Cathodoluminescence Microscopy and Spectroscopy of Micro- and Nanodiamonds: An Implication for Laboratory Astrophysics

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Abstract: Color centers in selected micro- and nanodiamond samples were investigated by cathodoluminescence (CL) microscopy and spectroscopy at 298 K [room temperature (RT)] and 77 K [liquid-nitrogen temperature (LNT)] to assess the value of the technique for astrophysics. Nanodiamonds from meteorites were compared with synthetic diamonds made with different processes involving distinct synthesis mechanisms (chemical vapor deposition, static high pressure high temperature, detonation). A CL emission peak centered at around 540 nm at 77 K was observed in almost all of the selected diamond samples and is assigned to the dislocation defect with nitrogen atoms. Additional peaks were identified at 387 and 452 nm, which are related to the vacancy defect. In general, peak intensity at LNT at the samples was increased in comparison to RT. The results indicate a clear temperature—dependence of the spectroscopic properties of diamond. This suggests the method is a useful tool in laboratory astrophysics.

Key words: cathodoluminescence, scanning electron microscopy, nanodiamond, astrophysics

INTRODUCTION

Diamonds play an important role not only in the material sciences but also in Earth and Planetary Science. For example, nanodiamonds may be one of the most important types of stardust in primitive meteorites, with their origin linked to supernova explosions, as indicated by the isotopic compositions of trace elements that they carry (Ott, 2003, 2009 and references therein). Such nanodiamonds are also among the samples studied in the work reported here.

Color centers in diamond have been studied over the past years (e.g., Davies & Hamer, 1976; Zaitsev, 2001). According to Tizei and Kociak (2012), these centers are punctual defects, created by the presence of substitutional or interstitial atoms or vacancies in different configurations. Cathodoluminescence (CL) has emerged as an alternative to other methods to study individual emission centers with a better spatial resolution. To date, there are limited CL investigations of natural micro- and nanodiamonds (Grund & Bischoff, 1999; Heiderhoff et al., 2001; Kumar et al., 2001; Zaitsev, 2001; Pratesi et al., 2003; Orlanducci et al., 2008; Karczemska, 2010; Kopylova et al., 2010; Shiryaev et al.,

2011). The technique has been applied more frequently to synthetic diamond, for example, chemical vapor deposition (Kawarada et al., 1988; Robins et al., 1989; Yacobi et al., 1991; Katsumata, 1992; Won et al., 1996; Kanda et al., 2003), high pressure high temperature (HPHT; Katsumata, 1992; Kanda & Watanabe, 2004; Stevens-Kalceff et al., 2008), and ultradisperse detonation diamonds (Gucsik et al., 2009).

Groups of diamonds should be divided into four types, which are based on the local configuration of impurities within the carbon lattice, as follows (Walker, 1979; Zaitsev, 2001). The most common diamond type is Type I in which the nitrogen concentration is around 0.1%. According to their optical absorption and luminescence properties, the Type I class is further classified into the Type Ia and Type Ib diamonds. Almost all natural diamonds belong to Type Ia, where the nitrogen impurities are clustered within the crystal lattice of carbon atoms. Such diamonds absorb blue light that provides a significant narrow band centered at around 415 nm, which is assigned to the N3 centers (where the diamonds contain clusters of three nitrogen atoms). Additionally, a relatively weak line at 478 nm is related to the N2 nitrogen center (blue fluorescence). The green band at 504 nm (H3 center) is often accompanied by a weaker shoulder or broad band centered at 537 and 495 nm (H4

center containing four substitutional nitrogen atoms and two lattice vacancies), which occurs in brown, green, or yellow diamonds, respectively (Walker, 1979; Zaitsev, 2001). Almost all synthetic diamonds belong to the Type Ib class, which contain hydrogen and nitrogen defects as well as impurities. However, the origin of their color is still uncertain (Iakoubovskii & Adriaenssens, 2002). Compared to Type Ia diamonds, the Type Ib class occurs in synthetic diamonds and shows more intense green, yellow, and brown colors (De Sa & Davies, 1977; Walker, 1979; Zaitsev, 2001). They contain a relatively small amount of nitrogen (0.1%) atoms that occupy isolated sites within the crystal structure.

In a comparison with the Type I diamonds, Type II diamonds (formed under high pressure) do not contain nitrogen impurities and do not show absorption lines in the visible light range of the electromagnetic spectrum. Type IIa colorless nature might be attributed to the imperfections, which were formed under the HPHT conditions. Type IIb (extremely rare in nature) shows boron impurities that lead to the typical green, blue, and red colors (Walker, 1979; Zaitsev, 2001).

As noted above, diamonds may also have a role in interstellar space. In the last decades, a number of authors have proposed different models for the dust particles that might constitute the basis of circumstellar dusty matter. Some models are based on laboratory studies, while others are purely theoretical and invoke data of astrophysical observations (Mathis et al., 1977; Li & Greenberg, 1997; Weingartner & Draine, 2001; Smith & Witt, 2002). An important feature is the extended red emission of reflection nebulae. After it was interpreted as photoluminescence (PL) of dust, a lively discussion developed regarding the physical properties and chemical composition of the dust particles responsible for this phenomenon.

The extended red emission in the spectra of reflection, protoplanetary, and planetary nebulae is a structureless band over the range 5,400–9,400 Å. A source for this emission has been proposed by Duley (1985). In his model, each individual dust particle contains carbon grains, which are enriched in hydrogen. Under ultraviolet irradiation, such a dust particle is capable of luminescing within the abovementioned spectral range. It is worthy of note, however, that in conducting laboratory experiments and creating theoretical models and concepts, it is necessary to bring the modeled conditions closer to the natural ones given the extensive abundance of a whole series of compounds in the universe. Often the experiments have been done at 298 K, while the actual temperature of the dust in nebulae is entirely different most of the time. This is especially important when the quantum yield of luminescence is elevated at low temperatures. The present study involves scanning electron microscope-cathodoluminescence (SEM-CL) spectroscopy to address the question of whether the SEM-CL technique is capable of documenting temperature-related effects by performing analyses at temperatures of 298 K [room temperature (RT)] and 77 K [liquid-nitrogen temperature (LNT)]. We also aimed at determining whether investigation of the CL characteristics of diamond has a useful
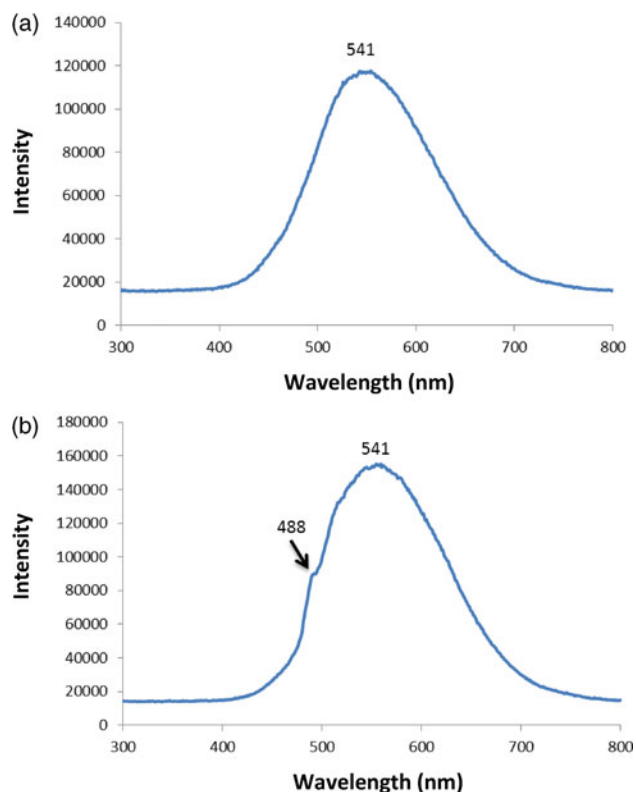

Figure 1. CL spectra of natural diamond at (**a**) 298 K (RT) and (**b**) 77 K (LNT) temperature showing a significant CL band centered at 541 nm.

astromineralogical application. To contribute to this subject, SEM-CL of selected samples from natural and synthetic diamonds has been done.

Experimental Procedure

Cathodoluminescence was measured for carbon-coated thin sections polished by silicon colloids, which were mounted in and fixed by two-component nonradiative epoxy. CL spectroscopy was performed by an SEM-CL system, which was comprised of an SEM (JSM-5410LV, JEOL Ltd., Tokyo, Japan) combined with a grating monochromator (Mono CL2, Oxford Instruments, Abingdon, Oxfordshire, UK). The SEM was operated at 2 nA, the spectrometer was stepped in 1 nm steps, and the flood gun used a 60 s exposure. The CL emitted from the samples was collected using a retractable parabolic mirror coated with aluminum (collection efficiency: 75%). The CL was dispersed by a grating monochromator, which has the following characteristics: 1,200 grooves/mm, a focal length of 0.3 m, limit of resolution of 0.5 nm, and slit width of 4 mm at the inlet and outlet. Dispersed CL was recorded by a photon counting method using a photomultiplier tube (R2228, Hamamatsu, Hamamatsu City, Japan) and converted to digital data.

All CL spectra were corrected for total instrumental response determined using a calibrated standard lamp (Quartz Halogen Lamp, Eppley Laboratory, Newport, RI, USA). This correction prevents errors in the peak position
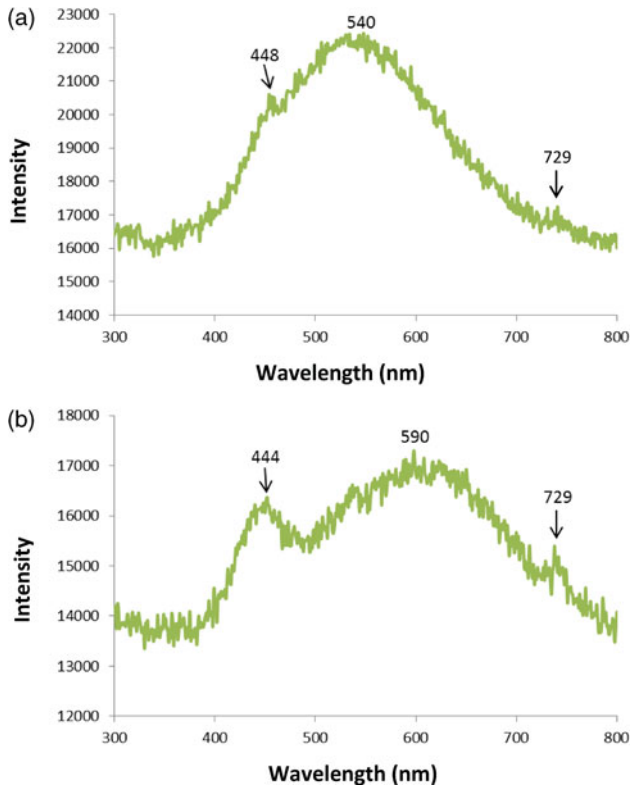
Figure 2. (**a**) CL spectrum of the synthetic HPHT diamond sample obtained at RT exhibits a broad band at 540 nm with two shoulder peaks 448 and 729 nm. (**b**) There is a peak shift as well as peak broadening of a band at 590 nm and peaks at 444 and 729 nm show increasing peak intensity in the LNT-CL spectrum.

of emission bands and allows quantitative evaluation of CL intensity. The spectral response varies smoothly between 300 and 800 nm with a maximum at 550 nm and shows steps at approximately 450 and 730 nm. The intensity units on the figure are arbitrary.

RESULTS

Cathodoluminescence Spectral Properties of Micro- and Nanodiamond Samples

Cathodoluminescence spectra of the natural diamond sample (HPHT diamond sample from an igneous rock) show a significant broad band centered at around 541 nm at both 298 K (RT) and 77 K (LNT) temperatures (Figs. 1a, 1b). Compared to the CL spectrum obtained at RT, an additional weak shoulder peak appears at 488 nm at LNT (Fig. 1b). The cause of the large *y*-axis offset in the spectrum may be related to the dark noise of the detector. The grain sizes of these diamond samples are typically a few hundred micrometers in size. The RT-CL spectrum of the synthetic diamond is dominated by a broad band centered at 540 nm (Fig. 2a), whereas the LNT-CL spectrum shows a broad band at 590 nm (Fig. 2b). Both CL spectra also have bands at around 445 nm (448 nm at RT and 444 nm at LNT) and 729 nm, which are more prominent in the LNT spectrum (Fig. 2b). The source of the above-mentioned peak shift between 448 and 444 nm
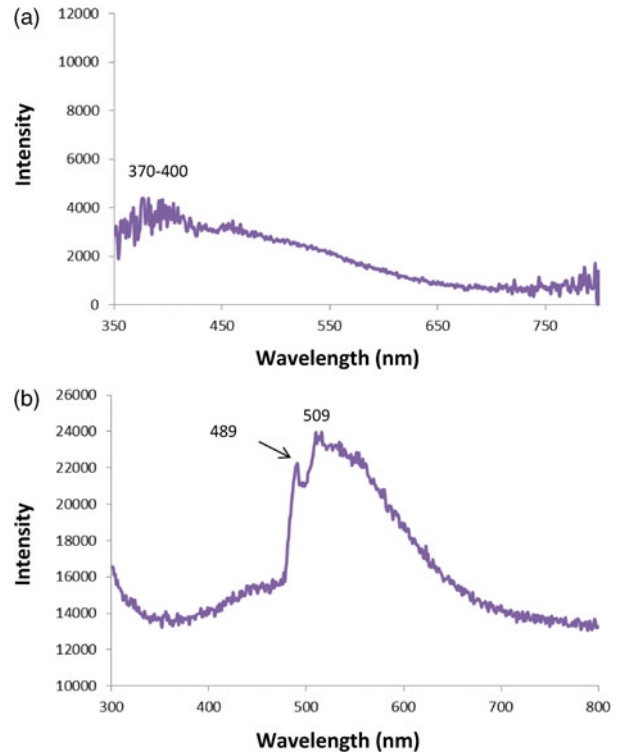

Figure 3. The CVD diamond sample contains almost no CL peaks in RT (**a**) whereas a broad band centered at 509 nm is dominant in the LNT-CL spectrum (**b**).

is not well known. In addition to the 444 and 590 nm peaks, the 540 nm peak might still be there in Figure 2b. In this case, a deconvolution of this peak as a part of further investigations should provide more insight.

The chemical vapor deposition (CVD) diamond sample at RT is dominated by a noisy broad band ranging from 370 to 400 nm; otherwise almost no CL spectral features are obtained at RT (Fig. 3a). A broad band centered at 509 nm with a shoulder peak at 489 nm is dominant in the spectrum at LNT (Fig. 3b). The maximum grain size of these diamond samples is around 250 nm. Figure 3a also shows a step at 450 nm. The origin of noise at each end of the spectrum in Figure 3 as well as the relatively lower background of Figure 3a is still poorly understood.

The ultradisperse detonation (UDD) nanodiamonds were manufactured by detonation synthesis from explosives containing graphite (Greiner et al., 1988 and references therein). The individual grain sizes of the UDD samples vary between 3 and 9 nm. CL spectra at RT are dominated by two broad bands at 388 and 422 nm (Fig. 4a), whereas spectra obtained at LNT exhibit a significant broad peak centered at 550 nm containing three shoulder peaks at 448, 476, and 590 nm (Fig. 4b).

Boroskino (CM2) is a carbonaceous (C) chondrite of the Mighei-type (M), which contains a relatively large fraction of fine-grained matrix and abundant hydrated mineral phases (Grady, 2000). The samples were extracted using two-step ultracentrifugation of colloidal diamonds, which were prepared for heavy noble gas measurements to avoid contam-
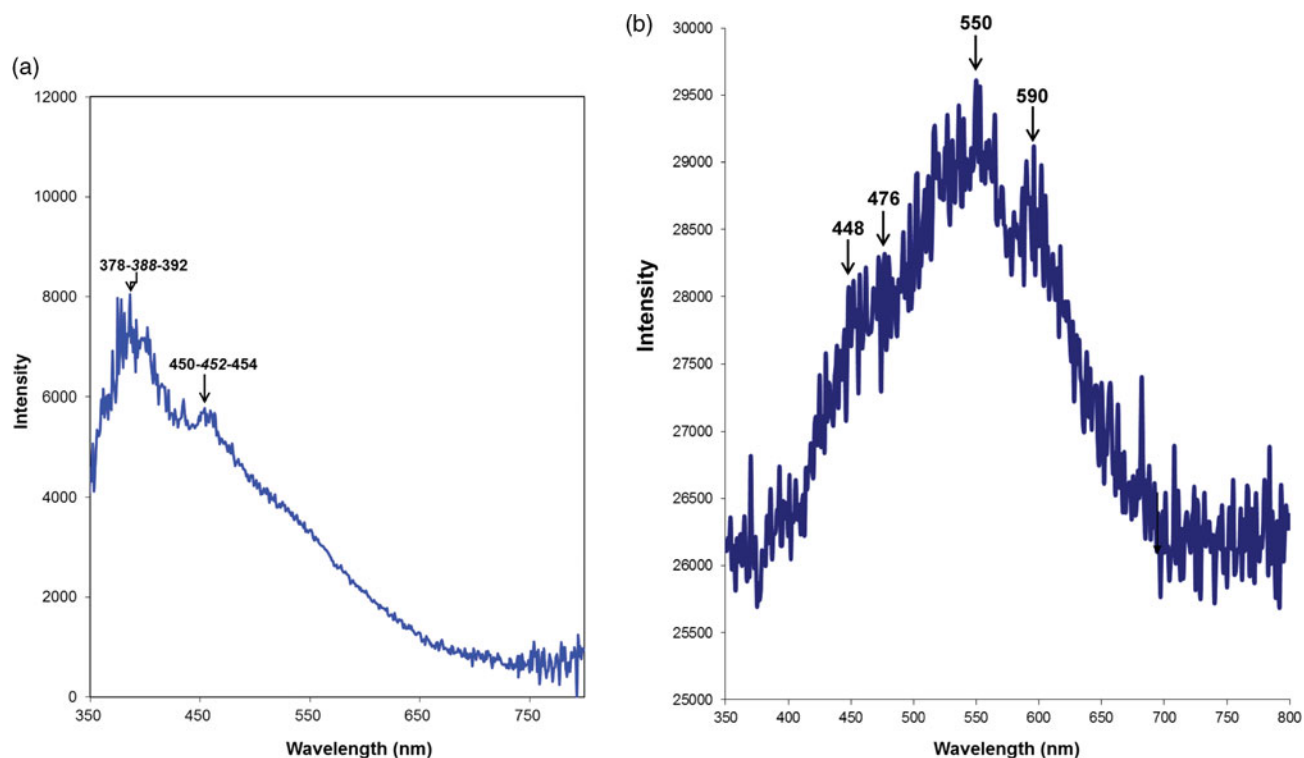
Figure 4. (**a**) The RT-CL spectral features of the UDD samples are related to centers at 388 and 452 nm and (**b**) the LNT-CL spectrum is dominated with only one peak at around 550 nm with three shoulder peaks at 448, 476, and 590 nm.

ination by other mineral phases. Details of the preparation method of the Boroskino meteorite diamonds can be found in Verchovsky et al. (1999) and Fisenko et al. (2002).

In contrast to the CVD samples, the CL spectrum of the nanodiamonds from Boroskino shows a broad band centered at 540 nm at RT (Fig. 5a), but it is noisy and almost peakless at LNT (Fig. 5b).

DISCUSSION

Cathodoluminescence Peak Assignment of Diamond

According to Kanda and Jia (2001), the band at around 390 nm has been observed in CVD and HPHT diamonds, respectively. This may be associated with a radiation damage defect center suggesting that this imperfection occurred during defective crystal growth.

The 451 nm center might be assigned to rhombic symmetry or A-E transition at a tetragonal center (Mohammed et al., 1982; Jorge et al., 1983), which has been described from natural brown diamonds (Zaitsev, 2001). This peak was also described in diamond samples from meteorites by Karczemska (2010).

The emission peak at 487 nm is related to the intrinsic defect center (divacancy, TH5), which has been observed in Type Ia and IIa diamonds following an electron irradiation (Zaitsev, 2001 and references therein).

The assignment of emission bands at around 540 nm is not always straightforward, but they correspond to disloca-
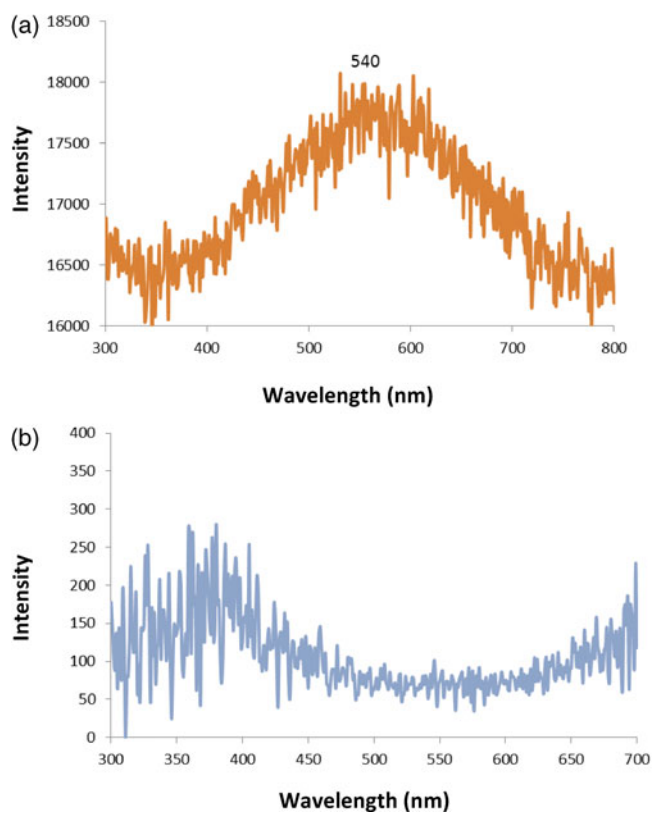
Figure 5. Nanodiamond from the Boriskino meteor shows a (**a**) significant broad peak at 540 nm in the RT-CL spectrum, but (**b**) its LNT-CL does not contain any peaks.

tion defects associated with nitrogen atoms. The CL spectra suggest a low concentration of nitrogen in the diamonds and give indications for distinguishing these emission bands. A nitrogen content of even less than 20 ppm (Type II diamonds) can be sufficient to provide luminescence of diamonds (Zaitsev, 2001).

A broad band at 550 nm and a shoulder peak at 590 nm in the UDD samples are related to the dislocations (Zaitsev, 2001 and references therein).

Lindblom et al. (2005) studied the luminescence properties of the HPHT, boron-doped, and synthetic diamonds grown with a nitrogen getter, as well as of natural diamonds. They found a CL peak at 729 nm, which is related to the nickel-related center. We also note that the peak at 729 nm could be assigned to an artifact in the instrument response correction. However, this is a matter of further investigations.

An Astromineralogical Context

It is generally accepted that the Sun formed due to the gravitational collapse of the original solar nebula. In the accretion disk around the proto-sun, both terrestrial and giant planets were formed. Nano- and micro-sized dust particles (including diamonds) in meteoroids may in principle have two possible sources: (1) geological evolution of the terrestrial (rocky bodies) derived from solar nebula matter and (2) penetration of presolar (interstellar) particles into the solar nebula during the gravitational collapse. Obviously solar and interstellar nanodiamonds should differ in their physico-chemical parameters. Possible differences are (a) isotopic composition, (b) abundance of impurities, and (c) crystal lattice/structure. The following two paragraphs are aimed to provide new insights to possible formation mechanisms of diamond particles in planetary nebula and meteorites.

Diamonds in Planetary Nebula

According to Simonia and Mikailov (2006), circumstellar dust of nebulae undergoing the permanent influence of electromagnetic and corpuscular radiation from the central star can carry information on the origin and evolution of the system. Based on a comparative analysis, it has been shown that several emissions in the optical spectrum of NGC 7027 (Simonia & Mikailov, 2006 and references therein) and other nebula (i.e., NGC 7023) correspond to CL and PL of fine-dispersive circumstellar diamond dust. The optical lines at 503, 577, and 578 nm are present in the spectral properties of both planetary nebulae. These lines are in a good agreement with our CL spectral properties of UDD samples. Based on this consistency, diamond particles in nebulae NGC 7023 and NGC 7027 may have originated due to ejection of the outer parts of the Red Giant parent star during planetary nebula formation.

Duley (1988) described the first possible presence of nanodiamonds in the protoplanetary nebula environment. Taking into account that PL and CL of solid substances are physically similar phenomena, our laboratory results might be applied to interpretation of an extended red emission

(ERE) source. Particularly, we conclude that spectral position and profile of nanodiamond CL (data obtained in our lab experiments) has a correlation with ERE spectral properties. It means that a relatively cool nanodiamond is also a candidate to an ERE source.

Nanodiamonds from Meteorites

There are two scenarios existing for the formation process of nanodiamonds from meteorites (e.g., Daulton et al., 1996 and references therein), as follows: (1) CVD and (2) shock origin. Transmission electron microscopy investigations, in particular, seem to suggest that formation by a CVD process is most likely (Daulton et al., 1996). The latter one is also supported by our study, according to the CL data of diamond particles from the Boroskino meteorite.

Conclusions

SEM-CL properties of micro- and nanodiamond samples prepared by CVD as well as explosively (ultradispersive detonation diamonds) were studied at both liquid nitrogen and room temperatures. Also studied were natural specimens including HPHT diamonds and meteoritic diamonds, with emphasis on the application of the method to laboratory astrophysics. The preliminary results of this work suggest that the SEM-CL is a useful tool in laboratory astrophysics. Further systematic investigations must be done to identify the defect centers in the selected diamond samples using the electron spin resonance technique (Casabianca et al., 2011; Shames et al., 2012) combined with infrared spectroscopy (Baranov et al., 2009, 2011).

Acknowledgments

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