JOURNAL OF MATERIALS SCIENCE 25 (1990) 4273–4278

Infrared absorption of β-SiC particles prepared by chemical vapour deposition

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Infrared absorption characteristics of β-SiC particles prepared by chemical vapour deposition were studied. These particles were either solid or had a silicon core and/or were hollow. The solid particles exhibited a single absorption peak between the transverse optical frequency ($\omega_{TO} = 794\,cm^{-1}$) and the longitudinal optical frequency ($\omega_{LO} = 976\,cm^{-1}$) of β-SiC. This absorption peak shifted to a lower frequency with increasing lattice parameter of β-SiC and increasing free silicon content. The particles containing a silicon core and/or were hollow exhibited double absorption peaks close to ω_{TO} and ω_{LO}. The peak at the LO side shifted to a lower frequency and that at the TO side to a higher frequency with decreasing silicon core size and increasing hollow size. Using the calculations based on the effective medium theory assuming surface phonon mode, the relationship between the infrared absorption characteristics and microstructures of the β-SiC particles are explained.

1. Introduction

Silicon carbide (SiC) is a promising material for engineering and electrical uses due to its superior mechanical and electrical properties at high temperatures. Control of the microstructure of the starting SiC powder is very important when fabricating an SiC body through a sintering process. Solid and spherical β-SiC particles are required if a dense SiC body is to be prepared [1]. Recently, it was shown that hollow β-SiC particles are useful starting materials for fabrication of a thermoelectric device [2]. The SiC body prepared using hollow particles showed a low thermal conductivity and high Seebeck coefficient due to the uniformly dispersed micro-voids.

Several methods, including chemical vapour deposition (CVD), plasma CVD, laser-derived CVD and carbothermic reduction of silica, have been used to synthesize SiC powders. Among these, CVD is known to be the best method to control the microstructure of the particles. Earlier, the authors prepared solid and silicon core and/or hollow β-SiC particles by CVD using $(CH_3)_2SiCl_2 + H_2$ and $SiH_4 + CH_4 + H_2$ as source gases and reported the structure and properties of the particles [3, 4].

Conventionally, transmission electron microscopy (TEM), BET absorption, X-ray diffraction (XRD), chemical analysis have been used to characterize the fine particles. In addition, infrared absorption spectroscopy is also an effective method to investigate the microstructure of fine particles [5].

In general, bulk crystal shows a significant infrared absorption at the frequency of transverse optical (TO) mode by the interaction between phonon and photons. However, when the size of the crystal decreases to the order of the wavelength of the photons, a series of absorption peaks due to the surface phonon mode appear between the transverse optical (TO) and longitudinal optical (LO) frequencies. Because infrared absorption by surface phonon mode is strongly influenced by the crystallinity, composition and shape of particles, much useful information concerning particle microstructure can be obtained by analysing the infrared absorption spectroscopy.

Many studies on infrared absorption due to the surface phonon mode of particles such as MgO [6], ZnO [7], CdS [7], α-Fe_2O_3 [8], KCl [9], NaCl [10], NiO [11], ZnO containing a zinc core [12], CdO containing a CdTe core [13], MgO containing a magnesium core [13], have been reported. However, no report on the infrared absorption by the surface phonon mode of β-SiC particles has been found. In the present work, the relationship between infrared absorption and microstructure of CVD β-SiC particles either solid or having a silicon core and/or hollow was investigated. Calculations based on the effective medium theory were compared with the experimental results.

2. Theory

The effective medium theory provides a frequency (ω) relationship to infrared absorption coefficient (α) as shown by Equation 1, assuming small spherical particles are embedded in a non-absorption medium [5].

$$\alpha = (\omega/c)\ \mathrm{Im}\,[\varepsilon_{av}(\omega)]/\mathrm{Re}\,\{[\varepsilon_{av}(\omega)]^{1/2}\} \qquad (1)$$

where c is the velocity of light, and Re and Im denote the real and imaginary parts of an average dielectric function $\varepsilon_{av}(\omega)$. For a small spherical particle composed of a core and a shell, Yamamoto *et al.* [14] gives the expression $\varepsilon_{av}(\omega)$ as

$$\varepsilon_{av}(\omega) = \frac{f\varepsilon_c A(r_c/r)^3 + f\varepsilon_s B[1 - (r_c/r)^3] + \varepsilon_m(1 - f)}{fA(r_c/r)^3 + fB[1 - (r_c/r)^3] + (1 - f)} \qquad (2)$$

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where, ε_c, ε_s and ε_m are the dielectric constants of the core, shell and medium, respectively, f is the volume fraction of the particles in the medium. r_c and r are the radii of core and shell, respectively. A and B are represented by Equations 3 and 4, respectively.

$$A = \frac{3\varepsilon_s}{(\varepsilon_c - \varepsilon_s)} \frac{K}{r_c^3} \tag{3}$$

$$B = \frac{(\varepsilon_c + 2\varepsilon_s)}{(\varepsilon_c - \varepsilon_s)} \frac{K}{r_c^3} \tag{4}$$

where

$$K = \frac{3\varepsilon_m(\varepsilon_c - \varepsilon_s)r_c^3}{(\varepsilon_s + 2\varepsilon_m)(2\varepsilon_s + \varepsilon_c) - 2(\varepsilon_s - \varepsilon_m)(\varepsilon_s - \varepsilon_c)(r_c/r)^3} \tag{5}$$

In the present work, the core consists of silicon and/or a hollow. For this case the average dielectric constant of silicon ($\varepsilon_{Si} = 11.9$) and the hollow ($\varepsilon_{vacuum} = 1$) should be used for ε_c as in Equation 6.

$$\varepsilon_c = 1 + 3f_{Si} \frac{\varepsilon_{Si} - 1}{\varepsilon_{Si}(1 - f_{Si}) + (2 + f_{Si})} \tag{6}$$

where f_{Si} is the volume fraction of silicon in the core. ε_s can be calculated from Equation 7.

$$\varepsilon_s(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\gamma\omega} \tag{7}$$

where ε_0 and ε_∞ are the static and high-frequency dielectric constants of β-SiC ($\varepsilon_0 = 10.0$, $\varepsilon_\infty = 6.7$) [15], respectively, γ is the damping factor ($\gamma = 8.5\,\text{cm}^{-1}$) [15], ω_{TO} is the TO frequency of β-SiC which varies with the lattice parameter as given by Equation 8 [16].

$$\omega_{TO} = \omega_{TO}^0 - D(a - a_0)/a_0 \tag{8}$$

where $\omega_{TO}^0 = 794\,\text{cm}^{-1}$ [15] and $a_0 = 0.43589\,\text{nm}$ [17]. D is a constant [16].

In the case of a solid spherical particle, r_c is equal to 0, and $\varepsilon_s'(\omega)$ indicated by Equation 9 should be used instead of $\varepsilon_s(\omega)$ given by Equation 7 in Equations 2 to 5.

$$\varepsilon_s'(\omega) = \varepsilon_{Si}\left\{1 + \frac{3(1 - f_{Si}')(\varepsilon_s(\omega) - \varepsilon_{Si})}{\varepsilon_s(\omega)f_{Si}' + \varepsilon_{Si}(3 - f_{Si}')}\right\} \tag{9}$$

where f_{Si}' is the volume fraction of silicon in the solid spherical particles.

It is known that the measured infrared absorption spectra of the surface phonon mode agree well with the calculations if the damping constant is multiplied by 3 to 5 due to the large anharmonicity of the particle surface [18]. In the present calculations, the damping constant was multiplied by 5.

3. Experimental procedure

Solid and silicon core and/or hollow β-SiC particles were prepared by CVD at reaction temperatures (T_{rea}) from 1273 to 1673 K using $(CH_3)_2SiCl_2 + H_2$ and $SiH_4 + CH_4 + H_2$ as source gases. The detailed procedures for the powder preparation were reported earlier [3, 4]. The particles were mixed with KBr ($\varepsilon_{KBr} = 2.33$) powder and pressed into pellet form for the measurement of infrared absorption spectra. The infrared absorption spectra were measured using a spectrophotometer (Japan Spectroscopic: IR-G) at room temperature in the frequency range 400 to $4000\,\text{cm}^{-1}$.

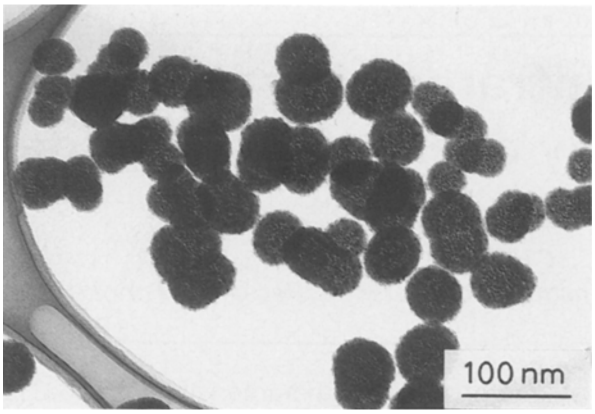

Figure 1 Electron micrograph of solid β-SiC particles prepared from the $(CH_3)_2SiCl_2 + H_2$ system at $T_{rec} = 1673\,\text{K}$.

Fig. 1 shows a transmission electron micrograph of solid spherical particles prepared by the $(CH_3)_2SiCl_2 + H_2$ system. The particles obtained at $T_{rea} = 1673\,\text{K}$ are single-phase β-SiC, while those obtained below $T_{rea} = 1573\,\text{K}$ are composites of β-SiC and silicon. Fig. 2 shows hollow β-SiC particles prepared by the $SiH_4 + CH_4 + H_2$ system. At $T_{rea} = 1673\,\text{K}$, the particles obtained were single-phase β-SiC having a hollow, while those obtained below $T_{rea} = 1623\,\text{K}$ had a silicon core and a hollow within the core. Table I lists the size, lattice parameter, and the radii of the silicon core (r_c) and the hollow (r_{c1}). These values were used in the calculations of infrared absorption spectra. The values of r_c and r_{c1} were calculated from the composition (x: SiC/(SiC + Si)wt %) and measured density (ρ) using Equations 10 and 11 [4].

$$r_c/r = (1 - x\rho/\rho_{SiC})^{1/3} \tag{10}$$

$$r_{c1}/r = [1 - x\rho/\rho_{SiC} - (1 - x)\rho/\rho_{Si}]^{1/3} \tag{11}$$

4. Results and discussion

Fig. 3 shows the measured infrared absorption spectra of solid particles prepared from the $(CH_3)_2SiCl_2 + H_2$ system. A distinct absorption peak between 800 and $900\,\text{cm}^{-1}$ was observed for the particles obtained at all

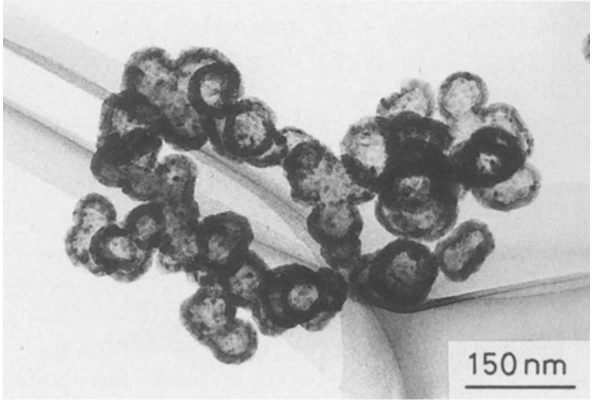

Figure 2 Electron micrograph of hollow β-SiC particles prepared from the $SiH_4 + CH_4 + H_2$ system at $T_{rec} = 1673\,\text{K}$.

TABLE I Preparation conditions and properties of particles

Reaction temperature (K)	Gas concentration (mol %)			β-SiC lattice parameter (nm)	Free silicon content (wt %)	Diameter (nm)		
	$(CH_3)_2SiCl_2$	SiH_4	CH_4			Outer (r)	Silicon core (r_c)	Hollow (r_{cl})
1373	7.0	–	–	0.43700	38.7	50	–	–
1473				0.43635	22.5	45	–	–
1573				0.43615	8.6	45	–	–
1673				0.43604	0	45	–	–
1523	–	2.0	4.0	0.43620	–	46	40.8	25.1
1573				0.43600	–	54	46.7	31.7
1623				0.43590	–	68	53.4	48.8
1673				0.43590	–	73	–	54.3
1523	–	3.6	7.2	0.43630	–	70	65.8	24.5
1573				0.43615	–	64	57.6	21.5
1623				0.43595	–	64	53.3	39.6
1673				0.43590	–	79	58.8	58.5

reaction temperatures. The peak frequency increased with increasing reaction temperature.

The calculation assuming the surface phonon mode also predicted one absorption peak between ω_{TO} and ω_{LO} for solid spherical particles. The calculations also showed that this peak frequency decreased with increasing free silicon content and lattice parameter of β-SiC, as shown in Figs 4a and b. When the particle contains no free silicon and its lattice parameter is equal to the value of bulk β-SiC (a_0 = 0.435 89 nm), this peak frequency is given by 874 cm^{-1}.

Fig. 5 shows the effect of reaction temperature (T_{rea}) on the measured and calculated peak frequencies. The calculated values are in good agreement with the measured values. The calculated spectra were also compared with the measured ones and are seen to agree well in Fig. 6. However, the measurements give a weak absorption at about 1100 cm^{-1} for the particles prepared below T_{rea} = 1473 K, while the calculation gives no such absorption. This absorption may have been caused by impurity such as SiO_2 particles contained in the powder [19–21].

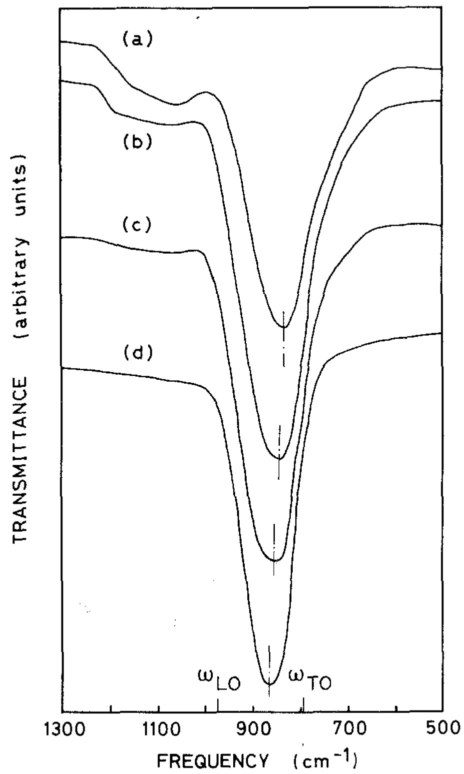

Figure 3 Measured infrared absorption spectra of solid particles prepared from the $(CH_3)_2SiCl_2$ + H_2 system at (a) T_{rec} = 1373 K, (b) 1473 K, (c) 1573 K and (d) 1673 K.

Fig. 7 shows the measured infrared absorption spectra of particles prepared from the SiH_4 + CH_4 + H_2 system. Two absorption peaks are observed at about 810 and 940 cm^{-1} for the particles obtained at T_{rea} = 1523 to 1623 K. These particles consist of an SiC shell having silicon core and an inner hollow. The interval between the two peak frequencies as well as the peak intensity at the LO side, decreased with increasing reaction temperature. The peak at the LO side nearly disappears and appears as a shoulder for the particles obtained at T_{rea} = 1673 K. At this temperature the particle consists of an SiC shell and a hollow but not of a silicon core.

Fig. 8 shows the absorption spectra calculated assuming that the particles consist of an SiC shell and a silicon core of different radii but no inner hollow. Under this assumption, the calculation predicts the presence of two absorption peaks. Eventually, when r_c/r = 1, that is when the β-SiC shell becomes infinitely thin, the two peak frequencies are predicted to be equal to ω_{TO} and ω_{LO} of β-SiC. The interval between the two peaks decreases with decreasing silicon core radius (r_c) as shown in Fig. 8. Both peak frequencies will slightly increase with increasing lattice parameter

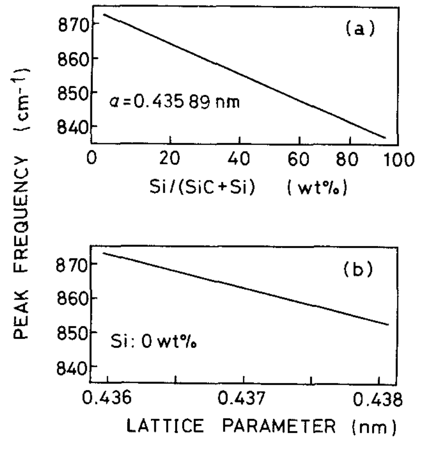

Figure 4 Effect of (a) free silicon content and (b) β-SiC lattice parameter on the calculated peak frequency for solid particles.

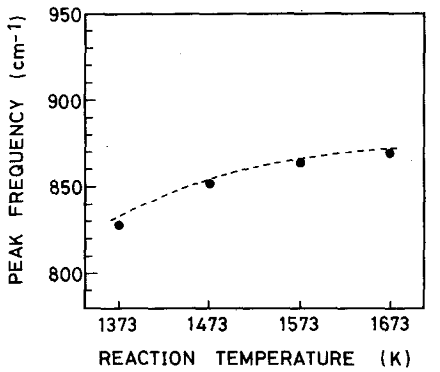

Figure 5 Effect of reaction temperature (T_{rec}) on the (●) measured and (– – –) calculated peak frequency of solid particles prepared from the $(CH_3)_2SiCl_2 + H_2$ system.

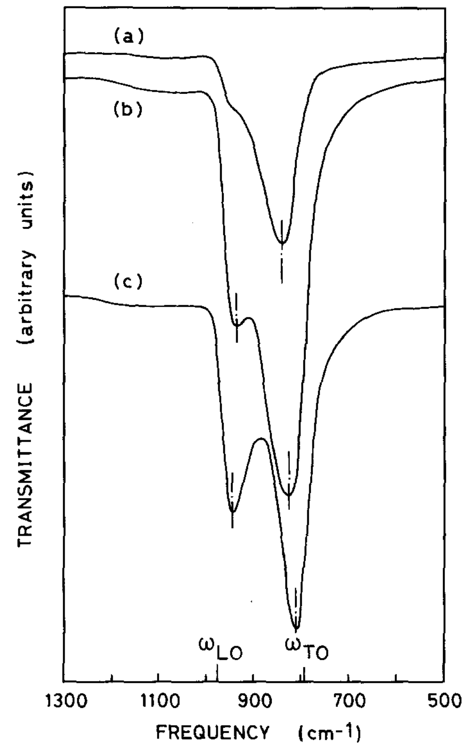

Figure 7 Measured infrared absorption spectra of silicon core and/or hollow particles prepared from the $SiH_4 + CH_4 + H_2$ system at (a) T_{rec} = 1673 K, (b) 1623 K and (c) 1573 K.

of β-SiC just as in the case of the solid particles shown in Fig. 4b. However, the decrease in peak intensity at the LO side, as shown in Fig. 7 cannot be predicted by the above calculations based on the assumption of the existence of the silicon core alone. Thus, the effect of a hollow within the silicon core can be considered as follows.

Fig. 9 shows the infrared absorption spectra calculated by assuming the presence of a hollow within the silicon core. It is clearly shown that the peak intensity at the LO side decreases with increasing hollow radius (r_{cl}). When $r_{cl} = r_c$, that is only a hollow but no silicon core exists within the particles, the absorption at the LO side will appear as a shoulder.

Fig. 10 shows the effect of the radii of the silicon core (r_c) and the hollow (r_{cl}) on the two peak frequencies. Both measured and calculated values are presented in Fig. 10. The measured peak frequencies at the LO side are slightly smaller than the calculated values and are slightly larger for the TO side peaks. This difference may be caused by the measurements of powder density. Because the particles were agglomerated, as seen in Fig. 2, the measured density might be smaller than the true values due to the existence of pores among the agglomerated particles. Consequently, r_c and r_{cl} calculated from Equations 10 and 11 tend to be larger than the true values. This result might lead to the difference in the peak frequencies found between the measurements and calculations. If the true values of r_c and r_{cl} could be obtained, the measured peak

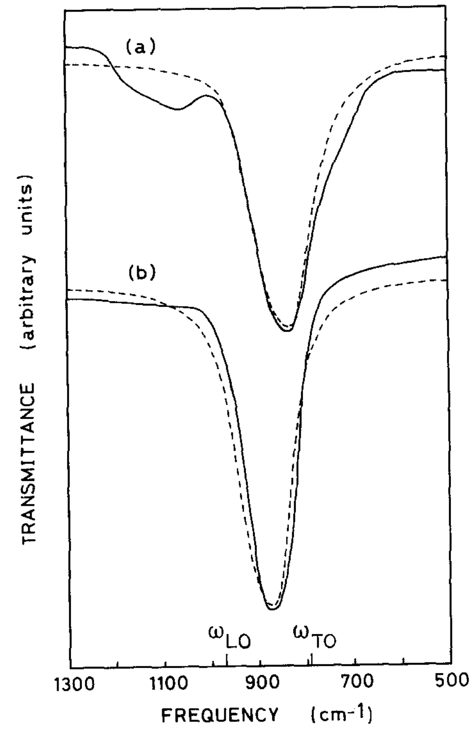

Figure 6 Comparison of (– – –) calculated and (——) measured absorption spectra of solid particles prepared from the $(CH_3)_2SiCl_2 + H_2$ system at (a) T_{rec} = 1373 K and (b) 1673 K.

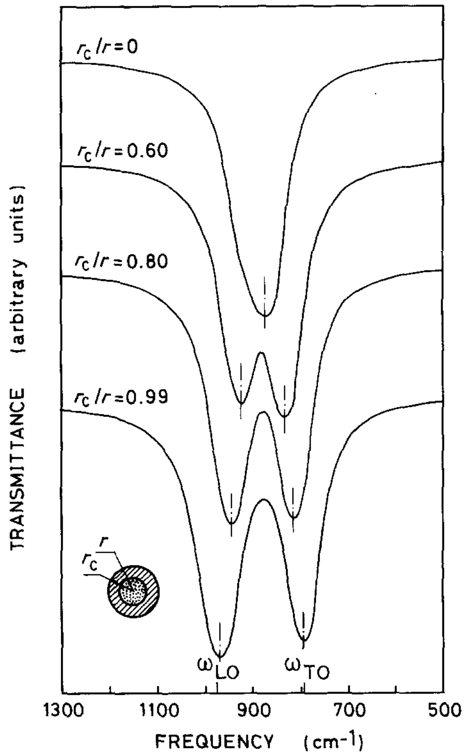

Figure 8 Effect of silicon core radius on the calculated absorption spectra (r = 50 nm is assumed).

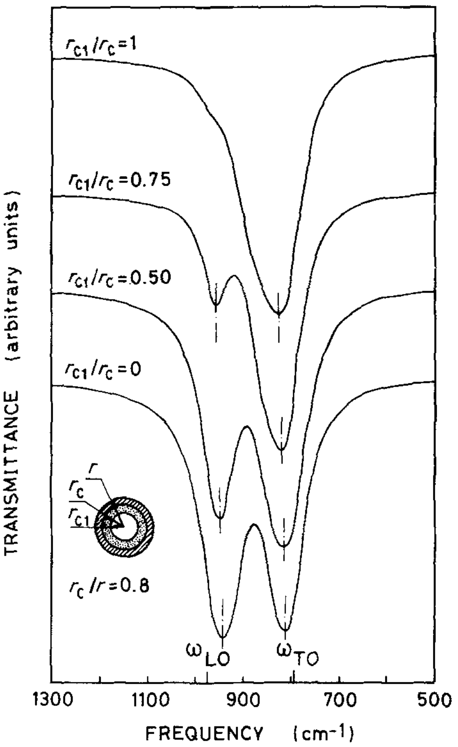

Figure 9 Effect of hollow radius on the calculated absorption spectra (r = 50 nm, r_c/r = 0.8 are assumed).

frequencies would probably match the calculations exactly.

Fig. 11 shows the comparison between calculated and measured infrared absorption spectra of the particles prepared from the $SiH_4 + CH_4 + H_2$ system. The general shapes of the calculated spectra are in good agreement with the measured ones, just as found for the case of the solid particles prepared from the $(CH_3)_2SiCl_2 + H_2$ system, as shown in Fig. 6.

5. Conclusion

Infrared absorption characteristics of two types of β-SiC particles (solid, silicon core and/or hollow) prepared by CVD were experimentally measured and the results were compared with the theoretical calculations based on the effective medium theory, assuming the surface phonon mode.

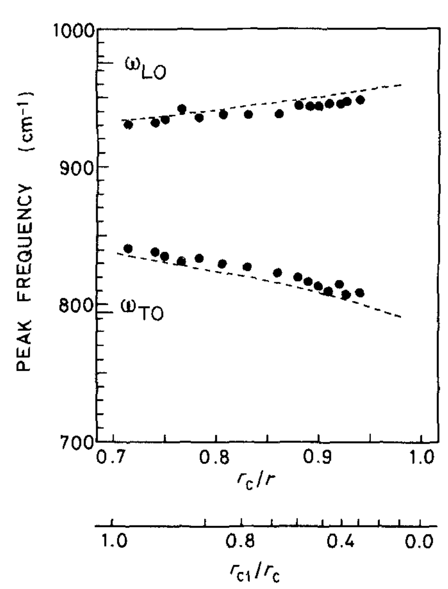

Figure 10 Relationship between peak frequencies and size factors (r_c/r, r_{c1}/r_c) for silicon core and/or hollow particles prepared from the $SiH_4 + CH_4 + H_2$ system. (– – –) Calculated, (●) measured.

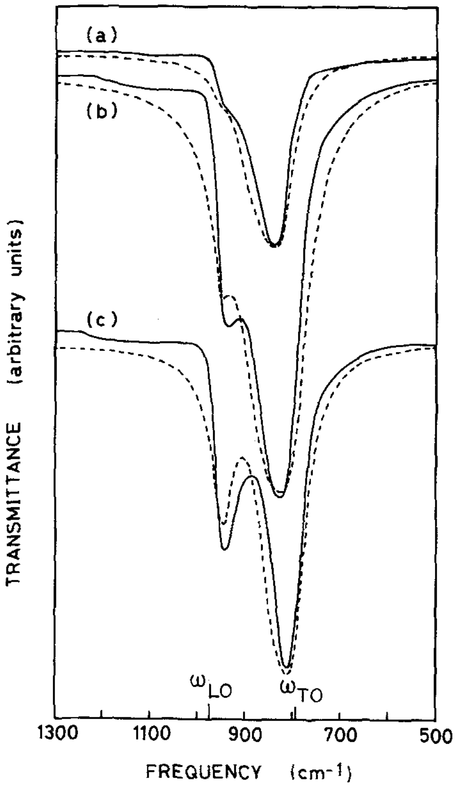

Figure 11 Comparison of (– – –) calculated and (——) measured absorption spectra of silicon core and/or hollow particles prepared from the $SiH_4 + CH_4 + H_2$ system at T_{rec} = (a) 1673 K, (b) 1623 K and (c) 1573 K.

The solid particles prepared from the $(CH_3)_2SiCl_2 + H_2$ system showed a distinct absorption peak between ω_{TO} and ω_{LO}. The peak frequency decreased with increasing lattice parameter of β-SiC and free silicon content in the particles. The silicon core and/or hollow β-SiC particles prepared from the $SiH_4 + CH_4 + H_2$ system showed two absorption peaks close to ω_{TO} and ω_{LO}. The peak frequency at the TO side increased but at the LO side decreased with decreasing silicon core size and with increasing hollow size. The effect of preparation conditions, microstructure and properties of the β-SiC particles on infrared absorption peak frequencies and intensities were well described by the effective medium theory, assuming the surface phonon mode.

Acknowledgements

The authors thank Dr Y. Sasaki, Tohoku University, for helpful advice on the calculation, and Mr F. Chida for measurement of infrared absorption spectra. This research was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Scientific and Culture under Contract nos. 60 430 019 and 60 850 130.

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Received 17 May
and accepted 29 September 1989