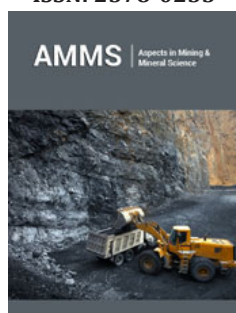


# Growth of SiC Whiskers in Beryl by a Natural Supercritical VLS Process

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## Abstract

This short paper shows the unusual occurrence of SiC whiskers grown in beryl by a supercritical VLS (vapor-liquid-solid) process. The beryl sample is from a small beryl-quartz veinlet related to the Variscan tin deposit Ehrenfriedersdorf in the Saxon Erzgebirge. The SiC or moissanite, often twisted along the c-axis, is of the hexagonal 6H-SiC polytype and generally forms needle- or whisker-like crystals parallel to the c-axis of beryl. Up to now, the growth mechanism is not precisely known, especially for the nature of the VLS liquid catalyst. Nanodiamonds in the supercritical fluid take over the role of the growth trigger. The maximum temperature of the beryl and moissanite crystallization is 720 °C.

**Keywords:** SiC whisker; Beryl; Supercritical fluids; Nanodiamonds as the catalyst; Raman spectroscopy; Ehrenfriedersdorf tin deposit

## Introduction

By careful microscopic and Raman spectroscopic looking through old samples from rare beryl-quartz veinlets related to the Variscan tin deposit Ehrenfriedersdorf (Sauberg mine) in the German Erzgebirge, unexpected SiC needles and whiskers in beryl were found. It will discuss shortly the origin of this unexpected paragenesis. To understand the related tin mineralization, the paper from Schröcke [1] & Hösel [2] are recommended, which comprehensively describes this famous deposit. However, a description of the small beryl veins is missing. Only Kumann & Leeder [3] discuss this very shortly in their contribution and show such veins' appearance. However, they have not studied the beryl. This short contribution concisely describes the unusual beryl-moissanite paragenesis and the method used for the unequivocal proof. The VLS process for the SiC whisker growth discussed in this paper stands V for vapor feed, L for liquid catalyst, and S for solid SiC whisker growth (see further below).

## Sample Material & Methods

The sample is from a 6cm thick beryl-quartz veinlet from the Ehrenfriedersdorf Sauberg mine (Prinzler Liegendtrum, sample BAF F64-18) composed of about 28% beryl and 72 % quartz. Figure 1 shows a piece from this beryl-quartz veinlet. The beryl is transparent and pale green and contains many secondary fluid inclusions. Primary melt inclusions (tH ~720 °C, see [4]) are rare. Besides numerous small (10-20µm) mineral inclusion like beryl-II, zircon, OH-rich topaz, sphalerite, and arsenopyrite, often spherical or elliptical, many needles and whisker-like black crystals of SiC (moissanite) are present. Larger beryl crystals show indications of tectonic demand perpendicular to the c-axis resulting in a dispersal of large SiC needles. Double-polished thick sections with a thickness of 500µm for the study were used. All microscopic and Raman spectroscopic studies are performed with a petrographic polarization microscope with a rotating stage coupled with the RamMics M532 Raman spectrometer working in the spectral range of 0-4000cm<sup>-1</sup> using a 50mW single-mode 532nm laser. The Olympus long-distance LMPLN100x as a 100x objective lens was used for Raman spectroscopic routine measurements. Details are given in Thomas [5].

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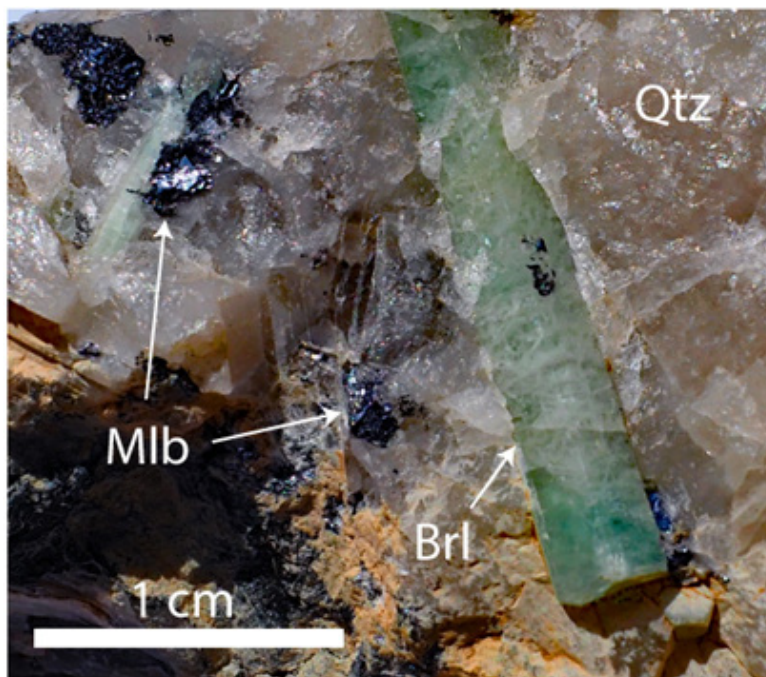
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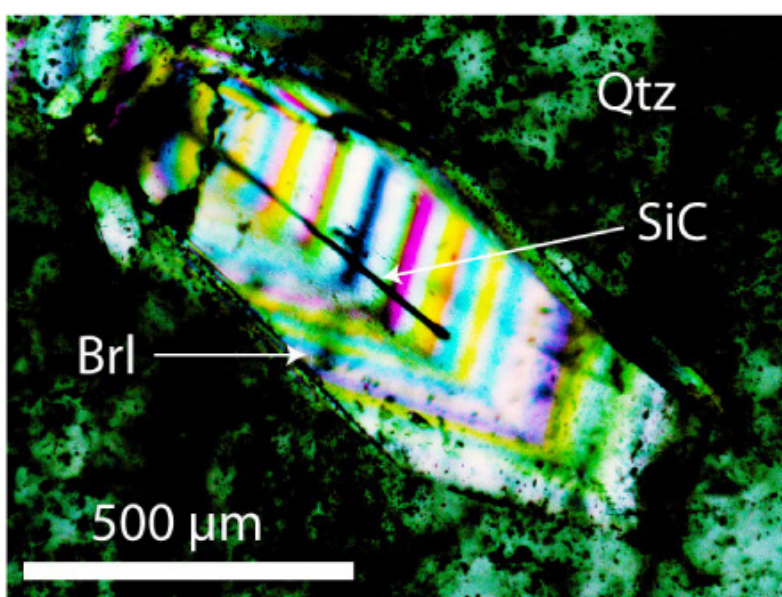


**Figure 1:** Detail of the studied quartz-beryl sample from the Sauberg mine near Ehrenfriedersdorf: Brl-green beryl, Mlb-molybdenite, Qtz-quartz.

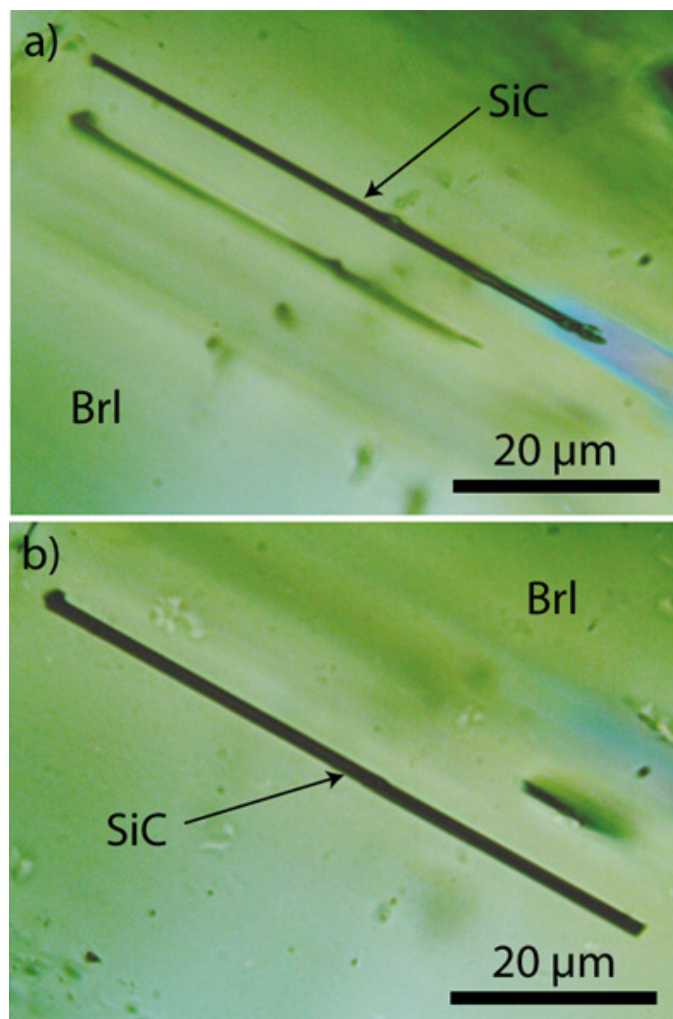
## Result

The beryl of the studied samples contains many black whisker-like needles of moissanite arranged generally parallel to the c-axis of the beryl. About 15000 to 35000 such SiC crystals per  $1\text{cm}^3$  were counted. Figure 2 shows a SiC whisker in the center of a beryl crystal. Up to now, the most extended needle is  $1540\mu\text{m}$  long. Depending on the cutting slope, the cross-section is spherical to elliptical. The whiskers are often twisted along the c-axis, and Raman spectroscopic studies show this SiC is of the hexagonal polytype 6H-SiC [6,7]. Figure 3 presents several such SiC whiskers

parallel to the c-axis of a beryl crystal (same position, however different depths). Table 1 compares the Raman measurements on natural SiC (whiskers and needles) in beryl and technical SiC. Figure 4 depicts a typical Raman spectrum of a SiC whisker. The linewidths of the main Raman band at about  $770\text{cm}^{-1}$  is  $25\text{cm}^{-1}$ , and that is for the natural SiC 4 fold more extensive than the synthetic/technical one. Figure 5a shows the start point of the SiC whisker growth in Figure 2 by the VLS process. The Raman spectrum in Figure 5b represents the nanodiamonds (nD) at the basis of the supercritical VLS catalyst ball.



**Figure 2:** An about  $600\mu\text{m}$  long moissanite (SiC) whisker in the center of a beryl (Brl) crystal (crossed Nicols). Qtz-quartz.



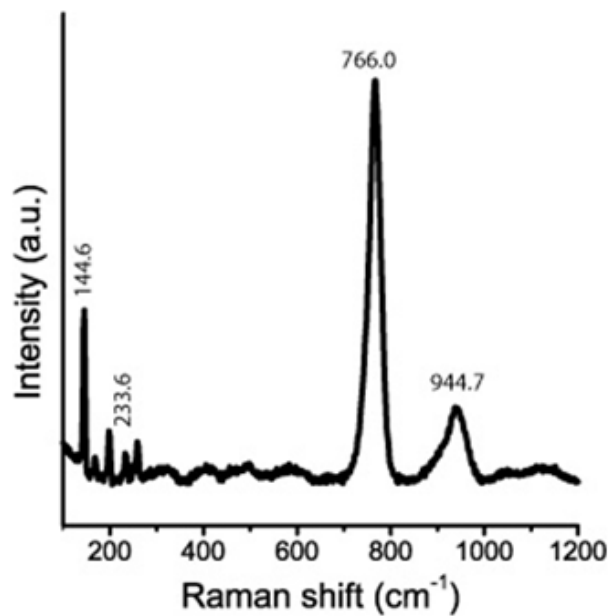
**Figure 3:** Several such SiC whiskers parallel to the c-axis of a beryl crystal (Brl) from the Ehrenfriedersdorf Sauberg mine. Figures a) and b) show the same position in different depths.

**Table 1:** Experimental Raman-active vibrational modes of the SiC polytype 6H-SiC in beryl from Ehrenfriedersdorf, Erzgebirge, Germany, and a synthetic/technical reference. n-number of studied SiC crystals; vibration modes according to [6,7]: AA-Axial Acoustic Mode, LA-Longitudinal Acoustic Mode, LO-Longitudinal Optic Mode, PA-Planar Acoustic Mode, PO-Planar Optic Mode, TA-Transversal Acoustic Mode, TO-Transversal Optic Mode. Intensity: vw-very weak, w-weak, m-medium, s-strong, vs-very strong; FWHM-line widths(full width at half maximum).

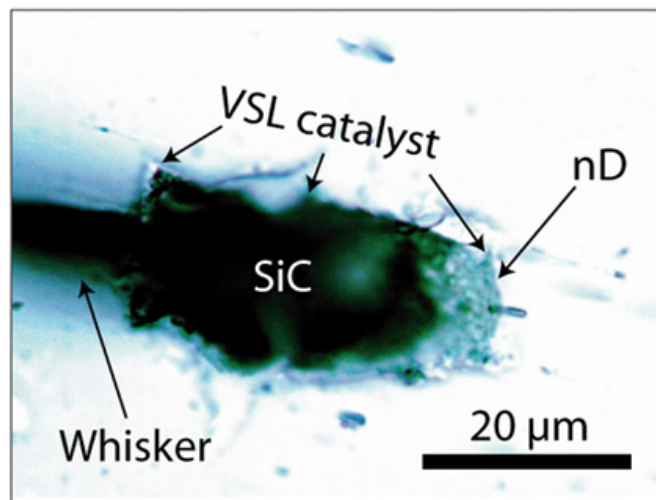
Polytype: 6H-SiC			
	Vibration Modes	Intensity	FWHM (cm <sup>-1</sup> )
SiC Needle: Perpendicular to the c-axis			
145.6±1.1	E <sub>2</sub> (PA)	m to s	6.0±1.8
234.6±2.3	E <sub>1</sub> (PA)	vw	
259.9±2.0	E <sub>2</sub> (PA)	vw	
498.0±2.8	A <sub>1</sub> (AA)	vw	
753.80±14.6	E <sub>2</sub> (PO)	m	21.7±11.1
775.4±10.6	E <sub>1</sub> (TO)	s to vs	23.7±9.8
948.0±16.8	A <sub>1</sub> (LO)	m	27.3±13.0
n=15			
SiC Needle: Parallel to the c-axis			
145.0±0.8	E <sub>2</sub> (PA)	m	5.5±0.8
233.4±1.0	E <sub>1</sub> (PA)	w	
497.0±5.0	A <sub>1</sub> (AA)	vw	21.3±3.2



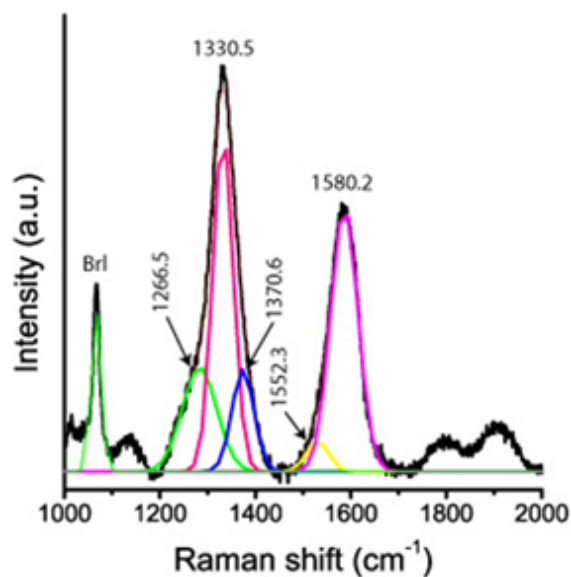
748.4±9.6	E <sub>2</sub> (PO)	s	26.0±10.6
771.9±5.9	E <sub>1</sub> (TO)	vs	24.7±4.5
925.8±5.6	?	w	
950.1±6.3	A <sub>1</sub> (LO)	m	
n=12			
<b>SiC: Polytype 6H-SiC Synthetic</b>			
147.6	E <sub>2</sub> (PA)	w	6.6
238.3	E <sub>1</sub> (PA)	vw	75.0
504.9	A <sub>1</sub> (AA)	vw	12.6
766.0	E <sub>2</sub> (PO)	w	9.0
786.8	E <sub>2</sub> (PO)	vs	6.0
796.6	E <sub>1</sub> (TO)	m	9.0
968.7	A <sub>1</sub> (LO)	w	8.7



**Figure 4:** Typical Raman spectrum of a SiC whisker in the Ehrenfriedersdorf tin deposit beryl.



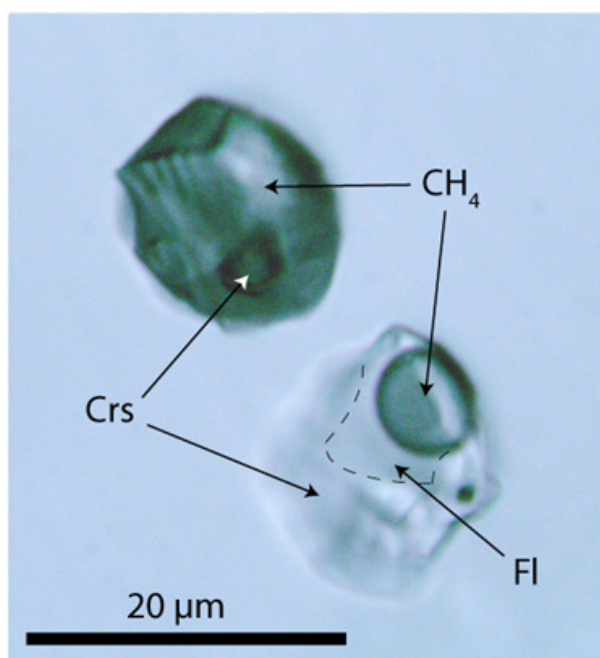
**Figure 5a:** The supercritical VLS catalyst ball is the starting point for the growth of the SiC whisker in Figure 2. Carbon (as supercritical methane) and silicon atoms in the supercritical fluid feed the Be-rich catalyst melt droplet on the beryl substrate.



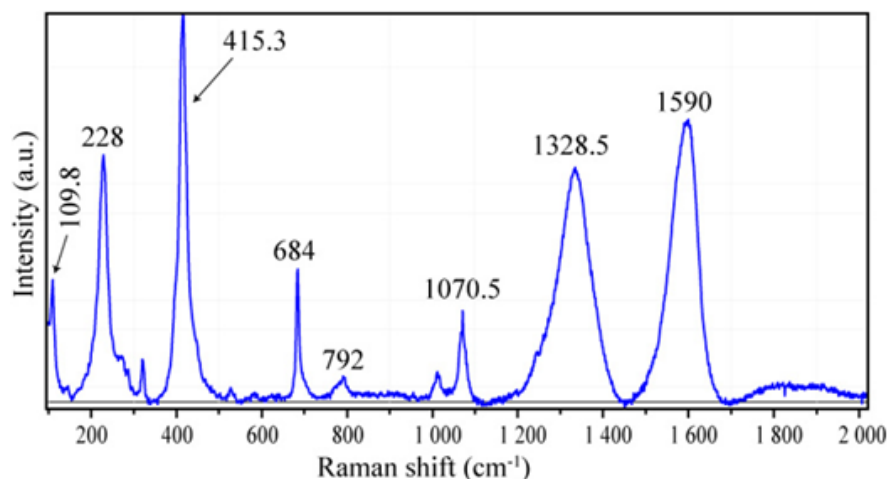
**Figure 5b:** Raman nanodiamond (nD) spectrum in the supercritical VLS catalyst ball. BrI–beryl.

McMahon et al. [8] give an idea about the growth mechanism of silicon carbide whiskers. The composition and structure of the VLS liquid catalyst (Figure 5a) is the task for further sophisticated studies. Noteworthy is that this elliptical catalyst ball is composed of SiC, graphitic carbon, and nanodiamonds. The composition of the liquid phase of the catalyst is unclear – maybe a metastable Be-bearing supercritical melt droplet on the growing beryl substrate [9]. Beryl, SiC, and nanodiamonds in the catalyst ball are noteworthy. The vapor phase, methane, is often seen as a supercritical high-pressure phase inclusion in beryl (Figure 6). The vapor phase consists exclusively of methane ( $\text{CH}_4$ ), and cristobalite (Crs) forms the solid phase of both inclusions. A necking-off process creates

both inclusions (Roedder [10], p. 59). Cristobalite in the methane inclusion is stable under laser light and is metastable in the water-bearing fluid inclusion (forming quartz). With the used Raman spectrometer, in no case hydrogen using the pure rotational lines  $S_0$  ( $354.8\text{cm}^{-1}$ ),  $S_1$  ( $587.4\text{cm}^{-1}$ ),  $S_2$  ( $815.0\text{cm}^{-1}$ ), and  $S_3$  ( $1034.9\text{cm}^{-1}$ ) could be determined - See [9]. The cristobalite was primarily water-rich stishovite or coesite, giving the supercritical fluid a minimum pressure of 7GPa. Figure 7 shows a Raman spectrum of the cristobalite in the  $\text{CH}_4$ -rich inclusion of Figure 6. Conspicuous are the strong nanodiamond band at  $1328\text{cm}^{-1}$  and the strong carbon band at  $1590\text{cm}^{-1}$ . The catalyst ball was partially distorted or destroyed during the further growth of beryl.



**Figure 6:** Two supercritical inclusions in beryl (BrI).  $\text{CH}_4$ -methane, FI-aqueous liquid phase. Cristobalite (Crs) in both inclusions gives in the Raman spectrum strong lines at  $112.6$ ,  $229.8$ ,  $418.6$ , and  $1072.1\text{cm}^{-1}$ , respectively.



**Figure 7:** Raman spectrum of cristobalite, nanodiamond, and carbon in the CH<sub>4</sub>-rich inclusion of Figure 6. The Raman bands at 109.8, 228, 414.3, 792, and 1070.5 cm<sup>-1</sup> correspond to cristobalite. The 1328.5 and 1590 cm<sup>-1</sup> bands correspond to nanodiamonds and carbon, respectively.

## Discussion

The finding of SiC whiskers in beryl is astonishing because the crystallization of SiC whiskers generally happens at very high temperatures. In the given example, moissanite forms with beryl around 720 °C, which is very low in contrast to the growth of β-silicon carbide whiskers at about 1400 °C by the VLS process [11]. The low temperature corresponds to the idea presented by Schmidt et al. [12]. Also, the nanodiamond participation at such low temperatures is remarkable. Following Buchner et al. [13], nanodiamonds as a catalyst can play a crucial role in the growth of moissanite at significantly lower temperatures. The essential step is changing from the supercritical state to the critical/under critical condition.

Furthermore, the present study shows that the supercritical fluid is rich in nanodiamonds. Nearby all SiC whiskers contain nanodiamonds. A supercritical fluid or melt is responsible for the VLS process; further studies are necessary to illuminate this process in more detail. A concise description of the beryl-moissanite-graphite paragenesis related to the Variscan tin mineralization of the Erzgebirge, Germany, will be given in a forthcoming paper by the author.

## Acknowledgment

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