

# Micro-Raman study of nanodiamonds from Allende meteorite

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**Abstract.** We 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 nanodiamond show a narrow peak at 1326 cm<sup>-1</sup> and a broad band at 1590 cm<sup>-1</sup>. Compared to the intensities of these peaks, the background fluorescence is relatively high. A significant frequency shift from 1332 to 1326 cm<sup>-1</sup>, peak broadening, and appearance of a new peak at 1590 cm<sup>-1</sup> 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.

**Keywords.** (Stars:) supernovae: general, shock waves, ISM: evolution, meteors, meteoroids

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## 1. Introduction

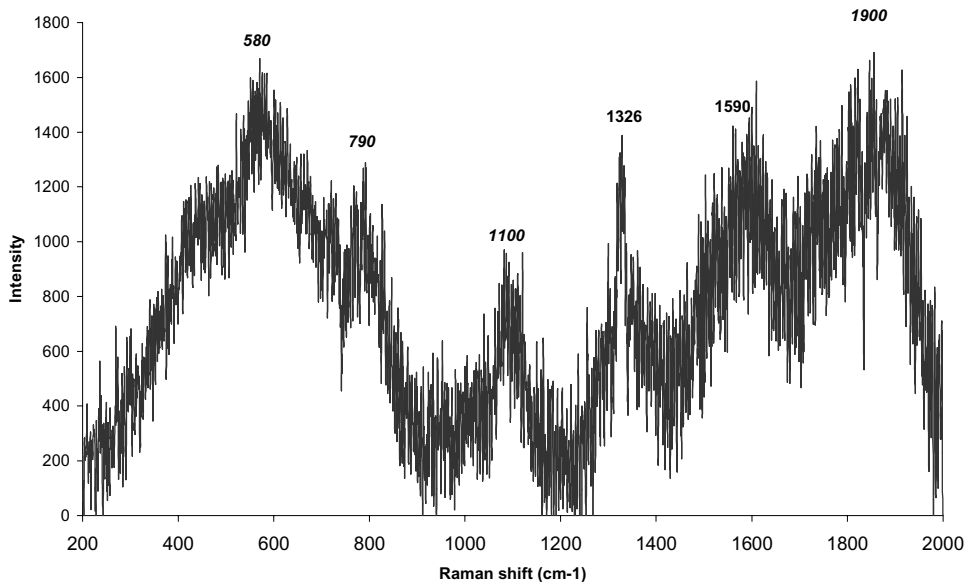
Primitive meteorites contain abundant (up to 1500 ppm) amounts of nanodiamonds (Huss 1990). At least some subpopulation must be of pre-solar (stardust?) origin, as indicated by the isotopic composition of trace elements the diamonds carry, in particular noble gases (e.g., Huss & Lewis 1994, 1995) and tellurium (Richter *et al.* 1998). On the other hand, the isotopic composition of the major element, carbon, is unremarkable, i. e., within the range reasonably expected for Solar System materials (e.g., Russell *et al.* 1991). 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 (e.g., 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, we 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.

## 2. Results

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  $\sim 1 \mu\text{m}$  diameter of the laser excitation beam on the surface of the sample. The Raman spectra of the nanodiamonds exhibit two broad bands centered at  $\sim 1326$ , and  $\sim 1590 \text{ cm}^{-1}$  (Figure 1). In general,

peak intensities of these bands are relatively low, which indicates the strong background fluorescence. This may be due to lack of well-crystalline parts of the sample; alternatively, it may (also) be related to the small grain size. Following the data correction, the band at  $1326\text{ cm}^{-1}$  shows a  $14.4\text{ cm}^{-1}$  FWHM and a  $6\text{ cm}^{-1}$  peak shift from the  $1332\text{ cm}^{-1}$  peak position of standard or reference nanodiamond (Zhang & Zhang 2005, Karmenyan *et al.* 2007).



**Figure 1.** Raman spectral features of nanodiamonds from Allende meteorite ( $1326$  and  $1590\text{ cm}^{-1}$ ), and glass holders at  $580$ ,  $790$ ,  $1100$ , and  $1900\text{ cm}^{-1}$ . 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 (Argon line  $\lambda=514.5\text{ nm}$ ).

### 3. Discussion and Conclusions

The Raman spectra of single crystal diamond is dominated by a Brillouin zone-center point as  $T2g$  mode at  $1332\text{ cm}^{-1}$  (strong or very strong peak for carbon  $sp^3$  bonding) with approximately  $5\text{--}10\text{ cm}^{-1}$  FWHM (Ferrari & Robertson 2004, Zhang & Zhang 2005, Karmenyan *et al.* 2007, Karczemska *et al.* 2008). This relatively sharp and single peak is frequently used as a signature of high crystalline quality. In previous studies, several additional peaks have been described in the Raman spectra of micro- and nanodiamond samples, 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  $1450\text{ cm}^{-1}$  (trans-polyacetylenes; Ferrari & Robertson 2001). 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  $1350\text{ cm}^{-1}$  and at  $1590\text{ cm}^{-1}$ . The  $1350\text{ cm}^{-1}$  feature is related to the D-band, which is a normally Raman inactive  $A1g$  mode. It is activated due to the finite crystal size (Filik *et al.* 2006, and references therein). The G-band at  $1590\text{ cm}^{-1}$  is assigned to carbon  $sp^2$  bonding graphitic structures (Nasdala *et al.* 2004).

Frequency shifts of the  $1332\text{ cm}^{-1}$  band by a few  $\text{cm}^{-1}$  ( $6\text{ cm}^{-1}$  in this case) may be due to strained nanodiamond caused by shock waves or high-pressure-induced deformation,

**Table 1.** Micro-Raman properties of nanodiamonds separated from CVD, meteoritic, and shock metamorphic samples.

| Origin            | Raman Bands ( $\text{cm}^{-1}$ ) |      |           |                   |      |      |      | References  |
|-------------------|----------------------------------|------|-----------|-------------------|------|------|------|---|
| CVD               | 500                              | 1150 | 1240-1280 | 1332              | 1350 | 1450 | 1590 | Ferrari & Robertson (2001)<br>Ferrari & Robertson (2004)<br>Filik <i>et al.</i> (2006)<br>Karmenyan <i>et al.</i> (2007)<br>Karczemska <i>et al.</i> (2008) |
| Meteoritic        |                                  |      |           | 1332 <sup>1</sup> |      |      | 1580 | Greshake <i>et al.</i> (2000)<br>Karczemska <i>et al.</i> (2008)  |
| Shock metamorphic |                                  |      |           | 1332 <sup>1</sup> |      |      | 1590 | El Goresy <i>et al.</i> (2001)<br>Kenkmann <i>et al.</i> (2002)<br>Chen <i>et al.</i> (2004, 2006)<br>Dunlop <i>et al.</i> (2007)                           |

Note

<sup>1</sup>Peak shift to the lower frequency modes

but may also be due to disorder in the nanodiamond structure. Similar frequency shifts, broad bands ( $10\text{-}20\text{ cm}^{-1}$  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) as well as in shock recovery experiments (Kenkmann *et al.* 2002). We note, however, that the frequency shift of the band at  $1332\text{ cm}^{-1}$  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  $1590\text{ cm}^{-1}$  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 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  $1326\text{ cm}^{-1}$  in nanodiamond could indicate a change of the C-C bond strength caused by the phase transition at high pressure and temperature.

In conclusion, our 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 after 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, Le Guillou & Rouzaud 2007). Other processes that are possible in principle (see also Anders & Zinner 1993), but have received less attention, are photolysis of hydrocarbons (Buerki & Leutwyler 1991), annealing by UV photons (Nuth & Allen 1992) and transformation by energetic particle irradiation (e.g., Ozima & Tatsumoto 1997). Note that Raman peak shifts were observed after irradiation by neutrons (Guo *et al.* 2004), but otherwise information is lacking concerning the effects of these processes on the Raman spectral properties of nanodiamonds.

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## Discussion

FLYNN: We looked at the carbon XANES of diamonds from Allende a few years ago and also we were unable to find the diamond exciton feature which is characteristic of CVD diamond but is not characteristic of shock diamonds, so we also have some indications that there are not well crystallized diamonds.

GUCSIK: This is a good comment because we selected the Allende meteorite on the basis of the phase equilibria diagram by Carl Agee. He estimated that the maximum pressure

for the internal pressure of the parent body of the Allende meteorite wasn't more than 30 GPA. This is kind of a low shock regime of the meteoritic background because you can see here that we need at least 40 GPA for the phase transformation between graphite and diamond. So I think there are 10 GPA of pressure that might be missing in this model.

NITTLER: For a contrasting view, there was a very detailed study by Tyrone Dalton some years ago who did a very detailed high resolution transmission electron microscopy study of the meteoritic nanodiamonds and compared the microstructures of diamonds produced by chemical vapor deposition and diamonds produced by shock using the same technique in the same instrument. He found that the microstructures looked much more like the CVD diamonds than the shock diamonds and argued the exact opposite of what you are arguing.

GUCSIK: I have a surprise for you. I was playing around with the shock wave calculator of the normal shock wave front coming from a supernova explosion. This shock wave calculator can be found on the net. And I managed to get 40 GPA pressure circumstances required for having the phase transformation between graphite and diamond, and the shock wave calculator found 2400 Kelvin as a temperature for the post shock effects. I think both processes, the shock wave front and post shock temperature effects, might both be leading processes for the formation of the meteoritic diamonds. On the basis of very preliminary data I can conclude this kind of behavior of nanodiamonds.

GUCSIK: It is important to note that, in general, although CVD diamonds show Raman shift of a peak at  $1331\text{ cm}^{-1}$ , they do not exhibit a coexistent peak at around  $1600\text{ cm}^{-1}$  and the peak shifting. Moreover, compared to CVD diamonds, our Allende meteoritic nanodiamonds do not contain some major Raman bands at around  $1150$  and  $1450\text{ cm}^{-1}$  ( $sp^2$ , transpolyacetylene) peaks.

HENNING: Actually I have a comment. There is another mechanism that is able to produce nanodiamonds - ion radiation of small particles. This may actually be a mechanism that is operating in the environment of young stars because these nanodiamonds seem to be different from the meteoritic nanodiamonds. It would be worth while to study nanodiamonds that are produced by ion irradiation as well.

GUCSIK: Yes. But the coexistence of peak shifting of the peaks at  $1331\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  have only been known from the shock metamorphic nanodiamonds. This can aid (or even support) understanding more about the supernova-driven shock wave front and its effect on the graphite-diamond high pressure transition in the interstellar medium.



Catherine Cesarsky being asked to put red paint on the the eye of the lion with a brush in order to liven up the lion.