Polymeric Precursor Synthesis of the Superconducting Metal Boronitride $La_3Ni_2B_2N_3$

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The recent discovery of superconductivity in a variety of quaternary metal borocarbides[3] (including RPt_2B_2C, R = Y, La, Pr; and RNi_2B_2C, R = Y, Tm, Er, Ho, Lu, Ln) and the metal boronitride, $La_3Ni_2B_2N_3$[4] (Figure 1) has spurred interest in the development of systematic methods for the preparation of boron-containing intermetallic compounds. While the metal borocarbides can be readily prepared by the direct reaction of the elements, the synthesis of $La_3Ni_2B_2N_3$ has required the high-temperature arc-melting of La, Ni, and B powders in a N_2 atmosphere. This process is limited to small scales and has the inherent difficulty of controlling the nitrogen content of the product due to the gas/solid reaction.

The discovery[5] that titanium nitride/titanium boride composites could be synthesized by the pyrolysis of titanium powder dispersed in the boron−nitrogen polymer polyborazylene, $[B_3N_3H_{\sim 4}]_x$,[6] suggested that ternary or quaternary metal boronitrides could also be synthesized in a similar manner. Indeed, we report here the convenient preparation of $La_3Ni_2B_2N_3$ from the 1000 °C pyrolysis of lanthanum and nickel powders dispersed in polyborazylene, as indicated in eq 1.

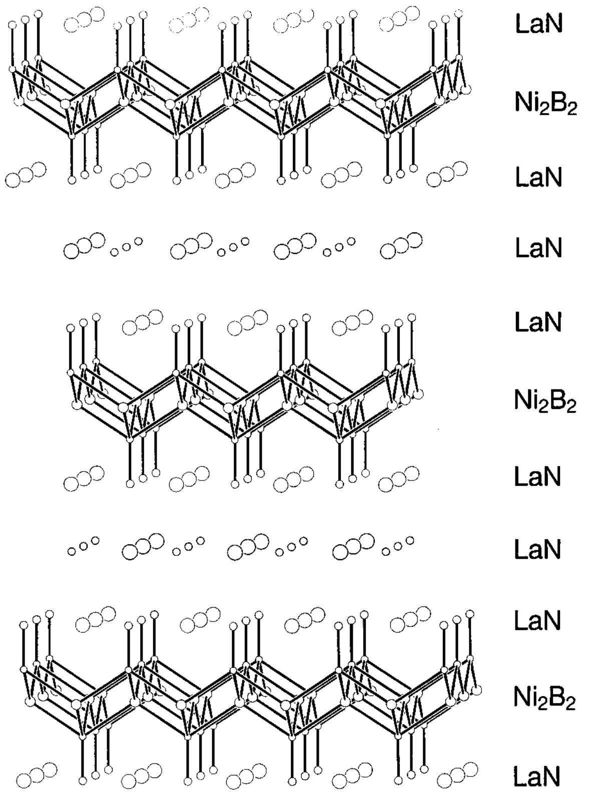

Figure 1. Stucture of the $La_3Ni_2B_2N_3$ lattice.[4]

$$3La + 2Ni + [B_3N_3H_{\sim 4}]_x \xrightarrow[-H_2]{1000\ °C,\ Ar} La_3Ni_2B_2N_3 + B \qquad (1)$$

In a typical reaction, 5.53 g (39.8 mmol) of lanthanum powder (Alpha/AESAR, 250 mesh, 99.9%), 1.55 g (26.4 mmol) of nickel powder (Alpha/AESAR, 2.5−3 μm, 99.99%), and 1.14 g (~14.5 mmol of borazinyl units) of $[B_3N_3H_{\sim 4}]_x$ were charged under an inert atmosphere into a 100 mL one-piece glass reaction flask equipped with a high-vacuum stopcock. The flask was sealed, removed to a vacuum line, and evacuated, and ~10 mL of glyme was vacuum transferred into the flask at −196 °C. Upon warming to room temperature, the polymer dissolved and the mixture was sonicated for 30 min (67 kHz, 200 W) at room temperature while the solvent was slowly evaporated. The sample was further dried at 70 °C for 12 h in vacuo. The material was then removed from the flask under an inert atmosphere and isolated as a dark gray solid. The powder XRD spectrum of the polyborazylene/metal dispersion showed diffraction from only La and Ni.

Pyrolysis of a 1.72 g sample of the polyborazylene/metal dispersion at 1000 °C under argon (99.999%) for 48 h produced $La_3Ni_2B_2N_3$ in high ceramic (1.68 g, 97.7%) and nearly quantitative chemical (98.4%) yields. Elemental analyses show retention of nitrogen and are consistent with the $La_3Ni_2B_2N_3$ stoichiometry: Anal. Calcd for $La_3Ni_2B_2N_3$: La, 69.71%; Ni 19.64%; B, 3.62%; N, 7.03%. Anal Fd: La, 69.7%; Ni 16.7%; N, 5.49%. The powder XRD spectrum of this material[7] (Figure 2a) agrees with both the theoretical pattern (Figure 2b) generated[8] from the previously reported[4b] atomic coor-

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(7) XRD spectra of the mixture sintered for only 1 h showed the $La_3Ni_2B_2N_3$ phase, but with slightly lower crystallinity.

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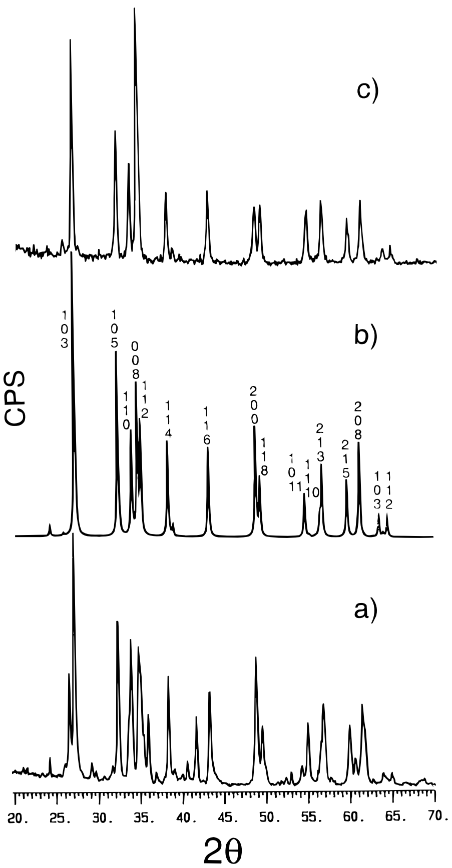

Figure 2. Powder XRD spectra of $La_3Ni_2B_2N_3$ (a) prepared by the polymer precursor route, (b) generated[8] from the previously reported[4b] atomic coordinates, and (c) prepared by arc melting.[4a]

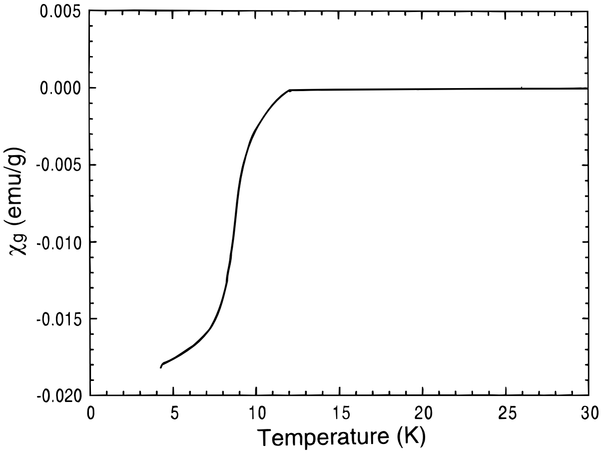

Figure 3. Temperature-dependent ac susceptibility of $La_3Ni_2B_2N_3$ prepared by the polymer precursor route.

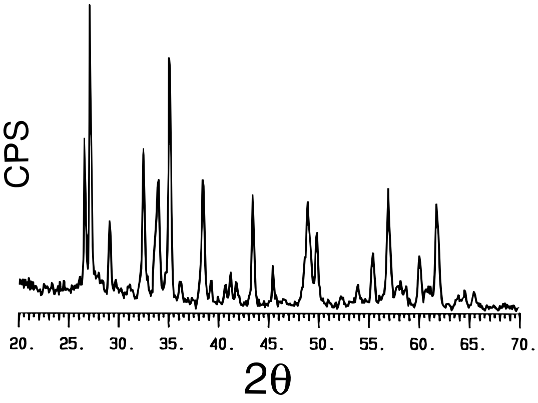

Figure 4. Powder XRD spectrum of $La_3Co_2B_2N_3$.

dinates of $La_3Ni_2B_2N_3$, as well as the spectrum (Figure 2c) from an authentic sample prepared by the arc-melting process.[4a] Consistent with the fact that the polymer contains excess boron compared to the $La_3Ni_2B_2N_3$ stoichiometry, small amounts of impurities were observed in the XRD spectra. However, these could not be matched to any known phase on the JCPDS data base.

Diffuse reflectance infrared (DRIFT) spectra of the mixture sintered to 1000 °C showed no B−H, N−H, or B−N stretches characteristic of polyborazylene suggesting that the ceramic conversion was complete. Furthermore, the absence of the B−N stretch also indicated that boron nitride, which is the pyrolysis product of pure polyborazylene,[6] was not present in the sample.

The ac susceptibility (Figure 3) of the mixture pyrolyzed to 1000 °C, measured in a Lake Shore Cryogenics susceptometer at an 0.1 Oe applied field, showed a T_c slightly over 12 K with a large shielding signal (approximately 100%), with the majority of the transition near 9 K. The relative broadness of the transition could be due to poor connectedness between small superconducting crystallites or could represent a true nitrogen nonstoichiometry, as has been observed in a refinement of the structure by powder neutron diffraction (REF).[9]

The 1000 °C pyrolysis of a Ni/polyborazylene dispersion produced only BN and Ni, with no binary or ternary metal containing phases. The 1000 °C pyrolysis of a mixture of a La/polyborazylene, however, produced both LaN (JCPDS Card No. 15-0892c) and LaB_4 (JCPDS Card No. 24-1015I). Powder X-ray diffraction of a La/Ni/polyborazylene dispersion pyrolyzed to only 600 °C for 1 h under argon showed the formation of LaN. It therefore appears that the initial formation of the LaN rock-salt layers (Figure 1), which determine the *a* and *b* cell contants,[4b] is an important step in the formation of the $La_3Ni_2B_2N_3$ intermetallic. A key point that enables this reaction is that polyborazylene functions as a solid-state source of nitrogen that is reactive at moderate temperatures.

The above results further suggest that the pyrolysis of other lanthanum/transition metal dispersions in polyborazylene could serve as a precursor route to a range of metal boronitrides, and we have, in fact, used this approach to prepare the previously unknown $La_3Co_2B_2N_3$ by the 1200 °C pyrolysis of lanthanum/cobalt/polyborazylene dispersions. Since the covalent radii of cobalt and nickel are nearly identical (1.16 vs 1.15 Å), the powder XRD pattern of the $La_3Co_2B_2N_3$ (Figure 4) is very similar to the $La_3Ni_2B_2N_3$ spectrum (Figure 2a). Initial magnetic susceptibility measurements for the $La_3Co_2B_2N_3$ material showed no superconducting transition above 4 K.

Although initial attempts to form $Y_3Ni_2B_2N_3$, $La_3Fe_2B_2N_3$, and $La_3Cu_2B_2N_3$ have not yet been successful, we are currently investigating using this approach to produce other unknown $Ln_3M_2B_2N_3$ [Ln = La, Y and M = Pd, Pt, Rh, Fe, Ag, Cu] phases.

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[8] Theoretical diffraction spectra were generated using Cerius^2 Molecular Simulations software.

[9] Huang, Q.; Chakoumakos, B. C.; Santoro, A.; Cava, R. J.; Krajewski, J. J.; Peck, W. F., Jr. *Physica* **1995**, *244C*, 101.

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