Elementary Reactions of Nitrogen and Oxygen with Boron and Carbon at High Pressures and Temperatures

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The direct elementary reactions among the first and second row elements often yield novel superhard, high energy density, and wide band-gap optical materials. The reactions of oxygen and nitrogen with boron and carbon have been investigated at high pressures and temperatures by using an integrated technique of diamond-anvil cell, laser-heating, x-ray diffraction, Raman spectroscopy. A wide range of products has been synthesized and characterized *in-situ* at high pressures, including α -CO₂, B₂O₃-I, B₂O₃-II, *c*-BN, *h*-BN, *h'*-BN, amorphous carbon nitrides. The elementary reactions occur exothermically and result in highly polycrystallized products with an exception in carbon-nitrogen reactions. The implication of the elementary reactions to energetic materials applications is discussed.

[direct elementary reaction, CO₂, BN, B₂O₃, carbon nitride, amorphous carbon, superhard materials]

1. Introduction

The microscopic understanding of novel materials with advanced properties requires knowledge at a molecular or atomistic level of their crystal structure, phase stability, electronic, optical, vibrational, and mechanical properties, all of which can be altered by application of high pressure and temperature. Recent advances of high pressure and temperature technologies, thus, provide extended opportunities in materials research for discovery of new properties and phenomena, invention of new exotic materials, and modification of chemical bonds and crystal structures for advanced and desirable properties.

Novel materials composed of the first- and second-row elements like diamond and cubic-boron nitride (*c*-BN) often exhibit a covalently bonded three-dimensional network structure and low compressibility. Such an extended network structure of hard material contrasts to the molecular form of same elements like nitrogen or oxygen. These simple diatomic molecules typically contain strong covalent intramolecular bonds; whereas, there is only weak van der Waals interaction between the molecules. The highly localized nature of electrons in intramolecular covalent bonds minimizes the potential energy, makes the bonds extremely stable, and acts as a barrier to reactions leading to the network structure.

In contrast, the network structure is ubiquitous at high pressures, as unsaturated chemical bonds become unstable at high pressures with respect to associative, cross-linking reactions forming denser, more saturated species [1]. This is because at high pressure the kinetic energy of electrons dominates and the intermolecular interaction of isolated molecules becomes mostly repulsive in nature. Therefore, the electrons localized in isolated molecules at low pressures should eventually delocalize at sufficiently high pressure. Thus, applying high pressure is an excellent way to increase chemical reactivity of many molecules with strong covalent bonds.

Pressure increases the chemical reactivity; yet, there may exist a high activation barrier preventing the reaction from initiating. A natural solution to this problem is high temperature, which can be obtained by either ohmically heating the sample in a diamond-anvil cell to several hundred degrees or laser-heating it to a few thousand degrees. On the other hand, such an activation barrier could also exist in the reverse process, providing opportunities to quench new materials and metastable phases at ambient condition.

Over the past few years, we have studied various chemical reactions at high pressures and temperatures, particularly among the first and second row elements. Two types of reactions have been encountered: (1) endothermic reactions leading to metastable phases or high energy density materials and (2) exothermic reactions yielding wide-band gap, hard materials. The examples of endothermic reactions include copolymerization of diatomic molecules [1,2], hydride forming reactions, and metallization[3] at high pressures. The latter type, on the other hand, includes the reactions forming various nitrides, oxides, and carbides. In this paper, we describe the exothermic reactions of light elements such as boron and carbon with diatomic covalent molecules such as nitrogen and oxygen, yielding mostly hard and glass materials.

2. Experimental Method

The synthetic route used in this study is to induce the direct reaction between a sample (boron or carbon) and a pressure medium (nitrogen or oxygen) at high pressure and temperature. Various forms of carbon were used to provide an optimum condition for the synthetic route, including C₆₀, graphite, diamond, and amorphous carbon. Fine (<1 μ m) boron powders were used. The pressure medium is loaded by an immersion technique

The reactions were initiated by laser-heating of the sample in a diamond anvil cell. The reaction products were then characterized by synchrotron x-ray diffraction [4] and micro-Raman spectroscopy. An angle-resolved x-ray diffraction method was used for *in-situ* investigation of the sample and products, by using a monochromatic x-ray beam and an imaging plate detector. A few samples, particularly quenched ones, were also examined by an energy-dispersive x-ray diffraction method. Because of highly preferred orientation of molecular crystals and/or low x-ray scattering of first- and second-row elements, these two x-ray methods were complementary for the study. The details of the experimental method were reported elsewhere [5].

Temperature of the sample was determined by measuring thermal emission from the laser-heated area and fitting the spectrum to a gray-body radiation. However, because the elementary reactions described in this paper are highly exothermic and also rapidly occur in an order of ms or less, it is difficult to determine the actual temperature during the reaction.

Therefore, we report only an approximated temperature measured prior to initiation of the exothermic reaction. Pressure of the sample was determined by Ruby luminescence before and after the reaction. It was often observed a pressure change after the reaction, in which case we report the average value.

3. Elementary Reactions with Oxygen

The objective of our studies on elementary oxygen reactions with boron, aluminum, carbon, and silicon is to synthesize high density glass such as the orthorhombic form of B_2O_3 -II, Al_2O_3 or SiO_2 , or a hypothetical CO_2 glass at high pressures and temperatures. In this section, we summarize the result of oxygen reactions with boron and carbon as shown in Fig 1 and 2.

Fig. 1. The angle-resolved x-ray diffraction of carbon-oxygen reaction products, showing the formation of α - CO_2 . Several broad features between 12.5° and 14.5° are also apparent. The band marked with an asterisk (*) is the 110 reflection of α -Fe from the gasket. This spectrum was obtained by integrating the imaging-plate record.

Figure 1 shows the angle-resolved x-ray diffraction pattern of carbon-oxygen reaction products quenched from about 2000 K at 9 GPa, yielding the α (cubic)-phase of CO_2 and an amorphous C/O product. All the sharp features in Fig 1 can be well indexed to a mixture of β - O_2 and α - CO_2 with the volumes of 19.494 and 18.786 cm^3/mol , respectively; whereas, there are also a few broad features between 12.5° (2.4 Å) and 14.5° (2.8 Å), which have not been well characterized. These broad features are reproducible in the reaction with other forms of carbon; for example, diamond-oxygen reactions. The carbon sample after the reaction becomes nearly transparent with pale pink color likely due to unreacted β -oxygen. It indicates that the broad feature is not from disordered carbon, but is possibly from an amorphous C/O product. Furthermore, the diffraction line of disordered carbon is expected to appear above 3.0 Å. No new transparent material is recovered at ambient pressure. Therefore, it is feasible that the broad feature may represent a metastable C/O glass.

The reaction of boron and oxygen at 6.5 GPa and about 2300 K results in a mixture of both low pressure hexagonal B_2O_3 -I (labeled as hkl_0) and high pressure orthorhombic B_2O_3 -II

(labeled as hkl_0), as shown in Fig 2. A few sharp diffraction lines in Fig 2 are also well indexed to β - O_2 . Both B_2O_3 -I and -II are quenchable at ambient condition. The densities of quenched B_2O_3 -I and -II are, respectively, 2.640 and 3.134 g/cm^3 , in reasonable agreement with the previously reported values, 2.56 and 3.11 g/cm^3 [6,7]. No features are apparent for other forms of boron oxide including B_2O .

Fig. 2. The angle-resolved x-ray diffraction of boron-oxygen reaction products, showing the formation of B_2O_3 -I (labeled as h) and B_2O_3 -II (labeled as o). This spectrum was obtained by integrating the imaging-plate record.

It is interesting to note that both B_2O_3 -I and II were synthesized at 6.5 GPa. This is in contrast to other elementary reactions typically resulting in a product stable at the P,T condition. Considering relatively low melting temperatures of B_2O_3 (about 1400 K at 6.5 GPa [6]), the boron-oxygen reaction occurred in the melt. Therefore, the products were likely formed during the process of quenching, resulting in a mixed phase.

4. Elementary Reactions with Nitrogen

The objective of our studies on nitrogen reactions with carbon and boron is to synthesize superhard nitrides such as c -BN, α - C_3N_4 , or β - C_3N_4 [8,9]. The boron-nitrogen reactions yield various forms of boron nitrides, h -BN, c -BN, and a new hexagonal allotrope h' -BN depending on pressure and initial composition. Highly polycrystallized h -BN is formed below 7.5 GPa, in contrast to other chemical methods resulting in a highly disordered form of h -BN or t (turbostatic)-BN. c -BN is formed above 10 GPa directly from the boron-nitrogen reaction. Highly transparent low density allotrope of h' -BN is formed in nitrogen-rich conditions and is likely a nitrogen-rich metastable form. c -BN has been typically synthesized by converting h -BN at high pressures and temperatures often with catalytic or seed materials. Neither has the attempt of direct synthesis of h -BN been successful at ambient pressure [10]. Therefore, this study is the first to show the synthesis of both c -BN and h -BN directly from the elements without by-products. The details of boron-nitrogen reactions were previously described elsewhere [5].

In contrast to other elementary reactions, carbon-nitrogen reactions typically result in an amorphous product. The most distinctive change of the sample after the reaction is in its

appearance; for example, the diamond sample becomes black after laser-heating. However, there is little indication of crystallites in the x-ray diffraction pattern (Fig 3), suggesting that the product is likely amorphous.

Fig. 3. The angle-resolved x-ray diffraction of boron and oxygen mixtures before and after the laser heating at 4.5 GPa. The broad band marked with an asterisk (*) is the 110 reflection of α -Fe from the gasket. These spectra were obtained by integrating the imaging-plate records.

All the sharp diffraction lines are indexed to β -N₂ with the volumes 19.348 (before the reaction) and 19.936 (after) cm³/mol and unreacted diamond with $a=3.549$ (before) 3.546(after) Å. It is evident that the reflections of β -N₂ becomes substantially more intense after the reaction, indicating that nitrogen is more preferably oriented before the reaction than after. Clearly, no additional sharp features are evident for the reaction product.

Raman spectrum of the product shows a broad feature in the region between 1200 and 1600 cm⁻¹. This feature is somewhat distinctive from amorphous carbon or graphite, centered between 1580 and 1600 cm⁻¹ depending on crystallinity, and is extended toward substantially lower wavenumbers. The proposed C₃N₄ is expected to have a vibrational band near 1200 to 1300 cm⁻¹.

We have also investigated other forms of carbon, yielding again an amorphous form of carbon-nitrogen products. For example, the product of C₆₀-nitrogen reaction exhibits a broad x-ray diffraction at near 3.15 Å, similar to the feature overlapping with the 100 reflection of β -N₂ near 3.17 Å in Fig 3(after heating). The reactions in the other phases of nitrogen, for example in a more miscible phase of δ -N₂, do not alter the nature of the reaction.

The amorphous nature of the carbon-nitrogen reaction product is quite distinctive from a prototype silicone-nitrogen reaction product resulting in highly polycrystallized β -Si₃N₄ [11]. Clearly, further studies are required to characterize the nature of carbon-nitrogen reactions and their products.

5. Energetic and Applications

The reactions reported here do not occur to 50 GPa at ambient temperature; whereas, those proceed highly exothermically even at a few GPa at high temperatures. Therefore, it is likely that these reactions proceed with a high

kinetic barrier. Considering highly exothermic nature of the reactions, it is clear that the forward reactions are favored in energetic. In fact, most of the elementary reactions forming oxides, nitrides, and carbides occur like laser combustion or explosion.

The exothermic nature of these reactions can be utilized for increasing energy in propellants and high explosives. In fact, so-called "paste high explosives", metal (aluminum or boron)-powder dispersed oxygen-rich high explosives, utilize the exothermic nature of metal-oxygen reactions. In a similar concept, it is quite feasible to make new paste explosives even in nitrogen-rich systems such as N₂H₂, a major propellant used for rocket fuel. In fact, the energy release in boron-nitrogen reactions, >10 KJ/g, is greater than or at least comparable with that in carbon-oxygen reactions, ~9 KJ/g, a major energy source in high explosive.

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