

Diamonds in meteorites - Raman mapping and cathodoluminescence studies

A.T. Karczemska*

Technical University of Lodz, Institute of Turbomachinery,
219/223 Wolczanska Street, Łódź, Poland

* Corresponding author: E-mail address: anna.karczemska@p.lodz.pl

Received 26.09.2010; published in revised form 01.11.2010

Materials

ABSTRACT

Purpose: The aim of this paper is to show abundance of diamonds existing in the Universe and diamonds diversity among the diversity of other extraterrestrial carbon phases. The main subject of research shown here are example meteorites consisting diamonds: ureilites DaG 868 and Dho 3013. Results are compared with previous investigations. Diamonds exist in many different meteorites, interplanetary dust particles (IDPs) and in comets dust. Origin of different diamonds is still debated among the scientists, two main possibilities are taken into consideration CVD process or shock metamorphism. Understanding laboratory techniques of manufacturing diamond helps in understanding the processes taking place in the Space. From the other side, the new findings and discoveries give the new insight to material science and laboratory techniques.

Design/methodology/approach: The samples were examined with different methods, the most investigations presented here are Raman Mapping and Cathodoluminescence (CL).

Findings: Diamonds have been found in different samples with different shock stages. It means that not all diamonds in urelites could have shock origin. Diamonds from examined samples show high diversity, they exist in different sizes, from nanodiamonds to micrometer sizes diamonds and in different polytypes. Shifts of Raman diamond peaks indicates this.

Research limitations/implications: Results show the possibilities of creating the new diamond-based materials similar to those found in meteorites. Diamond polytypes are not well characterized yet and could give some surprises for materials science. For future research it would be interesting to apply more methods such as X-ray diffraction or HRTEM.

Originality/value: SEM+BSE+EDS+CL results and Raman imaging results of DaG 868 and Dho 1303 ureilites are shown for the first time.

Keywords: Nanomaterials; Diamond; Polytypes; Meteorite

Reference to this paper should be given in the following way:

A.T. Karczemska, Diamonds in meteorites – Raman mapping and cathodoluminescence studies, Journal of Achievements in Materials and Manufacturing Engineering 43/1 (2010) 94-107.

1. Introduction

It is a great interest of materials science in diamond because of its extraordinary mechanical, physical and bio-medical properties [1,2]. Diamond finds many interesting applications in science, technology and recently medicine [2-5]. Diamond-based materials are manufactured in laboratories around world, with different purposes and different methods.

What is the origin of diamonds in the Universe? Or better to ask: what are their origins because different could be. In laboratory, there are many known technologies to manufacture diamond. We have diamonds grown with HPHT technique, CVD method or detonation. Diamonds can be formed in very different conditions, in high pressures and high temperatures and in low pressures and even room temperatures (look at the phase diagram of carbon in Fig. 1). Theories concerning diamond formation in the Space are changing since new methods of diamond formation in laboratory are developed (Fig. 2).

Carbon is common in space and so diamonds are. Astrophysicists have found nanodiamonds around stars and in interiors of dying stars. Diamonds have been also found in many meteorites, for instance carbonaceous chondrites Allende, Murchison), iron meteorites (Canyon Diablo) or ureilites (Novo Urei) [6,7].

In the most primitive matter as the carbonaceous chondrites are, there are presolar diamonds of the sizes of nanometers [8], they have been formed before our Solar System begun. In ureilites [9] there are many diamonds and conglomerates of diamonds of the sizes of few micrometers. In iron meteorites they are also few micrometers diamonds originated in shock event. The first diamonds in meteorites have been found in Novo Urei meteorite in 1888 and in Canyon Diablo iron meteorite in 1891.

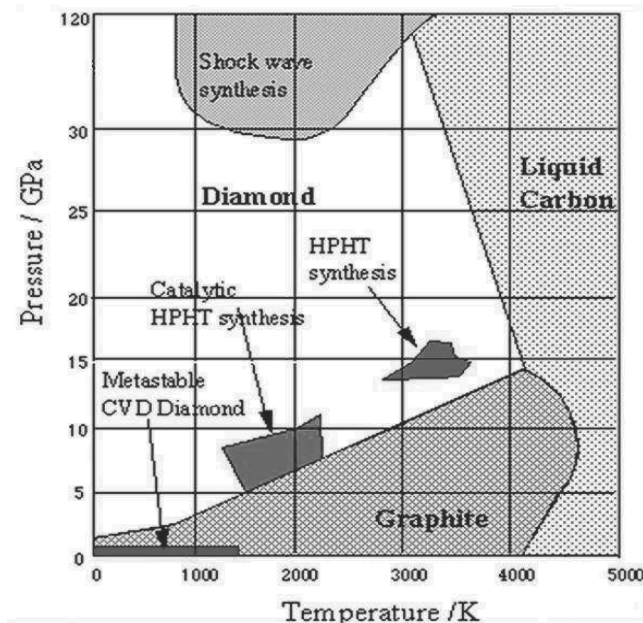


Fig. 1. Phase diagram of carbon [11]

Carbon in space exists in different molecules. Kroto in 1988 [10] has shown the existence of different molecules consisting carbon in the Universe, they are shown in Tab. 1.

Carbon exists even in more different forms in the vapor phase around stars. Astrophysicists detected long carbon chains and carbon clusters consisting many more atoms, among them fullerenes. There are many evidences of existence of organic molecules with extraterrestrial origin. Also nanodiamonds should be abundant in the interstellar medium [13]. Evidence of diamonds of the sizes >50 nm has been detected in HD 97048 and Elias 1 Herbig Ae/Be stars. Also the smaller nanodiamonds and diamondoids have been detected.

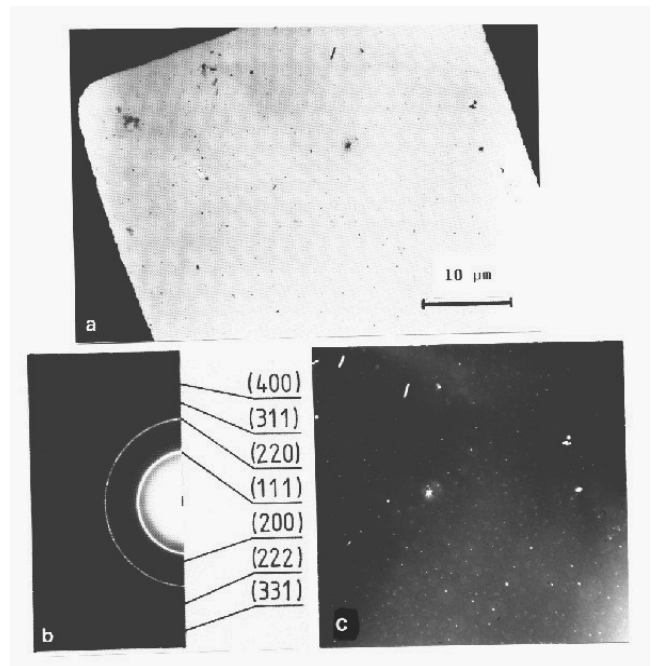


Fig. 2. Diamonds can be formed in the gas phase under reduced pressure [12]

Terrestrial diamonds are cubic, however extraterrestrial diamonds possess different crystalline forms, it means polytypes with cubic, hexagonal or rhombohedral symmetry [14]. There are different diamond polytypes as for example: 3C (cubic), 2H (hexagonal lonsdaleite), 4H, 6H, 8H 15R, 21 R. Different diamond polytypes can be recognized with Raman spectroscopy and X-ray diffraction (Tab. 2). The best known polytype of diamond is lonsdaleite (2H diamond), in 1967 it was discovered in Canyon Diablo iron meteorite and at the same time it was manufactured in laboratory.

Very interesting are nanodiamonds in the Space, as mentioned before they are abundant in the Universe, found in meteorites, interplanetary dust particles, comets, carbon rich stars. From the other side, nanodiamonds find an interest as a very interesting material for science, technology and medicine.

Table 1.
Different interstellar molecules consisting carbon by Kroto [10]

Number of atoms in the molecule	Interstellar molecules consisting carbon
2	CH, CH ⁺ , C ₂ , CN, CO, CS
3	HCN, HNC, HCO, HCO ⁺ , [HCO ⁺], HCS ⁺ , C ₂ H, OCS, C ₂ S
4	H ₂ CO, H ₂ CS, HCNH ⁺ , HNCO, HNCS, HOCO ⁺ , C ₃ H, C ₃ N, C ₃ O, C ₃ S, C ₂ H ₂ , C ₂ H ₄
5	H ₂ C ₂ O, H ₂ CNH, H ₂ NCN, HC ₃ N, HCOOH, C ₃ H ₂ , C ₄ H, CH ₄
6	HCONH ₂ , CH ₃ CN, [CH ₃ CN], CH ₃ OH, CH ₃ SH, C ₅ H
7	HC ₅ N, HCOCH ₃ , CH ₃ C ₂ H, CH ₂ CHCN, NH ₂ CH ₃ , C ₆ H
8	HCOOCH ₃ , CH ₃ C ₃ N
9	HC ₇ N, (CH ₃) ₂ O, CH ₃ CH ₂ CN, CH ₃ CH ₂ OH, CH ₃ C ₄ H
10	CH ₃ C ₅ N, CH ₃ COCH ₃
11	HC ₉ N
13	HC ₁₁ N

Table 2.
Summary of Raman investigations of carbon, examples from experimental and computed (6H, 8H) values [15-17]

Material	Vibration mode	Frequency [cm ⁻¹]
Diamond	T _{2g} stretching	1332
Graphite	E _{2g} stretching	1580
Fullerene C ₆₀	A _g bond alteration	1469
Trans-poly(acetylene)	C-C stretching	1100
	C=C stretching	1500
Poly(diacetylene)	C=C stretching	1500
	C≡C stretching	2100
Diamond 6H polytype	A _{1g} E _{1g}	1332
	2E _{2g}	1298
	2A _{1g}	1270
	E _{2g}	1210
	2A _{1g}	1208
Diamond 8H polytype	A _{1g}	732, 1112, 1332, 1357
	B _{1g}	384, 987, 1322, 1360
	E _{1g}	405, 546, 1304, 1353
	E _{2g}	236, 519, 1265, 1337

2. Description of work methodology, materials for research and experiments

2.1. Samples

Two ureilites samples (Fig. 3) have been used in this research. Dar al Gani 868 (DaG 868), 40.3 g stone, was found in Libyan desert in the year 2000, it has shock level S2. Dhofar 1303 (Dho 1303) was found in Oman in the year 2002 as 404 g stone, it has shock level S3. Ureilites are rare type of meteorites named after meteorite Novo-Urei, Russia that fell in 1886 and was the first known meteorite containing diamonds (discovered in 1888). Ureilites contain olivines and pyroxenes with filling of the

intergranular spaces by carbon veins consisting graphite, amorphous carbon, diamonds, lonsdaleite, carbides and probably other carbon phases. Diamonds may have formed from graphite during impact event [18,19], but it is also possible that they have formed in CVD like process [20].

CVD diamond was manufactured in General Physics Institute, Russian Academy of Science, with Microwave Plasma Chemical Vapor Deposition Method (MW CVD). Carbonado sample is natural polycrystalline diamond from Brazil.

2.2. Methods

The cathodoluminescence analyses (CL) were carried out on polished thin sections by means of the CCL 8200 mk3 device cold cathode (Cambridge Image Technology Ltd.) combined with the polarizing microscope Optiphot 2 (Nikon) and on Scanning

Electron Microscope LEO, type 1430 with microprobe EDS-ISIS 300 and cathodoluminescence device type VIS-View with spectrometer in Polish Geological Institute in Warsaw.

SEM with EDS microprobe, BSE, CL imaging and spectral analysis have been used in samples investigations. The combined BSE+EDS+CL method enables to define geochemical features. BSE imaging allows to distinct minerals. EDS microprobe detection gives information about chemical composition. Cathodoluminescence is a phenomenon of emitting light under electron beam bombardment. The lattice structure, for instance defect like vacancies, broken bands, incorporated additional ions or molecules, represents luminescence centres.

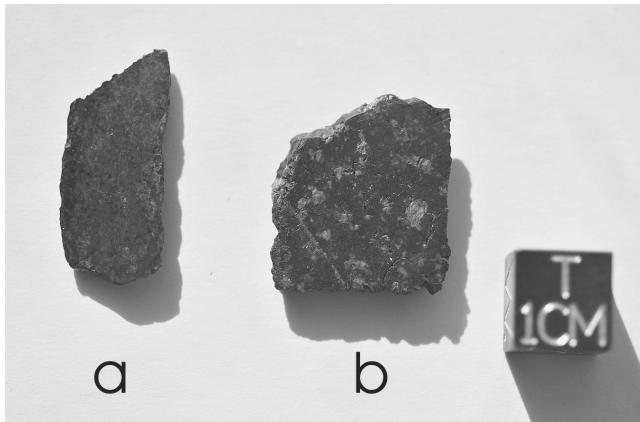


Fig. 3. Polished slices of ureilites a) Dhofar 1303 (Dho 1303) and b) Dar al Gani 868 (DaG 868)

Raman spectroscopy was done in Department of Molecular Physics in Technical University of Lodz – Poland, with usage of confocal micro-Raman spectrometer T-64000 (Jobin-Yvon) equipped with the BX-40 microscope (Olympus). The 514.5 nm Ar line was used for sample excitation. Acquisition time and laser power were adjusted to obtain spectra of sufficient quality. The laser beam diameter was c.a. 1.5 μm . All spectra were deconvoluted with Peakfit 4 software (Jandel) after the baseline correction.

Raman mapping was done in WITec Instruments Corp. in Ulm – Germany, with use of WITec alpha RA instrument equipped with an one grating (600 g/mm, BLZ=500 nm) UHTS 300 spectrometer, Newton-CCD camera (1024 x 127 pixels) and Nikon 100x (NA=0.95) objective. Frequency doubled NdYAG laser (532 nm line) was used for sample excitation. A complete Raman spectrum was acquired at every image pixel, leading to a 2D array of few thousands Raman spectra. By evaluating intensities of different Raman bands, various Raman images can be evaluated.

3. Results and discussion

3.1. CL results

Meteorites thin sections exposed to the bombardment of electron beam emit light in visible region. The source of emitted light are

luminescent centres: defects like vacancies, incorporated additional atoms or molecules etc.

Pictures in Figures 4-7 are made with use of CCL 8200 mk3 device cold cathode. Figure 4 presents the image of DaG 868 ureilite. Diamonds are seen as the bright-yellow spots, they are seen in vein-like carbon areas. Olivines shine with red color.

Figure 5 presents CL image of Dho 1303 ureilite. Diamonds can be seen also in this sample, however there are not so many as in DaG 868 and in some places they form strange chain-like shapes. Figure 6 presents CL image of polycrystalline diamond manufactured with MP CVD method. CVD diamond shines with blue color. Figure 7 shows CL image of carbonado – natural polycrystalline diamond with probably extraterrestrial origin, it shines with yellow color.

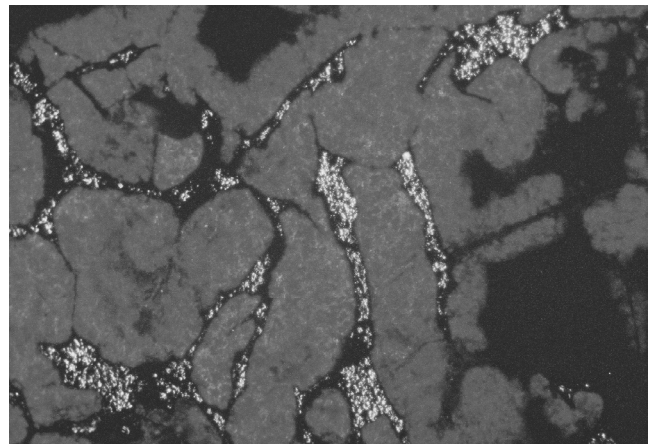


Fig. 4. CL image of DaG 868 ureilite, bright-yellow spots are diamonds (CCL 8200 mk3 device cold cathode)

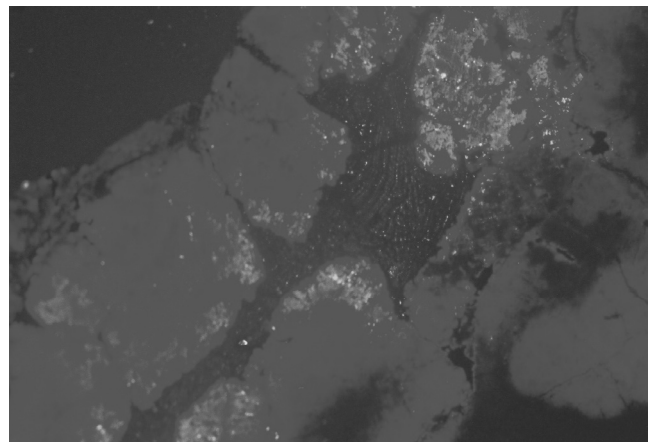


Fig. 5. CL image of Dho 1303 ureilite (CCL 8200 mk3 device cold cathode), diamonds are seen in the carbon vein-like area as the bright-yellow small spots

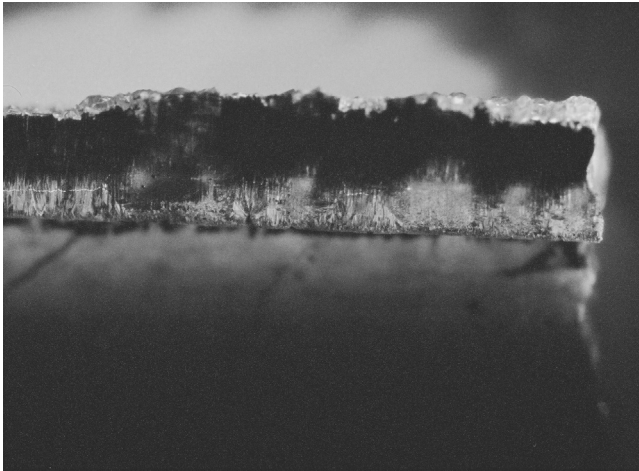


Fig. 6. CL image of CVD diamond manufactured with MP CVD method (CCL 8200 mk3 device cold cathode)

Figures 8-19 show results of DaG 868 and Dho 1303 ureilites made with Scanning Electron Microscope (SEM) LEO type 1430

equipped with cathodoluminescence detector. Figures 20-21 show results obtained for CVD polycrystalline diamond.

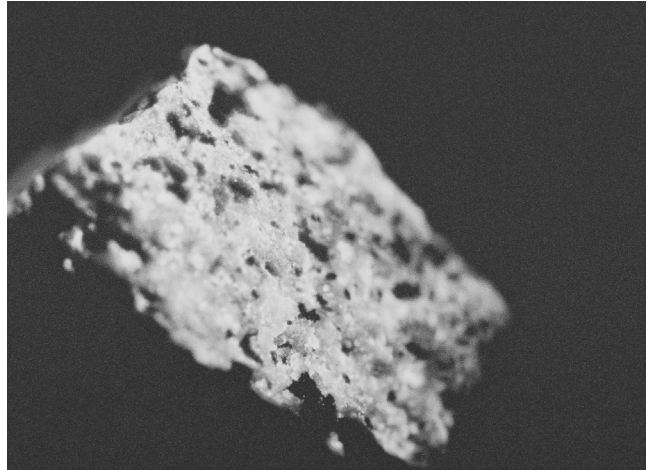


Fig. 7. CL image of carbonado – natural polycrystalline diamond with probably extraterrestrial origin (CCL 8200 mk3 device cold cathode)

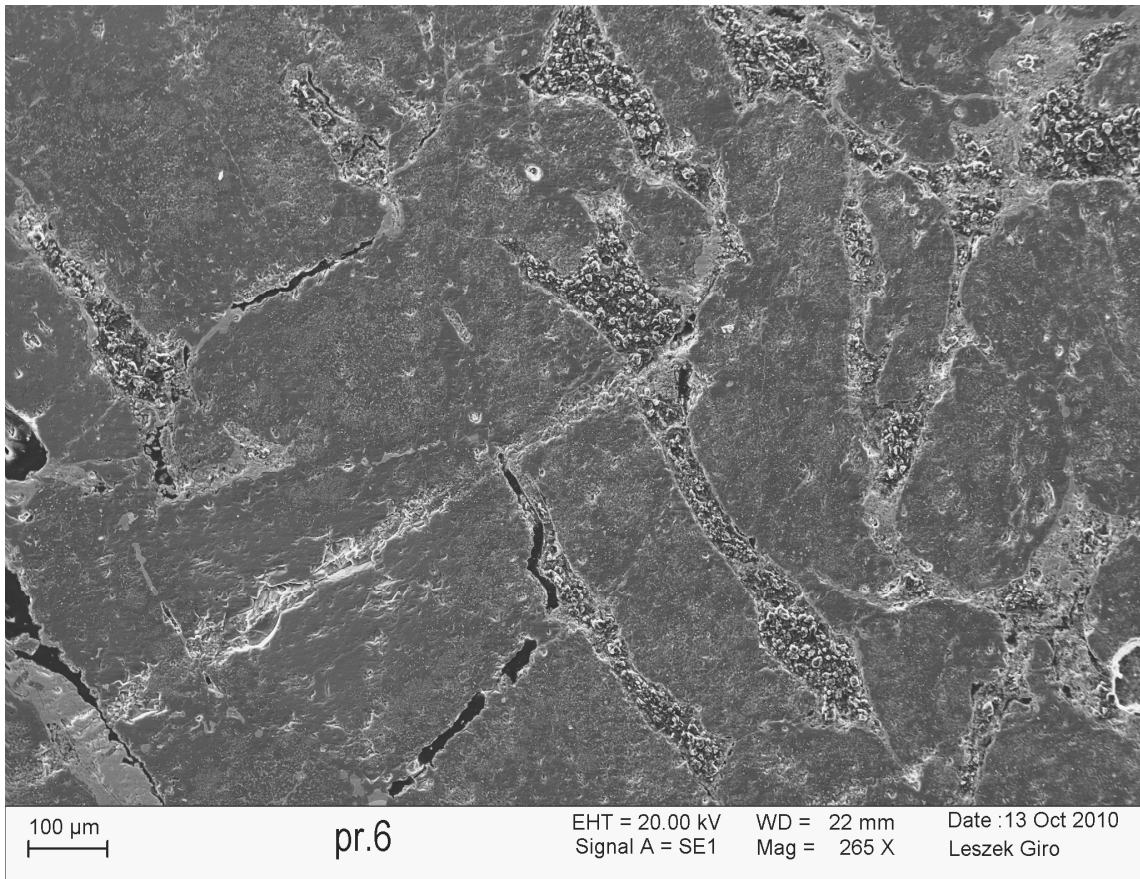


Fig. 8. SEM image of DaG 868 ureilite, there are seen vein-like carbon areas consisting diamonds

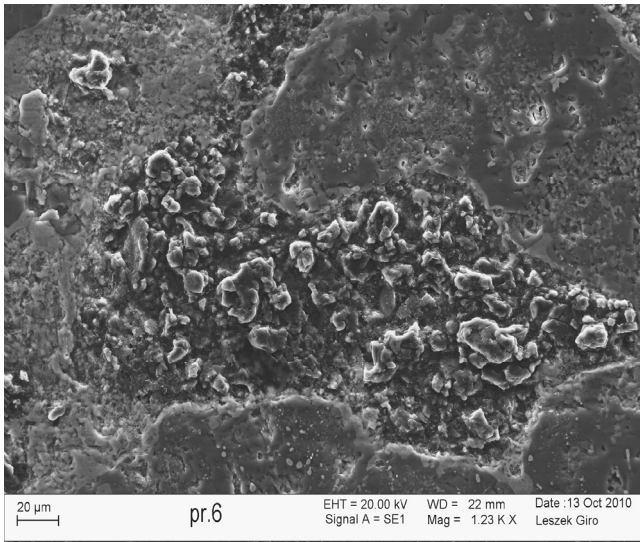


Fig. 9. SEM image of vein-like carbon area of DaG 868 ureilite, diamonds are seen

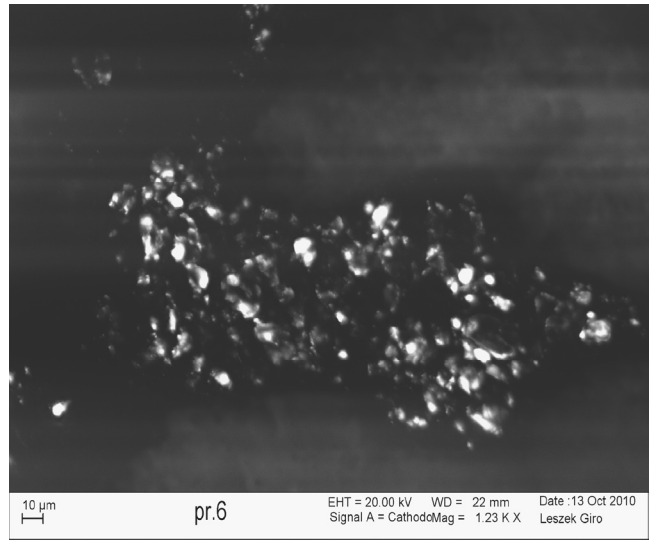


Fig. 10. CL image of vein-like area of DaG 868 ureilite (the same as in Fig. 10), diamonds are seen as the bright spots

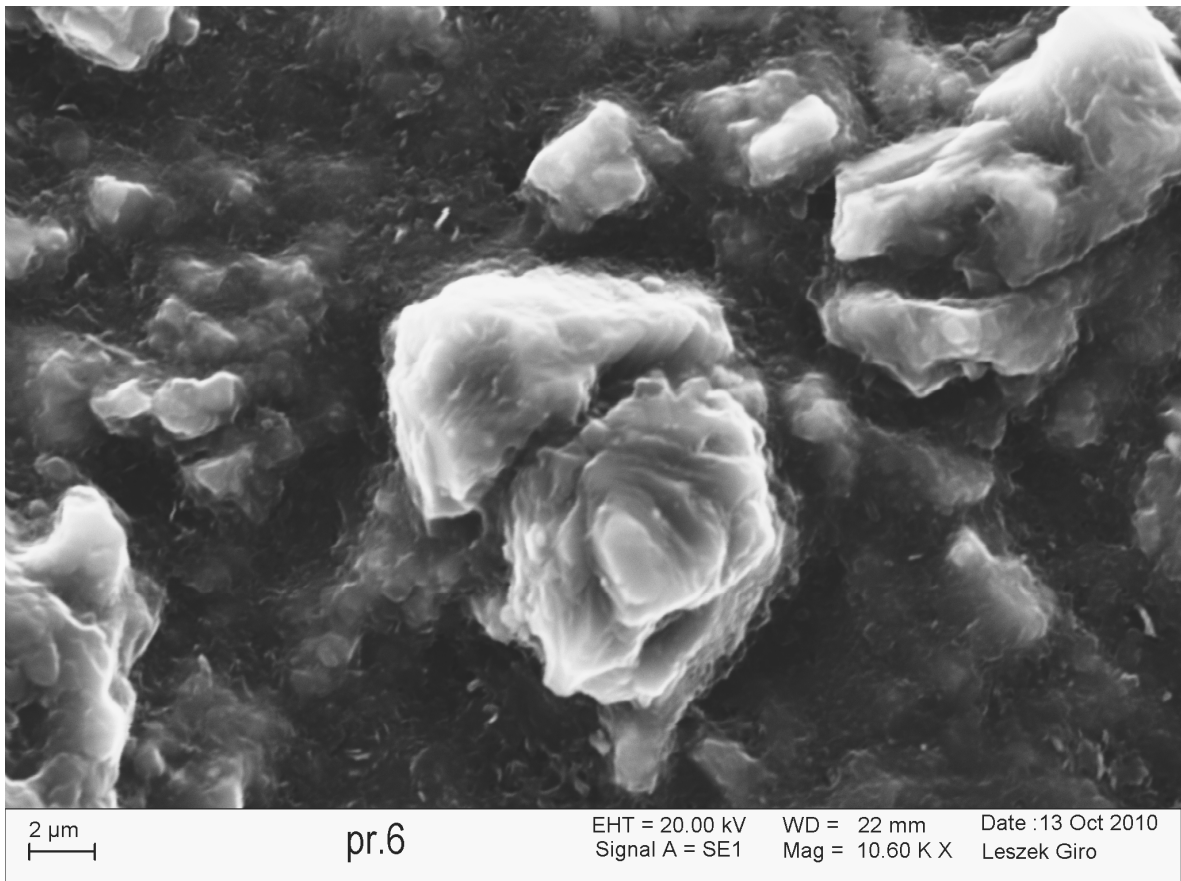


Fig. 11. SEM image of diamonds in DaG 868 ureilite

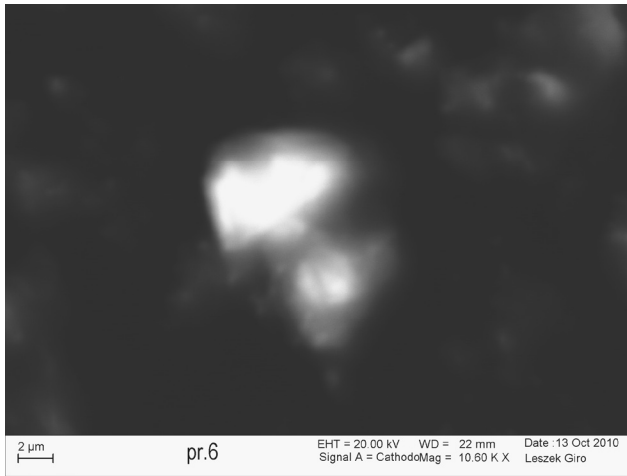


Fig. 12. CL image of diamonds in DaG 868 (from Fig. 12), diamonds are seen as the bright spots

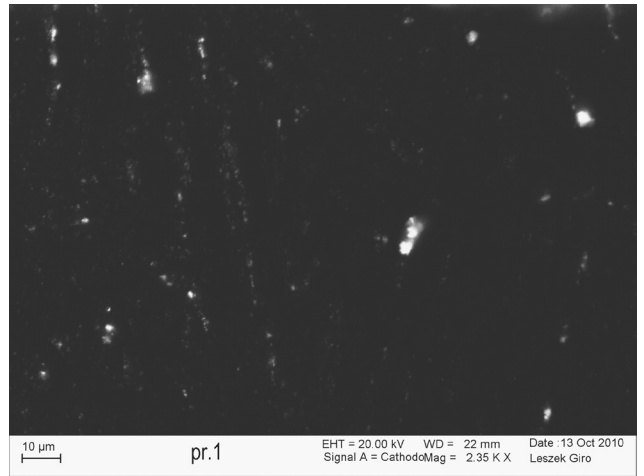


Fig. 15. CL image of Dho 1303 ureilite at the same place as Fig. 14, the bright spots are diamonds

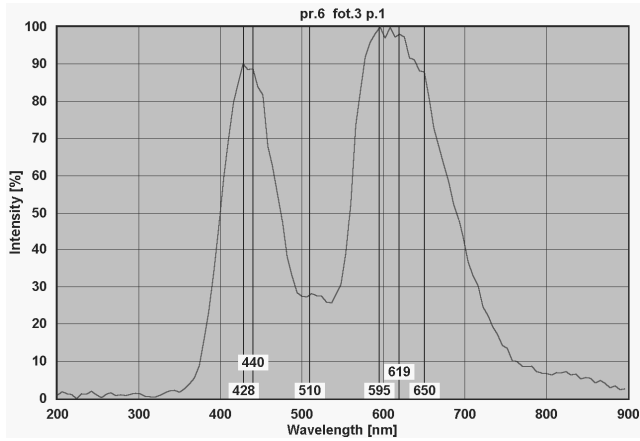


Fig. 13. CL spectra of diamond (from Fig. 11-12) from DaG 868 ureilite

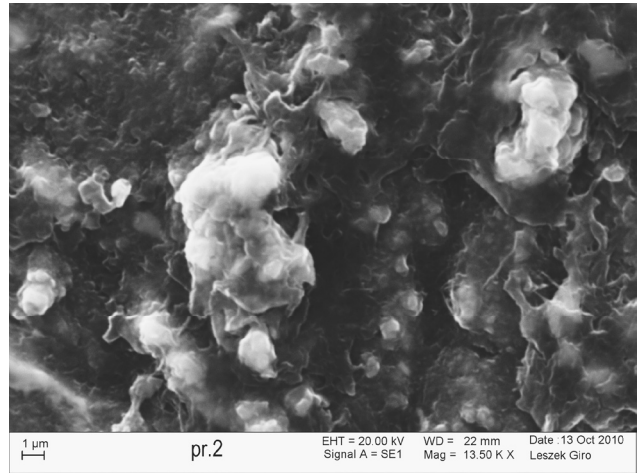


Fig. 16. SEM image of diamonds in Dho 1303 ureilite

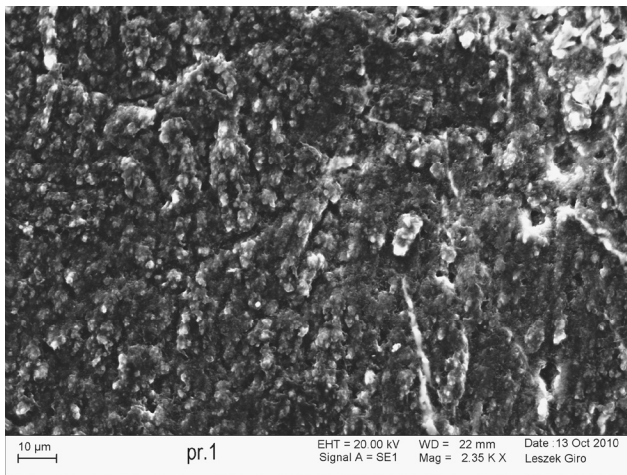


Fig. 14. SEM image of Dho 1303 ureilite

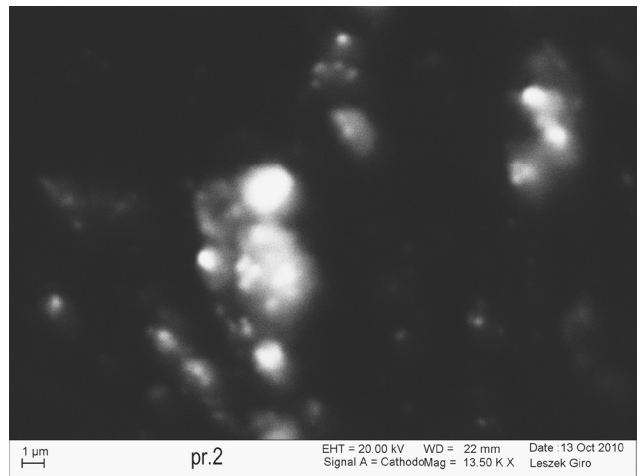


Fig. 17. CL image of diamonds in Dho 1303 ureilite

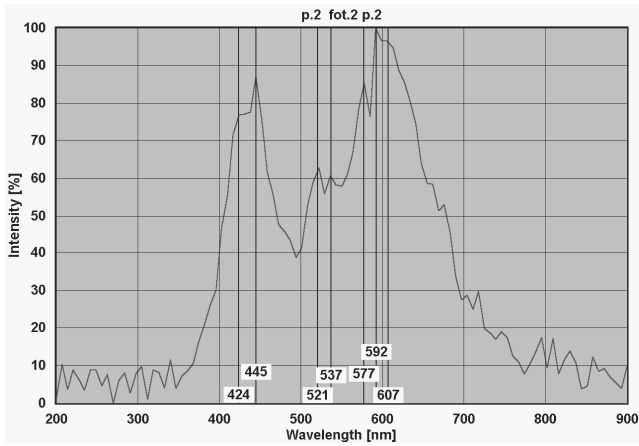


Fig. 18. CL spectra of diamond (from Figs. 16-17) in Dho 1303 ureilite

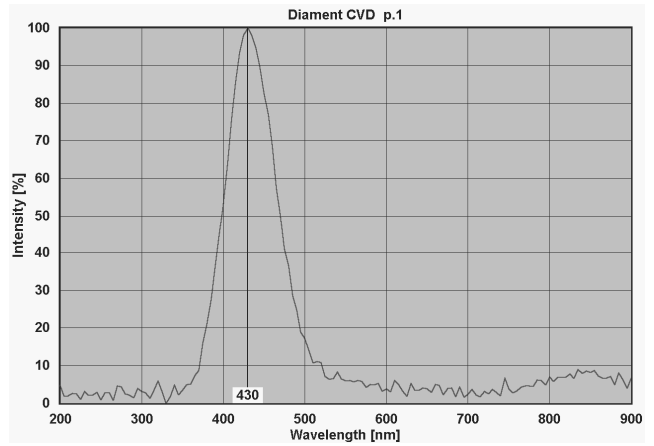


Fig. 21. CL spectra of CVD polycrystalline diamond

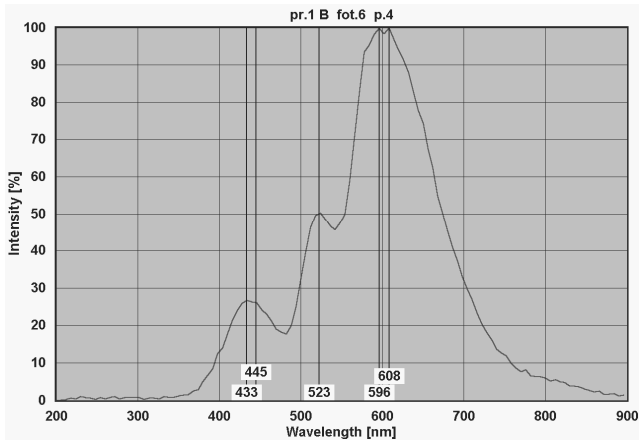


Fig. 19. Example CL spectra of diamond in Dho 1303 ureilite

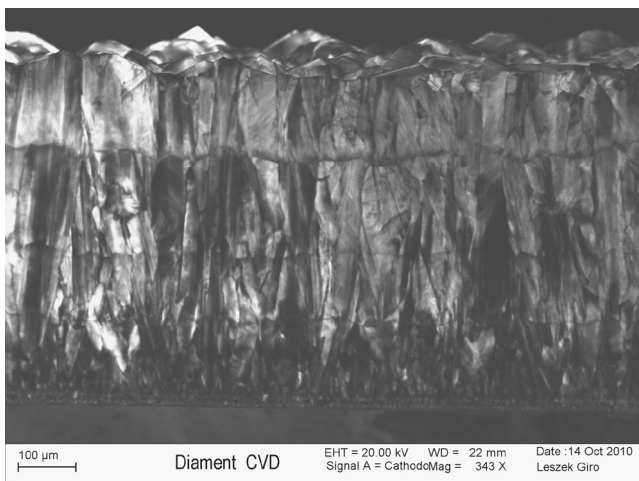


Fig. 20. CL image of CVD polycrystalline diamond

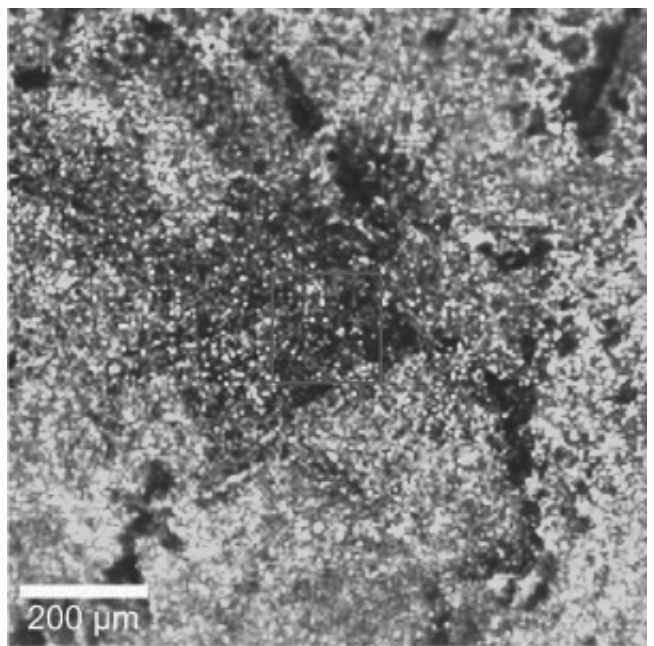


Fig. 22. Video images of DaG 868

3.2. Raman mapping

Raman spectroscopy is a powerful, non-destructive tool to investigate the structure of carbon materials. Even more powerful tool for carbon research is Raman imaging (mapping), described more precisely elsewhere [21]. It allows to examine the distribution and diversity of carbon phases in the sample. For materials engineering research, it allows to control material quality, uniformity and for instance is used for analyzing internal stresses inside the sample. It is important for instance in examining CVD polycrystalline diamond and its quality.

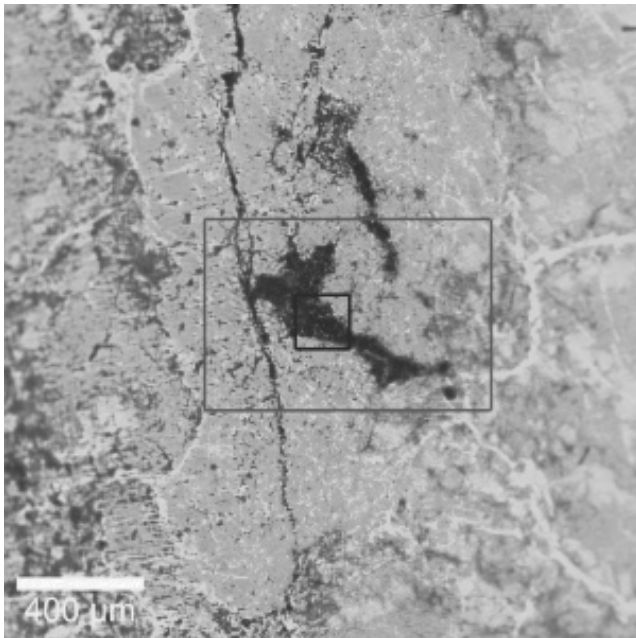


Fig. 23. Video image of Dho1303

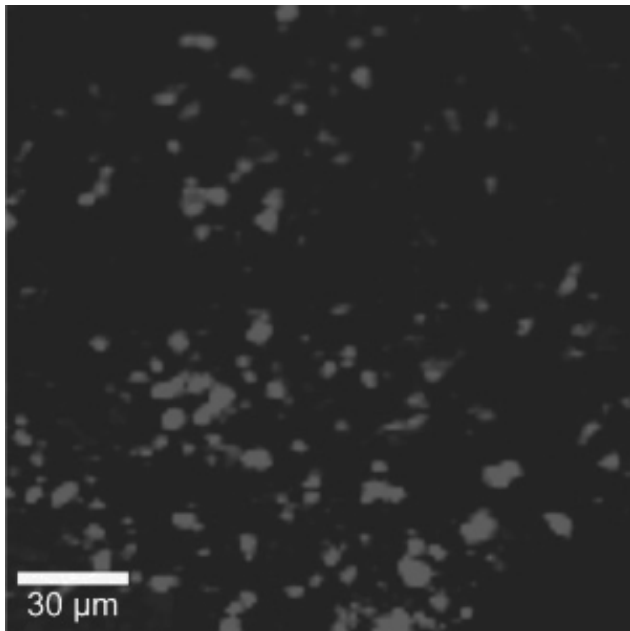


Fig. 24. Color-coded Raman image of DaG 868 ureilite, excitation 532 nm, $170\ \mu\text{m} \times 170\ \mu\text{m}$ and 120×120 pixels with an integration time/spectrum of 150 ms

Figures 22 and 23 show the video images of investigated samples. Red rectangle in Figure 22 and blue rectangle in Figure 23 show the investigated areas. Color coded 2D images of several thousand Raman spectra, of DaG 868 and Dho 1303, are shown in the Figures 24 and 26. Averaged Raman spectra are shown in the

Figures 25 for DaG 868 and Figure 27 for Dho1303. Colors in the images correspond to the colors of spectra for each sample.

Strong and narrow peak of $1334\ \text{cm}^{-1}$ appears in the Figure 23 (blue spectra), peaks around $1420\ \text{cm}^{-1}$ and $3100\ \text{cm}^{-1}$ are also seen. Red spectra shows peaks at $1359\ \text{cm}^{-1}$, small peak at $1426\ \text{cm}^{-1}$, strong peak at $1587\ \text{cm}^{-1}$ and peaks at $2700\ \text{cm}^{-1}$ and broad peak at $3150\ \text{cm}^{-1}$.

Red Raman spectra in Figure 25 shows peaks at 1356 , 1588 and $2704\ \text{cm}^{-1}$. Blue spectra shows peaks at $1334\ \text{cm}^{-1}$, $1466\ \text{cm}^{-1}$ and $3200\ \text{cm}^{-1}$. Green spectra shows peaks at 239 , 342 , 401 , 542 , 680 and $1023\ \text{cm}^{-1}$.

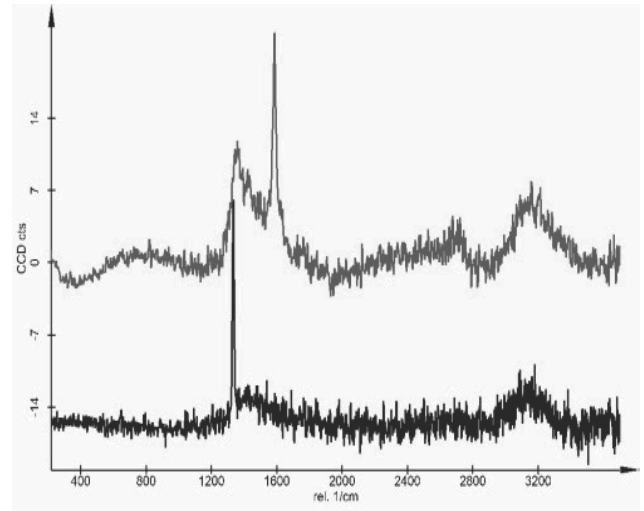


Fig. 25. Averaged Raman spectra for DaG 868, corresponded to Fig. 21

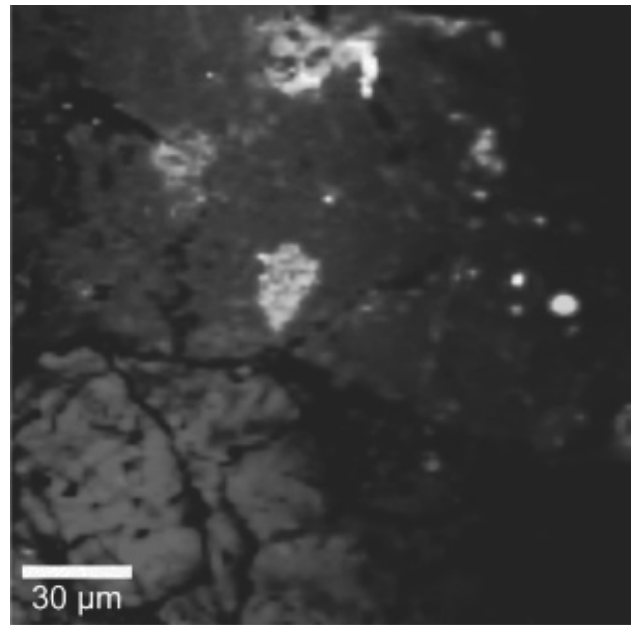


Fig. 26. Color coded Raman image of Dho 1303 ureilite, excitation 532 nm, $170\ \mu\text{m} \times 170\ \mu\text{m}$ and 120×120 pixels with an integration time/spectrum of 100 ms

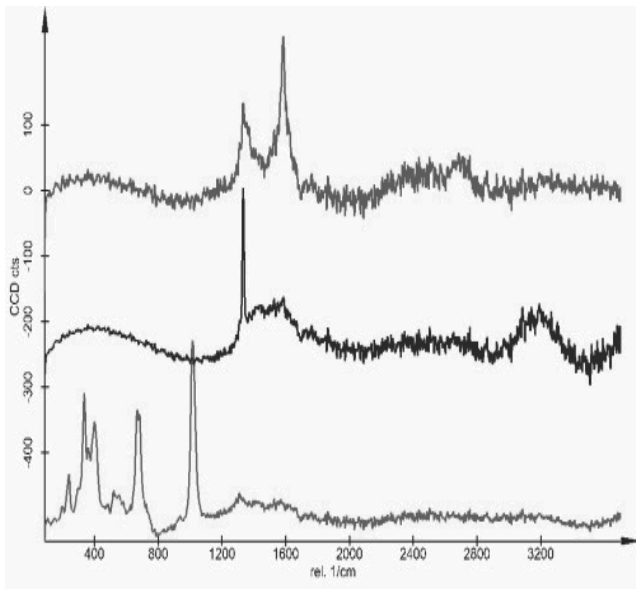


Fig. 27. Averaged Raman spectra in Dho 1303, colors correspond to Fig. 23

3.3. Discussion

Red luminescence of olivines and yellow luminescence of diamonds is seen in Figures 4-5. High abundance of micrometer sizes diamonds or conglomerates of diamonds (bright-yellow spots) is seen in carbon veins filling places between olivines and pyroxenes. CVD diamond manufactured with MP CVD method has blue luminescence (Fig. 6). Carbonado has yellow luminescence (Fig. 7).

SEM+CL investigations allow the more precise research.

Pratesi [23] reviews diamonds CL bands according to CL centres. The closest bands to my investigations are:

- 415 nm (2.98 eV) the N3 CVD center,
- 424 nm (2.92 eV) a center detected in type IIa diamonds, easily destroyed by electron irradiation,
- 435 nm (2.88 eV): the A-band is observed in all natural, CVD and HPHT diamonds and is one of the most characteristic features of type IIa diamonds with mosaic texture,
- 438 nm (2.83 eV) a weak line sometimes detected in IIb diamonds,
- 440 nm (2.82 eV) has been observed in brown diamonds and in high-silicon natural diamonds,
- 451 nm (2.75 eV) observed in brown diamonds which emit a yellow luminescence under excitation at a wavelength of 365 nm,
- 500 nm (2.48 eV) a center (B-line) detected in natural brown diamonds showing yellow luminescence under a 365 nm ultraviolet lamp,
- 503 nm (2.46 eV) the H3 center, along with N2 center, is the most typical naturally occurring feature of diamonds containing nitrogen,

- 516 nm (2.40 eV) center may be observed in natural brown diamonds showing yellow luminescence under a 365 ultraviolet source,
- 525 nm (2.36 eV) a broad band, associated with the H3 center, may be detected in natural brown diamonds.

Grund et al [19] uses cathodoluminescence for diamonds investigations in ureilites. From their measurements, diamonds in ureilites have two dominant spectral peaks appearing with different intensities: 435 nm and 615 nm. A small emission was found at 520 nm. Similar CL-spectra have been obtained for shock-induced Ries crater diamonds so authors conclusion is that ureilitic diamonds are also shock-induced.

Results presented in this paper for ureilites DaG 868 and Dho 3103 are in agreement with those mentioned above, CL-spectra show peaks appearing with different intensities around 435 nm, small peak at 520 nm and around 600 nm (Figs 13, 18 and 19). CL-spectra of CVD polycrystalline diamond shows one peak at 430 nm (Fig. 21), referred by Pretasi as the A band. However, it is possible to obtain CVD diamonds similar to ureilitic diamonds. Seo et al [29] show CL spectra of CVD nitrogen incorporated diamonds with peaks around 430 nm, 600 nm and additionally with strong peak at 750 nm.

Carbonado is natural polycrystalline diamond recovered from two places in the Earth: Brazil and Central Africa. It is aggregate of randomly polycrystallized microdiamonds of the sizes not exceeded 20 μm , with porous structure, filled with the other minerals. Its origin is still unclear. Ozima et al [30] propose radiation-induced diamond crystallization as the possible method of carbonado synthesis. Origin of carbonado is still unclear, however there are evidences that it was part of meteorite and that these special diamonds fell down from the sky.

Diamonds can be formed also in the interiors of dying stars.

Inside white dwarf BPM 37093, which is about 50-light years from the Earth, there is diamond of the size of about 4000 km. After discovery in 2004 [31,32], astronomers nicknamed this special object – Lucy, after the Beatles song “Lucy in the Sky with Diamonds”. It is possible that meteorite which brought carbonado diamonds to the Earth was just part of such interior of white dwarf, similar to Lucy, which arrived to our Solar System.

Rondeau et al [33] show CL-spectra for carbonado sample possessing several lines: a group of emissions at 415, 428, 439, 452 and 463 nm (N_3V center), a group of emissions at 503, 511 and 520 nm (N_2V center), a group of emission at 575, 588, 602 and 620 nm (N-V^0 defect). N_3V center is group of three nitrogen atoms around a vacancy. N_2V center is a pair of nitrogen atoms combined to a vacancy. N-V^0 defect corresponds to a nitrogen atom associated to a neutral vacancy.

Bischoff et al [18] show that presence or absence of diamonds in ureilites is related to the shock level of meteorite. Their investigations show that low-shock ureilites don't contain diamonds, diamonds are present in S3 or higher levels of shock. For the higher levels of shock, it means above S2, no correlation between the level of shock and diamonds abundance was found. Authors have shown CL images of ureilitic diamonds. In Dar al Gani ureilite diamonds are arranged in chains.

In this paper, similar CL images are presented. Diamonds are arranged in chains in some areas of Dho1303 ureilite (Figs 5, 14 and 15). High abundance of diamonds is seen in DaG 868 meteorite with shock level S2, Dho 1303 with shock level S3 doesn't show so high abundance of diamonds.

In ureilites olivine is used to study shock stages. Shock stages are divided to few groups according to Stöffler scale corresponding to pressures levels: S0 and S1 - unshocked (< 4-5 GPa); S2 - very weakly shocked (5–10 GPa); S3 - weakly shocked (10–15 GPa); S4 - moderately shocked (25–30 GPa); S5 - strongly shocked (40–60 GPa); S6 - very strongly shocked (75–90 GPa) [24]. Comparing the shock stage to results of impact diamonds from Ries crater (Germany), the theory of formation by a solid state martensitic phase transformation from graphite at pressures of 45-55 GPa was proposed (Stöffler 1971, Schmitt 2005). The post-shock temperature of 1175-1775 K was estimated.

However there are ureilites with low shock stage and possessing diamonds. Almahata Sitta, unshocked meteorite with S0 shock stage, possesses diamonds [25]. Our preliminary investigations of Almahata Sitta meteorite also prove that (PhD thesis of Tomasz Jakubowski). Another interesting thing is that DaG 868 (S2) possesses more diamonds than Dho 1303 (S3).

Does it mean that diamonds in ureilites (maybe part or all of them) are formed in different process than HPHT? Is their origin similar to CVD process?

Have diamonds been formed in the young Solar System from the gas phase? Diamonds (nanodiamonds) have been found in interplanetary dust particles falling down from the sky to our planet every day and in cometary dust (for instance Stardust project). How abundant they are in the Universe? How different they are from diamonds on Earth?

From the previous Raman investigations it is seen that there is diversity of carbon phases in meteorites [21, 22, 26-28], and diversity of extraterrestrial diamonds. For instance even in small, few micrometers square area of ureilite, diamonds of different Raman shifts are present, as seen in Figure 33 [21].

Diamonds in ureilites coexist with graphite and other carbon phases which also show high diversity. From Raman investigation it is seen that graphite in ureilites exists with different levels of order. 1580 cm^{-1} sharp peak indicates the presence of highly ordered graphite. If graphite becomes more disordered, additional peaks appear at 1350 cm^{-1} and 1620 cm^{-1} . Another important parameter is full width at half maximum (FWHM), it gives information about structural order.

Classical diamond (3C) Raman peak, so common for diamonds on Earth, is 1332 cm^{-1} . In meteorites this value is often shifted. Sharp and strong band indicates the monocrystalline structure of diamond. Diamonds from Space show also diversity of FWHM parameters, they have different level of order (disorder) [21].

Different diamond Raman peaks can characterize different polytypes of diamond, but also can indicate internal stresses inside diamonds crystals, different isotopic crystals composition or smaller crystal sizes (presence of nanodiamonds). It is proved that different diamond polytypes such as 2H, 6H, 8H, 10H, 21R, occurs in different ureilites [14]. Raman imaging investigations are with agreement to the previous results of Vdovykin from 1970-ies, cited by Phelps in [14], but they give new light to these results. Different polytypes of diamond coexist together, in the small area of the sample (look at Figure 34).

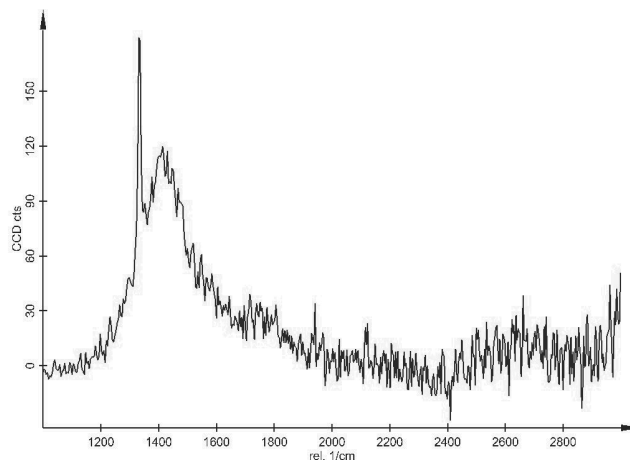


Fig. 28. Example Raman spectra of DaG 868 ureilite, peaks at 1333 cm^{-1} and 1430 cm^{-1} are seen.

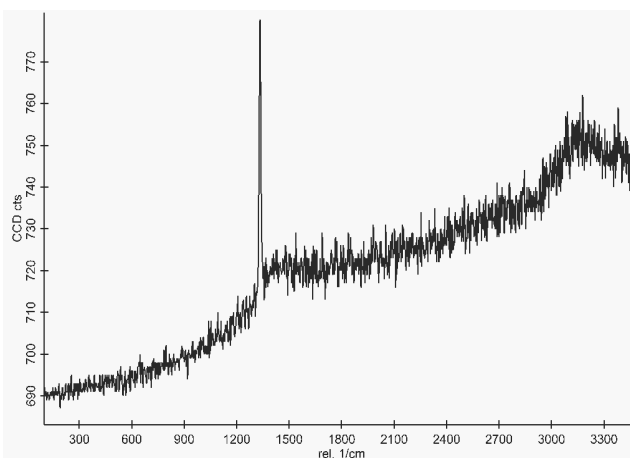


Fig. 29. Example Raman spectra of DaG 868 ureilite, peak at 1334 cm^{-1} is seen.

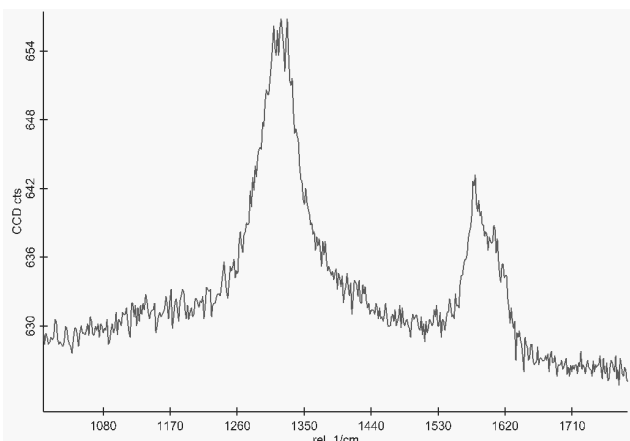


Fig. 30. Example Raman spectra of carbon phases of Dho 1303 ureilite, peaks at 1317 cm^{-1} , 1580 cm^{-1} and 1604 cm^{-1} are seen.

For DaG 868 there are diamond Raman shifts from 1319 cm^{-1} to 1339 cm^{-1} . For Dho 1303 there are diamond Raman shifts from 1310 cm^{-1} to 1340 cm^{-1} . Figures 28-33 show example raw Raman spectra for DaG 868 and Dho 1303 meteorites showing diversity of diamond Raman shifts and FWHM parameters (full width at half maximum). FWHM parameters are from about 10 cm^{-1} to few tens cm^{-1} .

The additional broad band at 1430 cm^{-1} may be caused by carbon phase chaoite [34].

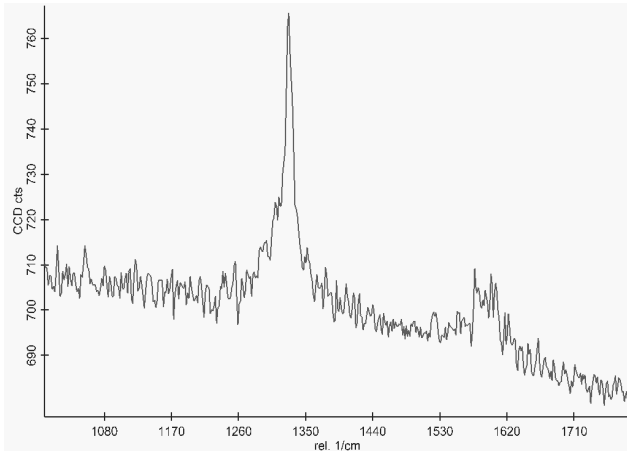


Fig. 31. Example Raman spectra of carbon phases of Dho 1303 ureilite, peaks at 1329 cm^{-1} and 1590 cm^{-1} are seen.

Presolar nanodiamonds separated from Allende meteorite in Max-Planck Institute in Mainz have been examined with Raman spectroscopy with usage of confocal micro-Raman spectrometer T-64000 (Jobin-Yvon) equipped with the BX-40 microscope

(Olympus) in Department of Molecular Physics in Technical University of Lodz. Raman spectra for presolar nanodiamonds was obtained for the first time (Fig. 31) [28]. Peaks at 580, 790, 1100, 1326, 1590 and 1900 cm^{-1} have been detected. Carbonaceous chondrites as the Allende meteorite is, are very interesting group of meteorites because they are the most primitive matter from our Solar System. This is kind of matter from what our Solar System was formed.

Diamonds from carbonaceous chondrites of the sizes of 2-5 nanometers are called presolar, because all or part of them have been formed before our Solar System was formed

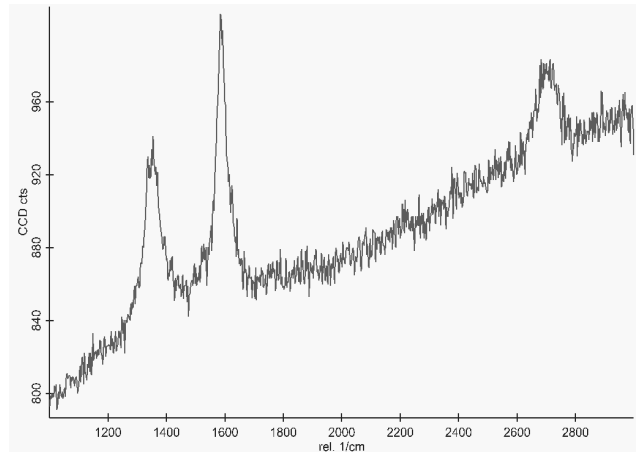


Fig. 32. Example Raman spectra of carbon phases of Dho 1303 ureilite, peaks at 1355 cm^{-1} and 1588 cm^{-1} and 2700 cm^{-1} seen..

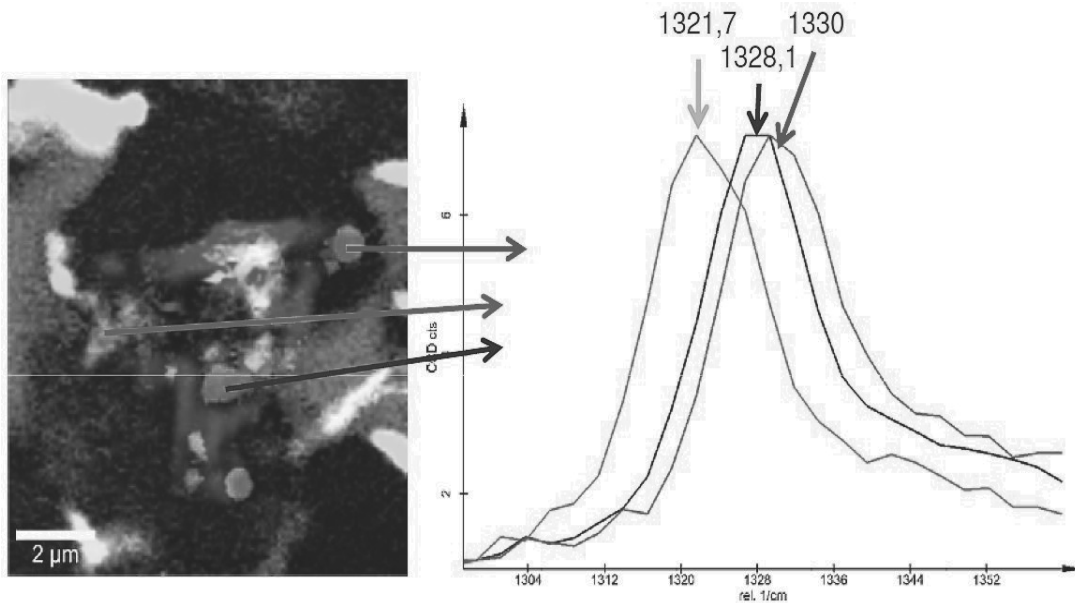


Fig. 33. Diversity of diamonds in JaH 054 ureilite, different colors represent different Raman spectra [21]

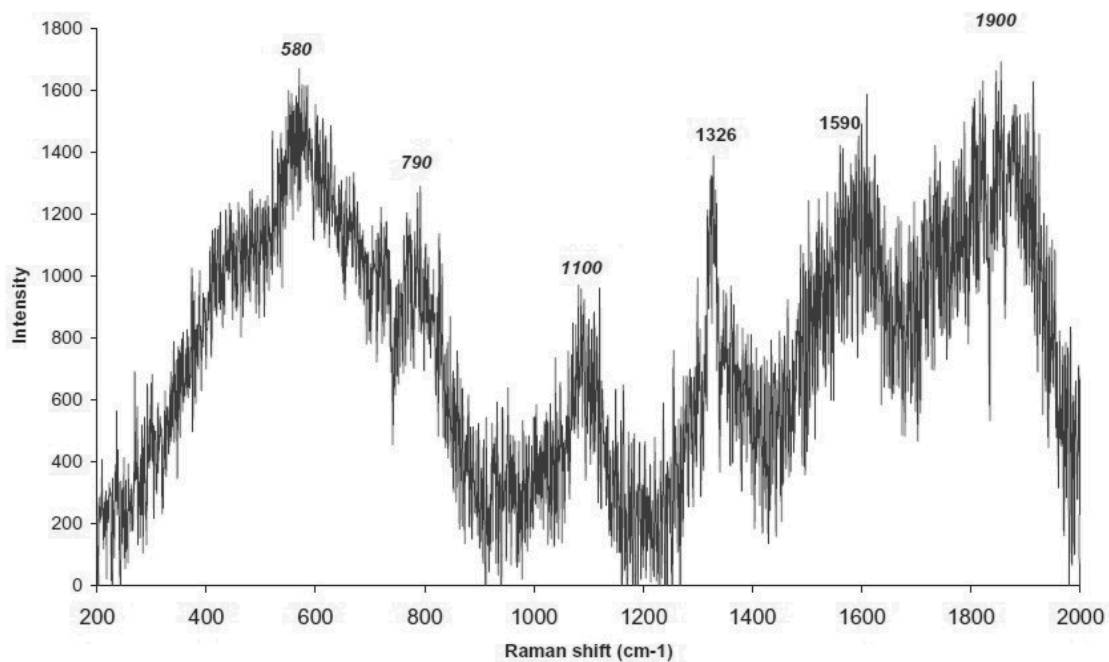


Fig. 34. Raman spectroscopy of presolar nanodiamonds from Allende meteorite [28]

4. Conclusions

There are different diamonds in the Universe of different origin, different sizes and different polytypes. Meteoritic diamonds, their diversity and richness, show us the beauty of nature. There is still a lot of questions concerning the origin of diamonds falling down from the sky. The origin of ureilitic diamonds is still unclear. However, we can be sure that diamonds in the Universe are formed in many ways and in many different places.

The new findings in the area of meteoritic carbon can lead us to conclusion that we can still learn a lot from the nature and that carbon can give us many surprises. Research on diamond polytypes and nanodiamonds found in meteorites can bring new insight to materials science, this knowledge can help in designing and manufacturing new carbon materials. Understanding of diamonds origin can allow to develop the technologies of diamond manufacturing in laboratory.

Scanning Electron Microscopy with Cathodoluminescence and Raman Mapping are the powerful tools for investigations of carbon phases in meteorites. They allow to show the distribution of diamonds in the samples and to study the diversity of carbon phases.

Acknowledgements

I would like to thank people who helped me in this research and shared with me fascination of meteorites and diamonds: Mgr

Tomasz Jakubowski, Dr Marian Szurgot, Dr Marcin Kozanecki, Doc. Dr hab. Magdalena Sikorska-Jaworowska, Mgr Leszek Giro, Dr Ulrich Ott, Dr Arnold Gucsik, Dr Jan Toporski, Andrea Jaus, Prof. Aleksandra Sokołowska, Prof. Stanisław Mitura, WITec Instruments Corp. Thank you for all fruitful discussions and collaboration. Additionally I would like especially thank prof. Leszek Dobrzański for his invitation to write this article.

References

- [1] L.A. Dobrzański, Fundamentals of Materials Science and Physical Metallurgy, Engineering Materials with Fundamentals of Materials Design, WNT, Warszawa, 2002 (in Polish).
- [2] S. Mitura, K. Mitura, P. Niedzielski, P. Louda, V. Danilenko, Nanocrystalline Diamond, its synthesis, properties and applications, Journal of Achievements in Materials and Manufacturing Engineering 16/1-2 (2006) 9-16.
- [3] J. Grabarczyk, D. Batory, P. Louda, P. Couvrat, I. Kotela, K. Bakowicz-Mitura, Carbon Coatings for Medical Implants, Journal of Achievements in Materials and Manufacturing Engineering 20/1-2 (2007) 107-110.
- [4] K. Fabisiak, E. Staryga, CVD diamond, from growth to application, Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 264-269.
- [5] K.T. Wojciechowski, R. Zybala, R. Mania, J. Morgiel, DLC layers prepared by the PVD magnetron sputtering technique,

- Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 726-729.
- [6] M.Szurgot, A.Karczemska, M.Kozanecki, Extraterrestrial diamonds, Nanodiam, PWN, Warszawa, 2006, 259.
- [7] A.Karczemska, M.Szurgot, M.Kozanecki, M.Szynkowska, V.Ralchenko, V.V.Danilenko, P.Louda, S.Mitura, "Extraterrestrial, terrestrial and laboratory diamonds - differences and similarities", *Diamond and Related Materials* 17/7-10 (2008) 1179-1185.
- [8] U. Ott, Nanodiamonds in meteorites, *Journal of Achievements in Materials and Manufacturing Engineering* 37/2 (2009) 779-784.
- [9] C. A. Goodrich, "Ureilites: critical review" *Meteoritics* 27 (1992) 327-352.
- [10] H.W. Kroto, "The chemistry of the interstellar medium", *Phil. Trans. R. Soc. Land. A* 325 (1988) 405-421.
- [11] F.P. Bundy, The P,T Phase and Reaction diagram for elemental Carbon, 1979, *J. Geophys. Res.* 85 (B12) (1980) 6930.
- [12] S. Mitura, Nucleation of diamond powder particles in an RF methane plasma, *Journal of Crystal Growth* 80/2 (1987) 417-424.
- [13] A.P. Jones, L.B. d'Hendecourt, "Interstellar Nanodiamonds" *Journal: Astrophysics of Dust, ASP Conference Series, Vol. 309*, Edited by Adolf N. Witt, Geoffrey C. Clayton and Bruce T. Draine., p.589.
- [14] A.W. Phelps, "Interstellar Diamond: I. Condensation and Nucleation", *Lunar and Planetary Science XXX*, Abstract 749.
- [15] L. Kavan, J. Kastner, Molecular and electron spectroscopy of carbene structures, R.B. Heimann et al. (eds.) *Carbyne and Carbynoid Structures*, Kluwer (1999) 342-356.
- [16] S.Bhargava, H.D. Bist, S. Sahli, M. Aslam, H.B. Tripathi, Diamond Polytypes in the chemical vapor deposited diamond films, *Applied Physic Letter* 67/12 (1995) 1706-1708.
- [17] Z. Wang, Y. Zhao, Ch-S. Zha, Q. Xue, R. T. Downs, *Adv. Mater.* 20, 3303 -3307, (2008).
- [18] A. Bischoff, C.A. Goodrich, T. Grund, "Shock-induced origin of diamonds in ureilites", *Lunar and Planetary Science XXX* (1999) Abstract 1100.
- [19] T. Grund, A. Bischoff, "Cathodoluminescence properties of diamonds in ureilites: further evidence for a shock-induced origin", 62nd Annual Meteoritical Society Meeting, Abstract 5074
- [20] M. Miyamoto and T. Takase and Y. Mitsuda, Raman spectra of various diamonds, *Mineralogical Journal* 16/5 (1993) 246-257.
- [21] A. Karczemska, T. Jakubowski, M. Kozanecki, I. Tsydel, A. Jauss, A. Gucsik, *AIP Conference Proceedings* 1163 (2009) 59-71.
- [22] A. Karczemska, T. Jakubowski, F. Vergas, Different diamonds in meteorites DaG 868 and NWA 3140 ureilites, *Journal of Achievements in Materials and Manufacturing Engineering* 37/2 (2009) 292-297.
- [23] G. Pratesi, Impact Diamonds: Formation, Mineralogical Features and Cathodoluminescence Properties, in. *Cathodoluminescence and its Application in the Planetary Sciences* Ed. A. Gucsik, Springer (2009) 61-86.
- [24] R.T. Schmitt, C. Lapke, C.M. Lingemann, M. Siebenschock, D. Stöffler, Distribution and origin of impact diamonds in the Ries crater, Germany, in *Large meteorite impacts III*, Ed. By T. Kenkmann, F. Hörz, A. Deutsch, Published by the Geological Society of America Inc. (2005) 299-313.
- [25] A.J. Ross, A. Steele, H. Downes, M. Fries, A.P. Jones, L. Kater, C.L. Smith, P. Jenniskens, M. Shaddad, M. Zolensky, Raman Analysis of Diamond in Almahata Sitta and Other Ureilites, 73rd Annual Meteoritical Society Meeting (2010) Abstract #5062.
- [26] T. Jakubowski, A. Karczemska, M. Kozanecki, A. Gucsik, A. Stanishevsky and S. Mitura, "Micro-Raman spectroscopy of diamonds from hot desert ureilites", 40th Lunar and Planetary Science Conference, Abstract #1382 (2009).
- [27] A. Karczemska, T. Jakubowski, M. Kozanecki, "Raman Spectroscopy Studies of Diamond and Graphite Phases in JaH 054 Ureilite", 72nd Annual Meteoritical Society Meeting, #Abstract 5382 (2009).
- [28] A. Gucsik, U. Ott, E. Marosits, A. Karczemska, M. Kozanecki, M. Szurgot, "Micro-Raman study of nanodiamonds from Allende meteorite" *IAU SYMPOSIA, Organic Matter in Space Proceedings IAU Symposium International Astronomical Union 2008 S.Kwok & S.Sandford* 251 (2008) 335-339, doi:10.1017/S1743921308021893
- [29] S.H. Seo, T.H. Lee, J.S. Park, K.H. Auh, Cathodoluminescence characteristics of nitrogen incorporated diamond films grown by microwave plasma CVD, *Journal of Ceramic Processing Research* 4/4 (2003) 173-176.
- [30] M. Ozima, M. Tatsumoto, Radiation-induced diamond crystallization: Origin of carbonados and its implications on meteoritic nano-diamonds, *Geochimica and Cosmochimica Acta* 61 (1997) 369-376.
- [31] T.S. Metcalfe, M.H. Montgomery, A. Kanaan, Testing White Dwarf Crystallization Theory with Asteroseismology of the Massive Pulsating DA star BMP 37093, *Astrophys. J.* 605/2 (2004) 133-136.
- [32] <http://news.bbc.co.uk/2/hi/3492919.stm>
- [33] B. Rondeau, V. Sautter, J. Barjon, New columnar texture of carbonado Cathodoluminescence study, *Diamond and Related Materials* 17/11 (2008) 1897-1901.
- [34] C. Lapke, R.T. Schmitt, T. Kenkmann, D. Stöffler, Raman Microspectrometry of shocked graphite and impact diamonds from the Ries Crater, Germany, *Lunar and Planetary Science XXXI* (2000), Abstract #1040