrounded by eight RE atoms in the function of a slightly elongated cube.

The distances between neighboring bismuth atoms range from 385.83(3) to 399.11(3) pm (Table 3), which correspond to the a-axis of the respective compound, are too long for assuming a chemical bond. However, the bismuth atoms in each refined structure show significant anisotropy of thermal motion, which is expressed by the ratio of the maximum and minimum displacement parameters $U_{11}/U_{33} \approx 2.2$–$4.3$. This is indicating some local disorder, which gives freedom to assume real Bi–Bi distances shorter by approx. 28 pm ($= 2\sqrt{U_{11}}$, cf. Table 2). This value is independently confirmed by applying a split model for the Bi position ($8i$ site instead of $2a$). In elemental bismuth, the Bi–Bi distances are 307 pm, and within 1D Bi^- zigzag chains[9] or Bi_2^{4-} dumbbells[10] the distances are 322 and 329 pm, respectively, the latter are usually addressed as single bonds. In the 2D Bi^- square sheets, present in $EuBi_2$,

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Table 1. Crystal data, data collection, and refinement details at 298 K.

Compound	Nd_2BiO_2	Tb_2BiO_2	Dy_2BiO_2	Ho_2BiO_2
Formula weight	529.46	558.82	565.98	570.84
Space group (no.), Z	$I4/mmm$ (139), 2	$I4/mmm$ (139), 2	$I4/mmm$ (139), 2	$I4/mmm$ (139), 2
Lattice constants /pm	a = 399.11(3)	389.62(6)	387.61(3)	385.83(2)
	c = 1366.3(3)	1331.7(3)	1323.3(2)	1321.8(1)
	c/a = 3.423	3.418	3.414	3.426
V /Å^3	217.63(5)	202.16(6)	198.82(4)	196.77(2)
ρ_{xray} /g·cm^{-3}	8.080	9.180	9.454	9.635
Crystal size	$0.08 \times 0.06 \times 0.04$	$0.07 \times 0.07 \times 0.04$	$0.12 \times 0.06 \times 0.03$	$0.15 \times 0.10 \times 0.05$
Diffractometer	SMART APEX II, Bruker AXS			
X-ray radiation, λ /pm	71.073			
Absorption correction	multi-scan, SADABS[15]			
2θ range /°	$5.96 \le 2\theta \le 73.78$	$6.12 \le 2\theta \le 68.76$	$6.16 \le 2\theta \le 73.74$	$6.16 \le 2\theta \le 73.88$
Index range	$-6 \le h \le 6$, $-6 \le k \le 6$, $-22 \le l \le 22$	$-6 \le h \le 6$, $-6 \le k \le 6$, $-20 \le l \le 20$	$-6 \le h \le 6$, $-6 \le k \le 6$, $-22 \le l \le 22$	$-6 \le h \le 6$, $-6 \le k \le 6$, $-22 \le l \le 22$
Reflection collected	2785	1583	2432	2385
Data, R_{int}	201, 0.051	161, 0.033	185, 0.054	184, 0.028
No. of parameters	9	9	9	9
Transmision: t_{max}, t_{min}	0.185, 0.080	0.147, 0.074	0.195, 0.037	0.102, 0.028
$R_1[F^2 > 2\sigma(F^2)]$	0.022	0.019	0.036	0.016
$wR(F^2)$	0.048	0.050	0.107	0.041
Extinction coefficient	0.0043(5)	0.020(1)	0.010(1)	0.0019(3)
Deposition no.[17]	CSD-423917	CSD-423916	CSD-423915	CSD-423914

Table 2. Atomic coordinates and displacement parameters U_{ij} /pm^2 at 298 K ($U_{11} = U_{22}$, $U_{12} = U_{13} = U_{23} = 0$).

Atom	Site	x	y	z	U_{11}	U_{33}	U_{eq}
Nd_2BiO_2							
Bi	2a	0	0	0	203(2)	87(3)	164(2)
Nd	4e	0	0	0.33596(3)	66(2)	96(3)	76(2)
O	4d	0	½	¼	56(16)	149(26)	87(11)
Tb_2BiO_2							
Bi	2a	0	0	0	188(3)	61(3)	146(2)
Tb	4e	0	0	0.33422(3)	57(2)	63(3)	59(2)
O	4d	0	½	¼	80(15)	59(22)	73(11)
Dy_2BiO_2							
Bi	2a	0	0	0	195(4)	45(4)	145(3)
Dy	4e	0	0	0.33412(2)	67(3)	57(4)	64(3)
O	4d	0	½	¼	63(12)	107(23)	77(9)
Ho_2BiO_2							
Bi	2a	0	0	0	196(2)	88(2)	160(2)
Ho	4e	0	0	0.33374(2)	71(2)	94(2)	79(2)
O	4d	0	½	¼	58(10)	134(21)	83(8)

the Bi–Bi distances of 334 pm are considered to be “hypervalent“ Bi–Bi bonds.[9] In comparison, the Bi–Bi contacts of 360–370 pm encountered in RE_2BiO_2 compounds appear still too long. Thus at best non-covalently bonded Bi^{2-} anions can be assumed, which would be in agreement with the metallic conductivity observed.[2,6] It was suggested,[6] and later confirmed by band structure calculations,[2] that the partially filled 6p band of Bi^{2-} is responsible for this behavior.

In structural details the bismuthides are clearly distinct from the respective antimonides Ce_2SbO_2 and Pr_2SbO_2, where a ratio of $U_{11}/U_{33} > 15$ is observed, indicating pronounced Sb–Sb bonding interactions, which allows for the description of covalently bonded Sb_2^{4-} dimers, in agreement with their semiconducting behavior.[6]

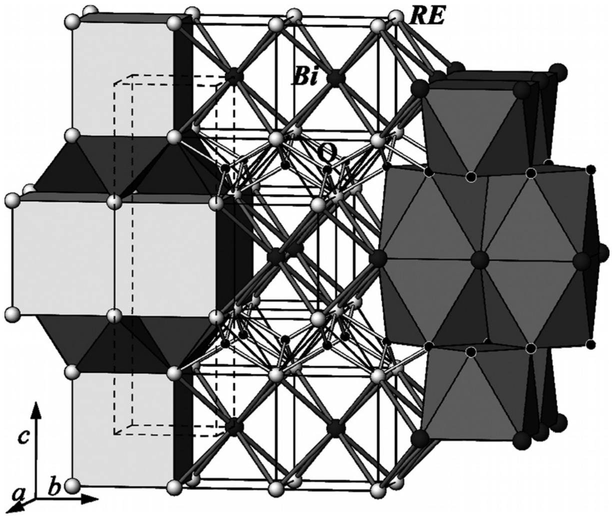

Figure 1. Perspective representation of the crystal structure of RE_2BiO_2 compounds (RE = Nd, Tb, Dy, Ho), showing the coordination of the anions (left) and cations (right) in polyhedral representation. The central part is drawn in ball-and-stick mode emphasizing the connectivity. The unit cell is drawn in dotted lines.

Table 3. Interatomic distances /pm at 298 K (RE = Nd, Tb, Dy, Ho).

Atomic contact		Nd_2BiO_2	Tb_2BiO_2	Dy_2BiO_2	Ho_2BiO_2	mult.
RE	–Bi	360.38(4)	353.04(5)	351.16(3)	350.32(3)	4
	–O	231.55(3)	224.79(3)	223.50(2)	222.42(2)	4
	–RE	367.17(7)	355.28(6)	353.10(5)	351.34(4)	4
Bi	–RE	360.38(4)	353.05(5)	351.16(3)	350.33(3)	8
O	–RE	231.55(3)	224.79(3)	223.50(2)	222.41(2)	4
Bi	–Bi	399.11(3)	389.62(6)	387.61(3)	385.83(2)	4

Conclusions

Nd_2BiO_2, Tb_2BiO_2, Dy_2BiO_2, and Ho_2BiO_2 have been synthesized by solid state reaction from elemental bismuth, *RE*Bi, and RE_2O_3, and characterized by single crystal diffraction. Their existence clearly demonstrates that there is no need for the rare earth metal to adopt the tetravalent oxidation state, and consequently bismuth must be present as Bi^{2-} anions. The particular bonding situation, as revealed for bismuth, clearly deserves further attention.

The title compounds complete the series of rare earth metal pnictide oxides: RE_4Pn_2O,[8] $RE_9Pn_5O_5$,[11–13] RE_2PnO_2,[2,5,6] $RE_8Pn_3O_8$,[1] and RE_3PnO_3.[1]

Experimental Section

Syntheses

The RE_2BiO_2 (*RE* = Nd, Tb, Dy, Ho) compounds have been synthesized in approx. 1 g batches from *RE*Bi, elemental bismuth, and RE_2O_3, respectively (ChemPur, Karlsruhe, Germany 99.9 %). The binary rare earth bismuthides were prepared from the elements in tantalum ampoules. The reactions were done in dynamic vacuums, when heating the ampoules at 1270 K for 48 h to remove potential impurities of hydrogen. Stoichiometric amounts of the starting materials were mixed and sealed in tantalum ampoules. The following temperature profile was applied: $298 \rightarrow 1770$ K (100 $K{\cdot}h^{-1}$, subsequent annealing for 72 h); $1770 \rightarrow 1470$ K (25 $K{\cdot}h^{-1}$, subsequent annealing for 72 h); $1470 \rightarrow 298$ K (50 $K{\cdot}h^{-1}$).

Structure Determinations

The diffraction data were collected at 298 K with a SMART-APEX-II CCD X-ray diffractometer (Bruker AXS, Karlsruhe, Germany) with graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). The reflection intensities were integrated with the SAINT subprogram in the Bruker Suite software package,[14] a multi-scan absorption correction was applied using SADABS.[15] The structures were solved by direct methods and refined by full-matrix least-squares fitting with the SHELXTL software package.[16] Experimental details are given in Table 1 and Table 2. Further details may be obtained from Fachinformationszentrum Karlsruhe.[17]

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