



## Letter to the editor

## Size-controllable synthesis of ultrasmall diamonds from halogenated adamantanes at high static pressure



## A B S T R A C T

We report on the use of dibromoadamantane  $C_{10}H_{14}Br_2$  as a promising precursor for the mass synthesis of ultrasmall diamonds at an industrially accessible pressure of 8 GPa. Under pressure, the formation of nanodiamonds upon decomposition of  $C_{10}H_{14}Br_2$  starts at the record low temperature of 1000 K. As a result of the decomposition, effective nucleation of diamonds and their slow growth at temperatures up to 2000 K provide favorable conditions for the size-controlled synthesis of nanodiamonds by changing the synthesis temperature. We show that chloroadamantane,  $C_{10}H_{15}Cl$ , is also a good candidate for producing nanodiamonds.

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Great attention to the synthesis of diamonds from hydrocarbons at high pressures arises in connection with the possibility of obtaining diamond nanocrystals, doped with electrically and optically active impurities for nanotechnology applications [1,2]. It is assumed that in comparison with the diamond production under metastable (CVD) or highly non-equilibrium conditions (explosive technologies), the synthesis under high static pressures (HPHT) can provide the diamond formation with the highest structure perfection. Reduction of the potential barrier for the formation of diamonds from hydrocarbons in comparison with that of the direct graphite-to-diamond transition, allows obtaining diamonds at pressures of 8–9 GPa. However, so far well controllable mass synthesis of nanodiamonds at high static pressures has been carried out only in case of the highly boron-doped diamond; 9-Borabicyclo[3.3.1]nonane dimer,  $C_{16}H_{30}B_2$ , was used as a precursor for the production [1]. Mass synthesis of pure nanodiamonds can be carried out from adamantane at 8–9 GPa, but in a very narrow temperature range of 1500–1600 K [2], which makes it impossible to control the process.

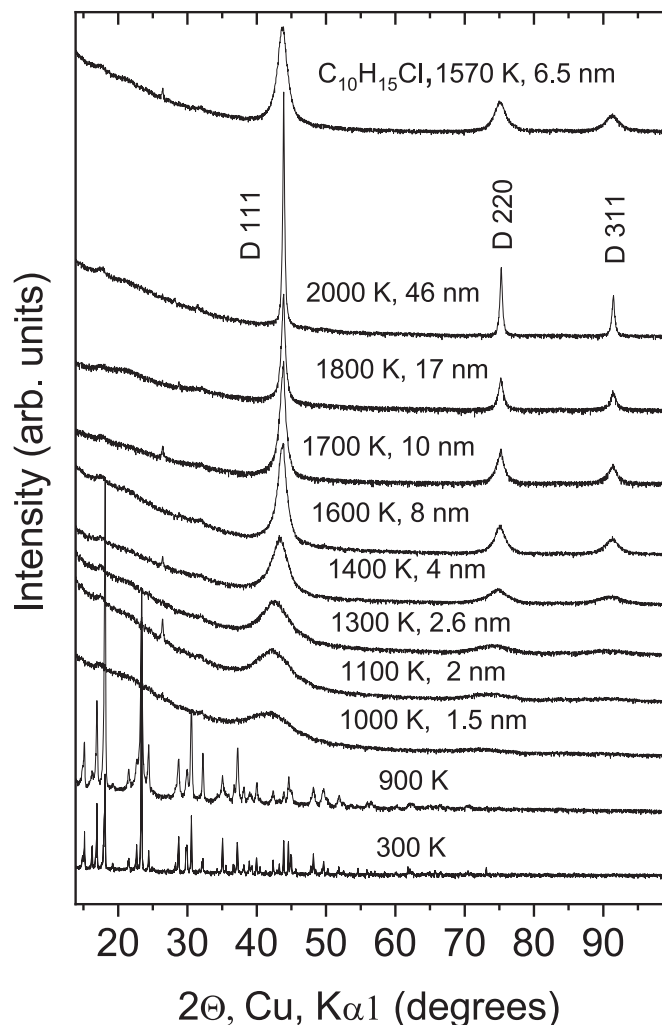
In this paper, we show that halogen derivatives of adamantane:  $C_{10}H_{14}Br_2$  (99% purity, Aldrich) and  $C_{10}H_{15}Cl$  (98% purity, Aldrich) are excellent precursors for mass synthesis of nanodiamonds at an industrially accessible pressure of 8 GPa. Possibility of the synthesis of ultrasmall diamonds with controllable crystal size is for the first time demonstrated on the example of  $C_{10}H_{14}Br_2$ .

The samples were obtained in a high-pressure chamber of the toroid type at a pressure of 8 GPa. Compressed tablet of the initial material 4 mm in diameter and 4 mm in height was loaded into a graphite crucible-heater and a container made of lithographic stone ( $CaCO_3$ ). The temperature was controlled by thermocouples, the junctions of which were placed on the outer side of the heater. The characteristic duration of the synthesis did not exceed 2 min. Diffraction patterns were obtained in the transmission

configuration using Mylar film as the sample holder. Micro-Raman measurements were performed at room temperature using 488 nm line of Ar<sup>+</sup> ion laser for excitation. To avoid overheating, the laser power was kept at a minimum (~0.2 mW at the sample) and the 10× objective was used for laser focusing.

Decomposition of dibromoadamantane, detected by the mass loss (about 10%), starts at a temperature of 900 K; most of the material is retained in the original crystal structure (Fig. 1). At further increase of temperature, the samples lose 50–60% of the mass, forming an easily fragmented transparent glassy substance (about 40–50 mg in mass) with diamond peaks in x-ray diffraction patterns. As the synthesis temperature rises, diffraction peaks of diamond become narrower, indicating an increase of size of the diamond crystals. Relative changes in the crystal sizes were traced with use of the Williamson-Hall (for samples obtained at 1400–2000 K) and Scherrer (for the 111 x-ray diffraction peak) methods for calculation of crystallite sizes. Both methods gave close values probably due to relatively small inhomogeneous strains in synthesized nanodiamonds. The dimensionless shape factor was taken equal to unity in the calculations; change in the shape of nanocrystals was not taken into account. According to the calculations, the average crystallite size monotonically increases from 1.5 nm to 46 nm with an increase in the synthesis temperature to 2000 K.

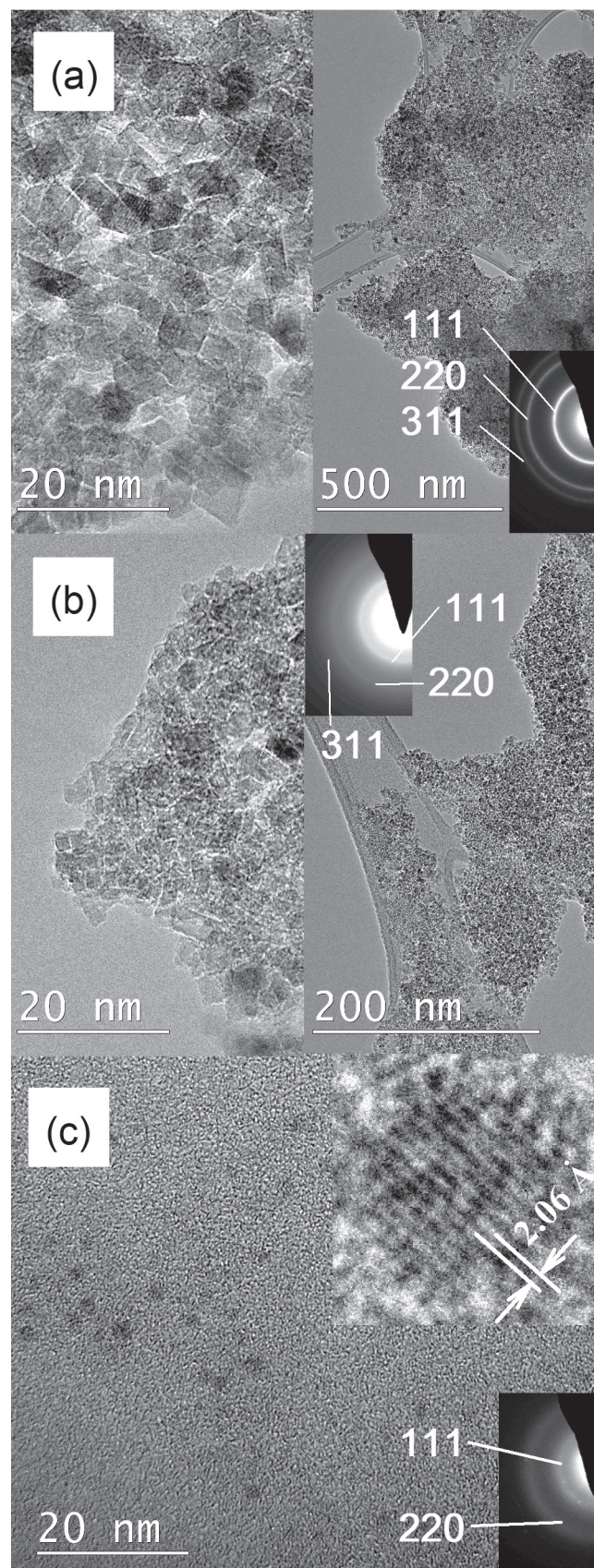
Direct measurements of nanocrystal sizes in the TEM images (Fig. 2) give values, well correlated with the calculated ones. The shape of diamond nanocrystals evolves from sphere-like to clearly faceted by the 111 faces with increasing synthesis temperature, which reflects the tendency to acquire an equilibrium shape depending on the ratio of surface and volume energies of crystals growing under certain conditions. Slightly elongated or flattened crystals, detected in samples (see Fig. 2a and b), were probably formed due to nonuniform temperature field in the reaction



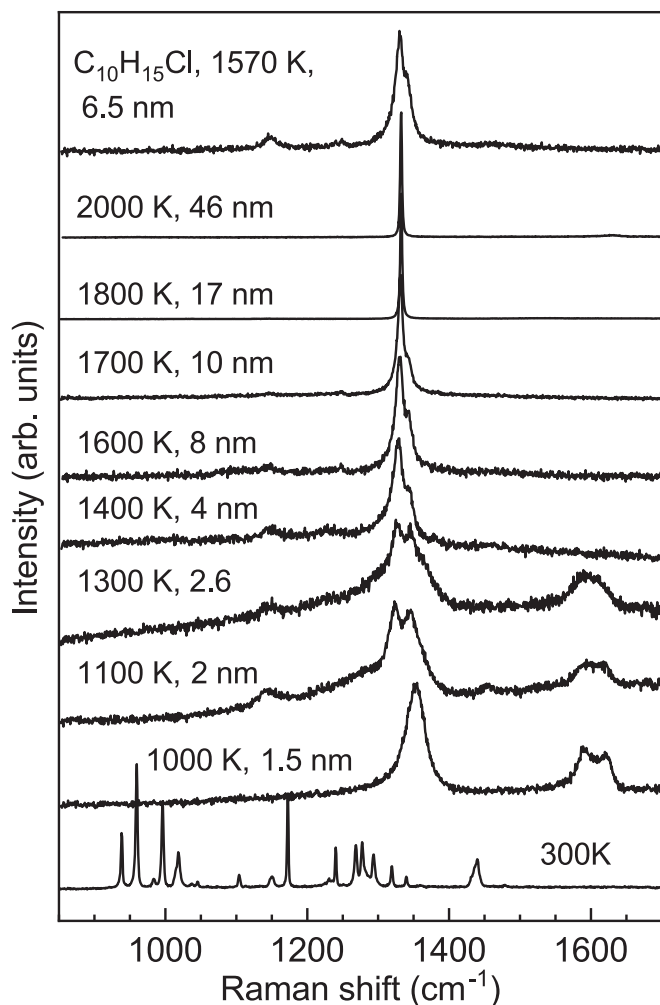
**Fig. 1.** Evolution of the x-ray diffraction patterns of samples and the average size of nanodiamonds (shown in the figure) obtained from 1,3-Dibromoadamantane with increasing synthesis temperature at a pressure of 8 GPa. As an example, the diffraction pattern of the sample synthesized at 1570 K from  $C_{10}H_{15}Cl$  is shown at the top of the figure. At small diffraction angles there are peaks originated from the Mylar sample holder (at 18 and 32°) and accidentally caught in the sample pieces of graphite heater (line 002 of graphite at 26°). D – diamond. (A colour version of this figure can be viewed online.)

volume. The data on Raman spectroscopy investigation of diamond samples are presented in Fig. 3. Apart from the diamond Raman line, the following features are detected in the spectra: lines at 1140 and 1450  $cm^{-1}$  assigned to the *trans*-polyacetylene fragments, broad bands of the disordered  $sp^2$  carbon at 1350 and 1590–1620  $cm^{-1}$  [3], and the line at 1340  $cm^{-1}$ . The intensities of all non-diamond Raman lines decrease with the increase of synthesis temperature and size of the synthesized nanodiamonds, indicating their association with the growth medium and surface states of nanodiamonds. In the sample obtained at 1000 K, the diamond Raman line is not detected. The high scattering cross-section of disordered  $sp^2$  carbon obviously shades the presence of the 1–2 nm diamonds in the sample. Systematic broadening and shift of the diamond Raman line from 1332 to 1324  $cm^{-1}$  were detected for nanodiamonds with a decrease in the average crystal size presumably due to the phonon confinement effect [4].

An interesting feature of the dibromoadamantane carbonization at 8 GPa is the absence of the stage of graphite formation, characteristic of pure hydrocarbons [2]. It is known that bromine, like



**Fig. 2.** TEM images of nanodiamonds obtained at (a) 1600 K (insert shows diffraction pattern taken from an area of 500 nm in diameter on the sample), (b) 1400 K (insert demonstrates diffraction pattern taken from an area of 500 nm in diameter on the sample) and (c) 1100 K (inserts show a diamond crystal with fine resolution and diffraction pattern from the displayed diamonds). (A colour version of this figure can be viewed online.)



**Fig. 3.** Normalized Raman spectra of pristine  $C_{10}H_{14}Br_2$  (300 K) and nanodiamonds of various sizes. As an example, the Raman spectrum of the sample synthesized at 1570 K from  $C_{10}H_{15}Cl$  is shown at the top of the figure. The spectra are shifted vertically for clarity. (A colour version of this figure can be viewed online.)

other halogens, actively reacts with unsaturated hydrocarbons and practically does not interact with saturated ones in the absence of catalysts or special conditions. For this reason, the bromination reaction is commonly used as a test to distinguish between saturated and unsaturated hydrocarbons. It can be assumed that during the decomposition of dibromoadamantane, bromine inhibits the formation of graphite with unsaturated bonds and stabilizes carbon clusters with  $sp^3$  hybridized carbon, giving rise to diamond nucleation and growth. At the same time, adsorption of bromine at the diamond surface is the most probable reason for very slow growth (recrystallization) of diamond crystals even at temperatures of 2000 K. If it is the case, the crystal growth is to a great extent

controlled by chemical reaction at the crystal surface.

The appearance of the  $1340\text{ cm}^{-1}$  line in the Raman spectra and the absence of strong broad-band fluorescence, characteristic of nanodiamonds produced from pure adamantane [2], may be connected with the adsorbed bromine.

In a few of experiments, we have found that thermobaric treatment of  $C_{10}H_{15}Cl$  also gives the same results as processing  $C_{10}H_{14}Br_2$  in similar conditions (see Figs. 1 and 3).

The results obtained suggest that the cage molecule structure and specific bromine chemistry ensures the effective nucleation of diamonds and their slow growth in the C–H–Br system at temperatures up to 2000 K, providing favorable conditions for the controllable synthesis of nanodiamonds. We have shown that chlorinated adamantane is another good precursor for the synthesis of nanodiamonds, and it can be expected that other halogenated adamantanes will also be effective in producing nanodiamonds.

#### Funding

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