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Syntheses, structures and properties of the pnictide oxides R_2PnO_2 (R = Ce, Pr; Pn = Sb, Bi)

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ABSTRACT

Compounds with the chemical formula R_2PnO_2 (R = Ce, Pr and Pn = Sb, Bi) were prepared by reactions between adequate amounts of Ce_2O_3 (Pr_4O_7), Pn and RPn in sealed tantalum ampoules at 1770 K. Both bismuth compounds crystallize in the *anti*-$ThCr_2Si_2$ type of structure ($I4/mmm$, $tI10$). In the case of R_2SbO_2 a ($4 \times 4 \times 1$) super cell of the *anti*-$ThCr_2Si_2$ structure type is observed. Compared with the basis structure, the antimony atoms are displaced from the ideal positions forming Sb—Sb bonds perpendicular to the c-axis. The magnetic susceptibility measurements indicate that the rare earth metals are in the trivalent state, and the electrical conductivity measurements show semiconducting behavior for R_2SbO_2 and metallic conductivity for R_2BiO_2, respectively. Both, the Sb—Sb bond formation in the semiconducting antimonides, and the metallic conductivity of the bismuthides are in accordance with the description as $[R^{3+}]_2[Pn^{2-}][O^{2-}]_2$.

1. Introduction

There has been a lasting dispute of whether oxygen might be included in La_2Sb type compounds (R_2Pn) [1], which is nourished by oxygen-stuffed variants, like Eu_4Pn_2O [2,3], known to exist. However, it appears reasonable that the latter stuffed variants have been found only for europium and ytterbium so far, since electron precise compounds would require divalent cations. For other rare earth metal pnictides the oxidation of 2:1-alloys leads to the formation of $R_9Pn_5O_5$ compounds (R = La, Ce, Pr, Sm, Dy; Pn = Sb [4,5]). Their structures can be regarded as sheared, defect variants of La_2Sb, filled up with oxygen. These pnictide oxides host two excess electrons: $(R^{3+})_9(Sb^{3-})_5(O^{2-})_5 + 2e^-$, and show accordingly metallic conductivity. Thus, the question arises, to which extent oxygen can be included without forming pnicogene–oxygen bonds. Ce_2SbO_2 and Ce_2BiO_2, already reported by *Benz* [6], were proposed to crystallize in the *anti*-$ThCr_2Si_2$ type of structure, as was derived by a "*trial-and-error*" approach from powder-diffraction data. The presence of both, Ce^{3+} and Ce^{4+}, together with the formation of Pn^{3-}were assumed to stabilize the compounds. This detail is in accordance with the electron counts applying to the isotypic, electron precise tellurides R_2TeO_2, with $Te^{2-}$and R^{3+} [7]. To complete the series of 2:1:x rare earth metal pnictide oxides, we have reinvestigated the cerium compounds, and studied analogous praseodymium representatives. The latter ones appeared particularly interesting because of the additional degree of freedom in forming Pr^{3+} and Pr^{4+}.

2. Experimental

The R_2PnO_2 (R = Ce, Pr) compounds have been synthesized in ~1 g batches from RPn, the pnicogene elements, Ce_2O_3 or Pr_4O_7, respectively (ChemPur, Karlsruhe, Germany 99.9%). The binary rare earth pnictides 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 → 1770 K ($100\,\mathrm{K\,h^{-1}}$, subsequent annealing for 72 h); 1770 → 1470 K ($25\,\mathrm{K\,h^{-1}}$, subsequent annealing for 72 h); 1470 → 298 K ($50\,\mathrm{K\,h^{-1}}$).

Magnetic susceptibility measurements were carried out on a Quantum Design SQUID magnetometer. The susceptibility was recorded at H = 0.001, 0.1, 1, 3 and 7 T in the temperature range of 2–300 K. Temperature dependent resistivity has been obtained for pressed pellets using the *van der Pauw* method [8] (5–290 K at 5 K intervals).

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Table 1
Crystallographic data for R_2PnO_2 (R = Ce, Pr and Pn = Sb, Bi).

Empirical formula	Ce_2BiO_2	Pr_2BiO_2	Ce_2SbO_2	Pr_2SbO_2
Formula weight (g mol^{-1})	521.22	522.80	433.99	435.57
Crystal system, space group	Tetragonal, $I4/mmm$ (no. 139)			
Unit cell dimensions	a = 4.0369(5)	a = 4.0149(1)	a = 4.0167(3)	a = 3.9957(3)
(Å)	c = 13.746(2)	c = 13.7017(6)	c = 13.710(2)	c = 13.580(2)
Volume (Å^3), Z	224.01(5), 2	220.86(1), 2	221.20(4), 2	216,82(4), 2
2θ range (°)	5.92–73.9	5.94–74.18	5.94–73.32	6.00–73.48
Index range	$-6 \le h \le 6, -6 \le k \le 6, -22 \le l \le 22$			
Reflections collected, R_{int}	2173, 0.0295	3061, 0.0330	2689, 0.0577	2708, 0.0429
Data, parameters	205, 9	205, 9	201, 11	199, 11
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0174, 0.0371	0.0131, 0.0286	0.0217, 0.0508	0.0299, 0.0845
$R1$, $wR2$ (all data) [11]	0.0207, 0.0383	0.0135, 0.0289	0.0218, 0.0509	0.0299, 0.0845
Extinction	0.0042(4)	0.0093(5)	0.0067(10)	0.013(2)

Table 2
Atomic coordinates and displacement parameters (Å^2) for R_2PnO_2 (R = Ce, Pr and Pn = Sb, Bi).

Atom	site	x	y	z	U_{11}	U_{22}	U_{33}	U_{eq}
Bi	$2a$	0	0	0	0.0233(2)	U_{11}	0.0087(2)	0.0184(2)
Ce	$4e$	0	0	0.33674(3)	0.0079(1)	U_{11}	0.0089(2)	0.0083(1)
O	$4d$	0	1/2	1/4	0.0065(13)	U_{11}	0.0117(21)	0.0082(9)
Bi	$2a$	0	0	0	0.0231(2)	U_{11}	0.0083(2)	0.0182(2)
Pr	$4e$	0	0	0.33622(3)	0.0077(2)	U_{11}	0.0086(2)	0.0080(1)
O	$4d$	0	1/2	1/4	0.0074(11)	U_{11}	0.0114(16)	0.0087(7)
Sb[a]	$8i$	0.0982(5)	0	0	0.0327(9)	0.0356(10)	0.0115(5)	0.0266(5)
Ce	$4e$	0	0	0.33782(3)	0.0086(2)	U_{11}	0.0233(3)	0.0135(2)
O	$4d$	0	1/2	1/4	0.0092(12)	U_{11}	0.0246(25)	0.0143(9)
Sb[a]	$8i$	0.0961(8)	0	0	0.0372(16)	0.0343(15)	0.0126(6)	0.0280(8)
Pr	$4e$	0	0	0.33769(5)	0.0106(3)	U_{11}	0.0226(4)	0.0146(3)
O	$4d$	0	1/2	1/4	0.0115(20)	U_{11}	0.0254(37)	0.0161(15)

[a] Site occupation factor of Sb on the site $8i$ is fixed to 1/4.

The diffraction data were collected on a SMART-APEX-II CCD X-ray diffractometer (Bruker AXS, Karlsruhe, Germany) with graphite-monochromated MoK_α radiation at 296(2) K. The reflection intensities were integrated with the SAINT subprogram in the Bruker Suite software package [9], a multi-scan absorption correction was applied using SADABS [10]. The structures were solved by direct methods and refined by full-matrix least squares fitting with the SHELXTL software package [11]. Experimental details are given in Tables 1 and 2. Further details may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247 808 666; e mail: crysdata at fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html on quoting the CSD numbers: 419606–419609).

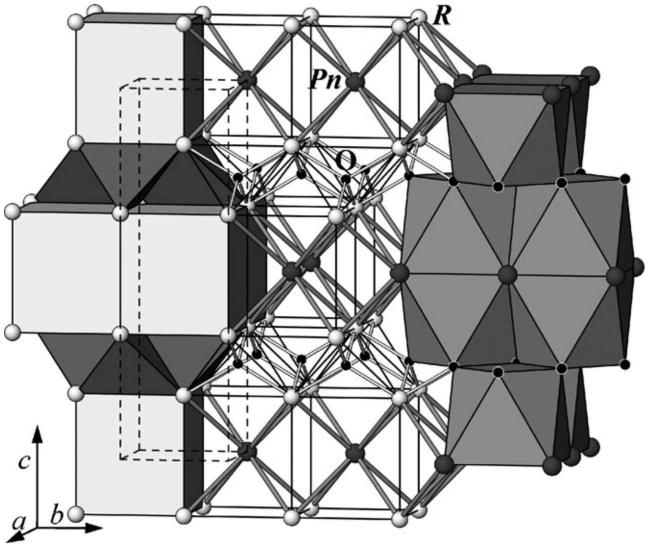

Fig. 1. Perspective view of the crystal structure of R_2PnO_2 (R = Ce, Pr; Pn = Bi), showing the coordination of the anions (left) and cations (right) in polyhedral representation. The central part is drawn in ball-and-stick mode to emphasize the connectivity. The unit cell is drawn in dotted lines.

3. Results and discussion

Starting from the respective pnicogene elements, pnictides and oxides, the compounds Ce_2SbO_2, Ce_2BiO_2, Pr_2SbO_2 and Pr_2BiO_2 have been synthesized by all-solid state reactions, and as single phase products.

The magnetic susceptibility measurements show *Curie–Weiss* behavior for all compounds. Onset of antiferromagnetic ordering has been observed to occur below 20 K, for all of them. Data analyses result for all compounds in magnetic moments close to the theoretical values of the trivalent states Ce^{3+} ($2.535\mu_B$) and Pr^{3+} ($3.578\mu_B$), respectively: $\mu_{eff} = 2.40\mu_B$ (Ce_2SbO_2), $2.41\mu_B$ (Ce_2BiO_2), $3.47\mu_B$ (Pr_2SbO_2), and $3.49\mu_B$ (Pr_2BiO_2).

The specific electrical resistivity of Ce_2BiO_2 (Pr_2BiO_2) has been determined to be 5(75) mΩ cm at 293 K, and slightly increases to 9(85) mΩ cm when cooled to 5 K. We attribute the very small increase in resistivity at lower temperatures to grain boundary effects, which is quite common for pressed pellets of moderately conducting metallic powders with possibly partially oxidized surfaces of the grains. In contrast, Ce_2SbO_2 (Pr_2SbO_2) shows a specific electrical resistivity of 18.8 (1.5×10^4) Ω cm at 293 K, which increases exponentially to 2.7×10^7 (2.5×10^7) Ω cm (limit of sensitivity of the measurement setup) when cooled down to 20(120) K, a typical behavior of a semiconductor.

The single crystal structure determination on Ce_2BiO_2 basically confirms the results of *Benz* [6], with significantly improved precision. This compound, and also the new Pr_2BiO_2, crystallize tetragonal in the space group $I4/mmm$ (no. 139) with a structure analogous to *anti*-$ThCr_2Si_2$ (Tables 1 and 2). The Ce or Pr cations are surrounded by eight anions in the shape of a square antiprism. Four oxygen atoms form a square basal face and four bismuth atoms are arranged similarly as a counterpart forming the opposite prism face (Fig. 1, left). The oxygen atoms are tetrahedrally coordinated by four rare earth metals forming PbO analogous slabs, and finally,

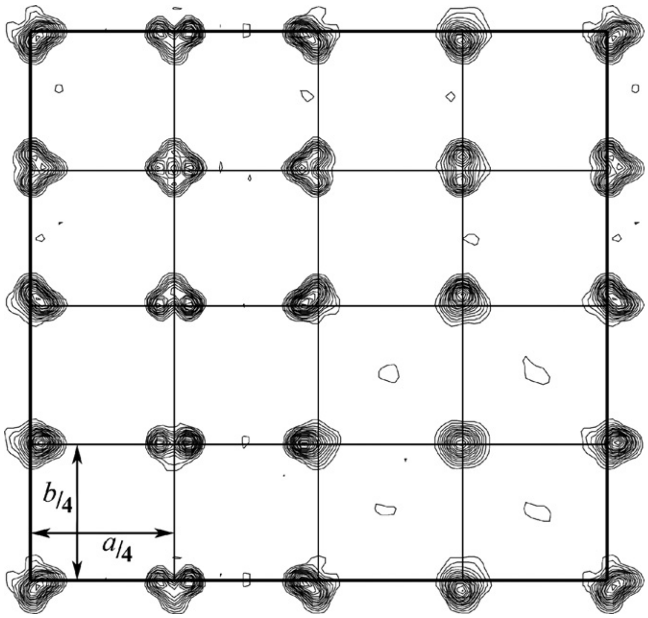

Fig. 2. Fourier map F_{obs} from Pr_2SbO_2, done with a "4 × 4 × 1 data set" within the space group $P1$. Depicted is the xy section at height $z = 0$.

the bismuth atoms are surrounded by eight R atoms in the function of a slightly elongated cube (quadratic prism), Fig. 1 (right). The antimony compounds Ce_2SbO_2 and Pr_2SbO_2 show the same building principle, at first glance, but with a strong anisotropy of the displacement parameters of the antimony atoms perpendicular to the c-axis ($U_{11} = U_{22} \sim 15U_{33}$). Refinement of the Sb atom on a split position (8i site instead of 2a) results in much better R values and the displacement parameters are more reasonable (Table 2). As a result, the Sb—Sb distances split into sets of 3.228(4) and 4.805(4) Å for Ce_2SbO_2, and 3.227(6) and 4.763(6) Å for Pr_2SbO_2, respectively. Carefully examining the diffraction data revealed super structure reflections for both antimony compounds, indicating a (4 × 4 × 1) super cell. Structure refinements on Pr_2SbO_2, carried out with and without the assumption of twinning (twinning matrix: 0 1 0; 1 0 0; $0\,0\,\bar{1}$), show that despite the large super cell dimensions there still remains a lot of disorder within the antimony layers, as can clearly be seen in electron density plots (Fig. 2). Most of the electron density accumulations, which correspond to the Sb positions, split into 2, 3 and 4 maxima, whereby the shortest Sb—Sb bonding distances are now in the range of about 3.0 Å.

The magnetic measurements indicate that all reported compounds contain rare metal cations in the trivalent state, justifying the description as $[R^{3+}]_2[Pn^{2-}][O^{2-}]_2$. The antimonides can be explained within the *Zintl–Klemm* concept, where Sb^{2-}, being isoelectronic with iodine, forms covalently bonded dimers ${Sb_2}^{4-}$, which is in agreement with semiconducting behavior of these electron precise compounds. Because of the metallic conductivity of the bismuthides the *Zintl–Klemm* concept is no longer applicable. These compounds seem to show similarities to Cu_2Sb. The latter does not consist of Cu^+, Cu^{2+} and Sb^{3-}, as expected, although this would be in accordance with its structural properties [12]. However, Cu_2Sb is diamagnetic and shows metallic conductivity. This is in agreement with the description of Cu^+ cations embedded in metallic Sb^{2-}, where the 5p electrons of antimony are the only one with appreciable contributions at the Fermi level [12]. A similar behavior may be adapted to Bi^{2-} in R_2BiO_2, where now the 6p electrons of bismuth will be responsible for the metallic behavior.

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