NITROGEN IN METEORITIC NANODIAMONDS: LATTICE IMPURITY IN DIAMOND CORE OR A CONSTITUENT OF AN ASSOCIATED CARBONACEOUS PHASES? A. A. Shiryaev1, A. V. Fisenko2, V. S. Krivobok3, I. I. Vlasov4, L. F. Semjonova1, 1Institute of Crystallography RAS, Leninsky pr. 59, Moscow 119333, Russia, shiryaev@ns.crys.ras.ru, 2Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Kosygina 19, Moscow, Russia, 3Physics Institute RAS, Moscow, Russia, 4General Physics Institute RAS, Moscow, Russia

Introduction: Understanding the origin of meteoritic nanodiamonds (MND) is as interesting cosmochronological problem, especially in view of trapped iso-topically anomalous xenon (Xe-HL), which might indicate that formation of at least a fraction of nanodiamonds grains was related to nucleosynthesis during type II supernovae explosion. One of the most promising ways to establish preferable formation mechanism is the investigation of microstructure and defects in nanodiamonds as well as detailed consideration of accessory phases.

Direct information about defects and structure of meteoritic nanodiamonds is very limited. Based on results of TEM investigation, Daulton et al. [1] suggested that MND were likely formed in CVD-like process. An electron paramagnetic resonance (EPR) study of meteoritic nanodiamonds [2] showed presence of the well-known H1 defect (proton+vacancy complex) which is common for CVD films, bulk nanodiamond prepared by HPHT synthesis and in carbonado [e.g., 3]. Unfortunately, no quantitative information about H1 concentration in MND is provided. Mass-spectrometry shows that H and N are the main chemical impurities in MNDs. The concentration of nitrogen may reach ~2 mass% with unusual δ15N [4]. Such concentrations of nitrogen significantly exceeds not only average, but also the maximal N content reported for terrestrial monocrystalline diamonds (0.04 and 0.3 mass%, correspondingly). Presumably, high stress introduced by relatively large N atoms into diamond lattice is the most important factor limiting N content of diamonds. In the same time, temperature-resolved oxidation shows that N releases simultaneously with carbon [5], suggesting its presence in the diamond lattice. This discrepancy raises fundamental questions whether nanodiamonds indeed differ in their lattice properties from the monocrystalline counterparts or this “extra” nitrogen is trapped in non-diamond carbon shell.

X-ray diffraction and spectroscopic investigation of synthetic ultradisperse nanodiamonds suggest that their structure could be represented by 2 shells: relatively perfect diamond core surrounded by non-diamond carbon shell [6]; existence of stressed diamond layer between the core and the outer shell is also plausible. It is very important to note that it is impossible to remove completely the non-diamond layer; largely due to unavoidable surface reconstruction and sorption from surrounding atmosphere. Therefore, methods of assessing structural impurities in diamonds such as UV-Vis-IR absorption spectroscopy are not applicable to nanodiamonds. The sp2-carbon shell contains various amounts of O, H, N-containing groups whose absorption significantly exceeds and overlaps with typical impurity-related bands in diamond lattice.

In this contribution results of investigation of structure and of spectroscopically-active defects in MND from Efremovka CV3 chondrite. One of the main aims is to understand what serves the main reservoir of nitrogen in MND.

Samples and methods: Nanodiamonds were extracted from the Efremovka CV3 chondrite meteorite using well established process involving multistage chemical treatment and centrifugation [5]. The samples were investigated using X-ray diffraction (XRD), Small-Angle X-ray scattering (SAXS), photoluminescence (PL) at room and at liquid He (LHe) temperatures and by Raman spectroscopy using visible (514 nm) and UV (244 nm) lasers.

Results: Structure of meteoritic nanodiamonds. The XRD patterns of the studied samples resemble those reported for many carbons: several relatively sharp Bragg peaks on a broad structureless background. The structureless halo is a clear indication of (semi)amorphous carbon, possibly enveloping diamond and graphite grains. The XRD results clearly confirm presence of nanosized diamond in the studied samples. Beside the diamond peaks, rhombohedral graphite and other carbonaceous phases are observed. One of the samples underwent a dry heating to the temperature of 300 °C at one of initial steps of the separation procedure. This heating has lead to partial graphitization of nanodiamonds. Remarkably, this graphite-like material could not be removed by repeated chemical treatment with hot acids. This newly formed phase may have important implications to understanding interaction of MND with the host meteorite and conditions of nanodiamonds preservation.

The SAXS signal from meteoritic samples is very strong. Size distribution of the scatterers is heavily...
polydisperse. It can be described as superposition of considerable fraction of particles with radii of 2-3 nm and a broad distribution of larger ones [8]. Such patterns are typical for nanodiamonds of different origin and the most plausible interpretation of the data suggests mixture of diamond grains (2-3 nm in size) with larger aggregates of various phases (e.g., non-diamond carbon, irregular aggregates of diamond grains). This is consistent with the XRD results.

Raman spectra of the MND’s obtained using visible laser (514 nm) are dominated by strong signal of graphite. The diamond peak is not observed. This is not surprising since the ratio of Raman cross-sections for $sp^2/sp^3$ carbon is very high for visible radiation. In addition, size effects and heating of the particles lead to broadening and downshift of the first order Raman peak, making its detection for nanodiamonds extremely challenging [e.g., 9]. However, with the UV excitation the $sp^3$-carbon scattering cross-section increases [review in 10]. The UV Raman spectra of two different samples of MNDs are shown on Fig. 1.

![Figure 1. UV Raman spectra of MND](image1)

Broad, asymmetric downshifted (1327 cm$^{-1}$) diamond peak is clearly observed along with broad bands due to graphite-like carbon and C=O bonds.

**Defects in diamond lattice.** Due to very small amount of available material and unavoidable contamination, absorption spectroscopy is barely useful. Instead, photoluminescence spectroscopy was employed. All samples show red luminescence of variable intensity (Fig. 2). Interpretation of the spectra is not straightforward. Such broad bands are often observed for nanodiamonds of different origin, and might be due to N-V defects (nitrogen-vacancy complex). However, examination of position of this band in our spectra as a function of temperature and excitation wavelength shows that assignment to combination of (NV)$^-$ and (NV)$^+$ defects is doubtful. The observed emission could be at least partly related to non-diamond carbon present in many CVD and detonation nanodiamonds. Another defect encountered after any irradiation of diamonds - GR1 (neutral vacancy) - is absent.

**Discussion.** From our point of view, results of the current study suggest that the meteoritic nanodiamonds are structurally similar to nanodiamonds produced in laboratory by various processes; they likely consist of diamond core surrounded by (semi)amorphous and graphite-like carbon. Chemical attack do remove most of $sp^2$-carbon, but fails to clean the diamonds completely.

Important result of the current study is the absence of obvious manifestations of nitrogen or radiation defects in MND. Reconciliation of absence of the spectroscopic manifestations of structural N with mass-spectrometry is not trivial. Assignment of all the N to the $sp^2$-carbon would require extremely high N (5-10 mass%) content of this phase. The presence of 2 mass% of N in diamond lattice requires an effective mechanism of stress release. If MND indeed contain such amounts of nitrogen, their formation process must be very fast and followed by immediate quenching to prevent nitrogen expulsion. In addition, an efficient non-radiative de-excitation channels should exist to prevent nitrogen detection by luminescence.

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