

A novel diamond sintering process implicated from chemical properties of natural polycrystal diamond (carbonado)

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Carbonado diamonds from Central Africa was found to exhibit very intense laser-induced photoluminescence due to the presence of radiation-damaged products. It suggests the intense irradiation by high energy particles into carbonado. From the spectral profiles of the photoluminescence, the carbonado stones were grouped into three groups and it was shown that one of the groups has not been exposed to temperature higher than 400°C.

Thermogravimetry and Differential Thermal Analysis (TG-DTA) clarified the difference in thermal properties between Group-A and Group-B. The DTA results suggest that structure and density of micropores in carbonado which would strongly affect the oxidation rate are distinct from each other, and the thermal conditions under which the carbonado grains studied had been formed are distinctly different between Group-A and Group-B.

Chondrite-normalized rare-earth element (REE) patterns of carbonado suggest a close relationship to the ordinary diamonds originating from the upper mantle. Furthermore, 1384 cm⁻¹ absorption band was observed in IR spectra of both Group-A and Group-B carbonado, which suggests the presence of nitrogen platelet in carbonado. Both REE and IR results imply the seed crystal of carbonado was formed at high pressure and high temperature and was subjected to the annealing process to generate nitrogen platelets.

Taken altogether, reconciliation of these experimental results lead us to a scenario concerning the genesis of some carbonado as follows; the microcrystals as a seed of carbonado had grown under high temperature and high pressure in the upper mantle. These diamond particulates were aggregated to form carbonado in the crust by sintering process with exposure to high-energy (order of MeV) α particles emitted from the decay of uranium and thorium, then underwent hydrothermal etching which had resulted in the difference in the optical and thermal properties. This scenario gave us a novel methods of diamond sintering; implantation of high energy ion into diamond micro-particle. This method would neither need high temperature nor high pressure, and would enable micro-processing by using microbeam of high energy particles.

1. Introduction

Carbonado is aggregate of randomly polycrystallized diamond particles with some non-carbonaceous inclusions, and its genetic history has been a question open to debate. They have inclusions (silicates, phosphates and oxides) potentially related to Earth's crust and contain polycyclic aromatic hydrocarbon (PAH), and their ¹³C/¹²C ratios are lower than diamond of kimberlite-origin, suggesting that the carbonado might contain biological carbon. On the basis of the above observations, Kaminskii¹ speculated that carbonados were formed in the crust from "coals" under exposure to the uranium and thorium radiation without undergoing the high pressure prevailing in the upper mantle. Recently, Ozima et al.² reported the noble gas isotope compositions revealing the presence of spontaneous fission products which is consistent with the Kaminskii's speculation.

On the other hand, it should be noted that, from a viewpoint of material science, the carbonados have a desirable quality for mechanical tools, because they are superior in a fracture toughness to single crystal diamonds. (But most carbonado have enough defects, poor diamond-diamond bonding and too much non-C material at grain boundaries to make them no stronger than single crystal of diamond.) It is also expected that information on the genesis of carbonado elucidated by the geochemical study would throw light on the artificial sintering process of diamond. All carbonado stones (uncrushed grains) studied here are from alluvial deposit in the Central African Republic, and their average grain size is 5 mm - 10 mm. Detailed experimental procedure and geochemical implications was published elsewhere³.

2. Photoluminescence spectra

Laser-induced luminescence spectra were obtained for 37 carbonado stones with a double monochromator at room temperature. The exciting radiation was 488.0 nm blue line of an Ar⁺ gas laser. All spectra were obtained covering 492 through 614 nm in wavelength.

All carbonado diamonds studied here showed very intense photoluminescence bands in visible light region, and the diamond Raman line at 1332 cm⁻¹ (522 nm in wavelength) derived from the lattice vibration cannot be detected because the Raman intensity is much weaker than that of the photoluminescence. Fig.1 shows typical luminescence spectra obtained from carbonado diamonds, and the spectral profiles can be classified mainly into three groups from their characteristic band shapes.

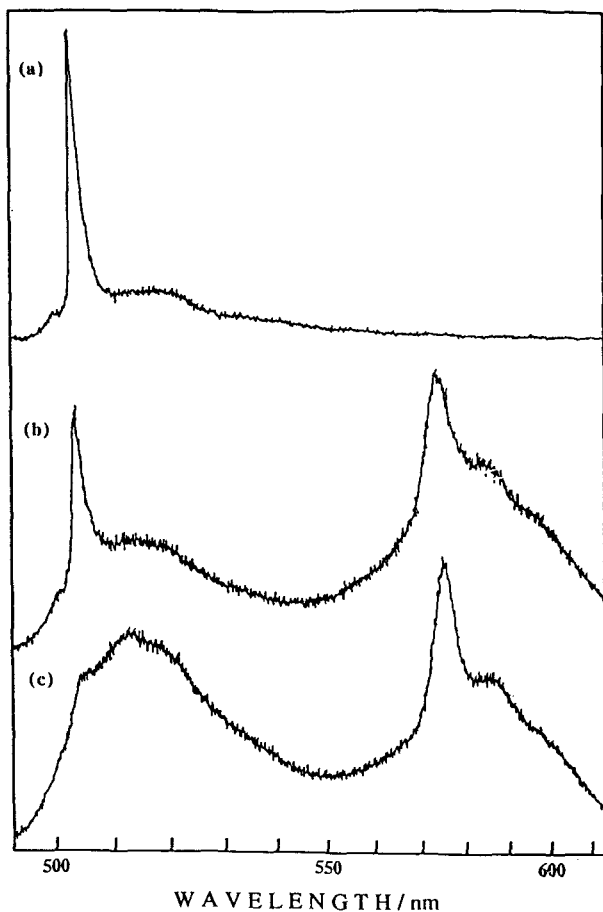


Fig. 1 Photoluminescence spectra of natural polycrystal diamonds, carbonado, excited by 488 nm blue line from Ar⁺ gas laser.
(a) Group-A carbonado (b) Group-B carbonado (c) Group-AB carbonado

The first one (Fig.1(a)) has one strong luminescence band at 504 nm with a weak adjacent background (Group-A carbonado). The second one (Fig.1(b)) has one strong luminescence band centered at 575 nm and two broad bands at 512 nm and 580 nm (Group-B carbonado). The third one (Fig.1(c)) has the intermediate type of photoluminescence which includes both spectral features of Group-A and Group-B. One can find that these observed photoluminescence bands can be assigned to radiation-induced defects⁴, which is consistent with the presence of fissiogenic noble gases in carbonado suggesting the influence of uranium and thorium². The 504 nm luminescence band is assigned to the 3H defect center. The photoluminescence band due to the 3H center is known to disappear upon annealing at 700 K in diamonds with high nitrogen content. Therefore, remarkable spectral changes can be expected after heating Group-A carbonado.

One of the crushed Group-A carbonado particles of submillimeter grain size was heated at 500°C for half an hour. The resultant spectrum shown in Fig. 2(a) exhibits the disappearance of the 3H band at 504 nm, and the heated Group-A carbonado shows a quite similar spectral profiles to those of Group-B carbonado displayed in Fig. 2(b). This transition takes place between 400 °C and 500 °C .

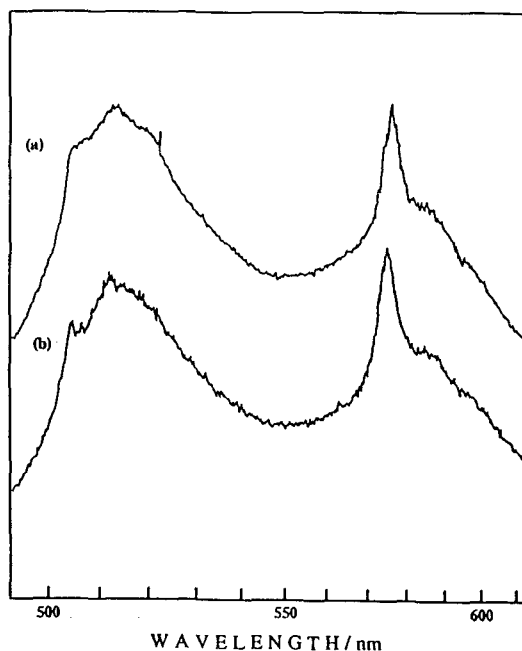


Fig. 2 Photoluminescence spectra of heated carbonado.
(a) Group-A carbonado heated to 500 °C for half an hour (b) Group-B carbonado

3. Thermal analysis

Thermogravimetry and Differential Thermal Analysis (TG-DTA) measurements were carried out in dry air using a Rigaku TG-DTA apparatus with a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$. Heating operation was carried out in the range of 100°C to 900°C .

Group-A carbonado gives one intense and narrow exothermic peak at $800\text{ }^{\circ}\text{C}$ associated with lowering of the TG curve. On the other hand, Group-B gives one broad exothermic band at $785\text{ }^{\circ}\text{C}$ with gradual lowering of the TG curve. One can recognize the tailing of exothermic curve of Group-B carbonado toward the lower temperature. The experimental results prove that the oxidation of Group-B carbonado begins at much lower temperature than that of Group-A carbonado, which means that the diffusion rate of oxygen gas is much higher in Group-B grain than in Group-A grain, or Group-B carbonado have much more or different kinds of defects. The remarkable difference in oxidation behavior between the two groups would imply the distinction of micro structures of differently grouped carbonado, which might have resulted from the difference in the formation conditions and thermal history of carbonado grains such as etching by hydrothermal fluid.

4. Infrared (IR) spectra

For IR measurement, carbonado sample was crushed in stainless vessel to the size about 0.1 mm . Prior to preparation of a KBr pellet for the measurement, the crushed grains were leached with a mixture of hydrochloric acid and hydrofluoric acid at several tens of degree for a few hours in order to remove oxide and silicate mineral inclusions. In Fig. 3, IR spectra for Group-A and Group-B carbonado are displayed in the 800 to 1500 cm^{-1} region, in which typical IR absorption bands for various kinds of diamond are observed. An intense broad band around 1100 cm^{-1} is attributable to the absorption by silicate minerals judging from its broad band shape and the high content of clay minerals in carbonado. In an IR region ranging from 1350 cm^{-1} to 1400 cm^{-1} , no well-defined absorption band can be given owing to the reported inclusion in carbonado such as serpentine, kaolinite, quartz, rutile, ilmenite and so on.

In this IR region, one sharp absorption peak free from the silicate-derived absorptions was observed at 1384 cm^{-1} both for Group-A and Group-B carbonado as shown in Fig. 3. The wavenumber of the

observed band (1384 cm^{-1}) seems to be slightly higher than the wavenumber of the B2 band (1370 cm^{-1}), but this energy deviation can be explained by the size effect of nitrogen platelets. Therefore, the 1384 cm^{-1} band observed in this study can be assigned to the nitrogen aggregate and the carbonado diamonds can be classified into type IaB both for Group-A and Group-B carbonado.

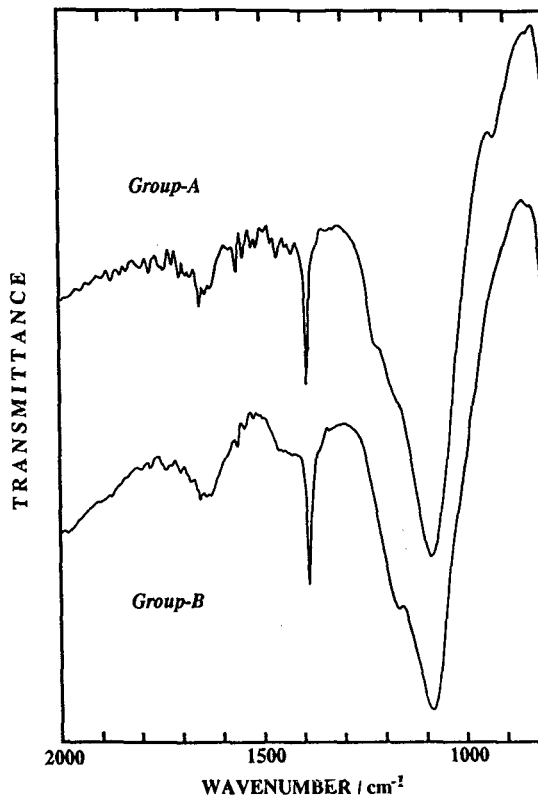


Fig. 3 IR absorption spectrum of Group-A and Group-B carbonado in the 800 to 1500 cm^{-1} region.

5. REE abundance

After the carbonado diamond was completely ashed, the sample solutions were examined with ICP mass spectrometer for the determination of REE abundances. Chondrite-normalised REE patterns for Central African carbonado are shown in Fig. 5. For all analysed samples, the chondrite-normalized La abundances are as large as 10^3 , while the normalized Lu abundances are of the order of 10. These REE patterns with steep gradient from La to Lu are very similar to those of kimberlite.

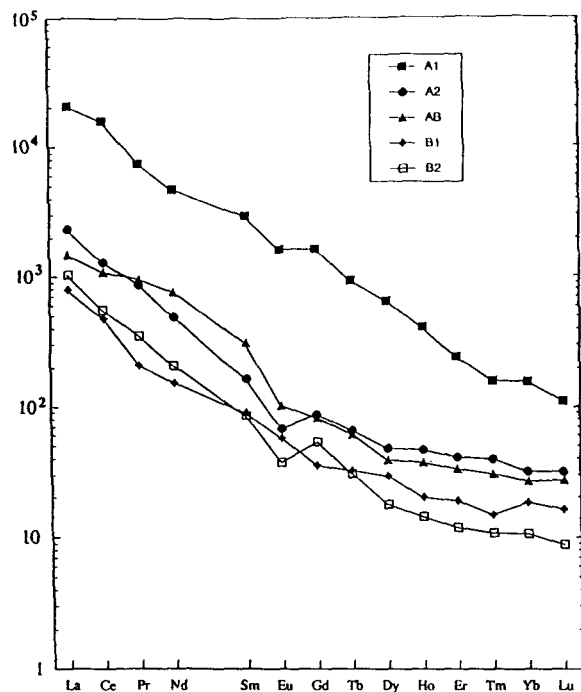


Fig. 4 Leedeey chondrite-normalised REE patterns of carbonado. A1 and A2 belong to Group-A carbonado, B1 and B2 to Group-B carbonado and AB to the intermediate group, respectively.

6. Genetic history of carbonado

Taken altogether, reconciliation of these experimental results lead us to a possible genetic history of carbonado as follows. In the first place, micro diamond crystallite as a source crystal of carbonado was formed at upper mantle under high pressure and high temperature, and nitrogen atoms in the diamond microcrystals were aggregated by annealing in the upper mantle prior to being ejected to the crust. Next, in the crust the microcrystals were sintered under exposure to α particles at the mild temperature and pressure. This process resulted in the genesis of color center in carbonado. After being sintered, they were etched by hydrothermal fluid, which gave rise to the elution of uranium ion and a part of REE contained in inclusions, the incorporation of minerals of crustal origin and the variety of the thermal properties and photoluminescence of carbonado.

On the basis of the versatile observed results, we inferred one of the possible genetic histories of carbonado, that is, crystallization of microdiamond by high pressure and high temperature in the upper mantle, sintering of the microcrystals in the crust

under the influence of radiation from uranium and thorium, and the hydrothermal etching resulting in the variety of physicochemical properties of carbonado.

7. A novel process for diamond sintering

The scenario for carbonado genesis speculated from the versatile experimental results is potential to propose a novel method for sintering diamond. As described above, natural carbonado consists of micron- or submicron-sized diamond particulates, and these microdiamonds are bonded with C-C covalence bonds. Employing the same processes as carbonado had suffered, one can expect that microdiamonds would be sintered artificially. A possible sintering process is as follows. High-energy ion beam is implanted into microdiamond particulates produced with CVD method or shock synthesis.

So far, diamonds have been sintered at high pressure and high temperature with an additive of transition metal binder⁵. On the contrary, neither high temperature nor high pressure is requisite for the sintering method described in the present paper, and micro-processing will be feasible using microbeam of high-energy ions. Further study is required to clarify the possibility of the novel sintering method.

Acknowledgements

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References

1. Kaminskii F.V. (1987) *Dokl. Akad. Nauk SSSR* 291, 439-440 (in Russian).
2. Ozima M., Zashu S., Tomura K. and Matsuhisa Y. (1991) *Nature* 351, 472-474.
3. Kagi H., Takahashi K., Hidaka H. and Masuda A. (1994) *Geochim. Cosmochim. Acta.* (in press)
4. Davies G. (1977) *Chemistry and Physics of Carbon* 13, 1-144.
5. Hall H.T. (1970) *Science* 169, 868.