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# Characterization of neutral boron-silicon clusters using infrared spectroscopy: The case of $Si_6B$

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ABSTRACT

Nano-size clusters are of great interest for understanding of fundamental properties and processes relevant for applied materials science such as heterogeneous catalysis. In this study, we present a newly developed dual-target dual-laser ablation source, suitable for the production of binary clusters and their spectroscopic characterization. With the current design, an almost arbitrary mixing ratio can be achieved by altering different parameters such as the laser fluences. Boron and silicon targets are chosen for cluster production, illustrating the possibility to control the outcome ranging from pure boron over mixed $Si_nB_m$ to pure silicon clusters. As a test system, $Si_6B$ clusters are characterized by means of infrared-ultraviolet two-color ionization (IR-UV2CI) spectroscopy, combined with quantum chemical simulations. The most stable structure of $Si_6B$ ($C_s$, $^2A'$) predicted in our previous work is confirmed by the present experiment. Doping of $Si_7$ with a single B atom has a drastic impact on the geometric, vibrational, and electronic properties.



## 1. Introduction

Nano-size silicon-based structures have attracted a lot of interest in the current miniaturization trend toward nanophotonics and nanoelectronics (e.g., [1–5]). Particularly, the understanding of material properties changing with size, composition, and charge plays an important role. It has been shown that nanostructures such as metal and semiconductor nanocrystals, quantum dots, and nanowires can be well described within the context of related isolated (gas-phase) atomic clusters [2,6,7]. As pure gas-phase silicon clusters are chemically reactive, doping with other elements has been considered as a solution in finding stable Si-based building blocks [8,9]. With the discovery of a superconducting transition at about 40 K in $MgB_2$ [10], there has been great interest in boron-doped materials as promising superconductors, including boron-doped diamond [11,12], silicon [13], and silicon carbide [14–16]. In crystalline phases, doping of group IV elements with boron as the source of hole-doping has been shown to induce superconductivity [12,13,17]. For sufficient boron doping (~100 ppm), silicon becomes metallic [18] and superconducting at a boron concentration of several percent with a critical temperature of $T_c \approx 0.35$ K [13]. Ab initio calculations combined with Raman measurements strongly suggest that doping is substitutional [13]. Interestingly, similar effects have also been predicted for small B-doped silicon clusters [19]. Efforts have been made to increase $T_c$ in B-doped silicon [16,20,21].

Studies on small B-doped silicon clusters are however rare, both in theory and experiment. For instance, heats of formation of gas-phase $Si_nB$ ($n = 1–3$) were measured by mass spectrometry [22]. Density functional theory (DFT) calculations for $SiB_2$, $Si_2B$, and $Si_2B_2$ found stable ring-like structures with strong π-bonding [23]. Anionic $Si_nB^-$ clusters ($n = 1–6$) formed by direct laser ablation from a mixed B/Si sample were studied by mass spectrometry and DFT calculations [24]. In that work, $Si_6B^-$ was predicted to have $C_{5v}$ symmetry ($^1A_1$), whereas its neutral counterpart was suggested to have $C_s$ symmetric geometry ($^2A'$) [25]. Recently, Tam *et al.* studied thermochemical parameters and the growth mechanism of B-doped silicon clusters ($Si_nB^q$, $n = 1–10$, $q = 0, \pm1$) using B3LYP, G4, and CCSD(T) approaches [19]. The ground state structures predicted for the neutrals suggest a growth mechanism, in which each $Si_nB$ is formed by adding a Si atom to $Si_{n-1}B$ rather than adding B into $Si_n$. For $Si_8B$, exohedral and endohedral structures become close in energy. Interestingly, pure boron clusters with sizes of up

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to 20 atoms have quasi-planar structures, while $SiB_7$ was predicted to have a 3D structure [26], indicating the importance of a single dopant atom on the properties of pure clusters. Surprisingly, no spectroscopic data are available for B-doped silicon clusters in any charge state. Here, we combine infrared-ultraviolet two-color ionization (IR-UV2CI) spectroscopy [27] with quantum chemical simulations to determine the structure of $Si_6B$, a strategy recently applied to a variety of (doped) silicon clusters [25,27–30].

Due to the high melting point of boron (>2000 °C), B-containing clusters are usually generated by laser ablation (see, e.g., [31,32]). An exhaustive review of laser ablation sources has recently been provided by Duncan [33]. To produce mixed clusters, various approaches have been demonstrated, such as single targets of alloys [34], binary compounds [35–37], pressed mixed powders [38,39], and dual-target (dual-laser) sources [40–44]. The dual-target dual-laser source designs allow for controlling the mixing ratios by changing the laser fluences, laser timing, and the rotation and/or translation speeds of the targets. Here, we describe a dual-target dual-laser ablation source developed for the production and spectroscopic measurement of binary clusters. We demonstrate that with this cluster source an almost arbitrary mixing ratio between the different components can be achieved. As an example for the spectroscopic characterization of the clusters produced in this source, we apply the IR-UV2CI technique to neutral $Si_6B$ to determine its geometric structure, as suggested previously [25].

## 2. Experimental and computational methods

### 2.1. Experimental setup

The experiments are performed in a cluster beam experiment connected to a beamline of the Infrared Free Electron Laser at the Fritz Haber Institute of the Max Planck Society in Berlin, Germany (FHI FEL) [45,46]. The cluster experiment has been described before [47] and is upgraded here with a new dual-target dual-laser ablation source (Fig. 1), with a design similar to the one reported by Banser et al. [44].

Mixed boron-silicon clusters ($Si_nB_m$) are produced by laser ablation of a silicon rod (natural isotopic abundance, ESPI metals, US) and an isotopically-enriched $^{11}B$ rod (99.5%, Ceradyne, US; rod manufactured by RHP-Technology, Austria) within a pulsed flow of helium carrier gas. The two cylindrical rods with 6.2 mm diameter are symmetrically located on opposite sides of the central gas channel. This channel has a diameter of 6 mm, and its volume can be adjusted with a teflon tube insert. Each rod is translated and rotated by a separate mechanism containing an in-vacuum stepper motor and a worm gear with a transmission ratio of 34:1 between motor and rod. This leads to a smooth and very slow movement of the target (few hours for one turn if required), always providing a fresh target. For ablation, two pulsed Nd:YAG lasers (Continuum Minilite, 10 Hz, 532 nm, ~5 ns) are focused by lenses onto the targets. The two parallel laser beams from the backside of the source are deflected to hit each rod at an angle of 60° with respect to the channel axis. This design ensures good spatial overlap of the ablation plumes, which is crucial for stable and controllable formation of binary clusters [43]. A solenoid valve (General Valve Series 9) is used to provide short helium carrier gas pulses (several 100 μs) at a backing pressure of about 4 bar. Through three-body collisions with carrier gas atoms, the atomic and molecular species contained in the ablation plasma are cooled down and form clusters. By tuning the laser fluence on each rod, either bare cluster distributions or binary cluster distributions with arbitrary mixing ratio can be produced (Fig. 2). Typically, pulse energies of about 4–6 mJ are used for Si and 5–8 mJ for B. The source is extended with a thermally insulated thermalization and reaction channel of 3 mm inner diameter and 40 mm length. The inlet for reaction gases is not used in the experiments described here. The temperature of the channel can be stabilized between 80 and 400 K using a flow of liquid nitrogen and/or an electrical heater. In the experiments reported here it was set to 90 K. At the channel exit, a converging/diverging nozzle of ~1 mm aperture is mounted to induce further cooling [48].

The molecular beam is collimated by a skimmer with 2 mm diameter. Before passing through a 1 mm aperture located further downstream and held at ~200 V to deflect charged clusters, the neutral $Si_nB_m$ clusters are irradiated with a counter-propagating IR laser beam from the FHI FEL and then post-ionized after a delay of 30 μs by an unfocused $F_2$ excimer laser (photon energy $E_{F2}$ = 7.87 eV) in the extraction zone of a reflectron time-of-flight mass spectrometer. The FHI FEL delivers pulsed radiation in the wavelength range from 3.5 to 48 μm, with up to 100 mJ within a macropulse of ~7 μs duration at about 0.4–1% full width at half maximum (FWHM) bandwidth. If the frequency of the FEL radiation is resonant with an IR active mode of a specific cluster, it can absorb IR photons followed by rapid intracluster vibrational energy redistribution, and thereby its internal energy increases. The ionization efficiency usually follows an S-curve behavior as a function of excitation energy, with a slope depending on the Franck–Condon factor for ionization [49]. An increase in the internal energy of the cluster upon IR absorption, therefore, results in an enhancement of the ionization yield. An IR-UV2CI spectrum is obtained from the relative ionization enhancement normalized by the IR photon flux as a

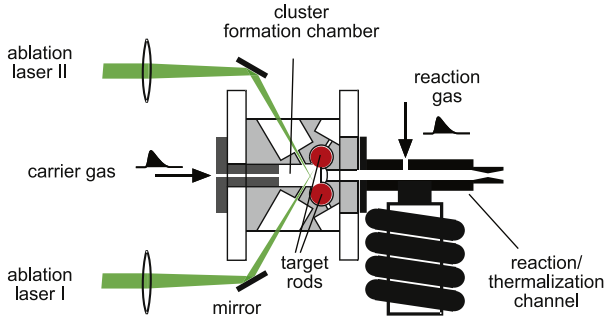


**Fig. 1.** Schematic view of the dual-target dual-laser ablation source for the production of mixed $Si_nB_m$ clusters.

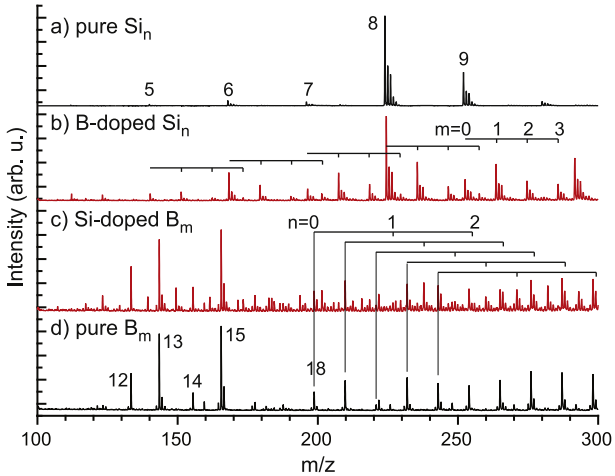


**Fig. 2.** Typical mass spectra of $Si_nB_m$ mixed clusters produced with the dual-target dual-laser ablation source. By altering the laser fluences, arbitrary mixing ratios of $Si_nB_m$ clusters, i.e., from pure $Si_n$ and $B_m$ to Si-rich and B-rich $Si_nB_m$ can be achieved. The used laser pulse energies are $^{Si}E_{abl}/^{B}E_{abl}$ = 6/0 mJ (a), 6/6 mJ (b), 6/8 mJ (c), and 0/8 mJ (d).