Ruthenium Intermetallics Grown from La-Ni Flux: Synthesis, Structure, and Physical Properties

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Introduction
La/Ni flux is composed of a highly reactive metal (lanthanum) together with a more inert component (nickel). When combined in a 88/12 wt. % ratio, these metals form a low-melting eutectic. Reactions of iron in this flux predominantly yield La/Fe/X phases, with no nickel incorporation. Syntheses with ruthenium were carried out to determine if this trend would also be seen with iron’s heavier congener. An interesting aspect of two-component flux systems is their ability to dissolve normally intractable elements. Carbon readily dissolves in La/Ni flux, and we are now finding that the solubilizing effect can be extended to boron. In the course of our exploratory synthesis aiming to produce new borides of ruthenium, we discovered three new compounds LaRu$_2$Al$_2$B, La$_2$Ni$_{2-x}$Ru$_x$Al, and La$_6$SnNi$_4$Ru$_{0.4}$Al$_{3.6}$.

Experimental
La, Ru, Sn, B, mixed in 1:1:1:1 mmolar ratio, were sandwiched between layers of La/Ni eutectic (~1.2 g) in an alumina crucible, which was placed in a silica tube. A second alumina crucible was filled with Fiberfrax and inverted above the reaction crucible to act as a filter during centrifugation. The silica tube was fused under vacuum of 10$^{-2}$ Torr; the ampoule was then heated to 1000 °C in 3 h, then cooled slowly to 600 °C in 6 days. At 600 °C the ampoule was removed from the furnace, inverted, and centrifuged for decanting of the molten flux. The slightly air-sensitive products were characterized using SEM-EDS for elemental analysis and single crystal XRD for structure determination. The boride LaRu$_2$Al$_2$B was further characterized using SQUID magnetometry, calculations of density of states and electron localization function, and heat capacity measurements (using the PPMS system in the Applied Superconductivity Center).

Results and Discussion
Crystals of three new intermetallic compounds were grown from reactions of ruthenium with other elements in La$_{0.8}$Ni$_{0.2}$ eutectic flux. The new boride LaRu$_2$Al$_2$B crystallizes in a filled CeMg$_2$Si$_2$ structure type (P4/mmm, a = 4.2105(5) Å, c = 5.6613(8); Z = 1, $R_1$ = 0.014), with Ru atoms forming a planar square net; B atoms center alternating Ru squares, which is an unusual coordination of boron by transition metals. Al atoms connect the Ru$_2$B layers, forming large voids where La ions reside. The chemical bonding analysis using electron localization function (ELF) reveals two-center covalent bonding between Al atoms, an absence of direct Ru-Ru interactions, and multi-centered bonds between Ru and B or Al atoms. The band structure calculation shows LaRu$_2$Al$_2$B to be metallic, which is in agreement with the observed temperature independent paramagnetism and heat capacity data. The crystal structure of La$_2$Ni$_{2-x}$Ru$_x$Al (HT-Pr$_2$Co$_2$Al-type; $x = 0.21(1)$ and $x = 0.76(1)$; C2/c; $a = 9.9001(3)$ Å, $b = 5.7353(1)$ Å, $c = 7.8452(2)$ Å, $\beta = 104.275(1)$; Z = 4, $R_1 = 0.016$ for $x = 0.76(1)$) features infinite [Ni$_2_x$Ru$_x$Al] spiral-twisted chains composed of Al$_2$M$_2$-rhombic units (M = Ni/Ru) seen in many La-Ni-Al intermetallics. The structure of La$_6$SnNi$_4$Ru$_{0.4}$Al$_{3.6}$ (Nd$_6$Co$_5$Ge$_2$-type; $P6m2$, $a = 9.620(1)$ Å, $c = 4.2767(9)$ Å; Z = 1, $R_1 = 0.015$) is comprised of a three-dimensional [Ni$_4$Ru$_{4.3}$Al$_{1.5}$]$_3^\infty$ network with large hexagonal channels accommodating interconnected tin-centered lanthanum clusters Sn@La$_9$.

Conclusions
La/Ni eutectic is an excellent solvent for a wide range of elements, and a rich growth medium for new materials. It is a reactive flux, producing lanthanum-containing polar intermetallic products. We are still working to determine the conditions under which the nickel component of the flux is inert. Synthesis of new borides in this medium may lead to phases displaying behavior such as superconductivity or metal-insulator transitions.

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References