Natural silicon carbide from different geological settings: polytypes, trace elements, inclusions

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Silicon carbide is a material of significant interest for various fundamental and applied fields: from high-power electronics to crystallography and the oxidation state of Earth's mantle. Since the stability of SiC requires extremely low fO_2 values, some geologists consider moissanite as a ''geological aberration''. However, a growing body of data confirms the rather widespread existence of small SiC grains in various geological settings. Moissanite has been found not only in mantle derived rocks (e.g., kimberlites, diamonds), but also in high- and low-grade metamorphic rocks, limestones and pegmatites (for a review see Derkachenko et al., 1972, Lyakhovich, 1980, Marshintsev, 1990). SiC is also reported in meteorites and interstellar dust. Interestingly, isotopic analyses show that SiC is always enriched in ^{12}C (Marshintsev, 1990, Mathez et al., 1995). The genesis of natural SiC remains a matter of debate.

In this work we report results of a detailed investigation by complementary techniques of natural SiC grains recovered from two contrasting geological settings: 1) from the heavy fraction of the Mir kimberlite pipe (Yakutia), and 2) from Triassic limestones in Bulgaria. Structural perfection, major and trace element chemistry of natural SiC grains and description of inclusions of other phases are presented.

Samples and methods

Issues of contamination were carefully addressed during extraction of kimberlitic SiC and the contamination is completely excluded in the case of Bulgarian samples. The rocks containing the latter set of SiC grains were collected at the geographical location and from strata described as moissanite-bearing by Gnoevaja and Grozdanov (1965). They were recovered from the heavy fraction of the acid-resistant residue of these rocks, containing well-preserved Triassic fossils. Note, that the SiC grains are genetically unrelated to the host limestones.

The kimberlitic moissanite grains (n=106) are up to 1 mm across and the Bulgarian grains (n=22) are less than 100 microns. The grains are usually transparent and show various colors, but usually are bluish-green. Similar to earlier observations (Derkachenko et al., 1972, Marshintsev, 1990) most grains are fractured, but some sides preserve well-formed crystallographic faces.

Raman microspectroscopy was employed to determine the polytypes, to assess degree of crystalline perfection, and to identify of some inclusions. Major and trace elements in SiC bulk and in inclusions exposed by polishing were measured using Electron Microprobe (EMP) and by LAM-ICP-MS. For comparative purposes we studied synthetic SiC samples produced by very different methods: the Acheson and the modified Lely (sublimation) methods. The SiC grains were cast in epoxy and polished prior to analyses. Transmission Electron Microscopy (TEM) was used for direct investigation of submicroscopic inclusions. Loose grains were mechanically crushed and suspension brought to the Cu grid.

Results

Raman spectroscopy

Due to differences in band gap the color of SiC is polytype-dependent. Therefore, already from optical examination the majority of natural SiC grains are identified as the 6H variety. However, doping strongly influences SiC coloration and a more reliable method should be employed to identify the polytypes. Raman spectroscopy is a powerful tool to identify SiC polytypes and to assess degree of lattice disorder (Nakashima and Harita, 1997). Typical spectra are shown in Fig. 1. Grains of pure 6H SiC make 55% of both samples sets. The second most abundant pure polytype is 15R: 8% of the kimberlitic population (pure 15R is not present in the more limited Bulgarian set). Some other grains show the presence of 6H+15R mixtures in different proportions. In total the grains made of pure or intermixed 6H and 15R polytypes make up 83% (73%) of kimberlitic (Bulgarian) sets. It is well-known that the 6H and 15R polytypes generally form at temperatures exceeding 1300 ºC. Several grains (~5%) contain mixtures of 6H and 4H polytypes. The rest of the studied populations consist of various mixtures of 6H, 8H, 15R and 21R polytypes; such crystals may be thought of as containing long-period polytypes. As is known, disorder in SiC is not completely random and disordered regions consist of mixtures of randomly disordered simple polytype

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domains and those containing stacking faults distributed periodically or near-periodically. Some of the grains (~10%) show extremely complex spectra clearly indicating heavily disordered structures.
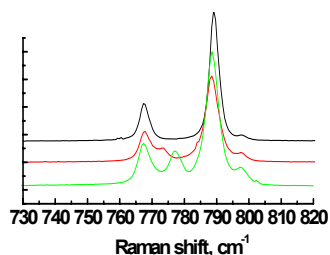

Fig. 1. Parts of the Raman spectra (TO modes) of SiC grains with various degree of perfection (disorder increases from top to bottom).

The shape and position of the LO phonon mode of SiC provides information about stresses and concentration of charge carriers. Only few spectra of the studied grains show stress-related features. At the same time, many grains show the presence of various levels of uncompensated charge carriers (presumably Al, B, perhaps N, see below), whose concentrations reach several hundred ppm in some grains. On average, the 15R grains contain higher concentrations of uncompensated impurities than the 6H ones. The Bulgarian set is, on average, also richer in dopants in comparison with the kimberlitic set.
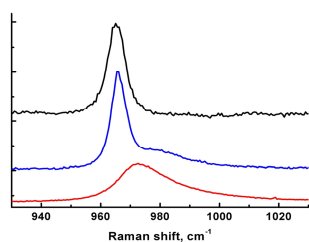

Fig. 2. LO phonon of SiC. Concentration of uncompensated dopants increases from top to bottom. The middle curve shows superposition of two domains.

The LO peak of some grains clearly reflects the superposition of at least two components (fig. 2). This suggests the existence of domains with markedly different type and/or concentration of uncompensated dopants. Judging from the size of the laser spot this heterogeneity is present at a scale of <10 microns. Cathodoluminescence images (Fig. 3) confirm the existence of such zoning. Recently Shiryaev et al., (2008) reported C and Si isotopic zoning in some of the grains.
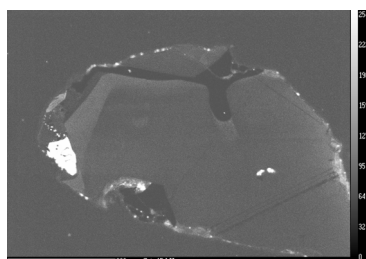

Figure 3. Cathodoluminescence of one of SiC grains showing growth(?) zoning and inclusions of Si.

Several grains (though the statistics are limited) show features in the OH vibrations region (fig. 4). However, it is not yet clear whether these bands are due to structural defects such as C-H complexes in SiC matrix or are due to microscopic H-rich inclusions.
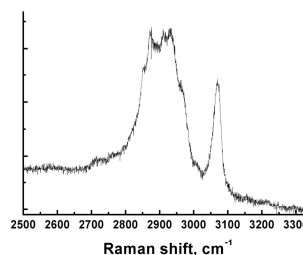

Fig. 4. H-related bands in Raman spectrum on a Yakutian SiC grain.

Major and trace elements

Moissanite grains are typically quite pure SiC with small admixture of oxygen (0.1-0.3 wt%). In the synthetic samples only Al, B, Ti, V, Sc were observed. These impurities (also N) are typical of synthetic SiC. Concentrations of these elements are roughly similar in synthetic and natural samples studied. However, the trace element chemistry of natural SiC is much richer than that of synthetic SiC samples. The most plausible explanation of chemical differences between natural and synthetic materials lies in amount of submicroscopic accessory phases. The SiC lattice is similar to diamond in its extremely low capacity for impurities except some subsitutional elements (Al, N, B). Therefore, it is believed that most trace elements are present in unresolved syngenetic inclusions and not in the SiC crystalline lattice. The contents of most trace elements in studied natural SiC grains are low (1-200 ppm), but several important conclusions can be drawn from the chondrite-normalised patterns.

- Al contents show a wide range, as do Cr and Ni;
- The contents of several chalcophile elements (Cu, Zn, Mo) are high compared to Ni, suggesting that no sulfide phase coexisted with the SiC;
- REE contents rise weakly from HREE to MREE, but decline on average from Nd to La;
- Sr shows a pronounced negative anomaly relative to Nd and Sm, and Y shows a negative anomaly relative to Dy and Ho; these features are also characteristic of trace elements in diamonds;
- Eu shows no anomaly relative to Sm and Gd;
- Contents of Sn are high and relatively constant;
- Zr/Hf is strongly subchondritic; limited data suggest the same is true of Nb/Ta; again, these features are characteristic of diamond trace-element patterns.

Several SiC grains from both localities contain inclusions of other phases. The most common is silicon metal, followed by an iron silicide ($FeSi_2$) and an oxygen-bearing Si(C,O) phase. Intergrowths of these phases in several grains indicate that they form a single primary assemblage. Raman spectroscopy provides unambiguous confirmation of presence of metallic Si. A slight shift of the Si Raman peak indicates residual pressure of several kbars. The presence of Si metal and various silicides in natural SiC was reported previously (Gnoevaja and Grozdanov 1965, DiPierro et al., 2003, Lyakhovich, 1980, Marshintsev 1990, Mathez et al., 1995). However, the chemical composition and crystal chemistry of previously reported compounds differ from our observations.

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A BSE image of an inclusion-bearing kimberlitic SiC grain is shown in fig. 5 (see also Fig. 3). A semi-euhedral crystal of SiC (150x350 μm) contains three inclusions with negative-crystal forms; each consists of Si^0 with blebs of $FeSi_2$ nucleated along the contacts. At the top of the grain, a large irregular grain of $FeSi_2$ is surrounded by a halo of cauliflower-shaped SiC grains set in a matrix of SiO_2. The SiO_2 also forms botryoidal outgrowths along the edge of the SiC crystal.
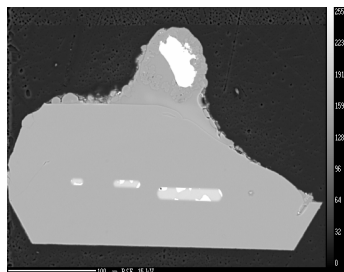

Figure 5. BSE image of inclusion-rich kimberlitic SiC grain.

The large $FeSi_2$ grain has a complex internal structure, with anastomosing "worms" of metallic Ti set in the $FeSi_2$ matrix (not shown); the microstructure strongly suggests exsolution of the Ti^0 from the $FeSi_2$, and the presence of subgrains within the $FeSi_2$. The Ti^0 strongly concentrates Ni and Mn.

The complex intergrowth of SiC and SiO_2 around the $FeSi_2$ grain suggests a secondary replacement process, which may have oxidised Si^0 and, to some extent, SiC. The relationships between the phases in these complex grains suggest that SiC coexisted with a melt phase dominated by Si^0 and Fe^0; this melt was trapped as inclusions in the SiC and formed a grain-boundary phase. On cooling, $FeSi_2$ appears to have crystallised (exsolved?) from the Si^0, typically along contacts with SiC. This relationship between Si and $FeSi_2$ makes trace element analysis of Si problematic due to contamination by microscopic silicide inclusions.

The TEM study shows presence of submicroscopic $FeSi_2$ inclusions dispersed in the SiC matrix (fig. 6) Electron diffraction confirms identification of the phase as a $FeSi_2$-based solid solution. Presumably, deviations of the composition from an ideal formula lead to absence of characteristic Raman signal.
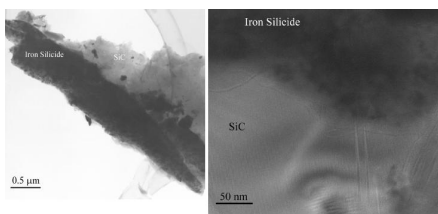

Figure 6. TEM image of $FeSi_2$ inclusion in a Bulgarian SiC.

Iron Silicide is compositionally variable: Fe ranges from 43.6-46.3 wt% (mean 45.4); Si from 49.2-55.4 wt% (mean 50.8). Ti varies widely; the mean value is 2.0 wt%, but many grains contain 2.5-3.8 wt% Ti, while others contain <0.3 wt%. Ni varies from 0.04 – 0.33 %, and Mn from 0.03 – 1.3 wt%. The calculated structural formula is $(Fe,Ti,Mn,Cr,Ni)Si_2$. This is clearly different from the Fe_3Si_7 composition reported as inclusions in moissanite by DiPietro et al. (2003).

The $FeSi_2$ phase has high contents of many trace elements; it appears to concentrate most of these elements in the system, and thus may give an indication of the nature of the environment in which the SiC and its associated phases formed. The key observations from the chondrite-normalised trace-element patterns are:

- High levels of elements such as Al, Cr, Mn, Fe;
- High levels of chalcophile elements, again indicating that no sulfide phase was present;
- A steep increase in REE contents from Lu to Ce, but chondritic (on average) La/Pr; Ba levels are low relative to La;
- A striking negative Eu anomaly; Eu is below detection limits in all analyses, even those with several hundred ppm of Nd and Gd;
- Smaller, but still marked, negative anomalies in Sm and Yb (as well as Y);
- High levels of Sn, as noted in the SiC;
- Zr/Hf ranges from subchondritic in some grains to suprachondritic in others; Nb/Ta is generally subchondritic.

The $FeSi_2$ phase clearly accepts highly charged, small ions (e.g., REE and HFSE). The REE pattern of the $FeSi_2$ suggests that nearly all Eu, and much of the Sm, has been reduced to the 2+ state and entered another phase. The lack of Eu and Sm anomalies in the moissanite suggests that the SiC does not discriminate against Eu^{2+} or Sm^{2+}. Without samples of other coexisting phases, it is not clear where the Eu and Sm are concentrated in this environment.

The Si-C-O phase contains 55-56 % Si, 9.6-12.0 wt% O; we assume that the balance is made up of C. The stoichiometry of this phase appears to be close to $Si_4(C,O)_7$, which would require a mixed valence (between 3 and 4) for Si.

The present study suggests that formation of natural SiC was related to the cooling of Fe-Al-Si-C melt. However, the geochemical environment of its genesis remains unclear.

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