

Synthesis of Large-Size Diamonds by Reduction of Dense Carbon Dioxide with Alkali Metals (K, Li)

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Octahedral and hexahedral diamond particles in the size range 4–450 μm were formed at temperatures of 400–600 $^{\circ}\text{C}$ by reduction of dense carbon dioxide with metallic lithium and potassium, respectively. The micro-Raman spectrum analysis shows that typical particles exhibit a sharp peak at 1332 cm^{-1} , which is the characteristic signature of cubic diamond. It is found that much larger diamonds can be yielded by using metallic potassium as reductant than that by using metallic lithium, which is explained in terms of the difference in molten characteristic between the two alkali metals.

Introduction

Diamond has long held a special place in the minds both of scientists and the public due to the fact that diamond is a material with uniquely attractive electronic, structural, or optical properties used in applications ranging from abrasives, tool coatings, bearing surfaces, microelectronics, and optics to corrosion protection.^{1–5} The broad range of valuable properties and applications have driven the development of routes to make synthetic diamonds. The diamond is grown commercially using high-pressure and high-temperature (HPHT),⁶ chemical-vapor-deposition (CVD) for thin films⁷ and shock-wave⁸ processes. Alternative approaches such as a hydrothermal process⁹ were also developed to prepare diamond. Recently, the synthesis of diamond-structured carbon from silicon carbide in chlorine-containing gases at temperatures not exceeding 1000 $^{\circ}\text{C}$ was also achieved.¹⁰ The diamonds made with the TNT detonation process were composed of nanometer-sized spherical particles. A hydrothermal process using carbon, metal, and water near 800 $^{\circ}\text{C}$ and at 1.4 kbar pressure can yield micrometer-sized diamonds, but diamond seed crystals were needed. CVD is a low-pressure process for the synthesis of polycrystalline diamond or diamond-like structure films. However, most CVD diamond has a polycrystalline structure with a crystal size of 0.1–10 μm . So far, only the resulting diamonds in the HPHT process are usually a few millimeters (seeds needed) in size and they are extremely useful as edges on cutting tools and drill-bits and for being compressed to generate very high pressures. Here we report on the synthesis of large-size diamond crystals by reduction of dense carbon dioxide with alkali metals (K, Li) at temperatures ranging from 400 to 600 $^{\circ}\text{C}$; the particle size of the yielded diamond is comparable to that of HPHT products.

Experimental Section

The synthesis was carried out in an autoclave (10 mL), in which an appropriate amount of carbon dioxide and metallic K or Li was added. The pressure was autogenetic, depending on reaction temperature and the amount of carbon dioxide used.

CO_2 is excessively used relative to K or Li to ensure CO_2 being in supercritical states at high temperatures and to avoid explosion during the postreaction treatments. A typical reaction, carried out at 460 $^{\circ}\text{C}$, 820 atm, used 0.162 moles of carbon dioxide and 0.065 moles of metallic potassium or lithium. The main products identified were carbon and carbonate after reaction for 10 h; the alkali metal carbonates were removed by washing with distilled water, and the insoluble carbonate was removed by treating the reaction products with 2.0 mol/L aqueous HCl. The solid precipitate, weighing 0.19 g, was confirmed containing diamond, graphite, and amorphous carbon. Graphite and amorphous carbon were removed by treating the solid precipitate with aqueous HClO_4 (70 wt %) at 180 $^{\circ}\text{C}$. The samples contain mainly diamond. As metallic K was used as reductant, the maximum transformation ratio for carbon dioxide to diamond was about 9.6% (mole ratio), while this value was as low as 0.58% for metallic Li.

The X-ray diffraction (XRD) analysis was performed on a Rigaku (Japan) D/max-rA X-ray diffraction meter equipped with graphite monochromatized Cu K α radiation ($\lambda = 0.154178 \text{ nm}$). The morphology of the samples was observed on a scanning electron microscope (SEM) (Hitachi X-650) and field emission scanning electron microscope (FESEM) (JEOL-6300F, 15 kV). The transmission electron microscope (TEM) studies were performed on a Hitachi H-800 transmission electron microscope. The Raman spectroscopy analysis was carried out on a LA-BRAM-HR Confocal Laser Micro-Raman Spectrometer at room temperature.

Results and Discussion

The Raman spectrum of the sample exhibits an intense first-order peak at 1332 cm^{-1} [Figure 1], which is the characteristic signature of the cubic diamond. The XRD of the product washed with distilled water was shown in Figure 2. It contains characteristic reflection peaks, indexed with 111, 220 and corresponds to cubic diamond with a lattice constant $a = 3.566 \text{ \AA}$ (PDF cards, JCPDS 75-0623). There is a peak at 26.2 $^{\circ}$, indicating the formation of graphite. Other peaks are assigned to FeCO_3 (PDF cards, JCPDS 29-696). The Fe may come from the components of the stainless steel cell. Figure 3a shows the SEM image of diamond particles picked out from a typical sample. The particles were proved to be diamond by the Micro-

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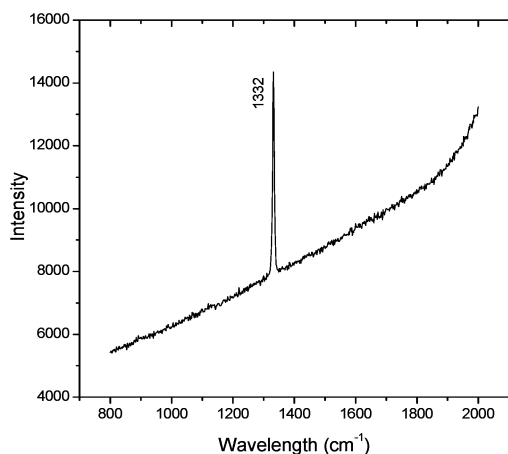


Figure 1. Raman spectrum of diamond microcrystals, using an excitation wavelength of 514.3 nm. The strong Raman peak at 1332 cm^{-1} is a characteristic signature of the cubic diamond. The measurements were performed on a LABRAM-HR Confocal Laser MicroRaman Spectrometer.

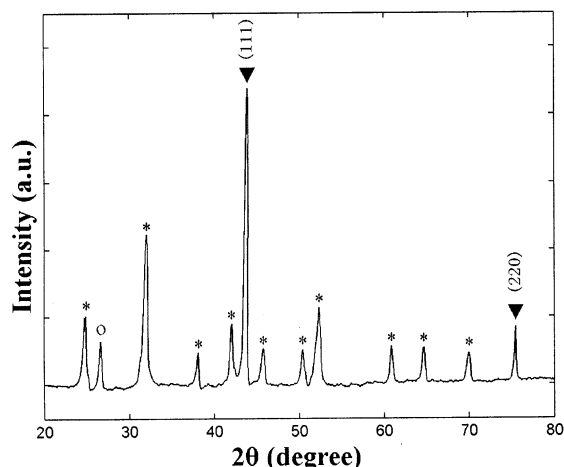


Figure 2. X-ray diffraction pattern for the sample produced in the CO_2 -K system, after washing with distilled water. The reflection peaks, indexed with 111, 220, correspond unambiguously to cubic diamond with a lattice constant $a = 3.568 \text{ \AA}$. Diffraction peaks of diamond were marked by \blacktriangledown , graphite by \circ , and FeCO_3 by *, respectively.

Raman spectroscopy analysis. Most of the diamond particles are around $200 \mu\text{m}$ in size; a large particle reaches up to $450 \mu\text{m}$. When the rectangle area shown in Figure 3b was enlarged, a $340 \mu\text{m}$ -crystal with hexahedral morphology was clearly seen.

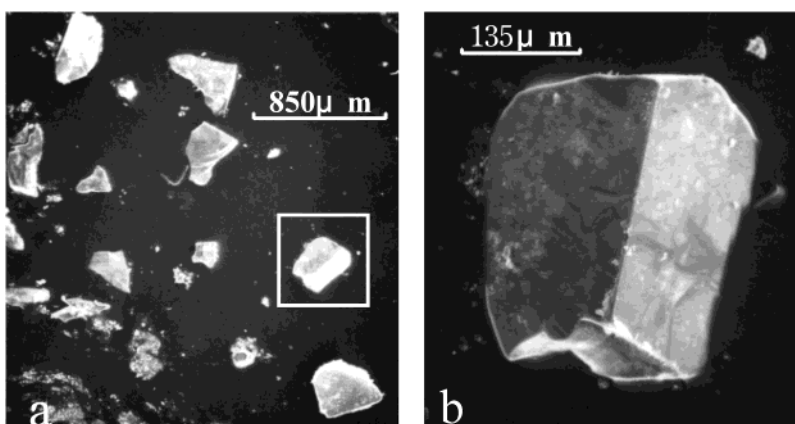


Figure 3. Photograph of diamonds produced in the CO_2 -K system, taken from a scanning electron microscope. Most of the diamond particles are around $200 \mu\text{m}$, a larger one can reach up to $450 \mu\text{m}$ (a); (b) is the enlarged image of the rectangular area shown in (a).

It was also found that diamond particles synthesized in the CO_2 -Li system are octahedron with sizes only several micrometers [Figure 4]. Figure 5 further shows the TEM image and the electron diffraction (ED) pattern of the sample. Octahedral particles with size around $4.3 \mu\text{m}$ were also observed (Figure 5A), which is in agreement with FESEM observations. ED pattern (Figure 5B) obtained from the edge area of the crystallite in Figure 5A can be indexed with the electron diffraction of cubic diamond, which confirms the particles imaged under FESEM and TEM are diamond. At temperatures lower than 400°C , no diamond was detected by XRD analysis, and no significant changes in particle size and yield of diamond were observed as the temperature was increased to 600°C .

It is hard to understand the lower yield and smaller size of diamonds in the CO_2 -Li system than that in the CO_2 -K system. It is found that the coexistence of supercritical CO_2 (ScCO_2) with molten alkali metal and the relatively high pressure in the initial stage of the reaction are two important factors determining diamond formation. The metallic Li melts at 180.5°C , and metallic K melts at 63.3°C . Carbon dioxide will be in ScCO_2 states beyond its critical point 31°C at 73 atm. The melting point for metallic Li is much higher than that of metallic K, and therefore CO_2 will react with solid Li for a longer time at the beginning of the reduction, as the temperature increased to the melting point of metallic Li, the pressure has already decreased, which is not favorable for the formation of diamond. While in the CO_2 -K system, the melting point of K is close to the critical temperature of CO_2 , the longer time of the coexistence of molten K with ScCO_2 might be responsible for the higher yield and larger particle size of diamond obtained in this system. This explanation was also supported by the results obtained in the CO_2 -Na (melting point of Na: 97.8°C) system,¹¹ in which diamond crystals as large as $250 \mu\text{m}$ were obtained and the yield reached up to 8.9%. From these results, it is expected that further work could lead to growing larger diamond crystals by optimizing the process. As shown in Figure 6, an optical microscope (with polarized model) reveals the diamond crystals are transparent and colorless, making them possible to be used as gems if the size can be further increased.

Carbon dioxide is a linear molecule in which the oxygen atoms are weak Lewis (and Brønsted) bases and the carbon is electrophilic. The standard potential of the $\text{CO}_2/\text{CO}_2^{\bullet-}$ couple in an aprotic solvent such as N,N' -dimethylformamide (DMF) containing a counteranion (Net_4^+) (tetraethylammonium), not giving rise to strong ion-pairing, is as negative as -2.2 V vs

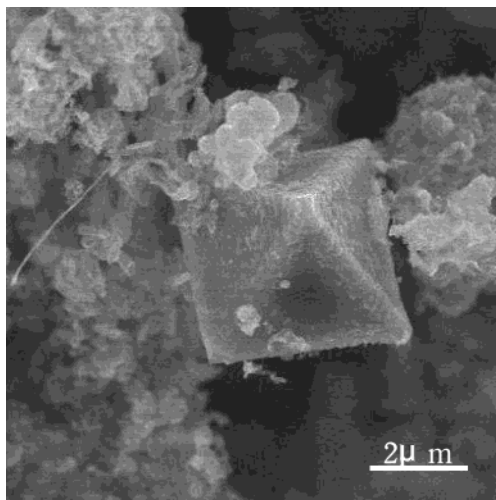


Figure 4. Field emission scanning electron micrograph of the product synthesized in the $\text{CO}_2\text{--Li}$ system at 600 °C. The octahedral diamond particle with a size about 4 μm was observed.

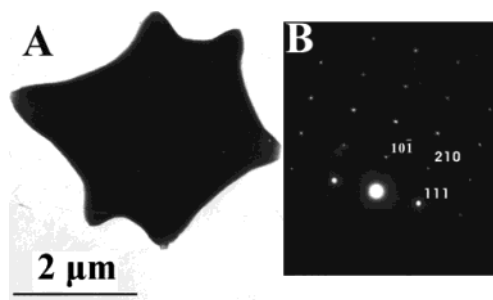


Figure 5. TEM image of the product synthesized in $\text{CO}_2\text{--Li}$ system at 600 °C. The octahedral diamond particles with sizes around 4.3 μm were observed (A). The electron diffraction pattern of the diamond was shown in (B).

SCE. The potentials for the redox couples K^+/K (−2.931 V) and Li^+/Li (−3.04 V) are negative enough for the CO_2 reduction to $\text{CO}_2^{\bullet-}$. The polarity of carbon dioxide can be increased by controlling its density; the dielectric constant of carbon dioxide ranges from 1 to 1.6,¹² therefore the ScCO_2 system could enhance the adsorption of carbon dioxide on the surface of liquid metallic Li or K, and may accelerate the electron transfer from them to carbon dioxide, leading to the formation of $\text{CO}_2^{\bullet-}$ radical anion. However, diamond is a form of carbon that is crystallized in a cubic structure with each carbon atom linked by a strong rigid chemical bond to four other atoms; the formation of this structure at pressures much lower than its thermodynamic stable limit needs to be understood.¹³ A metastable growth mechanism might be involved; much work should be done to reveal the mechanism of carbon dioxide reduction and diamond formation.

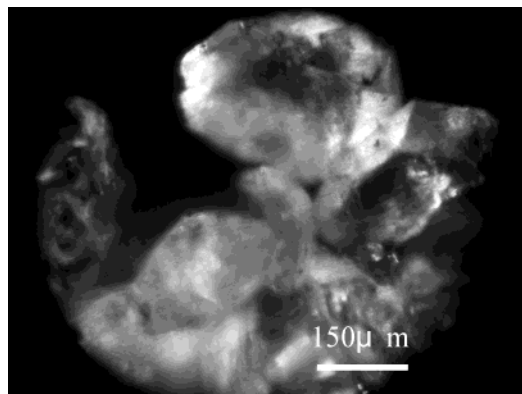


Figure 6. Photograph of diamonds produced in the $\text{CO}_2\text{--K}$ system, taken from an optical microscope.

Conclusions

In conclusion, the above studies illustrate a low-temperature diamond growth process, in which diamond as large as 450 μm can be prepared at 460 °C by reduction of dense carbon dioxide with metallic potassium. The yield of diamond is about 9.6%. It is found that the alkali metal with the lower melting point could result in higher-yield production of diamonds with larger size. Combined with our previous results obtained in a $\text{CO}_2\text{--Na}$ system, it is reasonable to expect larger diamond crystals would be obtained by optimizing the process. Diamond readily burns in oxygen to form CO_2 ; the inverse conversion of CO_2 to diamond could provide some clues for further exploring deep diamond mysteries because CO_2 exists within Earth in large quantity and the mantle was strongly reducing in the past.

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