

The effect of Li₃N addition by mechanical alloying on Nd₂Fe₁₄B—Formation of NdN₂

J. Tang, J. E. Troupe, C. J. O'Connor, A. U. Falster, and W. B. Simmons Jr.

Citation: *Journal of Applied Physics* **73**, 6485 (1993); doi: 10.1063/1.352588

View online: <http://dx.doi.org/10.1063/1.352588>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/73/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Texture formation of hot-deformed nanocomposite Nd₂Fe₁₄B/ \$\alpha\$ -Fe magnets by Nb and Zn additions](#)
J. Appl. Phys. **115**, 17A704 (2014); 10.1063/1.4860942

[Neutron diffraction analysis of melt spun 2:14:1 type \(NdPr\)—Fe—B compounds with Ti and Zr additions](#)
J. Appl. Phys. **91**, 7878 (2002); 10.1063/1.1453337

[Structure and magnetic properties of N-containing Nd—Fe—B alloys prepared by mechanical alloying](#)
J. Appl. Phys. **87**, 5332 (2000); 10.1063/1.373338

[Longterm stability of FeBNdDy alloys made by Dy₂O₃ additions](#)
J. Appl. Phys. **64**, 5311 (1988); 10.1063/1.342402

[Formation and properties of NdFeB prepared by mechanical alloying and solidstate reaction](#)
J. Appl. Phys. **61**, 3583 (1987); 10.1063/1.338708



Not all AFMs are created equal
Asylum Research Cypher™ AFMs
There's no other AFM like Cypher

www.AsylumResearch.com/NoOtherAFMLikeIt

OXFORD
INSTRUMENTS
The Business of Science®

The effect of Li_3N addition by mechanical alloying on $\text{Nd}_2\text{Fe}_{14}\text{B}$ —Formation of NdN_2

J. Tang and J. E. Troupe

Department of Physics, University of New Orleans, Lakefront, New Orleans, Louisiana 70148

G. J. O'Connor

Department of Chemistry, University of New Orleans, Lakefront, New Orleans, Louisiana 70148

A. U. Falster and W. B. Simmons, Jr.

Department of Geology and Geophysics, University of New Orleans, Lakefront, New Orleans, Louisiana 70148

Curie temperatures of R_2Fe_{17} and RTiFe_{11} (R=rare earths) can be raised drastically by addition of interstitial nitrogen. Can one see similar effects in $\text{Nd}_2\text{Fe}_{14}\text{B}$? This question is particularly interesting because $\text{Nd}_2\text{Fe}_{14}\text{B}$'s relatively low Curie temperature has limited its applications in high temperature operations. Nitrogen additions by heat treating $\text{Nd}_2\text{Fe}_{14}\text{B}$ in flowing N_2 at different temperatures have been reported to raise its Curie temperature by 20–50 °C. We report an attempt of nitriding $\text{Nd}_2\text{Fe}_{14}\text{B}$ by mechanical alloying it with Li_3N . Our attempt resulted in the formation of a rare form of neodymium nitride, NdN_2 . The original goal to nitride $\text{Nd}_2\text{Fe}_{14}\text{B}$ by mechanical alloying it with Li_3N seems to be inapplicable.

$\text{Nd}_2\text{Fe}_{14}\text{B}$, discovered in 1981 by Croat,¹ possesses excellent permanent magnetic properties and is an ideal material to replace the most used Sm-Co magnets. However, a serious drawback of $\text{Nd}_2\text{Fe}_{14}\text{B}$ is its low operating temperature, i.e., the coercivity decreases so rapidly with increasing temperature that the practical operating temperature is only about 100 °C.² On the other hand, it was recently discovered that interstitial nitrogen addition to R_2Fe_{17} (R=rare earths) could raise its Curie temperature T_c by approximately 400 °C.³ A drastic increase in T_c (~200 °C) was also observed in RTiFe_{11} upon absorption of nitrogen.⁴ An obvious question is then how such nitrogen addition will affect the Curie temperature of $\text{Nd}_2\text{Fe}_{14}\text{B}$. Nitrogen addition by heat treating $\text{Nd}_2\text{Fe}_{14}\text{B}$ samples in flowing N_2 at different temperatures could only raise its T_c by 20–50 °C,^{5–7} possibly due to the limited number of nitrogen atoms going into the $\text{Nd}_2\text{Fe}_{14}\text{B}$ lattice. As a matter of fact, the interstitial sites available to nitrogen in $\text{Nd}_2\text{Fe}_{14}\text{B}$ are smaller in size and less in number than those in R_2Fe_{17} and RTiFe_{11} .⁸ It is unclear yet if the nitrogen atoms occupy interstitial or substitutional sites in $\text{Nd}_2\text{Fe}_{14}\text{B}$.

We report an attempt to improve the solubility of nitrogen in $\text{Nd}_2\text{Fe}_{14}\text{B}$, that is to nitride nanocrystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$ by mechanical alloying it with Li_3N . This approach is based upon the following observations and arguments. First, mechanical alloying offers one of the few methods for mixing two ordinarily immiscible materials.⁹ This is probably due to the intimate contact between two components and subsequent imbedding of one component into another brought by the high energy ball-sample-container collisions during mechanical alloying. We expect that mechanical alloying will increase the solubility of nitrogen in $\text{Nd}_2\text{Fe}_{14}\text{B}$. Second, Li_3N will be used as the source to provide nitrogen in a condensed state. Because of the relatively weak bonding in Li_3N , a possible solid state displacement reaction, i.e., reduction of Li_3N to pure Li and formation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ nitride, is anticipated. In fact, mechanical alloying induced displacement reactions have

been reported in several publications.^{10–12} Third, it is well known that mechanical alloying produces nanocrystalline particles.¹³ Such extremely fine particles will enhance the possibility that nitrogen atoms go into the bulk of sample during mechanical alloying. It will also maximize the reaction rate by providing a larger surface area.

The $\text{Nd}_2\text{Fe}_{14}\text{B}$ sample was prepared from elements by melting the constituents in an arc furnace under argon partial pressure. The amount of iron used was 9% less than the ideal 2:14:1 ratio, i.e., the actual atomic ratio Nd:Fe:B was 2:12.7:1. This was to minimize the amount of α -Fe that would be present in the product. During arc melting sample was turned over and remelted several times in order to reach homogeneity. After cooling down to room temperature, the sample was sealed in a quartz tube under helium atmosphere and heated to and maintained at 1100 °C for 2 h, and then quenched into a water bath. X-ray diffraction pattern of the powder sample was obtained using a SCINTAG diffractometer, and it showed the formation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase [see Fig. 1(a)]. A small amount of bcc α -Fe was still present as indicated by the peak marked in Fig. 1(a).¹⁴

Prior to mechanical alloying, an attempt was made to heat directly the mixture of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Li_3N powders in a sealed quartz tube under helium atmosphere to see if the anticipated displacement reaction would occur. Such attempts resulted in explosions as soon as the temperature reached near 400–500 °C due to decomposition of Li_3N . Therefore, a low temperature synthesizing process seemed to be necessary in order to overcome the problems associated with the decomposition of Li_3N . Mechanical alloying could offer us a possible solution because it is a low temperature process. As a matter of fact, mechanical alloying is normally conducted at room temperature, and the maximum local temperature where the ball-sample-container collision takes place is less than 300 °C.⁹ As will be seen later, however, our study indicated that mechanical alloying probably led to the decomposition of Li_3N as well.

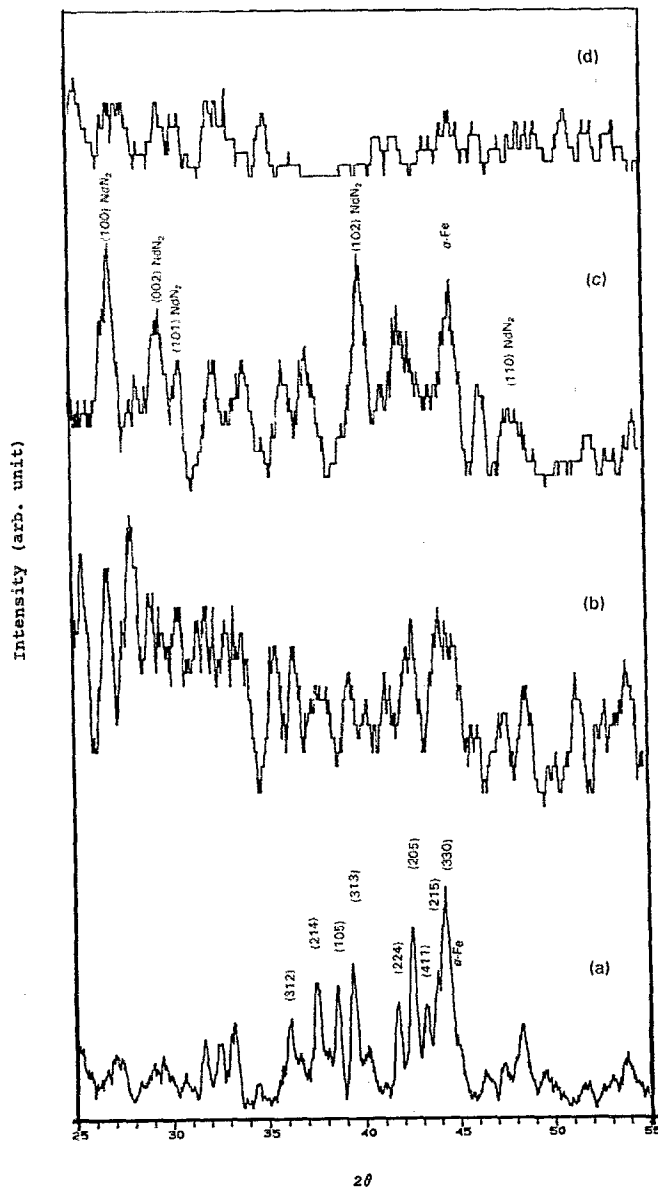


FIG. 1. (a) X-ray diffraction pattern of $\text{Nd}_2\text{Fe}_{14}\text{B}$; (b), (c), and (d) are the x-ray patterns of $\text{Nd}_2\text{Fe}_{14}\text{B-Li}_3\text{N}$ samples after 1, 5, and 26 h of mechanical alloying, respectively.

Mechanical alloying was carried out as follows. Powders of $\text{Nd}_2\text{Fe}_{14}\text{B}$ (obtained as described above) and Li_3N (purchased from Johnson Matthey) were mixed at a weight ratio of 8:1. This weight ratio corresponds to a molar ratio of about $\text{Nd}_2\text{Fe}_{14}\text{B}:\text{Li}_3\text{N}=1:4$. The mixture was poured into a tungsten carbide (WC) vial in a glovebox and sealed in an argon atmosphere. Also sealed in the WC vial was a 11-mm-diam WC ball. The weight ratio of ball to sample was about 2:1. The powders were mechanically alloyed by milling with a Spex 8000 mixer/mill. A portion of the sample was taken out for x-ray examination after milling for 1 and 5 h, respectively, and the remaining were milled again until a total of 26 h had been reached. Because the mechanical alloyed samples were very reactive in the air, they were loaded on the diffractometer sample

holder with N_2 flowing around them. During x-ray experiments sample chamber was kept under N_2 atmosphere.

Figures 1(b)–1(d) show the x-ray patterns of $\text{Nd}_2\text{Fe}_{14}\text{B-Li}_3\text{N}$ samples after 1, 5, and 26 h of mechanical alloying, respectively. The sample after 1 h of mechanical alloying had a rather complex x-ray pattern [Fig. 1(b)]. Although peaks from $\text{Nd}_2\text{Fe}_{14}\text{B}$ could still be identified, their intensities were reduced compared to that of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ sample before mechanical alloying. The appearance of some new phases is obvious as seen from the added peaks in its x-ray spectrum. These new phases are believed to be the combinations of NdN_2 (see below), Li_3N , $\alpha\text{-Fe}$, and some unidentified intermediate phases.

Figure 1(c) is the x-ray pattern of the sample after 5 h of mechanical alloying. This sample had a relatively well-defined x-ray spectrum. As a matter of fact, all of the major peaks in the spectrum could be indexed as the ones from hexagonal NdN_2 and bcc $\alpha\text{-Fe}$. The formation of NdN_2 and the substantial increase in the intensity of $\alpha\text{-Fe}$ peak indicated that $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Li_3N reacted in such a way during mechanical alloying that $\alpha\text{-Fe}$ precipitated out from the matrix and the excess neodymium formed NdN_2 . NdN_2 , which crystallizes in hexagonal La_2O_3 -type structure with lattice parameters $a=3.79 \text{ \AA}$ and $c=5.99 \text{ \AA}$, was first synthesized from Nd and N_2 under high pressure (30–300 atm) in an autoclave.¹⁵ We believe that the condition inside the WC vial during mechanical alloying was reminiscent of that in the autoclave. The high energy ball milling first led to the decomposition of Li_3N into Li and N_2 , and then N_2 pressure gradually built up as a result of the continuation of such decomposition. At the same time, reaction between N_2 and $\text{Nd}_2\text{Fe}_{14}\text{B}$ resulted in the precipitation of $\alpha\text{-Fe}$ and made the neodymium, probably in the form of NdN , available to further combine with pressured N_2 to form NdN_2 .

Shown in Fig. 1(d) is the x-ray pattern of the sample after 26 h of mechanical alloying. Those peaks from NdN_2 and $\alpha\text{-Fe}$ were smeared out, and virtually no peak was present at all. This represents the situation where the sample, after 26 h of mechanical alloying, has been ground into extremely fine particles, perhaps in the nanometer range, as reported in other cases.¹³ This sample could consist of nanocrystalline particles of NdN_2 , $\alpha\text{-Fe}$, and some minor impurity phases. There was no evidence that any substantial amount of $\text{Nd}_2\text{Fe}_{14}\text{B}$ was left in the sample. The magnetic measurement confirmed this conclusion. $\text{Nd}_2\text{Fe}_{14}\text{B}$ was, however, present in the sample after 5 h of mechanical alloying as shown in Fig. 1(c).

Magnetization M was measured as a function of temperature T from room temperature to $\sim 600 \text{ }^\circ\text{C}$ using a Faraday magnetometer. The magnetic field used was about 1 kG. Figure 2(a) shows the M vs T plot for the sample after 26 h of mechanical alloying. Because this sample is air sensitive, it was sealed in a small quartz tube during measurement. For comparison, the M vs T curve for a sample undergone no mechanical alloying (as quenched) is also shown [Fig. 2(b)]. The transition temperature of $310 \text{ }^\circ\text{C}$ for the as-quenched sample was consistent with the reported value of the Curie temperature of $\text{Nd}_2\text{Fe}_{14}\text{B}$. The

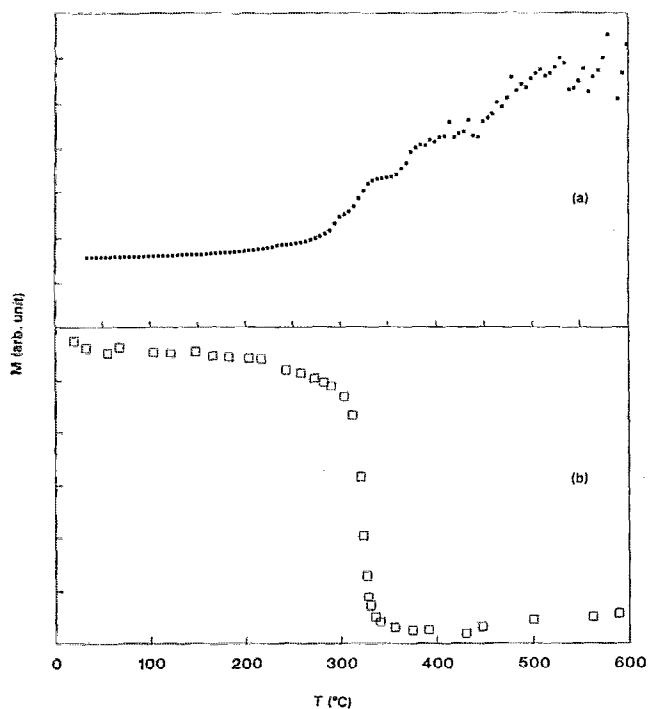


FIG. 2. (a) M vs T plot for the sample after 26 h of mechanical alloying; (b) the same plot for the as-quenched $\text{Nd}_2\text{Fe}_{14}\text{B}$ sample.

effect of the mechanical alloying was evident, i.e., there was no substantial amount of $\text{Nd}_2\text{Fe}_{14}\text{B}$ left after 26 h of mechanical alloying. This is seen from the absence of any drop in the M vs T curve near 310°C . The curving up above 300°C is probably due to the further alignment of the iron magnetic moments in the nanocrystalline particles, whose lattice relaxed from strain and allowed the realignment of iron moments as the result of increased temperature. Another possibility is that there was still some remaining $\text{Nd}_2\text{Fe}_{14}\text{B}$, and upon heating it decomposed into $\alpha\text{-Fe}$ and led to an increased M .

In summary, a rare form of neodymium nitride, NdN_2 , was synthesized as the result of mechanical alloying $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Li_3N . The original goal to nitride $\text{Nd}_2\text{Fe}_{14}\text{B}$ by mechanical alloying it with Li_3N seems to be inapplicable.

The authors wish to thank M. D. Davis, J. H. Zhang, and Y. S. Lee for their assistance in carrying out some of the experiments. This work was supported by the Louisiana Board of Regents and the National Science Foundation through the Louisiana Stimulus for Excellence in Research: the Louisiana EPSCoR Program, under Contract No. NSF/LaSER(1991)-RCD-06.

- ¹J. J. Croat, *Appl. Phys. Lett.* **39**, 357 (1981).
- ²R. Grossinger, *Modern Magnetic Materials*, Conf. Proceed., ERA No. Report 89-0278, (ERA Technol., Leatherhead, UK, 1989), 5.3/1-10.
- ³H. Sun, J. M. D. Coey, Y. Otani, and D. P. F. Hurley, *J. Phys. Condens. Matter* **2**, 6465 (1990).
- ⁴Y. Yang, X. Zhang, L. Kong, Q. Pan, and S. Gen, *Solid State Commun.* **78**, 317 (1991).
- ⁵M. Iwata and H. Harada, *Jpn. Kokai Tokyo Koho JP* 60, 176, 202.
- ⁶Y. Yang, S. Ge, X. Zhang, L. Kong, Q. Pan, Y. Hou, S. Huang, and L. Yang, *Proceedings of the 6th International Symposium on Magnetic Anisotropy and Coercivity in Rare Earth-Transition Metal Alloys* (Carnegie Mellon University Press, Pittsburgh, PA, 1990), p. 190.
- ⁷J. Tang, J. H. Zhang, and C. J. O'Connor, *Rare Earths, Resources, Science, Technology and Applications*, edited by R. G. Bautista and N. Jackson, (TMS, Warrendale, PA, 1991), p. 165.
- ⁸J. F. Herbst, *Rev. Mod. Phys.* **63**, 819 (1991).
- ⁹C. C. Koch, *Annu. Rev. Mater. Sci.* **19**, 121 (1989).
- ¹⁰G. B. Schaffer and P. G. McCormick, *Metall. Trans. A* **21**, 2789 (1990).
- ¹¹K. Tokumitsu, *J. Less-Common Metals* **172-174**, 153 (1991).
- ¹²E. P. Yelsukov, V. A. Barinov and L. V. Ovetchkin, *J. Mater. Sci. Lett.* **11**, 662 (1992).
- ¹³F. H. Froes, C. Suryanarayana, G.-H. Chen, A. Frefer, and G. R. Hyde, *J. Miner., Metals, Mater. Soc.* **44**, 26 (1992).
- ¹⁴M. Sagawa, S. Fujimura, M. Togawa, H. Yamamoto, and Y. Matsuura, *J. Appl. Phys.* **55**, 2083 (1984).
- ¹⁵R. Kieffer, P. Ettmayer, and S. Pajakoff, *Monatshefte Fuer Chem.* **103**, 1285 (1972).