Silicon Carbide: The Problem with Laboratory Spectra

A. K. Speck

University of Illinois at Urbana-Champaign, 1002 W. Green St., Urbana, IL 61801, USA

A. M. Hofmeister

Department of Earth & Planetary Science, Washington University, St Louis, MO 63130, USA

M. J. Barlow

University College London, Gower Street, London WC1E 6BT, UK

Abstract. The interpretation of astronomical observations of infrared (IR) silicon carbide (SiC) features in the spectra of carbon stars have revealed discrepancies between the work of astronomers and that of meteoriticists. The silicon carbide observed around carbon stars has been attributed to one type of SiC (α) while meteoritic samples believed to have formed around such stars are of another type of SiC (β). The key to solving this problem has been to understand the sources of laboratory data used by astronomers in order to interpret the IR spectra. Through comparison of thin film IR absorption spectra and spectra taken using finely ground samples dispersed in potassium bromide (KBr) pellets we show that the previously invoked "KBr matrix-correction" is unnecessary for powder dispersions obtained from very fine grain sizes of SiC. Comparison of our data and previous measurements show that dust around carbon stars is β-SiC, consistent with laboratory studies of presolar grains in meteorites. The implications of these findings affect twenty years of work. The IR spectroscopic laboratory data used by astronomers to identify dust species in space must be carefully scrutinized to ensure that the KBr correction is not responsible for further misattributions of minerals in astronomical dust features.

1. Introduction

Most of the solid material in the solar system is believed to have originated as small particles that condensed in outflows from evolved stars. However, most solar system solids (predominantly silicates) have been reprocessed and/or homogenized so extensively that even the most primitive meteorite silicate samples have lost the isotopic indicators of their presolar origins. However, some types

---

1This work was undertaken whilst at University College London
of dust particles in the solar system have not been reprocessed and can potentially be associated with their stellar origins. One such dust type, silicon carbide (SiC), has been found in primitive meteorites (Bernatowicz et al. 1987; Hoppe & Ott 1997 and references therein). The majority of these grains (~99%) have isotopic compositions indicative of formation around carbon-rich asymptotic giant branch (AGB) stars (otherwise known as ‘carbon stars’). Silicon carbide has been postulated to form in the outflows around carbon stars (Friedemann 1969; Gilman 1969) and a feature in their infrared (IR) spectra at ~11.3μm has been attributed to SiC (Gilrath & Code 1971; Hackwell 1972; Treffers & Cohen 1974). Therefore, meteoritic SiC is an important indicator of conditions in and around carbon stars.

There are in fact about seventy different forms of SiC, known as polytypes, and many papers have been published discussing which form most closely fits the observed feature ~11.3μm. All these polytypes are variants of the same basic structure, based on a tetrahedral group of silicon and carbon atoms (Taylor & Jones 1960). These seventy different forms of SiC can be divided into two basic groups: α- and β- SiC. The α-SiC form has a hexagonal or rhombohedral crystal structure and is very stable up to ~2700°C. The β-SiC form has a cubic structure, and is in general slightly less thermodynamically stable than α-SiC. β-SiC is the favoured type when condensation takes place in a vacuum. β-SiC will transform into α-SiC at temperatures above ~2100°C but it is thermodynamically unlikely that this process will work in reverse. Very little (a few percent at best) α-SiC will transform into β-SiC (I. P. Parkin; pers. comm.). The difference between these two forms is small, both structurally and thermodynamically (< 2100°C), but they can be distinguished by crystallographic techniques and by their IR spectra.

With the exception of a few nanometre-sized grains found in and amongst the presolar diamonds (Daulton et al. 1996), all of the presolar SiC grains recovered from meteorites are β-SiC (Bernatowicz 1997; Hoppe & Ott 1997 and references therein). However, astronomical observations of the 11.3μm feature in evolved carbon stars indicated that the grains were of the α- polytype (e.g. Speck et al. 1997 a&b; Groenewegen 1995). These investigations of the 11.3μm feature were based on previously published laboratory spectra of SiC. The physical properties of meteoritic SiC are determined by non-spectroscopic methods. The only spectra of meteoritic SiC taken to date (Andersen et al. 1999) suffer from problems due to large grain sizes and spectral artifacts and are therefore of little benefit in this problem. The discrepancy between meteoritic and astronomical results has been an enigma, the most plausible explanation being that until the dust around carbon stars and meteoritic SiC grains have been characterized by the same method, we cannot be certain whether we are observing the same types of grain (Speck et al. 1997 a&b). Here we present new laboratory spectra of α- and β-SiC and compare them to previous laboratory data. We find that the interpretation of astronomical observations was affected by erroneous interpretation of laboratory data and that the 11.3μm feature observed in the spectra of carbon stars is indeed consistent with β-SiC, resolving the most important discrepancy between the meteoritic and astronomical results.
2. The KBr Matrix-Correction Factor

Dorschner et al. (1978) undertook a study of the effects of the potassium bromide (KBr) matrix on the spectra of small grain-size silicate samples. They used reflection spectra of bulk samples, from which they derived optical constants using Kramers-Kronig analysis and then Mie theory to calculate the extinction due to small spherical particles of the same medium. They then compared these calculated spectra to the spectra obtained from small grains of the same medium embedded in a KBr pellet and found that there was a difference - the peaks of the spectral features were shifted. Hence they invoked a shift due to the KBr matrix which needed to be corrected before KBr pellet spectra could be used. There are several problems with this argument. Firstly, it assumes that the grains are spherical, which is almost certainly untrue. Second, the use of Kramers-Kronig analysis can be problematic as it requires an input spectrum over an extended wavelength range and extrapolation of the spectrum to infinity. Finally, care must be taken when using the KBr technique to avoid overloading the pellets or clumping the sample within the pellet as both these effects tend to produce more opaque pellets which in turn affects the spectrum they produce. A combination of these problems led to the wavelength shift rather than a real physical effect.

Subsequently, a similar treatment was performed for SiC by Friedemann et al. (1981). The problems with overloading pellets are compounded for SiC due to the extreme opacity of this mineral. The KBr matrix correction has since propagated through the astronomical literature and certainly needed further investigation.

We conclusively show through comparison of new thin film data (Speck et al. 1999) with previous IR data collected from KBr dispersed samples (e.g. Borghesi et al. 1985), that the matrix correction should not be applied to laboratory measurements of sub-micron grain size dispersions of SiC and that use of this is the cause of the discrepancy between the meteorites and astronomical results.

3. Comparison of Thin Film and KBr-dispersed Spectra

Mid-IR spectra were obtained from thin films of both α- and β-SiC. The thin films have a thickness of about 0.1μm which were created through compression of the sample in a diamond anvil cell (DAC) which was interfaced with the spectrometer. For further experimental details see Speck et al. (1999); Hofmeister (1995).

Fig. 1 shows the comparison of the uncorrected KBr-dispersed spectra obtained by Borghesi et al. (1985) with our new thin film data for both α- and β-SiC polytypes. For β-SiC, KBr-dispersed spectra obtained by Borghesi et al. (1985) for fine grain size sample (mean diameter modeled as 0.02μm) closely match our data, (see Fig. 1a). The greatest difference is that the transverse optic (TO) mode appears as a shoulder, rather than as a separate peak. The difference is due to sample thickness, because thinner films (not shown: see Speck et al. 1999) have a barely discernible shoulder at the TO position. The longitudinal optic (LO) mode occurs as a weak shoulder in the dispersion data.
The ~14μm peak seen in the thin film spectra is part of the Christiansen effect\(^1\). The peak barycentric wavelength is at 11.4μm, identical to the thin films.

For α-SiC, the KBr-dispersion spectrum of Borghesi et al. (1985)'s purest and smallest grains (mean diameter modeled as 0.04μm; 'SiC-600') closely matches the spectrum of the thinnest film (see Fig. 1b). Its peak position of 11.6μm equals our result, within experimental uncertainties. The positions of the shoulders are comparable to the LO and TO positions. Their sample 'SiC-N' was compromised by ~10% impurities, comprising equal amounts of C and SiO₂. 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 α-SiC grain sizes, but yielded similar spectral profiles, with a slight shift of the peak position to 11.8μm, consistent with the increase of peak wavelength with thickness seen for the thin films (Speck et al. 1999).

In both the α- and β- cases, the feature is broader in the thin film spectra than in the KBr dispersion data. This is due to experimental effects. The thin films, being imperfect, have some thick and some thin spots, which gives rise to features with rounder peaks and broader widths. This is particularly a problem with SiC as it is an extremely hard mineral and difficult to compress evenly. To avoid problems arising in the spectra from these imperfections, the films are progressively thinned until the positions and widths of the features remain constant. For the KBr spectra, if the sample dispersion is sufficiently dilute, any larger particles do not contribute to the spectrum so that the peaks can

\(^1\)The Christiansen effect gives a minimum in the absorbance when the optical interaction changes from absorption to transmission.
be narrow and a good representation of the intrinsic spectrum for a dispersion both dilute and fine-grained. Which of these situations is more applicable to the astronomical environments depends on the nature of the dusty region. If it is composed of a heavy blanket of very fine particles then the thin film spectra would be more applicable. For a less dense region, the narrower (uncorrected) KBr dispersion spectra would be more appropriate.

It is clear that applying a correction for a shift in wavelength due to the KBr matrix (e.g., Friedemann et al. 1981; Péroux 1988) is inappropriate, because the barycentric wavelengths for both α- and β-SiC fine grain size dispersions equal those of the corresponding thin film samples and the peak shapes are in excellent agreement. For the <0.1µm thickness thin films, absorption rather than scattering effects dominate in the vicinity of the intense peak, and thus the assumptions in scattering theory (Bohren & Huffman 1983) do not pertain. Only for extremely thick samples, ~1µm, or large grain sizes do the peak parameters of the particulate absorption spectra differ from those determined for bulk samples. The differences are due to internal scattering among the particulates and sampling effects caused by the zero transmission being incorrectly defined. Similarly the derivation of the KBr-matrix correction for various silicates (Dorschner et al. 1978) is problematic. Measurements taken by Colangeli et al. (1993, 1995) indicate minimal matrix effects for various silicate samples. In fact, Dorschner et al. (1978) applied a correction to their crystalline silicate spectra that shifted the well-known 11.3µm crystalline silicate feature to 11.0µm - a shift that is never used by the astronomical community.

4. Re-fitting the Astronomical Spectra

Having established that existing applications of laboratory SiC spectra to interpret astronomical spectra (Speck et al. 1997a&b, Groenewegen 1995, Breghesi et al. 1985; Friedemann et al. 1981) are erroneous due to the unnecessary application of a KBr correction factor, we have refitted our own observed astronomical IR spectra using the χ²-minimization routine described by Speck et al. (1997a) and equipped with uncorrected laboratory spectra. The laboratory data originally had a KBr matrix correction applied to them, however the values used here are the uncorrected data from Breghesi et al. (1985) which, as discussed earlier, have peaks and shapes comparable to our new thin film data. The observed carbon star spectra cover the 7.5 to 13.5µm waveband and were obtained with the CGS3 facility mid-infrared spectrometer at the 3.8m United Kingdom Infrared Telescope (see Speck et al. 1997a for details of observations).

The results from our fitting program are presented in Table 1 and several representative fits are shown in Fig. 2. Table 1 shows that there is an obvious predominance of the β-SiC phase and in fact no evidence for the α-SiC phase at all. This is in contrast to previous attempts to fit the SiC feature using similar, and in some cases the same, raw laboratory data which had been inappropriately corrected for the KBr dispersion technique. It was previously found that the best fits were obtained with α-SiC grains, with very little evidence for the presence of any β-SiC. The second column in Table 1 shows the wavelength at which the observed SiC features peak in the spectra of carbon stars. In most cases the peaks are in the 11.2–11.5µm range, consistent with the attribution to β-
<table>
<thead>
<tr>
<th>Source</th>
<th>$\lambda_{\text{peak}}$</th>
<th>SiC type</th>
<th>$T_{\text{BB}}$(K)</th>
<th>$T_{\text{SB}}$(K)</th>
<th>$\tau_{\text{SiC}}$</th>
<th>$\tau_{\text{TB}}$*</th>
<th>$\chi^{2}_{R}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRAS 21489+5301</td>
<td>11.28</td>
<td>$\beta$-SiC</td>
<td>450</td>
<td>260</td>
<td>—</td>
<td>—</td>
<td>0.515</td>
</tr>
<tr>
<td>IRC+10216</td>
<td>11.45</td>
<td>$\beta$-SiC</td>
<td>510</td>
<td>230</td>
<td>—</td>
<td>—</td>
<td>1.260</td>
</tr>
<tr>
<td>AFGL 5076</td>
<td>11.45</td>
<td>$\beta$-SiC</td>
<td>560</td>
<td>300</td>
<td>0.137</td>
<td>—</td>
<td>0.309</td>
</tr>
<tr>
<td>AFGL 2494</td>
<td>11.29</td>
<td>$\beta$-SiC</td>
<td>520</td>
<td>380</td>
<td>0.167</td>
<td>—</td>
<td>0.306</td>
</tr>
<tr>
<td>AFGL 3000</td>
<td>11.64</td>
<td>$\beta$-SiC</td>
<td>530</td>
<td>300</td>
<td>0.262</td>
<td>—</td>
<td>1.370</td>
</tr>
<tr>
<td>AFGL 5102</td>
<td>11.50</td>
<td>$\beta$-SiC</td>
<td>650</td>
<td>360</td>
<td>0.161</td>
<td>—</td>
<td>0.345</td>
</tr>
<tr>
<td>AFGL 2155</td>
<td>11.72</td>
<td>$\beta$-SiC</td>
<td>730</td>
<td>290</td>
<td>0.235</td>
<td>—</td>
<td>0.418</td>
</tr>
<tr>
<td>IRAS 02152+2822</td>
<td>11.33</td>
<td>$\beta$-SiC</td>
<td>550</td>
<td>520</td>
<td>0.223</td>
<td>—</td>
<td>0.504</td>
</tr>
<tr>
<td>IRC+40540</td>
<td>11.33</td>
<td>$\beta$-SiC</td>
<td>860</td>
<td>310</td>
<td>0.173</td>
<td>—</td>
<td>0.508</td>
</tr>
<tr>
<td>AFGL 2368</td>
<td>11.25</td>
<td>$\beta$-SiC</td>
<td>730</td>
<td>320</td>
<td>—</td>
<td>—</td>
<td>1.772</td>
</tr>
<tr>
<td>V Hya</td>
<td>11.24</td>
<td>$\beta$-SiC</td>
<td>1130</td>
<td>390</td>
<td>0.211</td>
<td>—</td>
<td>0.761</td>
</tr>
<tr>
<td>IRC+00365</td>
<td>11.38</td>
<td>$\beta$-SiC</td>
<td>1790</td>
<td>220</td>
<td>0.114</td>
<td>—</td>
<td>2.316</td>
</tr>
<tr>
<td>CIT</td>
<td>11.35</td>
<td>$\beta$-SiC</td>
<td>960</td>
<td>360</td>
<td>0.217</td>
<td>—</td>
<td>1.294</td>
</tr>
<tr>
<td>IRC+50096</td>
<td>11.20</td>
<td>$\beta$-SiC</td>
<td>940</td>
<td>460</td>
<td>—</td>
<td>—</td>
<td>2.166</td>
</tr>
<tr>
<td>R For</td>
<td>11.12</td>
<td>$\beta$-SiC</td>
<td>910</td>
<td>800</td>
<td>—</td>
<td>—</td>
<td>1.237</td>
</tr>
<tr>
<td>R Lep</td>
<td>11.13</td>
<td>$\beta$-SiC</td>
<td>1290</td>
<td>570</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>UU Aqr</td>
<td>11.22</td>
<td>$\beta$-SiC</td>
<td>2510</td>
<td>450</td>
<td>0.165</td>
<td>—</td>
<td>1.105</td>
</tr>
<tr>
<td>V Cyg</td>
<td>11.29</td>
<td>$\beta$-SiC</td>
<td>2560</td>
<td>570</td>
<td>0.139</td>
<td>—</td>
<td>1.014</td>
</tr>
<tr>
<td>CS 776</td>
<td>11.15</td>
<td>$\beta$-SiC</td>
<td>990</td>
<td>580</td>
<td>—</td>
<td>—</td>
<td>1.879</td>
</tr>
<tr>
<td>V414 Per</td>
<td>11.24</td>
<td>$\beta$-SiC</td>
<td>1100</td>
<td>920</td>
<td>0.177</td>
<td>—</td>
<td>0.579</td>
</tr>
<tr>
<td>AFGL 3008</td>
<td>10.81</td>
<td>$\beta$-SiC</td>
<td>390</td>
<td>60</td>
<td>0.030</td>
<td>—</td>
<td>0.092</td>
</tr>
<tr>
<td>IRAS 02408+5458</td>
<td>10.87</td>
<td>$\beta$-SiC</td>
<td>390</td>
<td>100</td>
<td>0.152</td>
<td>—</td>
<td>1.686</td>
</tr>
<tr>
<td>AFGL 2477</td>
<td>10.56</td>
<td>$\beta$-SiC</td>
<td>380</td>
<td>110</td>
<td>0.073</td>
<td>0.104</td>
<td>0.419</td>
</tr>
<tr>
<td>AFGL 5625</td>
<td>10.67</td>
<td>$\beta$-SiC</td>
<td>360</td>
<td>190</td>
<td>0.097</td>
<td>0.113</td>
<td>0.306</td>
</tr>
</tbody>
</table>

$\lambda_{\text{peak}}$ is the wavelength at which the observed SiC feature peaks
1 Fits with pure emission only
2 Fits with self-absorbed net emission
3 Fits with self-absorbed net absorption
* $\tau_{\text{TB}}$ is the optical depth at 9.7$\mu$m
† also requires Trapezium interstellar silicate absorption
‡ also requires $\mu$ Cep interstellar silicate absorption
SiC. The exceptions to this range are: the stars which exhibit the absorption features, discussion of which is beyond the scope of the present paper; R For and R Lep, which peak at 11.12 and 11.13μm respectively; and AFGL 2155 and AFGL 3099 which peak at wavelengths longer than 11.5μm. Furthermore, there are other carbon stars with SiC features which peak at λ > 11.5μm (e.g. AFGL 341, Y CVn; see Speck et al. 1997a, Speck 1998). These two carbon star spectra could not be fitted using the χ²-fitting routine due to strong features in the 7.5–9.5μm region (Speck 1998). It has been suggested that these longer wavelength peaks are due to α-SiC (L Little-Marenin, pers. comm.). However, even for AFGL 2155 and AFGL 3099, with peak wavelengths of 11.72μm and 11.64μm respectively, the fitting program was unable to find fits using α-SiC while very good fits were obtained using β-SiC. Even combining laboratory data for α- and β-SiC in the χ²-fitting routine did not yield fits to these spectra. Therefore, we do not preclude the existence of α-SiC around these stars, but have found little evidence for it. More detailed modeling of the contributions to these longer wavelength features may show evidence for some α-SiC. The case for R For and R Lep is a little different. Their peak wavelengths are shorter than expected for β-SiC, and therefore cannot be explained in terms of contributions from α-SiC. Indeed, the fits using β-SiC to these spectra are very good except for a “wing” on the short wavelength side of the feature. The best explanation for this is an increased contribution from the LO mode, possibly due to slightly larger grain sizes (see Speck & Hofmeister 2000).

5. Discussion

It is debatable whether thin film or uncorrected powder dispersion data are better for comparison with astronomical spectra. On the one hand, the environment of stars should have a wide range of particulates, and thus dispersion
may be more appropriate. On the other hand, the small size at which particles become opaque limits the utility of the KBr-dispersed data. This is because the laboratory zero point does not account for the opaque parts of the dispersed powder, so effectively zero transmission is incorrectly defined, and consequently mass extinction coefficients are incorrectly calculated. The astronomical spectra do not use a reference spectrum to determine intensity ratios and hence do not have this problem. For very fine particle dispersions, these distinctions are blurred, particularly because the thin films are not perfectly uniform, yielding nearly identical spectra from the two techniques. However, the detailed comparison shows that the KBr correction is unnecessary (Speck et al. 1999) and that previous laboratory data should be used with care.

It is worth noting that previous calculations of the KBr correction factor differ substantially (e.g., ~0.8 \( \mu m \), Bohren & Huffman 1983; ~0.4 \( \mu m \), Friedemann et al. 1981, Pégourie, 1988). Furthermore those workers who believe there is a need for the matrix correction now find that the supposed shift is much less significant, at probably ~0.1 \( \mu m \) (see Mutschke et al. 2000).

Assuming a KBr-dispersion correction factor of ~0.4 \( \mu m \), the application of this correction to laboratory spectra has led to a shifting of the peaks of the two SiC grain types to 11.0 \( \mu m \) for \( \beta \)-SiC and 11.4 \( \mu m \) for \( \alpha \)-SiC. Without this correction, and by a non-KBr dispersion method the peak wavelengths are found to be at 11.8 \( \mu m \) for \( \alpha \)-SiC and 11.4 \( \mu m \) for \( \beta \)-SiC. Obviously, the change in the peak wavelengths has a profound effect on the type of SiC which best fits the spectral observations of carbon stars whose observed feature peaks at about 11.4 \( \mu m \). Our fits to the observed spectra indicate ubiquity of the \( \beta \)-SiC phase and the absence of detectable \( \alpha \)-SiC grains in the circumstellar outflows around carbon stars. Even with a correction factor of 0.1 \( \mu m \) applied to the data, these results still stand. Thus, we conclude that \( \alpha \)-SiC is not observed around carbon stars and that the majority of SiC grains formed in these regions are of the \( \beta \)-SiC form. This resolves the previous discrepancy between the results obtained from astronomical observation and meteoritic samples.

6. Implications

This work has several implications. Firstly, we have demonstrated that mineral spectra produced using the thin film method are directly applicable to astrophysical contexts without further manipulation of the data. We are currently using this method to produce more mineral spectra of use to astronomers. Second, the original work that invoked the KBr matrix correction used silicate spectra (Dorschner et al. 1978). While the KBr correction has not been universally applied, it is important to investigate whether it has lead to any other erroneous attributions of minerals to astronomical IR spectral features. Furthermore, it is crucial to understand the reasons for the wavelength shift seen by Dorschner et al. (1978) in order to understand when laboratory spectra are reliable and applicable to astronomical environments. Finally, 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 merits
attention (see Speck et al. 1997a,b for a detailed discussion of the grain size problem; Speck & Hofmeister 2000 for possible observations of larger grains).

Acknowledgments. Support for AKS was provided by the United Kingdom Particle Physics and Astrophysics Research Council and by University College London. Support for AMH was provided by Washington University. We thank Tom Bernatowicz for suggesting this collaboration. We would also like to thank Irene Little-Marenin for her very constructive comments.

References


Friedemann, C., 1969, Physica, 41, 139


