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New Generation of Synthetic Diamonds Reaches the Market (Part A): **CVD-grown Blue Diamonds**

Peretti A. [1*], Herzog F. [2], Bieri W. [2], Alessandri M. [3], Günther D. [4], Frick D.A. [4], Cleveland, E. [5], Zaitsev A.M. [6], Deljanin B. [7]

[1]DR Peretti Co LTD, Thailand and GRS Laboratories
[2]GRS Gemresearch Swisslab AG, Switzerland
[3]GRS Lab (Hong Kong) Ltd, Hong Kong, China
[4]Laboratory for Inorganic Chemistry, ETH Zurich, Switzerland
[5]Delaware, USA
[6]The City University of New York, USA
[7]CGL-GRS Swiss Canadian Gemlab Inc., Canada

**Corresponding authour: adolf@peretti.ch*

Abstract

A new type of synthetic blue diamonds appeared on the market. These diamonds were identified as CVD-grown. Optical spectroscopy revealed that they are of type IIa and their colour is caused by strong absorption of very intense silicon-related SiV^- center (negatively charged Silicon and Vacancy centre). A structural and chemical layering was identified by SEM-CC analyses. Enhanced concentration of Bi and Pb elements was found by LA-ICP-MS method. Reliable identification of silicon-doped blue CVD diamonds can be performed in different ways and these diamonds can be unambiguously distinguished from their blue natural and HPHT-grown synthetic counterparts. The most effective identification methods are absorption and photoluminescence spectroscopy in the visible spectral range, which reveal extremely intense SiV^- (737nm) center. The silicon-doped blue CVD diamonds are not conductive. Thus the electrical conductance test is a method contributing to the recognition of these diamonds.

Keywords: Synthetic, CVD-grown, blue diamond, type IIa, SiV^- colour centres

Introduction

On October 18, 2013 Rapaport Diamond Report issued a trade alert warning "Buyers beware; Persistent reports indicate that large amounts of synthetic lab-grown diamonds are being mixed with natural diamonds in parcels of melee and pointers. Know your supplier and insist the phrase 'natural, untreated diamonds' to be included on all invoices". More than 600 undisclosed CVD-grown diamonds of less than 0.70 carats came through major laboratories in both Antwerp and Hong Kong for certification in 2012 [1]. As prices for natural diamonds in India rise, synthetic diamonds are also gaining attraction [2]. "The synthetic diamond market in India has captured around 1% of the overall diamond jewellery market," said Vipul Shah, chairman of the Gems and Jewellery Export Promotion Council (GJEPC). Therefore, disclosure of these new synthetic diamonds is also a matter of concern.

Orion PDC Diamonds, a company producing CVD diamonds, asserts in their marketing brochure entitled PDC Company that both genuine earth-mined and synthetic diamonds are 'real diamonds'. Although theoretically correct in that they both share the same physical and chemical properties, this statement, when used within the gem-diamond market, is very misleading. It implies that these lab grown diamonds are 'natural', which is certainly not the case.

Synthetic diamonds are indeed an important part of today's commercial gemstone industry and are being created by a variety of companies, like AOTC, Chatham, Scio Diamond, Gemesis, Washington Diamonds, and Orion PDC, all using various production methods (Fig. 1). To create different colours, a variety of treatments are applied to either natural or synthetic diamonds. Diamonds of practically any colour including colourless, yellow, blue, green, orange, and pink and their countless variations may result from the

Fig. 1: Scio Diamond Inc. facility in North Carolina, USA with many CVD-growers

controlled application of different combinations of irradiation, heat and high pressure. Commercial production of blue diamonds relies upon one of three methods:

1. ***electron irradiation with energy of a few MeV at moderate doses applied to practically any diamond (common treatment)***

2. ***high-pressure / high-temperature (HPHT) annealing of initially natural grey-colour (very rare) type IIb diamonds***

3. ***HPHT growth of synthetic boron-doped diamonds***

No other technique, including that of chemical vapour deposition (CVD) growth, has reportedly been used for commercial production of gem-grade diamonds with blue body colour. Of late, synthetic gem diamonds produced by CVD method could appear as brown, pink (post grown irradiated), yellow or colourless. But quite recently, CVD-grown diamonds of a greyish-blue colour have entered the marketplace (Fig. 2). The first characterisation and identification of these diamonds is the aim of this present publication.

Although published research does exist on CVD technique producing boron-doped blue colour diamond coatings, blue diamonds created by this method have not previously been seen as faceted stones in the marketplace. Synthetic blue diamonds appearing closest to their natural counterparts are usually produced by HPHT growth [5].

In September 2013, one of the authors (AP) conducted a survey at the Bangkok Gems & Jewelry Fair and discovered that synthetic blue diamonds over 1 carat in size (See Fig. 2b) appeared in the market along with a variety of other colours (See Fig. 2a). Later on, in Hong Kong, we were able to acquire a few reference samples of the blue diamonds from the producer, along with other samples for this study (see Tab.1).

In this effort, we express our discovery of a new type of synthetic blue diamond which had not been previously identified in scientific literature. This is a key finding for the gem trade especially in light of recent developments in CVD technology which turns out higher quality, greater colour range, and larger carat size synthetic diamonds.

Conclusion

A new type of CVD-grown synthetic blue diamond has been discovered. We discovered that some of these CVD-grown diamonds can be identified by their characteristic strain-pattern under cross-polarized light conditions. These diamonds are inert to SWUV and LWUV illumination and reveal no specific phosphorescence characteristic of HPHT-grown and natural blue diamonds. Comparative analysis of new blue CVD diamonds with their HPHT-grown and natural counterparts using FTIR, UV-VIS and PL spectroscopy has revealed that these diamonds are of type IIa. They do not owe their blue colour to boron impurity.

Because they are not doped with boron, the new blue CVD diamonds are not electrically conductive. Thus, the new CVD blue diamonds can be identified with the use of an electric conductivity tester for natural blue and HPHT synthetic blue diamonds which is available in the marketplace. This tester is useful for identification of irradiated blue natural diamonds which are of type Ia or IIa, and act as electric insulators.

The diamonds' blue colour is attributed to a high intensity of the silicon-related SiV^- centre, which produces preferential absorption in red spectral range. The SiV^- centre is so strong that it is the sole feature present in absorption and luminescence spectra taken in visible spectral range. By analysing the assembled data, we concluded that co-doping with silicon and some other impurity might be performed during the growth phase of blue CVD diamonds in order to stimulate efficiency of the SiV^- centre.

Chemical analysis performed on the blue CVD diamond has identified the elements Pb and Bi as the major contributing impurities. Pb and Bi are heretofore unknown impurities in diamonds, so their influence on optical properties of diamonds has not been studied. Therefore at this stage, we cannot presume that these impurities were intentionally introduced in diamonds for the purpose of stimulating the SiV^- centre. There is clearly more need for further research by LA-ICP-MS and alternative methods before every aspect of the new material is understood. Nevertheless, it is important to note that a new type of synthetic blue diamond has been discovered and identified (see also alert in "news section" at www.gemresearch.ch).

The trade and the public need to be made keenly aware of this discovery, particularly in light of the fact that the seller promotes this material as real diamonds in the marketplace [16]. Other types of synthetic blue diamonds (HPHT) are doped with boron corresponding to the trace elements found in nature. But they must be clearly described as lab-grown, and truthfully labelled as synthetic diamonds. This new generation of synthetic diamonds is different in that the origin of colour is related to Si and possibly a dopant. Therefore, these new synthetic blue diamonds origin of colour is not the same as is found in natural diamonds. Furthermore, they are synthetic and should not bear the conflicting misnomer of real diamonds. They may accurately be described as **"CVD-grown blue diamonds"**, however.

Major lab-created diamond manufacturers such as AOTC, Chatham, Gemesis, and Scio Diamond are transparent in their disclosure and cooperative within our trade. The majority of their diamonds are certified. Still, there are synthetic diamonds that reach laboratories undisclosed, and there are also synthetic diamonds brought in by individuals who bought them believing they are natural diamonds. Today, an increasing number of facilities grow diamonds, especially in Asia due to lower production costs. It appears that the CVD technology is increasingly employed to grow both near-colourless and coloured diamonds. This development makes it imperative to screen melee and small coloured diamonds parcels for determination of synthetic origin as well as for colour origin, especially in the Asian markets.

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***Table 1:** Summary of tested natural and synthetic blue diamonds of different producers and synthesis methods and results of examinations*

Producer	CVD-grown - Orion PDC *4 samples*	Natural *1 sample*	HPHT synthetic - Chatham *1 sample*	HPHT synthetic - Tairus *1 sample*	HPHT synthetic *3 samples*
Colour	light blue, fancy greyish blue, fancy light greyish blue	very light blue	fancy blue	fancy blue	fancy blue
Clarity	VS1 to VS2	SI2	I1	I1	SI to I
Solid Inclusions (at 60x magnification)	transparent crystals, clouds and pinpoints	none	black metallic inclusions, feathers	black metallic inclusions	black metallic inclusions, feathers
ED-XRF	none	none	Fe, Co	Fe, Co	Fe, Co
SEM-EDS	Pb, Bi	not measured	not measured	not measured	not measured
Fluorescence SWUV (254nm)	inert	inert	medium to strong milky green; phosphorescence	medium to strong milky yellowish green; phosphorescence	weak chalky green; phosphorescence
Fluorescence LWUV (365nm)	inert	inert	very weak light orange	inert	inert
Cross Polarized Filters (CPF)	irregular pattern or "tatami pattern"	weak pattern	no pattern	no pattern (straining around black metallic inclusion)	no pattern
FTIR spectroscopy (absorption, cm^{-1})	type IIa, weak bands at **1340** and **1332**cm^{-1}	type IIb, Boron related bands at **2455**, **2802**, **2928**, small **1332** and **1303**cm^{-1}	type IIb, very strong Boron related bands at **2455**, **2802**cm^{-1}, oversaturated above **2750**cm^{-1}	type IIb, very strong Boron related bands at **2455**, **2802**, oversaturated above **2750**, band at **1332** and **1292**cm^{-1}	type IIb, very strong Boron related bands at **2455**, **2802**, oversaturated above **2750**, band at **1332** and **1292**cm^{-1}
UV-Vis-NIR spectroscopy at LNT (absorption)	prominent **737** band, peaks at **830**, **833**, **856**, **870** and **946**, additional peaks around **530** (523.9, 529.9, 546.6) and at **676.8**nm	lack of sharp absorption bands, gradually increasing absorption towards near infrared (500 to 1000nm), slightly increasing towards the UV (420 to 300nm)	lack of sharp absorption bands, gradually increasing absorption towards near infrared (420 to 1000nm), slightly increasing towards the UV (420 to 300nm)	lack of sharp absorption bands, gradually increasing absorption towards near infrared (320 to 1000nm)	lack of sharp absorption bands, gradually increasing absorption towards near infrared (320 to 1000nm)
PL spectroscopy at LNT - 405nm	very strong **736** and **766** bands, peaks at **796** and **811**; small to pronounced **719** peak; valley at **946**nm	weak **741**nm (GR1) due to natural irradiation	no PL features	no PL features	no PL features
PL spectroscopy at LNT - 532nm	very strong **736** and **766** bands, peaks at **796** and **811**; small to pronounced **719**nm peak	weak **741**nm (GR1) due to natural irradiation	no PL features	no PL features	no PL features
Electrical conductivity	non-conductive	conductive	conductive	conductive	conductive

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