

THE SiC PROBLEM: ASTRONOMICAL AND METEORITIC EVIDENCE

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ABSTRACT

Presolar grains of silicon carbide, found in meteorites and interpreted as having had an origin around carbon stars from their isotopic composition, have all been found to be of the β -SiC polytype. Yet, to date, fits to the 11.3 μm SiC emission band of carbon stars had been obtained only for α -SiC grains. We present thin-film infrared (IR) absorption spectra that were measured in a diamond-anvil cell for both the α - and β -polymorphs of synthetic SiC, and we compare the results with previously published spectra that were taken using the KBr matrix method. We find that our thin-film spectra have positions nearly identical to those obtained previously from finely ground samples in KBr. Hence, we show that this discrepancy has arisen from inappropriate “KBr corrections” having been made to laboratory spectra of SiC particles dispersed in KBr matrices. We refitted a sample of carbon star mid-IR spectra, using laboratory data with no KBr correction applied, and show that β -SiC grains fitted the observations while α -SiC grains did not. The discrepancy between meteoritic and astronomical identifications of the SiC type is therefore removed. This work shows that the diamond-anvil cell, thin-film method can be used to produce mineral spectra that are applicable to cosmic environments without further manipulation.

Subject headings: infrared: ISM: lines and bands — infrared: stars — methods: laboratory — stars: carbon

1. INTRODUCTION

Most of the solid material in the solar system is believed to have originated as small particles that condensed in outflows from stars. However, most solar system solids (predominantly silicates) have been reprocessed and/or homogenized so extensively that even the most primitive meteorite silicate samples no longer contain evidence of their origins. But some types of dust particles in the solar system have not been reprocessed and can potentially be associated with their stellar origin. One such dust type, silicon carbide (SiC), is believed to be a significant constituent of the dust around carbon-rich asymptotic giant branch stars (Gilman 1969; Treffers & Cohen 1974). Silicon carbide grains can be divided into two basic groups: α -SiC, if the structure is one of the many hexagonal or rhombohedral polytypes, and β -SiC, if the structure is cubic (see, e.g., Bechstedt et al. 1997). Silicon carbide grains exhibit a strong mid-infrared feature between 10 and 12 μm , with the peak of the β -SiC feature occurring about 0.4 μm shortward of that for α -SiC. Until now, the observed peak wavelengths of the SiC feature in astronomical spectra have been interpreted as indicating α -SiC to be the dominant type of SiC around carbon stars (see, e.g., Baron et al. 1987; Pégourié 1988; Groenewegen 1995; Speck, Barlow, & Skinner 1997a, 1997b). In fact, Speck et al. 1997a, 1997b found no evidence of β -SiC in these circumstellar environments. Silicon carbide grains found in meteorites have isotopic compositions that imply that most of these grains were formed around carbon stars, with small amounts forming around novae and supernovae (see Hoppe & Ott 1997, Ott 1993, and references therein). To date, all studies of meteoritic SiC grains have found them to be of the β type (Bernatowicz 1997); β -SiC will transform into α -SiC above 2100°C, but the reverse process is thermodynamically unlikely. There is therefore an apparent discrepancy between the meteoritic and astronomical SiC types, which has been discussed in detail by Speck et al. (1997a, 1997b).

We present new infrared (IR) absorption measurements of thin films of α - and β -SiC that were created by compression in a diamond-anvil cell. Unlike some other methods, a dispersive medium (such as potassium bromide, KBr) is not used. This relatively new approach is quantitative, if sufficient care is taken to produce an appropriately thin and uniform film, as shown by a comparison of thin-film spectra of various minerals with reflectivity data from the same samples (Hofmeister 1995, 1997 and references therein). Moreover, thin-film spectra of garnets are nearly identical to single-crystal absorption data that were acquired in a vacuum (Hofmeister 1995); hence, thin film spectra can be applied to astronomical data without further manipulation. Our measurements strongly suggest, through a comparison of the new thin-film data with previous IR spectra collected for fine-grained KBr dispersions (in which the dust particles are dispersed in a KBr pellet), that the “matrix correction” wavelength shift, invoked by Dorschner, Friedemann, & Gürtler (1978) and adopted by other authors (see, e.g., Friedemann et al. 1981 and Borghesi et al. 1985), should not be applied to laboratory spectra of submicron grain-size dispersions of SiC: it was the use of this “KBr correction” that caused the above-mentioned discrepancy between the SiC types found in meteorites and around carbon stars. A companion paper (Hofmeister & Speck 1999) clarifies the roles of scattering, absorption, reflection, and baseline correction in laboratory measurements, sheds light on problems associated with the powder-dispersion technique, and discusses the conditions appropriate for the application of such data.

2. LABORATORY TECHNIQUES AND RESULTS FOR THIN-FILM SAMPLES

Single crystals of α -SiC were purchased from Alpha/Aesar (catalog No. 36224). This specimen is 99.8% SiC, consisting of hexagonal platelets of 50–250 μm in diameter and 5–15 μm thick. Less than 1% of the platelets had an amber color; the remainder were pale gray. All were transparent in the visible with smooth, highly reflective surfaces. Polycrystals of β -SiC were donated by Superior Graphite Co. The purity of this sample is also 99.8%. One batch consisted of 1 μm powder; the other was a conglomerate of equant crystallites of up to 25 μm

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in size. For this study, only the gray crystals of α -SiC were examined.

Mid-IR spectra were obtained from 450 to 4000 cm^{-1} (2.5–22.2 μm) at 2 cm^{-1} ($\sim 0.01 \mu\text{m}$) resolution using a liquid-nitrogen-cooled HgCdTe detector, a KBr beam splitter, and an evacuated Bomem DA 3.02 Fourier transform interferometer (FTIR). Thin films were created through compression in a diamond-anvil cell (DAC) that was interfaced with the spectrometer using a beam condenser. Type II diamonds were used. Film thickness was estimated from the initial grain size, by the relative relief and color seen among the various films and by the increase in grain diameter from the initial size during compression. Efforts were made to cover the entire diamond tip (0.6 mm diameter) with an even layer of sample, but slight irregularities in the thickness were inevitable. Reference spectra were collected from the empty DAC. Uncertainties in peak positions are related to peak widths because the accuracy of the FTIR spectrometer is high, $\pm 0.01 \text{ cm}^{-1}$. For procedural details, see Hofmeister (1997).

Spectra obtained from α -SiC (Figs. 1a and 1b) have an intense, broad band near 11.8 μm . The peak position lies between the longitudinal optic (LO) mode and transverse optic (TO) mode components observed by Spitzer, Kleinman, & Walsh (1959), and a shoulder is seen at the LO position. A shoulder also occurs at 12.2 μm . The sample thickness could not be determined precisely but was estimated to be submicron. Spectra obtained from β -SiC (Figs. 1c–1g) depend somewhat on thickness. For the thinnest films of submicron thickness (Figs. 1c and 1d), a fairly symmetric peak is found at 11.3–11.4 μm , and a weak shoulder exists at 10.7 μm , consistent with excitation of the LO mode component. Spectra from thicker film samples, $\sim 1 \mu\text{m}$ in thickness from visual inspection (Figs. 1e and 1f), have a peak at a similar position, with an asymmetric increase in intensity on the short-wavelength side, and display additional weak features. The 12.7 μm band is due to the TO feature. The weak, broad band at 13.4 μm is not an absorbance feature but is due to the Christiansen effect, which gives a minimum when the real part of the index of refraction is unity (Hapke 1993). The asymmetry of the main peak is due to the baseline rising toward the visible, probably a scattering effect from the grain boundaries. A spectrum from the thickest sample examined ($\sim 1 \mu\text{m}$) has high-absorbance values overall, with the Si–C stretching peak superposed (Fig. 1g). The appearance of the peak is intermediate between the peaks observed from the thin (Fig. 1d) and moderately thick samples (Fig. 1e) in that the main peak is symmetric, but a weak subsidiary feature exists at 12.7 μm . Below 8 μm , the absorbance in Figure 1g drops, rather than increasing as in the other spectra, because of interference fringes in the near-IR (not shown). These interference fringes indicate a distance of 5 μm , which is inferred to be the separation of the diamond anvils. The peak positions of the β -SiC samples are relatively independent of the thickness. No difference can be discerned between the two samples of β -SiC (fine grain size vs. mixed grain sizes). Figures 1c and 1g were made from a mixture of grain sizes, and Figures 1d–1f are from the 1 μm powder fraction. Additional spectra from both β -samples resembled those shown. The appearance of the spectra is consistent with being the result of pure absorption for the thinnest samples (Figs. 1c and 1d) and absorption with minor reflection for the thicker samples (Figs. 1e–1g), given that the LO-TO coupling is stronger in β -SiC than in α -SiC (Hofmeister & Speck 1999).

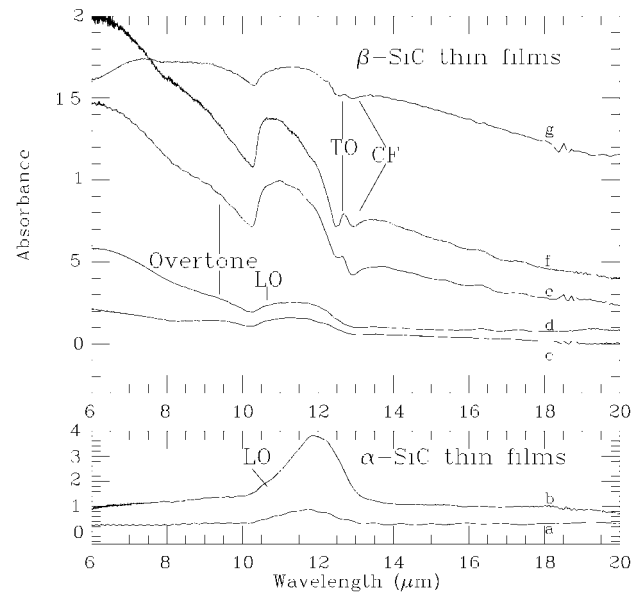


FIG. 1.—Representative thin-film IR spectra. *Bottom panel*: Submicron films of α -SiC, which have an intense broad band at (a) 11.70 and (b) 11.87 μm . *Top panel*: β -SiC spectra acquired from films increasing in thickness from less than 0.1 to $\sim 1 \mu\text{m}$. For clarity, plot d was offset by 0.2 absorbance units and plot b by 0.1 absorbance units. Absorbance clearly increases with thickness for β -SiC. The positions of the LO and TO modes of SiC are shown, as well as those of the overtone and Christiansen feature (CF).

3. COMPARISON WITH DISPERSED-SAMPLE RESULTS

KBr matrix spectra of β -SiC that were obtained by Borghesi et al. (1985) for a fine grain size sample (mean diameter modeled by them as 0.02 μm , average diameter observed in the transmission electron microscope [TEM] as 0.12 μm) closely match our own thin-film data, particularly the spectrum in Figure 1e (shown in Fig. 2a). The greatest difference is that the TO mode appears as a shoulder rather than a separate peak. This difference is obviously due to sample thickness, because the thinner film of Figure 1d has a barely discernable shoulder at the TO position. The LO mode occurs as a weak shoulder in their dispersion data. Their uncorrected peak barycenter was at 11.4 μm , which is the same as for our thin films. The match of Borghesi et al.'s dispersion data with Figure 1e is consistent with an estimated film thickness of less than 0.1 μm . The β -SiC spectrum of Papoular et al. (1998), with a maximum absorbance of 0.4, has a peak at 11.5 μm , in agreement with previous results and Figure 1. Papoular et al. (1998) also present two unusual spectra of β -SiC consisting of broad overlapping peaks at 10.9 and 12.2 μm . These positions are close to the TO and LO components. The very high absorbance units of 1 and 2.5 for these samples suggest overloaded pellets. For extreme concentrations of SiC (or large thicknesses), light is reflected between the TO and LO modes: the scattering in the pellet produces the dip in absorption. Problems occur at high absorption because the partial opacity induces a frequency-dependent baseline.

For α -SiC, the KBr-dispersion spectrum of Borghesi et al. (1985)'s smallest grained (mean diameter modeled by them as 0.04 μm , average diameter observed in TEM as 0.16 μm) and purest sample (SiC-600) closely matches the spectrum of our thinnest film (Fig. 1a; comparison shown in Fig. 2b). Its peak position of 11.6 μm equals our result, given the experimental uncertainties. The positions of the shoulders are comparable to

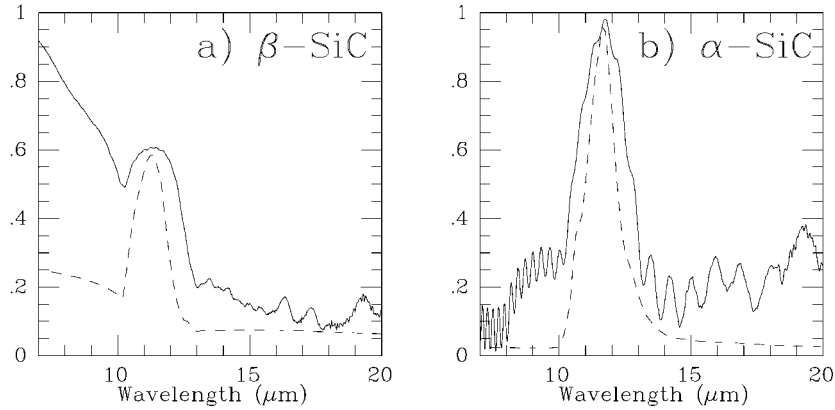


FIG. 2.—Our thin-film spectra (*solid lines*) and the uncorrected Borghesi et al. (1985) KBr dispersion data (*dashed lines*)

the LO and TO positions (Spitzer et al. 1959). Their sample SiC-N is compromised by $\sim 10\%$ impurities (C and SiO_2). Their SiC-1200 sample was 3–10 times larger grained, even for the ground and sedimented fraction, and is inappropriate for comparison. The study by Friedemann et al. (1981) involved larger grain sizes but yielded similar spectral profiles, with a slight shift of the peak position to $11.8 \mu\text{m}$.

It is clear that the introduction of a KBr matrix wavelength correction (see, e.g., Friedemann et al. 1981) is incorrect since the barycenter peak for KBr dispersions with fine grain sizes and reasonably low concentrations equals that of corresponding thin films, while the peak shapes are in excellent agreement. For these ($<0.1 \mu\text{m}$) grain sizes or film thicknesses, bulk absorption rather than surface effects dominates in the vicinity

of the intense peak. Only for extremely thick or large grain samples, $\sim 1 \mu\text{m}$, do the parameters of the dispersions differ from those of a bulk sample, but the differences are due to internal scattering among the particulates and sample opacity, leading to incorrect assumptions for zero transmission. This issue is discussed further by Hofmeister & Speck (1999). Similarly, the application of a KBr correction for silicates (Dorschner et al. 1978) is also problematic. Recent measurements by Colangeli et al. (1993, 1995) indicate minimal matrix effects for various silicates. Thin-film data, on the other hand, do not suffer from these problems.

4. IMPLICATIONS FOR THE SiC TYPE THAT BEST MATCHES CARBON STAR SPECTRA

Having established that previous fits of laboratory spectra for SiC to astronomical spectra have been erroneous because of the unnecessary application of a KBr correction factor, we have refitted our own UK Infrared Telescope (UKIRT) CGS3 spectra of carbon stars (Speck et al. 1997a, 1997b) without such a correction. We used the same χ^2 -minimization routine described by Speck et al. (1997a, 1997b), but the Borghesi et al. (1985) data for α -SiC (SiC-1200, SiC-600, and SiC-N) and for β -SiC, to which Speck et al. (1997a, 1997b) applied the usual KBr correction, were used uncorrected this time.

A detailed discussion of the fitting procedure can be found in Speck et al. (1997a). The routine was used on the flux-calibrated spectra, over the whole wavelength range ($7.5\text{--}13.5 \mu\text{m}$). All attempted fits involved either a blackbody or a blackbody modified by a λ^{-1} emissivity, together with some form of silicon carbide. The results are listed in Table 1, and representative sample fits are shown in Figure 3. The χ_R^2 values are the reduced χ^2 values, given by dividing the χ^2 value by the number of degrees of freedom. The fitting routine was unable to find fits for four of the spectra, those of AFGL 341, AFGL 2699, V Aql, and Y CVn. However, these four spectra are unusual in that they display a strong feature in the $7.5\text{--}9.5 \mu\text{m}$ region (see Fig. 2 of Speck et al. 1997a), possibly identifiable with α -C—H hydrogenated amorphous carbon (Baron et al. 1987; Goebel, Cheeseman, & Gerbault 1995), and need to be classified separately. Self-absorption by SiC grains is a possibility in some cases (Speck et al. 1997a, 1997b), so the fitting procedure was repeated using either a blackbody or a modified blackbody, together with silicon carbide in both emission and absorption simultaneously. The results of this fitting are listed in Table 1: 13 of the 20 spectra that could previously

TABLE 1

RESULTS OF THE χ^2 -FITTING FOR THE $7.5\text{--}13.5 \mu\text{m}$ FLUX-CALIBRATED CARBON STAR SPECTRA

Source	SiC Type	T_{BB} (K)	T_{SiC} (K)	τ_{SiC}	$\tau_{9.7}^a$	χ_R^2
IRAS 21489+5301 ^b	β -SiC	449	293	0.515
IRC +10216 ^b	β -SiC	511	230	1.260
AFGL 5076 ^c	β -SiC	557	298	0.137	...	0.369
AFGL 2494 ^c	β -SiC	516	383	0.167	...	0.306
AFGL 3099 ^c	β -SiC	726	329	0.242	...	1.370
AFGL 5102 ^c	β -SiC	650	355	0.161	...	0.345
AFGL 2155 ^c	β -SiC	734	288	0.235	...	0.418
IRAS 02152+2822 ^c	β -SiC	548	519	0.223	...	0.504
IRC +40540 ^c	β -SiC	859	313	0.173	...	0.508
AFGL 2368 ^b	β -SiC	727	321	1.772
V Hya ^c	β -SiC	1129	393	0.211	...	0.761
IRC +00365 ^c	β -SiC	1788	215	0.114	...	2.316
CIT 6 ^c	β -SiC	960	363	0.217	...	1.294
IRC +50096 ^b	β -SiC	940	455	2.166
R For ^b	β -SiC	906	800	1.237
R Lep ^b	β -SiC	1284	573	5.274
UU Aur ^c	β -SiC	2505	446	0.165	...	1.105
V Cyg ^c	β -SiC	2556	568	0.139	...	1.014
CS 776 ^b	β -SiC	993	576	1.879
V414 Per ^c	β -SiC	1102	920	0.177	...	0.579
AFGL 3068 ^d	β -SiC	394	62	0.030	...	0.092
IRAS 02408+5458 ^d	β -SiC	388	96	0.152	...	1.686
AFGL 2477 ^{d,e}	β -SiC	377	114	0.073	0.104	0.419
AFGL 5625 ^{d,f}	β -SiC	358	185	0.097	0.113	0.306

^a $\tau_{9.7}$ is the optical depth at $9.7 \mu\text{m}$.

^b Fits with pure emission only.

^c Fits with self-absorbed net emission.

^d Fits with self-absorbed net absorption.

^e Also requires Trapezium interstellar silicate absorption.

^f Also requires μ Cep interstellar silicate absorption.

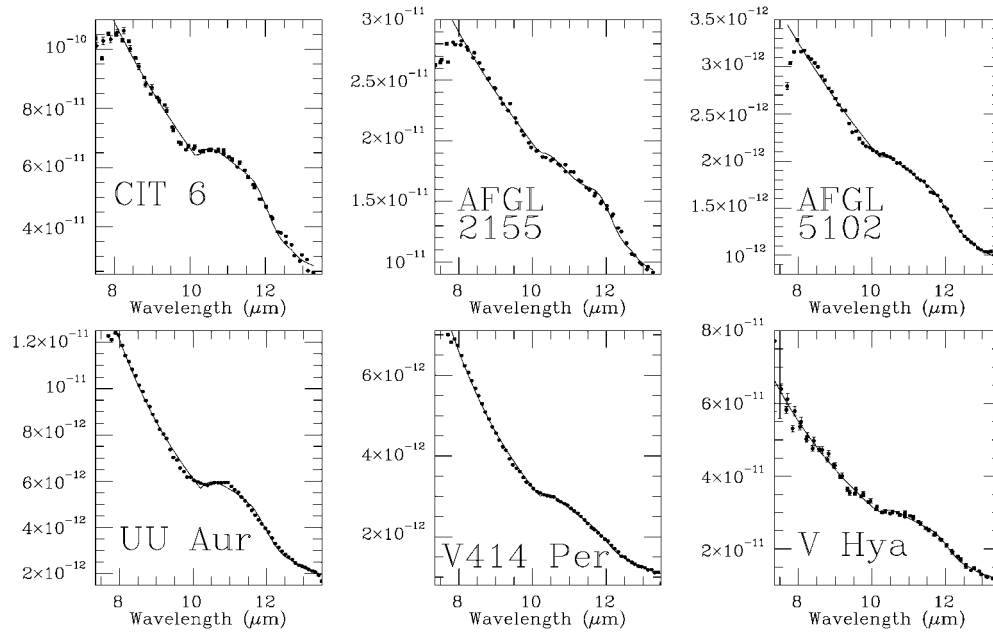


FIG. 3.—The β -SiC (plus blackbody) fits to several UKIRT CGS3 carbon star spectra (see text for details)

be fitted by SiC in pure emission produced better fits with self-absorption included. Four sources found to have SiC absorption features by Speck et al. (1997a) were also refitted, and the new results are shown at the bottom of Table 1. Two of these four sources required interstellar silicate absorption as well as circumstellar SiC absorption (see Speck et al. 1997a).

The results in Table 1 shows that there is an obvious predominance of the β -SiC phase and that there is now no evidence for the α -SiC phase at all. This is in contrast to previous attempts to fit the astronomical SiC feature using similar, and in some cases the same, raw laboratory data, but inappropriately corrected for the KBr dispersion. Previous work found that the best fits were obtained with α -SiC and had concluded that there was no unequivocal evidence for the presence of any β -SiC. Without the KBr correction, β -SiC matches the observed features, while α -SiC does not. Thus, there is now no astronomical evidence for the presence of α -SiC in the circumstellar regions around carbon stars. While α -SiC might exist in small quantities, all observations to date are consistent with the exclusive presence of β -SiC grains. This resolves the past discrepancy, reconciling astronomical observations and meteoritic samples

of silicon carbide grains. Having confirmed that SiC grains observed around carbon stars and those found in meteorites are of the same polytype, further discrepancies need to be addressed. In particular, the differences in grain sizes between astronomical models and meteoritic grains merit attention (see Speck et al. 1997a, 1997b for a detailed discussion).

Furthermore, the current work has demonstrated that mineral spectra produced using the DAC thin-film method are directly applicable to astrophysical contexts without further manipulation of the data. It is now appropriate to use the DAC thin-film method to produce more mineral spectra that would be of use to astronomers.

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