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Temperature measurements in CO_2-laser-induced pyrolysis flames for SiC and ternary SiC/C/B powder synthesis by means of CARS

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Abstract. The hot luminescent reaction zones of CO_2-laser-induced pyrolysis flames using SiH_4/C_2H_2 gas mixtures with different silane to acetylene ratios and with and without diborane additives were investigated by means of H_2 Q-branch CARS spectroscopy, leading to spatial temperature profiles in gas flow direction. In the case of B_2H_6 additive to the stoichiometric SiH_4/C_2H_2 mixture a high temperature plateau ($\approx$ 800–1000 K) of the reactant gas volume develops already several millimetres before reaching the CO_2-laser focus line. This precursor preheating zone could be explained by the catalytic effect of boron atoms or boron-containing intermediate species in the flame. A similar behaviour for acetylene-rich flames operating at half laser power was not observed.

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The advantages of laser pyrolysis for the production of nanosized ceramic powders are numerous, one of them the absence of contaminating walls or electrodes, another the formation of a spatially well defined reaction zone. The latter leads to very steep temperature gradients and cooling rates, which are necessary for high nucleation rates combined with small particle sizes. The experiments performed earlier in pure SiH_4 and SiH_4/C_2H_2 mixtures [1, 2] were extended to the ternary system $SiH_4/C_2H_2/B_2H_6$ [3, 4, 5]. Basing on the successful measurements of C_2H_2 and H_2 molecular densities and temperatures in SiH_4/C_2H_2 and SiH_4/C_2H_4 pyrolysis flames [6, 7], this work reports application of the CARS diagnostic to the ternary mixture.

1 Laser pyrolysis experiments

Construction of the setup (Fig. 1) is close to a previous experiment [4]. Main feature is a stainless steel reaction chamber with its central inlet nozzle for the reactant gas flow. An argon flow is used as protective gas to shield the reaction gas flow from the chamber walls and windows. Above the nozzle tip a CO_2 laser beam is focussed by a cylindrical lens to a horizontal line. The vertical stream of reactant gases intersects the focus line and forms a hot, luminescent reaction zone sustained by absorption processes of the silane molecule. As final products of the chemical reactions the SiC or boron doped SiC clusters and H_2 form the particulate plume, which enters an electrostatic filter, where the ultrafine particles deposit on the wall. To prevent undeposited clusters from contaminating the rotary pump and the motor valve a membrane filter follows behind the exit of the electrostatic filter. The residual reaction gases are led through a thermal decomposition unit where they are heated up to 900 K, sufficient for silane, diborane and the hydrocarbons employed in this experiment. Small amounts of residual silane are filtered by means of a scrubber unit containing NaOH and H_2SO_4 solutions.

All pyrolysis experiments were performed using gas mixtures of SiH_4 and C_2H_2 as hydrocarbon under a total pressure of 50 kPa. The experimental parameters were chosen in a way that the produced powders exhibited (besides SiC) merely a low boron concentration, because a diborane concentration of > 3 vol% gave rise to an uncontrolled burning reaction which was even still self-sustained with switched-off CO_2 laser. Such a mode of reaction had to be avoided, as it resulted in fast powder deposition on the nozzle tip and therewith in the emergency stop of the pyrolysis experiment. A synopsis of the experimental runs is given in Table 1.

2 CARS measurements

The narrow band scanning coherent anti-Stokes Raman scattering (CARS) diagnostic employed here is described exhaustively in [6, 7] and therefore not dealt with furtherly here. Different SiH_4/C_2H_2 and $SiH_4/C_2H_2/B_2H_6$ flames (runs P1–P4) were object of the CARS diagnostic. To define the spatial position of the scattering volume, Fig. 2 shows a schematic sketch of the reaction zone, together with an (x, z) coordinate system ($x > 0$ for positions between z axis and detection unit). All axial profiles were measured at $x = 0$.

An experimental Q-branch CARS spectrum of H_2 (cold band), recorded in the $SiH_4/C_2H_2/B_2H_6$ flame SiC/B P4 at $x = 0$ and $z = 3.5$ mm, is given in Fig. 2. It contains the vibrational-rotational lines $v = 0 \longrightarrow v = 1$ from $J = 0$ to $J = 5$. The same figure shows the fitted spectrum giving a

Table 1. Experimental conditions for powder synthesis

Run		Reactant gas			Laser power	IR absorption
		Φ_{SiH_4} [sccm]	$\Phi_{B_2H_6}$ [sccm]	$\Phi_{C_2H_2}$ [sccm]	P_L [W]	$1-(P_{L,T}/P_L)$ [%]
SiC/C	P1	333	—	397	50	26
SiC/C/B	P2	323	15	392	50	28
SiC	P3	333	—	167	100	14
SiC/B	P4	323	15	162	100	22

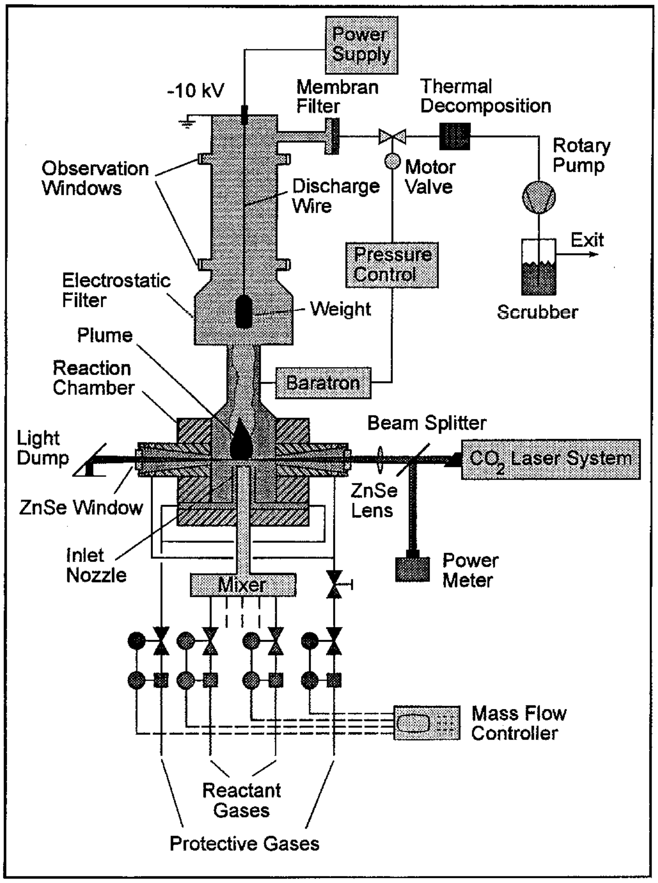

Fig. 1. Laser chemical setup

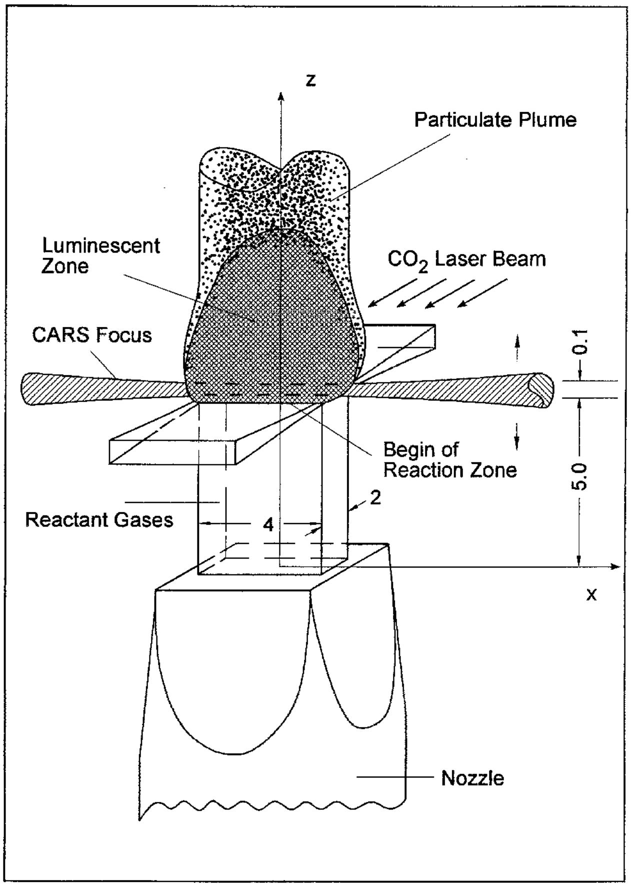

Fig. 2. Schematic of the reaction zone (values in mm)

rotational temperature of $T_{\text{rot}} = 881\,\text{K}$ (the fitting routines are described in detail in [6, 7]).

The experimental error of the CARS measurements is firstly due to spatial averaging over the finite scattering volume imposed by the steep axial temperature gradients in the flames. Its influence is estimated by means of the formulas applied in [7, 11], giving a maximum relative error of 10% for the highest gradients ($z \approx 4.5$ mm). For moderate gradients at $z < 3$ mm this error is considerably smaller. Secondly, the determination of the rotational temperature from CARS spectra is subject to statistical errors. To minimize these errors, rotational temperature measurements from different CARS spectra, recorded at identical spatial positions, were averaged. This leads to an error of 5% for temperature values in the preheating zone and of 10% in the region of the strong temperature rise. Summarizing, the overall error in temperature is approximatelly 20% for the steepest axial gradients and decreases rapidly down to 5% in the moderate regions.

3 Interpretation of CARS measurements

The diverse powder synthesis experiments listed in Table1 are now analysed with respect to the chemical processes occuring in the flame.

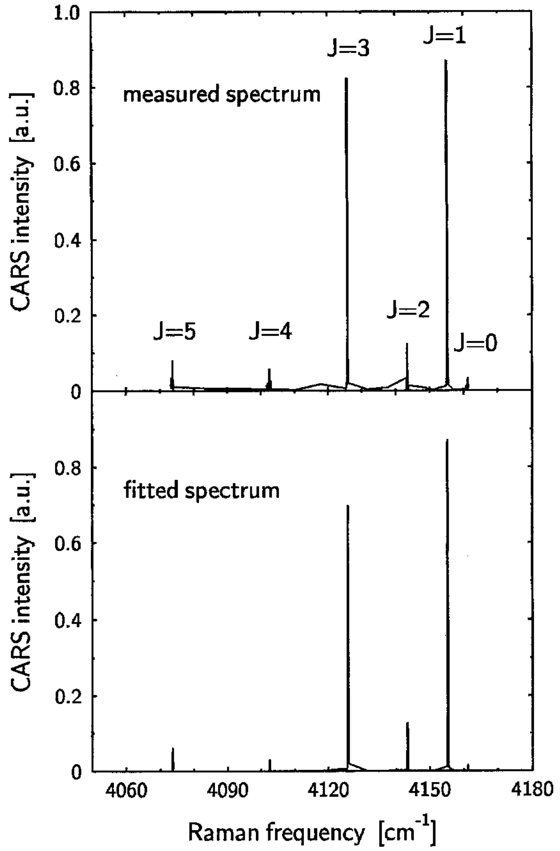

Fig. 3. CARS spectrum of H_2 measured in the pyrolysis flame run SiC/B P4 at $x = 0$ and $z = 3.5$ mm (*above*) and corresponding fitted spectrum for $T_{\mathrm{rot}} = 881$ K (*below*)

Table 2. Measured temperature gradients and corresponding heating rates

Run	P_L [W]	T' [10^6 K/m]	c_{gas} [m/s]	$\dot{T}$ [10^6 K/s]
SiC/C P1	50	2.5	3.3	8.3
SiC/C/B P2	50	2.2	3.3	7.3
SiC P3	100	3.1	2.3	7.1
SiC/B P4	100	3.1	2.3	7.1

3.1 Runs SiC/C P1 and SiC/C/B P2

The temperature curves for the flames SiC/C P1 and SiC/C/B P2 in Fig. 4 show a standard behaviour, which is very similar to the measured temperature profiles from [7]. In the case of diborane as gasphase precursor merely a slight increase in temperature can be stated. Temperature gradients and heating rates are 2.5 (2.2) × 10^6 Km^{-1} and 8.3 (7.3) × 10^6 Ks^{-1} (Table 2). The CO_2 laser beam absorption by the flame is high (26–28%).

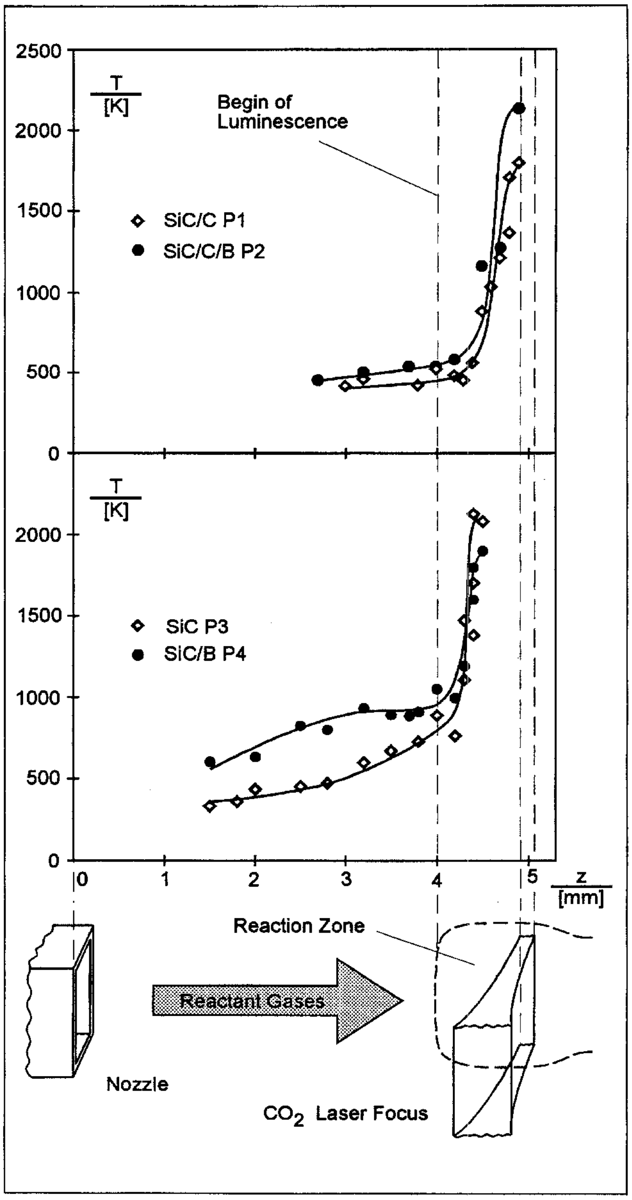

Fig. 4. Axial temperature profiles for runs SiC/C P1 and SiC/C/B P2 (above) and for runs SiC P3 and SiC/B P4 (below) obtained from H_2 CARS spectra

3.2 Runs SiC P3 and SiC/B P4

At run SiC/B P4, with $P_L = 100$ W and stoichiometric flow ratio (323 sccm : 162 sccm) of silane to acetylene, the temperature behaviour of the $SiH_4/C_2H_2/B_2H_6$ flame differs considerably from that of the corresponding SiH_4/C_2H_2 flame without diborane (run SiC P3). In the case of the latter the standard behaviour mentioned above is observed again, with a temperature rise position which is shifted towards smaller z values. With diborane addition a high temperature plateau (≈ 800–1000 K) of the reactant gas volume appears already several millimetres before reaching the CO_2 laser focus line (see Fig. 2).

Temperature gradients and heating rates are in the range of 3.1 × 10^6 Km^{-1} and 7.1 × 10^6 Ks^{-1} for both flames (Table 2). The preheating in the case of run SiC/B P4 is accompanied by a raise in CO_2 laser beam absorption from 14 to 22%.

A drastic increase in reaction enthalpy due to the anticipated different chemical reaction pathways when the boron compound is added can be ruled out as a reason for this preheating, because the diborane is strongly diluted within the SiH_4 and C_2H_2 flow ($\approx$ 3 vol%). For instance, a hydroboration mechanism [8] like

$$B_2H_6 + 4\,C_2H_2 \longrightarrow B_2H_2(CH = CH_2)_4 + \Delta H_0 \qquad (1)$$

should not possess reaction enthalpies clearly exceeding 100 kJ per mole C_2H_2, which is the same order of magnitude as the overall reaction enthalpy of the binary gas mixture:

$$2\,SiH_4 + C_2H_2 \longrightarrow 2\,SiC + 5\,H_2 + 217.3\,\mathrm{kJ\,mol^{-1}}\,. \qquad (2)$$

The strong increase in CO_2 laser beam absorption from 14 to 22%, caused by addition of 3 vol% diborane, can probably be explained by the formation of vinylboranes via reaction (1). The vinylboranes possess a high absorption of the 10*P*(20) laser photons, which also exceeds that of silane and of hydrocarbon. In contrast to this the diborane molecule only weakly absorbs the 10*P*(20) line at 944.19 cm^{-1} [9, 10]. Summarizing it can be concluded that the diborane or alternatively a boron-containing intermediate species in the flame must have a catalytic effect on the chemical process. Remarkable catalytic properties of boron atoms are indeed reported by Bilenchi et al. [9] for a SiH_4/B_2H_6 gas mixture. At high temperatures SiH_4 can easily act as a sensitizer for the dissociation of B_2H_6 [9], the Si-H bond in silane (3.2 eV) being considerably stronger than the BH_3–BH_3 bond in diborane (1.61 eV). Therefore as one possible mechanism

$$B_2H_6 \longrightarrow 2\,BH_3\,, \qquad (3)$$

$$2\,BH_3 \longrightarrow 2\,B + 3\,H_2\,, \qquad (4)$$

could be proposed, delivering via boryl radicals the boron atoms which then form the dominant catalysts for reaction (2).

If reaction (2) is catalyzed, it could start already below the CO_2 laser focus line, leading to the observed preheating in this spatial region. This assumption is further confirmed by test runs which were performed earlier and not mentioned here, varying the diborane concentration in the ternary gas mixture. These experiments showed that beyond a certain threshold ($\approx$ 10 vol% diborane) the reaction flame keeps burning also in the case of switched-off CO_2 laser, extending its luminescence down to the nozzle tip. When this occurred, the complete laserchemical setup was shut down immediately for safety reasons.

Further investigations will be necessary to elucidate the complex chemistry of the ternary gas mixture employed in this experiment, especially concerning the type of radicals (e.g. BH_3, BH) determining the characteristic pathway of the laserchemical process. Resonance enhanced CARS (RECARS) or degenerate four wave mixing (DFWM) seem to be suitable diagnostics for radical species occurring in the pyrolysis flame; nevertheless, up to now no literature dealing with this experimental field is known to the authors.

4 Conclusion

The CARS measurements presented here show that the addition of diborane to a laser induced stoichiometric silane/acetylene pyrolysis flame significantly influences the axial temperature profile of the luminescent reaction zone, revealing the catalytic role of the boron atoms with respect to the chemical process. The latter is observed to be clearly extended towards the presheath ranging from x = 2.0 to 4.0 mm.

It is remarkable that, although laser power is only 50 W, the absorption of the 10*P*(20) laser line is significantly higher for SiC/C P1 compared with SiC P3 (100 W), where in both cases no diborane is added to the gas flow. For a lower laser power, like in SiC/C P1, one should not expect a significant change of absorption because the flow rates of the absorbing molecules (silane) are the same for both flames.

A more plausible explanation for the increased absorption in SiC/C P1 is the fact, that due to the increased gas flow velocity of 3.3 ms^{-1} a higher amount of silane molecules reach the CO_2 laser focus line. This corresponds to a temperature rise which is much closer to the laser focus than in the case of SiC P3, where reaction starts earlier. The latter is caused by a 50% lower flow velocity combined with a doubled laser power (100 W).

Diborane addition does not change these absorption dependences, only a relatively high absorption for the lower gas flow (SiC/B P4) can be noticed now, which is due to the boron induced chemistry.

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