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Yet again, new compounds found in systems with known binary phase diagrams. Synthesis, crystal and electronic structure of Nd_3Bi_7 and Sm_3Bi_7

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The binary bismuthides Nd_3Bi_7 and Sm_3Bi_7 were synthesized and structurally characterized for the first time. The results from the calorimetric analysis show that both compounds are stable only up to about 500 °C, which may explain why they were overlooked during the original assessment of the corresponding phase diagrams.

Various solid-state compounds with the rare-earth elements (*RE*) are widely used as magnetic, catalytic and luminescent materials, and as components in construction.[1–4] We would like to bring attention to a specific sub-set of such compounds, those with the pnictogens, i.e., the elements of group 15 in the Periodic table (*Pn* = pnictogen hereafter), which offer a rich plethora of interesting properties. For example, $Yb_{14}MnSb_{11}$ was recently proposed as a highly efficient thermoelectric material at temperatures around 1000 K with the thermoelectric figure of merit zT close to 1.0 at these extreme conditions.[5] Similarly high zT values can be achieved at ca. 700 K for the rare-earth filled skutterudites REM_4Pn_{12}.[6] A number of Ce-based pnictides, such as $CeMPn_2$ (M = transition metal) exhibit heavy-fermion physics and a large variety of magnetic structures.[7–9] One cannot introduce the topic of pnictides without mentioning the superconducting iron-based arsenides which have captivated the condensed matter science communities for nearly a decade.[10]

From a more fundamental point of view, there are still vast gaps in the knowledge on the crystal chemistry of rare-earth pnictides. Whereas there are numerous studies on nitrides, phosphides, arsenides and even antimonides of the rare-earth metals, bismuthides, owing to the metallic nature of Bi, tend not to crystallize as easily as the compounds based on the lighter congeners. As a result, many multinary bismuthides that are likely to exist (based on periodic properties) are not known to date; in addition, the structures of some of them are simply "assigned" and not unambiguously established.[11,12] Even the binary *RE*–Bi systems, which appear to have been studied to a greater extent, with phase diagrams known for *RE* = La–Nd, Sm, and Gd–Lu,[13,14] can offer some surprises.

This communication details two such cases—for the very first time, we report the new binary bismuthides Nd_3Bi_7 and Sm_3Bi_7, the existence if which is *not* indicated in the corresponding phase diagrams. Both compounds were serendipitously observed as side-products during our exploratory work on bismuthides with complex structures in the ternary *RE*–*M*–Bi and quaternary Ca–*RE*–*M*–Bi systems.[15,16] Our initial efforts were focused on the synthesis of multinary bismuthides in the studied systems, since such compounds with heavy elements can display promising thermoelectric performance; high electrical conductivities and low lattice thermal conductance are the hallmark of many bismuthides with complex crystal structures. Zintl phases, i.e., electron-balanced compounds, which by definition demonstrate semiconducting properties are especially auspicious in this respect owing to the fact that they often possess an optimal combination of electronic and thermal behavior. Alongside the several multinary phases identified and reported already,[15,16] we also discovered the two new binary rare-earth-metal bismuthides, which are the subject of this communication.

Following the elucidation of the crystal structure via single-crystal X-ray diffraction methods, and the subsequent optimization of the reaction conditions, phase-pure samples were obtained by direct fusing of the elements 723 K (Fig. S1 in ESI). Needle-like single crystals with dimensions of up to several millimeters were grown from a Bi flux (see ESI for synthesis details).

The crystal structures of the newly obtained bismuthides were refined from X-ray diffraction data collected for several single crystals, picked out from different reaction batches. Nd_3Bi_7 and Sm_3Bi_7 are isotypic and crystallize in orthorhombic syngony with space group *Immm* (no. 71). Data collection details from representative crystals are tabulated in ESI. Formally, this structure can be classified with the $(U_{0.5}Ho_{0.5})_3Sb_7$ structure type (Pearson symbol *oI*40).[17]

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†Electronic Supplementary Information (ESI) available: synthesis details, single crystal X-ray diffraction, DSC, physical property measurements, first-principle calculations. See DOI: 10.1039/x0xx00000x

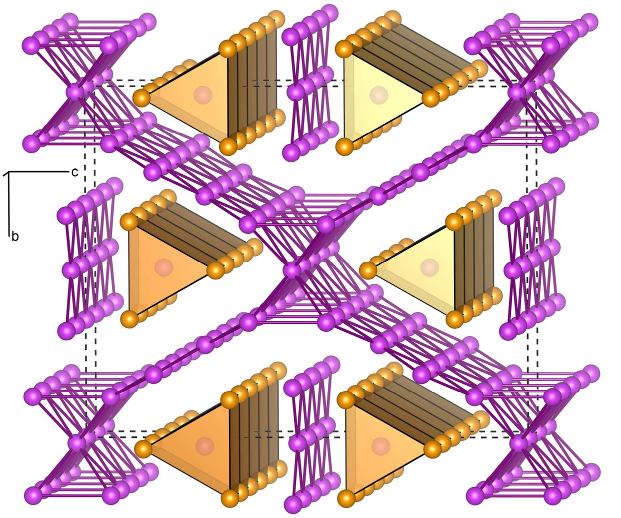

Fig. 1 Crystal structure of RE_3Bi_7 (RE = Nd, Sm). RE and Bi atoms are shown in orange and purple, respectively. The unit cell is outlined with dashed lines.

The structure is rather complex and features fully reduced Bi (the isolated Bi^{3-} anions in trigonal prismatic coordination of RE^{3+} cations, Fig.1) and extensive Bi–Bi bonding with simplest repeating units being Bi_2-dumbbells and Bi_4-squares. The Bi–Bi contacts in Nd_3Bi_7 and Sm_3Bi_7 fall in the ranges 3.18–3.46 Å and 3.16–3.44 Å, respectively, slightly shorter for the latter due to the lanthanide contraction. These values are typical for hypervalent Bi–Bi interactions.[15,18–20] As such, the Bi–Bi bonds do not satisfy the valence rules.[23] This notion is also confirmed by the analysis of the crystal structure of the prototypic $(U_{0.5}Ho_{0.5})_3Sb_7$,[17] where, U(IV) and Ho(III) are randomly mixed on the two crystallographically unique cation positions. Notice that while $(U_{0.5}Ho_{0.5})_3Sb_7$ can be viewed simply as a solid solution of U_3Sb_7 and Ho_3Sb_7 (both are not known to date), the end members will have different valence electron counts—47 e/f.u. for the former and 44 e/f.u. for the latter. Ternary derivatives of the discussed structure type are known too: $RE_6Zn_{1+x}Sb_{14}$ (RE = Sm, Gd–Ho)[24] and Ce_6ZnBi_{14}.[25] The structures of these antimonides and bismuthides accommodate interstitial Zn, occupying square-pyramidal sites between the Pn ribbons and $PnRE_6$ prisms, and tetrahedral sites between the Pn ribbons and sheets. The Zn atoms bring in extra electrons to augment the valence electron count in $RE_3Zn_{\sim 0.5}S_7$ and $Ce_3Zn_{0.5}Bi_7$ to ca. 45 e/f.u. Very similar structure is adopted by the antimonides RE_6MSb_{15} (RE = La–Pr; M = Mn, Cu, Zn, In).[26,27] The RE–Sb substructure of these phases can be constructed from the $(U_{0.5}Ho_{0.5})_3Sb_7$ type by replacing the Sb atom in the center of the unit cell by a Sb_2-dumbbell. These structurally similar antimonides also boast hypervalent bonding, which has been studied in detail on the example of La_6MnSb_{15}.[23,28]

Despite the apparent structural versatility, Nd_3Bi_7 and Sm_3Bi_7 are the only true binary compounds crystallizing in this structure. We have attempted to modulate the structure in analogy with the above-mentioned antimonides RE_6MSb_{15}, but these experiments were not successful. The RE_3Bi_7 samples produced in these reactions showed no significant variations of the unit cell parameters and the crystal structure refinements did not indicate the presence of interstitial atoms. It appears that an optimal geometric packing, i.e., proper atomic size match is realized for these two phases. Indeed, geometric constraints can be seen to play an important role in the structural stabilization, as Nd_3Bi_7 and Sm_3Bi_7 are the only two representatives among the potentially large RE_3Bi_7 family (RE = Y, La–Pr; Nd, Sm, Gd–Er, Lu).[29] All attempts to synthesize RE_3Bi_7 with other rare-earth metals failed, resulting in known binary bismuthides (see Table S1 in ESI for details). We can speculate that for the very early lanthanides, the larger size of the metals would yield too long Bi–Bi bonds in RE_3Bi_7, which in turn would destabilize the hypervalent bonding. Introduction of additional bonding interactions can counterbalance this effect, as observed for Ce_6ZnBi_{14}.[25] Similarly, contraction of the unit cell as in the case of the late rare-earth metals results in a "collapse", making RE_3Bi_7 with RE beyond Sm unstable. Here again, an insertion of interstitial atoms may stabilize the structure, the same way it is fulfilled for the antimonides $RE_6Zn_{1+x}Sb_{14}$ ($x \approx 0.5$).[24] Interestingly, for the latter, a much higher content of the interstitial metal is required in comparison with the earlier rare-earth metal antimonides RE_6MSb_{15} (RE = La–Pr; M = Mn, Cu, Zn, In)[26,27] and bismuthides (Ce_6ZnBi_{14}).[25] This is likely related to the stabilization effect stemming from the expansion of the unit cell upon insertion of additional Zn atoms, again emphasizing the importance of the size factor.

Band structure calculations were done on the hypothetical La_3Bi_7 taken as a model for the RE_3Bi_7 structure (see ESI for details). The electronic density of states (DOS) is shown in Fig. 3. Above the Fermi level (E_F), a strongly localized peak of La(4f) states is observed. Aside from this peak, the DOS in the vicinity of E_F is mainly composed of Bi(6p) and La(5d) states. The Bi(6p) states are mostly populated, whereas the La(5d) states are located predominantly above the Fermi level. However, the electron transfer from La to Bi is incomplete, as indicated by a considerable La(5d) contribution at E_F. In the region -12 eV < $E - E_F$ < -8 eV, a domain of strongly localized Bi(6s) states is evident, revealing the Bi lone pairs.[30]

The Fermi level (E_F) for La_3Bi_7 is located in a region of relatively high electronic density of states. This is indicative of metallic behavior, in line with the experimentally observed metallic properties of RE_3Bi_7 (RE = Nd, Sm). The DOS curve, however, displays a region of lower DOS just above E_F; using the rigid-band approximation, if the Fermi level were to be moved up to the pseudo-gap, the corresponding electron count will require ca. two extra electrons per formula unit.

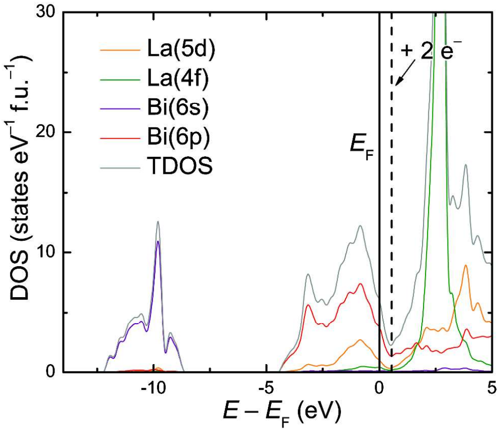

Fig. 2 Total and projected densities of states (DOS) for the hypothetical La_3Bi_7 structure.

The analysis of the chemical bonding in La_3Bi_7 (Fig. S5) suggests that the RE_3Bi_7 compounds can tolerate certain level of electron doping. More electrons in this average bonding arrangement can shift the Fermi level to region where there is a local minimum in the DOS. Since the electron doping must also destabilize the anionic Bi subunits, which are already electron-rich owing to their hypervalent nature, a Peierls-like distortion may occur leading to an opening of a bandgap. Taking into account the small thermal conductivity of the structurally related $RE_6Zn_{1+x}Sb_{14}$ (*RE* = Sm, Gd–Ho) phases,[24] such a transformation can result in promising thermoelectric properties due to an increased Seebeck coefficient in comparison with the metallic $RE_6Zn_{1+x}Sb_{14}$. In addition, an even lower lattice thermal conductivity can be expected for the bismuthides due to a larger atomic mass of Bi as compared to Sb. We believe that the optimal doping can be achieved by partial replacement of Bi by, e.g. Te, and by introduction of interstitial atoms. Obviously, electron and size factors will have to be considered to retain the structural stability.

Temperature dependence of the magnetic susceptibility of RE_3Bi_7 (*RE* = Nd, Sm) shows paramagnetic behavior at high temperatures (Fig. 2). In the case of Nd_3Bi_7, this kind of behavior persists down to 5 K with no magnetic ordering. Sm_3Bi_7 undergoes a transition of antiferromagnetic type with the Néel temperature T_N = 16 K. Fitting of the magnetic susceptibility with a modified Curie-Weiss expression $\chi = \chi_0 + C/(T-\Theta)$ yielded the magnetic moments of 3.72 μ_B and 0.81 μ_B per rare-earth atom for Nd_3Bi_7 and Sm_3Bi_7, respectively. These values are in good agreement with the theoretical moments for the Nd^{3+} (3.62 μ_B) and Sm^{3+} (0.85 μ_B) ground terms.[31] The Weiss constants Θ obtained from the fit are negative, indicating antiferromagnetic correlations. The absence of magnetic ordering in Nd_3Bi_7 and a moderately high frustration parameter $f = |\Theta|/|T_N \approx 2$ for Sm_3Bi_7 indicate some magnetic frustration, possibly originating from the triangular-like arrangement of the *RE* atoms in the RE_6Bi prisms.

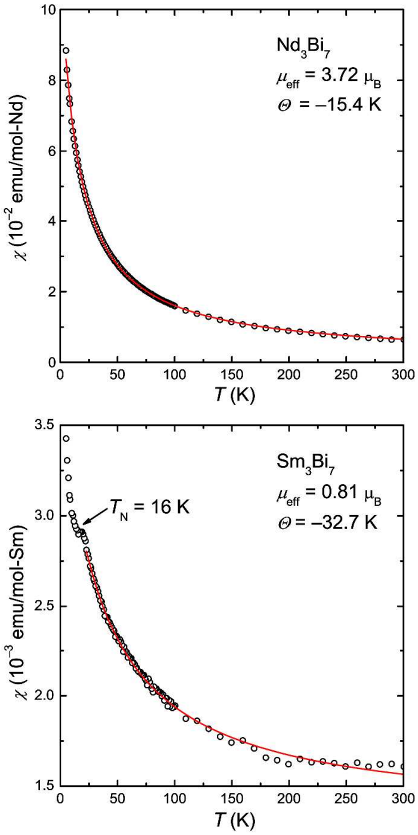

Fig. 3 Temperature dependence of magnetic susceptibility for RE_3Bi_7 (*RE* = Nd, Sm) under applied field of 5000 Oe. Red line – fit with a modified Curie-Weiss expression.

Electrical resistivity measurements on the single crystals of RE_3Bi_7 (*RE* = Nd, Sm) revealed bad metallic behavior (Fig. 3). At room temperature, the resistivity of the Nd sample was found to be about three times higher than that of the Sm phase, likely due to a stronger scattering of charge carriers by the localized magnetic moments of Nd^{3+}.

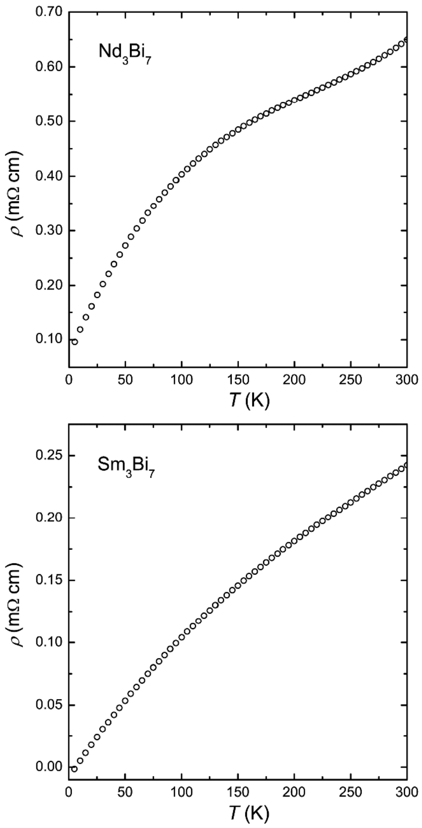

Fig. 4 Temperature dependence of electrical resistivity for RE_3Bi_7 (RE = Nd, Sm).

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Conflicts of interest

There are no conflicts to declare.

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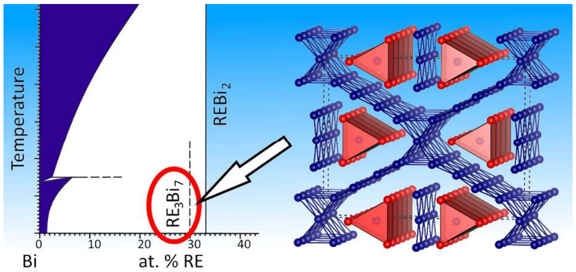

Reported, for the very first time, are the synthesis and structures of two new compounds, discovered in well-studied binary phase diagrams.