Novel High Energy Density Materials: Synthesis by Megabar Hot Pressing

H.E. Lorenzana, C.S. Yoo, M. Lipp, T. Barbee, III,
A.K. McMahan and C. Mailhot

RECEIVED

MAY 17 1996

OSTI

April 1996

Lawrence
Livermore
National
Laboratory

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (615) 576-8401, FTS 626-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

LDRD Final Report
(tracking code number 93-ERP-046)

**Novel High Energy Density Materials:
Synthesis by Megabar Hot Pressing**

H. E. Lorenzana, C. S. Yoo, M. Lipp, T. Barbee, III,
A. K. McMahan, and C. Mailhot

Lawrence Livermore National Laboratory
Livermore, CA 94550

Introduction

The goal of this work was to demonstrate proof-of-principle existence of a new class of high energy density materials (HEDM's). These proposed novel solids are derived from first and second row elements arranged in an uniform, three-dimensional network. Thus, every bond in these systems is energetic, in contrast to conventional energetic materials that store energy *only* within individual molecules. Recent predictions have suggested that a number of possible compounds including a polymeric form of nitrogen can be synthesized at high pressures and recovered metastably at ambient conditions. Specifically, polymeric nitrogen is predicted to have an energy density about *three times* that of a typical explosive.¹ Such extended solid HEDM's offer dramatic new opportunities as explosives, monopropellants, or as environmentally clean fuels. We utilized the laser heated diamond anvil cell as the synthesis route for establishing proof-of-principle existence. We conducted high pressure studies of pure molecular nitrogen samples and completely revised the previously published equation-of-state. We also pursued studies of carbon monoxide, a compound that is isoelectronic with nitrogen and exhibits very similar high pressure phase transformations. Carbon monoxide polymerizes under pressure into a solid that can be recovered and may be energetic.

Concept

Current conventional energetic compounds such as gasoline and liquid H_2/O_2 rely on strong covalent bonds *within* individual molecules for primary energy storage (Fig. 1a). These molecular liquids or solids are characterized by large equilibrium volumes resulting from weak bonds between neighboring molecules. These weak bonds—otherwise known as Van der Waals interactions—do not play a role in energy storage. Our goal was proof-of-principle synthesis of new compounds that achieve an unprecedented enhancement in energy density by completely replacing these weak interactions with highly energetic covalent bonds (Fig. 1b).

Figure 1. Concept of an energetic extended solid. (a) Conventional systems utilize only internal bonds for energy storage. (b) Extended solids replace weak, external bonds with energetic, covalent bonds, thereby increasing energy density.

Recent theoretical studies indicate that solid-state phases having such uniform and continuously bonded networks (extended solids²) offer entirely new and unexplored opportunities as novel energetic

materials.^{1, 3-7} These novel systems represent the analog of *infinite*, energetic molecules. Examples include a polymeric form of nitrogen,¹ an aluminum-like body-centered tetragonal (bct) phase of boron⁶, a distorted tetrahedrally coordinated form of carbon (bc8 C),^{5, 7} and the elusive monoatomic phase of hydrogen. We believe that hydrides of beryllium⁹ and boron offer related opportunities.¹⁰ The result is extended solid phases that have significantly *smaller volumes*, and correspondingly larger energy densities. Specifically, recent theoretical studies have predicted energy densities of 34, 26, and 21 KJ/cm³ for polymeric nitrogen,¹ metallic bct boron,⁶ and bc8 carbon,⁷ respectively. In comparison, the explosive HMX contains 12 KJ/cm³.

Synthesis route: The energetic phases presented here are actually the thermodynamically favored phases at high pressures, as calculated by theory. The megabar diamond anvil cell is, therefore, the perfect avenue for establishing proof-of-principle synthesis. High pressures is well known to greatly alter chemical bonds and the electronic nature of substances. Therefore, high pressure synthesis followed by pressure quenching is a natural processing route, especially since the stability fields of polymeric nitrogen and metallic boron are within current diamond anvil cell capabilities.

Energy Barriers: Energy barriers play a key role in our attempts to synthesize polymeric nitrogen using high pressures. Our most comprehensive *ab initio* total-energy calculations place the equilibrium phase boundary between the diatomic and the polymeric regimes near 650 kbar at room temperature.¹ On a surface like that sketched in Fig. 2, the metastable phase (higher energy state) would spontaneously decay to the stable phase (lowest energy state) were it not for the energy barrier. This barrier leads to metastability or hysteresis so that the diatomic $\rightarrow$ polymeric transition should occur at a *much higher* pressure than 650 kbar, while the reverse polymeric $\rightarrow$ diatomic transition should occur at a *much lower* pressure than 650 kbar. Our calculations support this scenario, and we predict that the polymeric phase should be stable *even at 1-atm*.^{1, 8}

Figure 2. Metastability of polymeric nitrogen. Metastable phase is higher in energy but conversion to the stable state is hindered by an energy barrier.

Experimental Techniques

Over the last two decades, the range of static pressures possible in a diamond-anvil cell has increased dramatically by approximately an order of magnitude. As a consequence, we can now vary

pressure pretty much as easily as temperature.⁹⁻¹¹ Judging from the predicted equilibrium phase boundaries between polymeric versus diatomic forms of nitrogen (~65 GPa),¹ or metallic versus covalent forms of boron (~210 GPa),⁶ this unique technique can create conditions which approach the stability limits of the very bonds one seeks to change. Combined with more recent but still well-established laser-heating methods which can be used to exceed residual energy barriers, one has the prospect of "hot pressing" at megabar pressures, a *truly unique* and largely unexplored materials synthesis and processing capability.¹² While limited to small (~50 μm) samples, the strength of such a facility lies in its diagnostic versatility combined with the capability of systematic exploration over a wide temperature-pressure regime. Such experiments are therefore ideally suited to proof-of-existence demonstrations coupled with wide-ranging material characterization, including stability and metastability fields, the results of which might then be used in the design of production scale-ups using alternate techniques such as large volume presses or shock-wave gas guns.

Of key importance in this study were the use and refinement of LLNL's diamond-anvil-cell laboratories. We significantly enhanced both our ability to access megabar pressures and our laser heating facilities with the implementation of innovative techniques and instrumentation. Experimental diagnostics that we employed included Raman scattering, video imaging, and visible absorption and fluorescence for phase identification and characterization.

Results

We have made significant progress toward realization of a new class of high energy density materials. As this class of materials represents phases of matter never before observed in the laboratory, we have concentrated our efforts on both the characterization and synthesis of the materials in the pressure regimes of interest.

We have completely revised the phase diagram of N_2 at high pressures and identified a new phase transition (see the enclosed report UCRL-JC-116590). The transition at ~70 GPa would appear to involve a crystallographic distortion (Fig. 2). Starting at about 120 GPa, N_2 gradually transforms with increasing pressure to a coffee-brown color, though we point out the system remains molecular (Fig. 3). This observation is interesting for two reasons: (1) because the bandgap in N_2 is showing indications that it is closing and possibly *en route* to becoming metallic and (2) because metallic behavior is expected on general grounds to weaken the molecular bond. From our data, we have also been able to make strong inferences about the high pressure crystal structure, and thus reach an important milestone, to *verify the robustness of our theoretical calculations*. In predicting the stability of polymeric nitrogen, we assumed a molecular phase that is very similar to the experimentally observed phase at high pressures, placing the prediction on solid ground. Moreover, we can directly quantify the strength of the molecular bond in the nitrogen molecule with increasing pressure using our spectroscopic analyses and theoretical modeling. What is notable is that we are now in the regime where the molecular character is measurably weakening, presaging a dissociation transition to perhaps the polymeric phase. We have not yet conclusively ascertained the dissociation of the molecular phase of nitrogen.

Fig. 2 Raman stretch modes in N₂ vs. pressure. Our analysis of the data demonstrates that the N₂ triple bond is severely weakening.

Fig. 3 Photograph of an N₂ sample at 129 Kbar. The Nitrogen has changed from a transparent phase to a coffee-brown colored phase.

We initiated experiments studying the properties of carbon monoxide. The properties of carbon monoxide are very relevant and interesting because it is isoelectronic to molecular nitrogen and exhibits remarkably similar phase transformations as a function of pressure and temperature to those observed in molecular nitrogen.¹³ We have verified the existence of a polymeric phase of carbon monoxide at ~50

Kbar and that this material is metastable upon pressure quenching (Fig. 4). The recovered material decomposes into graphitic-like byproducts and CO_2 , suggesting that the recovered polymeric CO is energetic. An important result from these experiments is that the concept of synthesizing and recovering metastable systems from high pressures is a reality. The lifetime and energetic-content issues have to be resolved for CO, but these results lend further confidence to recovery of polymeric nitrogen at ambient conditions, as the nitrogen bonds are expected to be stronger and more stable than those of CO.

Fig. 4 Photograph of CO sample at 182 Kbar. The diagram indicates the regions of sample that were irradiated by the laser beam.

In summary, our current progress leads us to be quite optimistic in regard to our ability to synthesize energetic extended solids, including a polymeric form of nitrogen. Our optimism is based on the extremely encouraging results obtained through this work, namely the recovered CO materials as well as the detailed studies of high pressure nitrogen.

References

- 1 C. Mailhot, L. H. Yang, and A. K. McMahan, Physical Review B **46**, 14419 (1992).
- 2 F. J. DiSalvo, Science **247**, 649 (1990).
- 3 A. K. McMahan and R. LeSar, Physical Review Letters **54**, 1929 (1985).
- 4 R. M. Martin and R. J. Needs, Phys. Rev. B **34**, 5082 (1986).
- 5 C. Mailhot and A. K. McMahan, Phys. Rev. B **44**, 11578 (1991).
- 6 C. Mailhot, J. B. Grant, and A. K. McMahan, Phys. Rev. B **42**, 9033 (1990).
- 7 D. B. Boercker, Phys. Rev. B **44**, 11592 (1991).
- 8 T. W. Barbee III, Physical Review B **48**, 9327 (1993).
- 9 C. S. Yoo and M. F. Nicol, J. Phys. Chem. **90**, 6726 (1986).
- 10 C. S. Yoo, J. J. Furrer, G. E. Duvall, *et al.*, J. Phys. Chem **91**, 6577 (1987).
- 11 H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, Physical Review Letters **63**, 2080 (1989).
- 12 C. S. Yoo, J. Akella, and C. Ruddle, EOS Trans. Amer. Geophys. Union **64**, 1489 (1992).
- 13 R. Mills, D. Schiferl, A. Katz, *et al.*, J. Physique **C8**, 187 (1984).