Micro-Raman study of the Allende meteoritic nanodiamonds: Supernova-driven shock wave origin is revisited

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I have studied the Raman spectroscopic signatures of nanodiamonds from the Allende meteorite, in which some portions must be of presolar origin as indicated by the isotopic compositions of various trace elements. The spectra of the meteoritic nanodiamonds show a narrow peak at 1326 cm^{-1} and a broad band at 1590 cm^{-1}. Compared to the intensities of these peaks, the background fluorescence is relatively high. A significant frequency shift from 1332 to 1326 cm^{-1}, peak broadening, and appearance of a new peak at 1590 cm^{-1} might be due to shock effects during formation of the diamond grains. Such changes may have several origins: an increase in bond length, a change in the electron density function or charge transfer, or a combination of these factors. However, Raman spectroscopy alone does not allow distinguishing between a shock origin of the nanodiamonds and formation by a CVD process, as is favored by most workers.

Key words: presolar grains, nanodiamond, shock waves, Raman spectroscopy

Introduction

Primitive meteorites contain abundant (up to 1500 ppm) amounts of nanodiamonds. At least some subpopulation must be of pre-solar (stardust?) origin, as indicated by the isotopic composition of trace elements the diamonds carry, in particular noble gases (Huss and Lewis 1994) and tellurium (Richter et al. 1998). On the other hand, the isotopic composition of the major element, carbon, is unremarkable, i.e. it is within the range reasonably expected for Solar System materials (Russel et al. 1992). As a consequence many workers believe that

the majority of the diamonds is of local, i.e. Solar System, origin and that the fraction that is pre-solar is relatively small (Zinner 1998). Two main theories exist for the formation process of the meteoritic nanodiamonds (e.g. Daulton et al. 1996 – and references therein): (1) Chemical vapor deposition (CVD), and (2) shock origin. TEM investigations, in particular, seem to suggest that formation by a CVD process is most likely (Daulton et al. 1996).

In this study, I present results of the study of meteoritic nanodiamonds from the Allende meteorite by means of Raman spectroscopy in an attempt to obtain further constraints with regard to the formation process and further interpretation of data obtained by Gucsik et al. (2008a).

Materials and methods

The Allende meteorite is a carbonaceous chondrite of type CV3 (Fig. 1). It is the meteorite where nanodiamonds, in the search for the carrier of isotopically anomalous noble gases, were first identified (Lewis et al. 1987). The abundance of nanodiamonds in this meteorite is ~250 ppm (Huss and Lewis 1995). The nanodiamonds investigated in this work were extracted from the meteorite using a variant of the microwave digestion procedure.

Fig. 1
A piece of the Allende meteorite showing typical features of the carbonaceous chondrite such as chondrules (white parts) (photo by author)

Raman spectra were recorded using the confocal Raman micro-spectrometer T-64000 (Jobin-Yvon) equipped with a BX-40 (Olympus) microscope at Technical University of Lodz, Poland. A small amount (less than 1 cubic micrometer) of nanodiamonds was placed on a microscope slide using an acupuncture needle and covered with a thin microcover glass. The slide was carefully positioned under the objective (×50), which was used to focus the excitation laser light (Argon line = 514.5 nm) onto the sample. The output power of the laser was 200 mW (~2 mW on the sample). A high background, which is typical for nanomaterials, limited the acquisition time to 90–300 s, dependent on the specific sample. In order to increase the signal/noise ratio two accumulation cycles were used. All spectra contain a significant contribution from the glass (peaks at 580, 790, 1100, and 1900 cm^{-1}) as a background, because the laser spot was larger than the diameter of the sample.

Results and discussions

Raman spectral features of the meteoritic nanodiamonds

The individual grain sizes of meteoritic nanodiamonds vary between 2 and 7 nm (e.g. Daulton et al. 1996), which is small compared to the ~ 1 μm diameter of the laser excitation beam on the surface of the sample. The Raman spectra of the nanodiamonds exhibit two broad bands centered at ~1326, and ~1590 cm^{-1}. In general, peak intensities of these bands are relatively low, which indicates strong background fluorescence. This may be due to lack of well-formed crystalline parts of the sample; alternatively, it may (also) be related to the small grain size. Following data correction, the band at 1326 cm^{-1} shows 14.4 cm^{-1} FWHM and a 6 cm^{-1} peak shift from the 1332 cm^{-1} peak position of standard or reference nanodiamond (Ferrari and Robertson 2001, 2004; Zhang and Zhang 2005; Karczemska 2010) (Fig. 2).

The Raman spectra of single crystal diamond is dominated by a Brillouin zone-center point as T2g mode at 1332 cm^{-1} (strong or very strong peak for carbon sp3 bonding) with approximately 5–10 cm^{-1} FWHM (Ferrari and Robertson 2001, 2004; Zhang and Zhang 2005). This relatively sharp and single peak is frequently used as a signature of high crystalline quality. In previous studies of micro- and nanodiamond samples several additional peaks have been described in the Raman spectra, as follows. The two most typical and significant ones in the spectra of artificially-produced chemical vapor deposited (CVD) nanocrystalline diamonds are at 1150 and 1450 cm^{-1} (trans-polyacetylenes; Ferrari and Robertson 2001; Karczemska 2010). It has been proposed that these peaks are related to phonon modes with q_0, which are activated by the disorder induced by small grain sizes in nanocrystalline or amorphous diamond (Filik et al. 2006). Additional medium or strong bands in the Raman spectra of nanocrystalline diamond samples are usually seen at 1350 and at 1590 cm^{-1}. The 1350 cm^{-1} feature is related to the D-band, which is a normally Raman inactive A1g mode.
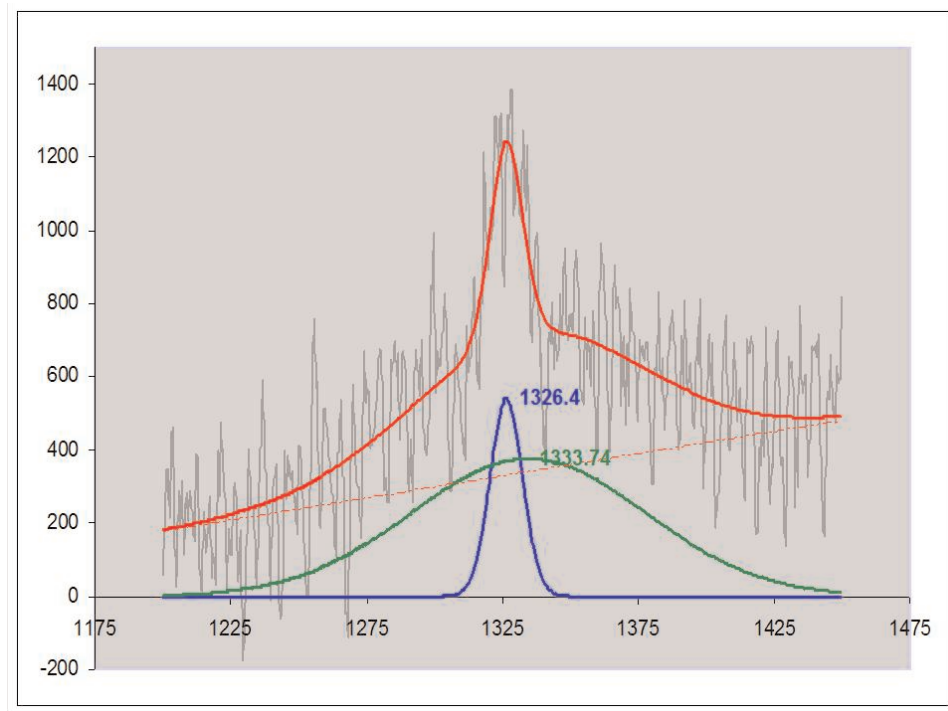
Fig. 2
Micro-Raman spectral features of the Allende meteoritic nanodiamonds. Data correction of a peak at 1326 cm^{-1}

It is activated due to the finite crystal size (Filik et al. 2006 – and references therein). The G-band at 1590 cm^{-1} is assigned to carbon sp2 bonding graphitic structures (Nasdala et al. 2004).

Raman frequency shift

Frequency shifts of the 1332 cm^{-1} band by a few cm^{-1} (6 cm^{-1} in this case) may be due to strained nanodiamond caused by shock waves or high-pressure-induced deformation but also due to disorder in the nanodiamond structure. Similar frequency shifts, broad bands (10–20 cm^{-1} at FWHM) and relatively high background fluorescence were observed in impact-induced diamond as well as in nanodiamond samples from different shock metamorphic environments such as terrestrial impact structures (El Goresy et al. 2001) and meteorites (Greshake et al. 2000; Mostefaoui et al. 2002; Gucsik et al. 2008a and b; Karczemska et al. 2009) as well as in shock recovery experiments (Kenkmann et al. 2002). We note, however, that the frequency shift of the band at 1332 cm^{-1} and the peak broadening from higher modes to the lower ones may also be assigned to the

effects of phonon/quantum confinement (Yoshikawa et al. 1995; Chen et al. 1999; Sun et al. 2000; Berg et al. 2008). Shifts were also observed after irradiation by neutrons (Guo et al. 2004). An additional peak at 1590 cm^{-1} was also described in the previous studies, which is probably related to the amorphous carbon phase present as the result of shock metamorphism (El Goresy et al. 2001; Kenkmann et al. 2002). These observations on shock-produced diamonds are in a good agreement with the Raman spectral properties of nanodiamonds from our Allende meteorite sample. The frequency shift may be associated with the modification of the local configuration of the sample by means of the transformation of graphite into nanodiamond (Dunlop et al. 2007). In particular, the difference in frequency values for the Raman C-C bonding vibrations between 1332 and 1326 cm^{-1} in nanodiamond could indicate a change of the C-C bond strength caused by the phase transition at high pressure and temperature.

Shock wave scenario

It is well known (based on shock recovery experiments) that the required shock pressure to produce impact-induced diamonds is around 40 GPa (Kenkmann et al. 2002). Since the Allende meteorite does not contain high-pressure polymorphs as evidence for a high shock stage, impact on the Allende parent body cannot be responsible for the formation of the nanodiamonds. This, of course, is also evident from the fact that nanodiamonds are present not just in Allende but in all primitive meteorites, with their relative abundance largely determined by losses due to metamorphism (Huss 1990; Huss and Lewis 1995). According to Klein et al. (1994) interstellar shock waves can be produced by the powerful stellar winds of massive stars, supernova explosions, cloud-cloud collisions, and spiral density waves. In the following paragraph I focus on the interaction of supernova-driven shock waves and interstellar cloud and their relationship to the linear growth rate of nanodiamonds.

Assuming a supernova shock wave front is responsible for the synthesis of diamond, its formation can be considered as a two-step process. According to the supernova shock wave experiment of Hansen et al. (2007) the first step is the transition of the secondary shock wave through interstellar media near the supernova explosion, resulting in grain-grain collisions. The initial shock wave occurs rapidly, which can provide the physical conditions such as high pressure and high temperature adequate for the formation of diamond, creating the second stage or the crystallization stage. A disadvantage of this process, however, is that pressures obtained during such collisions are often so high that shattering, sputtering and vaporization become dominant over phase transformation (Tielens et al. 1987; Jones et al. 1994, 1996), which limits the effectiveness of diamond formation. In this stage, according to the linear growth rate of diamond

(RD), the following relation between the linear size L of the growing diamond, the linear growth rate RD and growth time (time of crystallization) is given by

$$L\ (nm) = RD\ (nm/s)\, t\ (s) \tag{1}$$

For CVD diamonds, the RD rate of CVD ranges between 0.03 and 1.2–1.7 nm/s. Accordingly, for the meteoritic nanodiamonds with a mean size L of 2.6 nanometers the time of crystallization (t) would be between 1–2 s for relatively rapid growth and on the order of 100 s for slow growth. The structural property (i.e. startwin structure) of meteoritic nanodiamonds favors rapid growth and several seconds. In the case of the high pressure/high temperature (HPHT) processes, growth rates are high, in the order of 300–500 nm/s. This would result in growth times of 0.005–0.01 s (i.e. 5–10 ms), much shorter than for CVD processes (Battaile et al. 1997; Chung and Sung 2001; Aleksandrov and Sel'skaya 2002; Abbashian et al. 2005; Mokuno et al. 2006; Karczemska et al. 2008). According to Boss et al. (2008) the speed of the shock wave was calculated in a simulation of the triggered collapse of a presolar dense cloud core. In that case the transition would be 2.6 nm/20 km/sec (=0.13 picoseconds). It is also poorly understood whether or not nanodiamonds would be formed during such a very short period in the Universe. Of course, more detailed experimental work must be carried out focusing on the relationship to relatively rapid growth rate and speed of the shock wave front (Fig. 3).
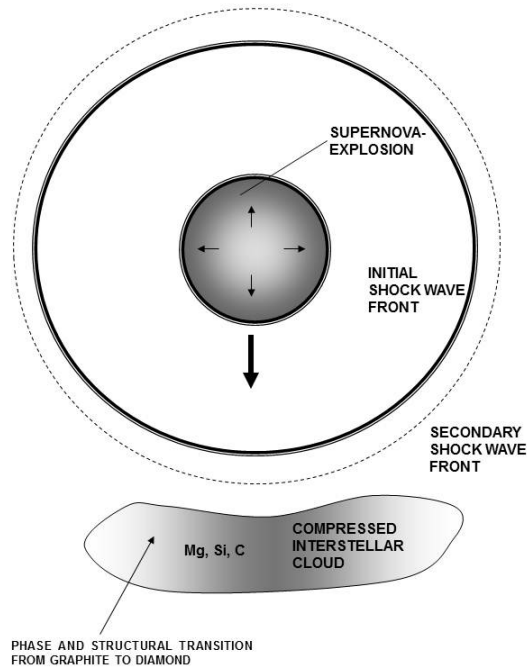

Fig. 3
A schematic figure showing a possible way to nanodiamond formation in the compressed interstellar cloud due to double supernova shock wave fronts following the Hansen model (Hansen et al. 2007). Scale: a few hundred light years in diameter

Alternatively, it is also important to note that the 2.6 nm average size of the meteoritic nanodiamonds may be related to the H-related self-terminating crystal growth process (Sun et al. 2004) in the shock-wave front. On the other hand, the surface chemistry of the nanodiamonds shows a poor thermal stability between 850–1350 °C (Lu et al. 2007), indicating the low-temperature crystallization process of the single diamond grains. These factors may also support the shock wave origin of the meteoritic nanodiamonds.

Conclusions

These results from Raman spectroscopy alone are not conclusive, especially since it is currently difficult to distinguish between the effects of shock transformation and small grain size. They leave open, however, the possibility that a significant fraction of the nanodiamonds in primitive meteorites were formed by shock transformation from graphite/amorphous carbon in the interstellar medium. As noted above, this possibility was immediately recognized following their discovery (Tielens et al. 1987), but more recent work has mostly concluded that a CVD-like process is more likely (e.g. Daulton et al. 1996; Le Guillou et al. 2006, 2007). Other processes that are possible in principle (see also Anders and Zinner 1998), but have received less attention, are photolysis of hydrocarbons (Buerki and Leutwyler 1991), annealing by UV photons (Nuth and Allen 1992), and transformation by energetic particle irradiation (e.g. Ozima and Tatsumoto 1997). Note that Raman peak shifts were observed after irradiation by neutrons (Chen et al. 2004), but otherwise information concerning the effects of these processes on the Raman spectral properties of nanodiamonds is lacking. As further measurements, it is also planned to use a multiple technological approach such as combination of Raman spectroscopy with Scanning Electron Microscope-Cathodoluminescence (SEM-CL) spectroscopy (Gucsik et al. 2009) and microscopy to carry out detailed analyses on the meteoritic nanodiamonds.

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