

# RAMAN AND LUMINESCENCE SPECTROSCOPY OF METEORITIC NANODIAMONDS.

A. A. Shiryayev<sup>1</sup>, A. V. Fisenko<sup>2</sup>, I. I. Vlasov<sup>3</sup>, L. F. Semjonova<sup>2</sup>, <sup>1</sup>Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Russia (shiryayev@phycr.ac.ru) for first author, <sup>2</sup>Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow, Russia, <sup>3</sup>General Physics Institute, Moscow, Russia.

**Introduction:** Meteoritic nanodiamonds (MND) are the most abundant protoplanetary Solar System relic phases in comparison with other compounds. We discuss results of extensive spectroscopic comparative investigation of meteoritic nanodiamonds from several chondrites with synthetic nanodiamonds produced by different methods: CVD and detonation (DND). The samples were analysed using luminescence and Raman spectroscopies, EELS and NEXAFS, X-ray diffraction and scattering [1].

## Results

**Raman spectroscopy:** Use of the UV laser allows detection of even small amounts of  $sp^3$ -carbon [2]. The analysed samples were embedded in copper to minimize laser heating. The UV Raman spectra of samples of Efremovka nanodiamonds are shown on Fig. 1 (left). Broad, asymmetric downshifted diamond peak is clearly observed along with broad bands due to graphite-like carbon and C=O bonds. The presence of the C=O bonds is due to oxygen, most likely chemisorbed on the nanodiamond grains during chemical oxidation. Such spectra are typical for DND.

At least two different phenomena which may act simultaneously could be responsible for the observed downshift of the Raman peak to  $1326\text{--}1327\text{ cm}^{-1}$ : 1) phonon confinement [3], and 2) presence of hexagonal diamond polytypes (hex-Dia).

The phonon confinement model gives the average size of the Efremovka nanodiamond grains of 4–6 nm. These values are higher than the median size of the nanodiamonds as determined from TEM and XRD (2.6–3 nm). The discrepancy might be explained by uncertainties due to selected phonon dispersion curves, but it is also possible that the Raman and X-ray scattering are dominated by the larger grains.

Though the fraction of purely hex-Dia particles is not very high, the MND grains often contain stacking faults and other similar imperfections [4]. From crystallographic point of view many types of stacking faults in cubic diamond lattice may be regarded as hexagonal polytypes. The Raman peaks of 2H and 6H diamond polytypes are observed between  $1319$  and  $1327\text{ cm}^{-1}$  [5]. At least partially the observed downshift may be due to such extended defects.

**Photoluminescence:** The photoluminescence spectra of the MND samples studied at room- and liquid helium temperatures are broadly similar indicating inhomogeneous, i.e. strain-related, line broadening as is expected for nanoparticles. The spectra are dominated by a broad band with a maximum around

560 nm (red emission) with shoulders around 530 and 610 nm and are similar to recorded for DND (fig. 1, right). The broad band represents overlapping signals from non-diamond carbon and from defects on the surfaces of diamond grains.

The spectra were recorded in a broad wavelength range which allowed observation of a remarkable feature at 737 nm (1.681 eV) with a weak shoulder at 750 nm. This feature is an unambiguous manifestation of well-known “silicon” defect, most probably consisting of silicon ion in the divacancy (commonly called a silicon-vacancy complex or Si-V [6]). The observed band is broad and the fine structure is not observed due to size/stress effects. We emphasize that the observed signature of the “silicon” defect should not be confused with SiC or Si in amorphous carbon.

A defect present in all types of irradiated diamonds – the GR1, is absent in spectra of the studied samples.

**Conclusions:** We show that the phase compositions of the meteoritic and the synthetic detonation nanodiamonds are similar, suggesting that both types of nano-

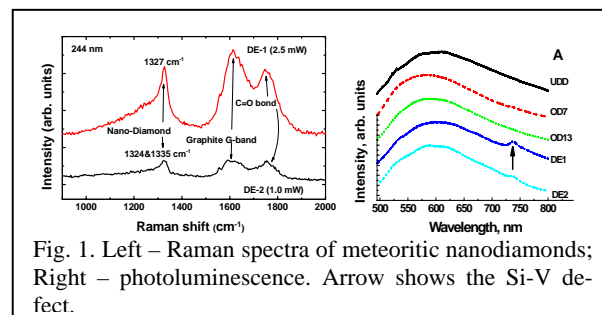


Fig. 1. Left – Raman spectra of meteoritic nanodiamonds; Right – photoluminescence. Arrow shows the Si-V defect.

diamonds consist of a diamond core surrounded by (semi)amorphous and graphite-like carbon.

For the first time the silicon-vacancy complex has been observed in meteoritic nanodiamond by photoluminescence. This is the first observation of this defect in dispersed nanodiamonds of any origin.

**References:** [1] Shiryayev et al. (2011) <http://arxiv.org/abs/1102.0880>; [2] Ferrari A.C. and Robertson J. (2004) *Phil.Trans.R.Soc. Lond A* 362, 2477, [3] Lipp M. et al., (1997) *Phys.Rev. B* 56, 5978, [4] Daulton T.L. et al., (1996) *GCA*, 60, 4853, [5] Knight D. and White W. (1989) *J. Mater. Res.* 4, 385, [6] Zaitsev A., (2001) *Optical properties of diamond*, Springer.