Description of the results – 2nd stage of the project (January – December 2018)

Title of 2nd stage: Determination of the local, atomic structure and of the electron properties of intrinsic and impurity associated defects in crystalline cubic boron nitride (cBN) with yellow-gold and dark coloration prepared by industrial high pressure-high temperature (HP-HT) synthesis, determined by correlated EPR, microstructure and optical investigations (continuation of the 1st stage). Changing the aggregation state of impurities and defects in yellow-gold and dark cBN by thermochemical and/or irradiation treatments. Identification and characterization of the resulting dispersed impurity states.

Estimated results of the research activity:

- Identification of the structure and nature of the aggregates of impurities and/or lattice defects localized in the yellow-gold and dark colored cBN crystallites prepared by industrial HP-HT synthesis (continuation of the 1st stage) .
- Procedure for the dispersion of the impurity aggregates in the yellow-gold (amber) and dark colored cBN crystallites.
- The nature and structure of the dispersed impurities and intrinsic defects.

Activity 2.1. Optical (photoluminescence –PL and Raman) investigations of the photosensitive centers in cBN. Determination of the energy levels in the band structure associated with these centers.

The EPR investigations performed in the first stage of this project concluded that several types of impurities associated with the observed paramagnetic defects should be present. Based on the specific properties of their EPR spectra (absence of hyperfine structure and broad Lorentzian lineshape) it has been also concluded that a non-uniform distribution of impurities, including aggregates of impurities consisting of atoms with mainly zero nuclear moment natural abundant isotopes should be present.

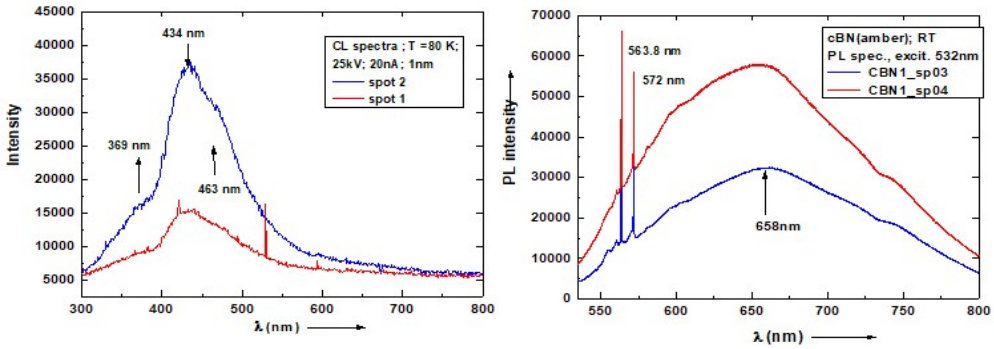

Figure 1. *The CL spectra (left) and the PL spectra (right) of a CBN-400 amber colored plate-like crystallite recorded at two distinct spots.*

The confirmation of the non-uniform distribution of natural impurities in the investigated cBN crystals has been obtained from cathodo-luminescence (CL) and micro-photoluminescence (μ-PL) investigations performed in this (2^{nd}) stage of the project. Thus, enlarged images of the amber colored cBN single crystals obtained in a scanning electron microscope (SEM) equipped for detecting the CL induced by the microscope electron beam, evidenced a variation in the intensity of the resulting CL across the investigated cBN crystallites.

CL spectral measurements in the visible range did prove that the observed CL spatial variation is determined only by changes in the concentration of the luminescent impurity centers(see Figure 1 - left) . The μ-PL measurements at room temperature (RT) under excitation with the 2^{nd} harmonic of a YAG:Nd^{3+} laser (532 nm) on two different spots of the same cBN crystallite have also evidenced variations in the PL intensity emission, with no special variation in the spectral distribution of the PL emission (Figure 1 - right).

Further information about the energy levels of the photosensitive impurities in the band structure of the cBN, based on EPR measurements, are presented in the Activity 2.3 section.

Activity 2.2. <u>Changing the aggregation state of impurities in crystalline cBN by thermo-chemical/irradiation treatments.</u>

Changes in the aggregation state of impurities induced by thermal treatments in vacuum at high temperatures have been investigated for amber colored CBN500 60/70 mesh and dark CBN Type 1 60/70 mesh samples. The thermal treatments were performed on such cBN crystalline powders inserted in fused pure silica tubes closed to one end (ampoules) and connected at the other end to a vacuum station. The closed end of the ampoule containing the cBN powder was inserted in a furnace, and heated from RT to 950 ^{0}C in 30 minutes, under a vacuum of better that 10^{-4} mbar. After 4 hours of thermal treatment in vacuum at 950 ^{0}C the ampoules were withdrawn from the furnace and cooled to RT in less than 1 minute.

The visual inspection of the silica ampoule containing the treated samples exhibited, for both amber and dark colored cBN crystalline powder cases, the formation in the cooler part, where the ampoule exited the furnace, of a white deposit. The EPR spectra of the investigated cBN samples subjected to such thermal treatment in vacuum exhibited changes described and analyzed in section: Activity 2.3.

The microstructural analysis of the composition and microstructure of samples from the white deposit (reported under Activity 2.4) offered additional valuable information about the nature and structure of the impurity aggregates in the cBN crystal, as well as about their thermal induced dispersion and ejection from the lattice host.

Activity 2.3. <u>Observing and monitoring by EPR and optical spectroscopy the dispersion of the impurities in the crystalline cBN.</u>

Comparing the EPR spectra of the two investigated CBN-500 (amber) and CBN Type 1 (dark) samples before and after the thermal treatment in vacuum, revealed changes in the intensity of the component EPR lines, resulting from thermal induced variations in the concentration of the paramagnetic centers responsible for the observed lines. Thus, the EPR spectrum of the amber colored CBN-500 samples exhibit following the thermal treatment only an insignificant variation in the intensity of the main, broad g=2.0037 centered line, while the small intensity, narrow line centered at g = 2.0027 practically vanishes. Meanwhile, in the dark colored CBN-Type 1 samples, while the main, broad line centered at g =2.0079 does not change significantly, the narrow line centered at g = 2.0029 decreases dramatically following the thermal treatment. It is obvious that the concentration of the paramagnetic centers responsible for the g =2.0028 +/- 0.0003 centered narrow line decreases during the thermal treatment.

We have also performed "*in-situ*" illumination experiments with the sample in the EPR spectrometer microwave cavity cooled to cryogenic temperatures. The experiments were performed with the specially developed "*in-situ*" monochromatic illumination set-up which allows to illuminate samples inserted in the probing head- microwave measuring cavity of the Bruker ESR spectrometers equipped with low temperature cryostats for operation at temperatures as low as 3.6 K. The set-up is described in a paper under preparation. Thus we found changes in the intensity of the EPR lines of the dark colored CBN-Type 1 samples during illumination with UV light (λ =365 nm) at T =100K. While the main broad line centered at g =2.0079 did increase in intensity by such illumination, the narrow line centered at g = 2.0029 did exhibit only a small intensity decrease. The change in the intensity of the EPR lines reflecting corresponding changes into the concentration of the paramagnetic centers is explained by the trapping of the electrons photo excited into the conduction band by the UV light of 3.4 eV energy. Thus, in the case of the QD center responsible for the broad line centered at g =2.0079, its concentration increase by illumination can be explained by the existence of an e-charged EPR silent QD^- precursor center which loses an electron by UV ionization into the conduction band. It means that its energy level is localized in the gap at $E(QD^-)$ = 6,4 – 3.4 = 3.0 eV below the conduction band, where E_g = 6.4 eV is the band gap of cBN. One should mention that such photo induced effects were not observed in the amber colored cBN-500 samples

Activity 2.4. **<u>Observing and monitoring by HRTEM and HRSTEM the dispersion of the impurty / defect aggregates in cBN (1st part). Analysis of the white powder deposited in the cold zone of the silica ampoule with cBN subjected to thermal treatment.</u>**

The analysis of samples from the white powder deposited in the cold zone of the silica ampoule during the thermal treatment has been performed with the analytical HRTEM microscope JEOL JEM ARM 200C. Using several microstructural and microanalytical techniques it is demonstrated that the

main component of the white powder consists of nanocrystallites of SnO_2 with tetragonal symmetry ($P4_2/mnm$). The Sn-O composition of the white powder was further confirmed by elementary mapping with EDS. The SnO_2 structure has been observed in the white powder resulting from the thermal treatment of both amber colored cBN-500 and dark colored cBN Type 1 crystalline powders.

Activity 2.4. **Observing and monitoring by HRTEM and HRSTEM the dispersion of the impurty / defect aggregates in cBN (1st part). Investigating the impurity aggregates in cBN crystalline powders.**

Microstructural investigations, to evidence the presence of impurity aggregates and their dispersion by thermal treatments, have been performed by HRTEM and STEM on cBN crystals before and after being subjected to thermal treatment in vacuum for 4 hours at T > 900 ^{0}C. To perform such investigation we had to prepare extremely thin samples (thickness < 50 nm) of crystalline cBN .

(a) Evidencing the presence of impurity precipitates/aggregates by (HR)TEM/STEM in dark cBN Type 1 crystals before the thermal treatment.

Investigating by TEM such thinned samples, extracted from untreated dark cBN Type 1, one could observe small precipitates (size < 5 nm) with amorphous structure (Figure 2a), as well as larger precipitates with sizes in the 20 to 50 nm range exhibiting a crystalline structure (Figure 2b) . As shown in figures 2, they are better observed in the STEM mode, where the contrast is proportional to Z^2, where Z is the atomic number of the atoms contained in the precipitate. Measurements in the HRTEM mode of the interatomic distances in the larger precipitates resulted in the determination of the following interplanar spacing values $d_{1\text{-}11}$ = 0.37 nm si d_{220} = 0.23 nm. According to the JCPDS file 87-0794 they correspond to metallic tin (Sn) of cubic structure and lattice parameter a = 6.489 Å.

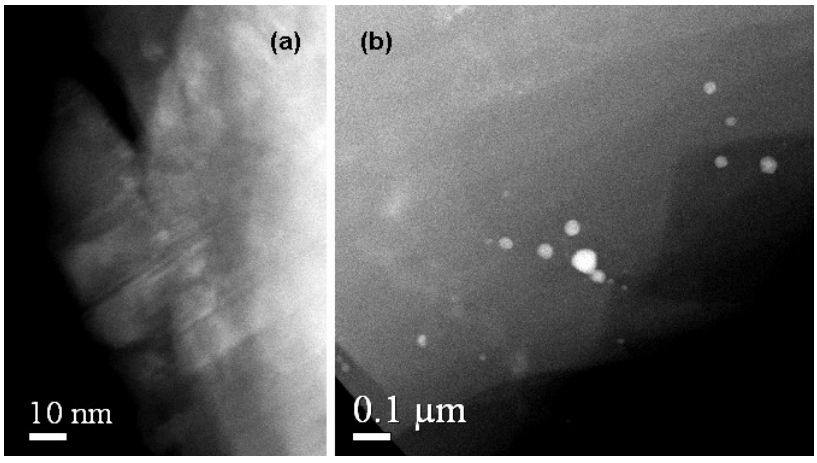

Figure 2. *Impurity precipitates, with Sn composition, observed in the STEM images of dark cBN – type 1 samples as white spots: (a) small precipitates, and (b) larger precipitates.*

(b) Evidencing the dispersion of the impurity aggregates in the dark cBN Type 1 samples thermally treated in vacuum at 950 ^{o}C.

The HRTEM/STEM measurements on samples extracted from dark cBN Type 1 crystals subjected to thermal annealing in vacuum at T =950 ^{0}C revealed the dispersion of the agglomerates observed in the untreated/as received crystals. Indeed, comparing Figures 2 form an untreated with the STEM image of a sample extracted form a dark cBN Type 1 crystal subjected to the thermal treatment of 4 hours in vacuum at T =950 ^{0}C , one observes in this last case/image (Figure 3) the absence of any aggregate.

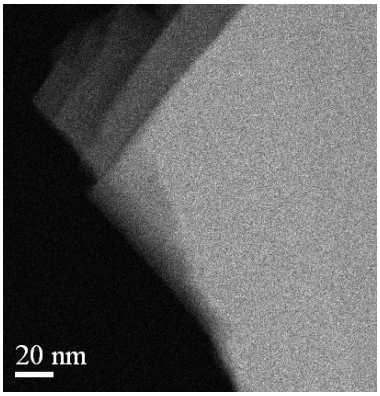

Figure 3*. STEM image of a dark cBN Type 1 crystallite subjected to thermal treatment in vacuum for 4 hours at T =950 ^{0}C.*

Conclusions

- The observation by microstructural techniques of impurity aggregates in cBN crystals confirms the conclusions based on EPR and optical investigations about the non-uniform distribution of impurities, with formation of aggregates in the cBN crystals.
- It has been shown that by thermal treatment in vacuum at 900 ^{0}C < T < 950 ^{0}C for several hours the cBN crystals are losing substance in the form of a white powder deposited on the cooler part of the treating ampoule.
- It has been demonstrated that the white powder produced by the thermal treatment of cBN crystals consists of SnO_2 nanocrystals resulting from the dispersion of Sn aggregates observed in the as-received cBN crystals, which diffuses at the surface of the cBN during the thermal treatment, evaporates and deposits in the cooler part of the silica ampoule as SnO_2.
- The microstructural investigations have confirmed the dispersion of Sn aggregates observed in the untreated samples, and their diffusion at the surface of cBN crystals.

Activity 2.5. <u>Presentation of the original results as communications at international scientific conferences and their publication as papers in internationally recognized (ISI) scientific journals.</u>

The original scientific results obtained from the research activities performed in the frame of the present research project PN-III-P4-ID-PCE-2016-0079, have been presented as communications at international scientific conferences and published as original papers in reputed internationally recognized (ISI) scientific journals, as follows:

Publications:

1."Production and annealing of the paramagnetic defects in as-grown and oxygen doped floating zone silicon irradiated with high fluence 3.5 MeV and 27 MeV electrons", A. C. Joita and S. V. Nistor, Mater. *Science in Semicond. Processing* 83, 1 (2018).

2. "Structure of defects in semiconductor crystalline cubic boron nitride. A microstructural and micro analytical investigation". L. C. Nistor, A. M. Vlaicu and S.V. Nistor, *Radiation Measurements*, submitted Oct. 16, 2018;

3. "Presence and distribution of impurity defects in crystalline cubic boron nitride. A spectroscopic study". S. V. Nistor, L. C. Nistor, A. M. Vlaicu and A. C. Joita, *Radiation Measurements*, submitted Oct. 16, 2018.

4. "Investigating photo-active ESR centers in semiconductors by high intensity *in-situ* illumination", S. V. Nistor and A. C. Joita, in preparation, *Proc. Romanian Acad*., series A; FI(ISI) = 1.65.

Presentations at conferences (year 2018):

1. "About the nature and distribution of defects in crystalline cubic boron nitride wide band-gap semiconductor", S. V. Nistor, L. C. Nistor, A. M. Vlaicu and A. C.Joita, The 10th International Conference on Luminescent Detectors and Transformers of Ionizing Radiation, LUMDETR-2018, Prague, 9-14 Sept. 2018 (oral presentation).

2. "Structure of defects in semiconductor cubic boron nitride. A microstructural and microanalytical investigation", L. C. Nistor, A. M. Vlaicu, R. F. Negrea and S. V. Nistor, The 10th International Conference on Luminescent Detectors and Transformers of Ionizing Radiation, LUMDETR-2018, Prague, 9-14 Sept. 2018 (poster presentation).

3. "Impurity type defects in crystalline cubic boron nitride. A correlated ESR, ESM and CL study on cBN crystals", A. C. Joita, S. V. Nistor, L. C. Nistor and A. M. Vlaicu, The 10th International Conference on Luminescent Detectors and Transformers of Ionizing Radiation, LUMDETR-2018, Prague, 9-14 Sept. 2018 (poster presentation).

General conclusions:

- We have evidenced by micro-photoluminescence the presence in amber and dark colored cBN crystallites, 200 microns maximum size the presence of a non-uniform distribution of optically active impurities, very likely with formation of aggregates of various sizes as well.
- Investigations by HRTEM and HRSTEM have evidenced the presence in the dark cBN crystallites of metallic Sn precipitates/aggregates with cubic structure.
- We have developed a procedure for dispersing the Sn-aggregates by thermal treatment at T = 950 ^{0}C in vacuum in fused silica ampoules. Such thermally treated cBN crystallites exhibited changes in their EPR spectra as well as the disappearance of the Sn-aggregates observed by HRTEM in the untreated samples.
- In the next (3rd) stage of investigations one expects to obtain, according to the working plan, by correlating the EPR, optical, microstructural and analytical data, new information concerning the nature of the aggregates in various degrees of dispersion in the cBN crystal lattice, including in molecular/atomic state of dispersion.