

Effects of Grain Morphology and Impurities on the Infrared Spectra of Silicon Carbide Particles

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Abstract. In this paper we demonstrate that distinguishing between the polytypes of silicon carbide by means of infrared features in small-grain spectra is impossible. Therefore, the infrared spectra of carbon stars, unfortunately, do not provide a means for drawing comparisons between the crystal structures of grains condensed in these environments and found in meteorites.

This is proven first by comparing theoretical band profiles calculated for ellipsoidal particles, which show clearly a strong dependence on the axis ratio of the ellipsoids but negligible differences for the two most common polytypes. Second, spectra measured on submicron particle samples in the laboratory do not show any obvious correlation of band position or shape to the polytype. However, we demonstrate by measurements with SiC whiskers that grain shape is able to determine the spectrum completely. A further strong systematic influence on the band profile can be exerted by plasmon-phonon coupling due to conductivity of the SiC material. The latter fact probably is responsible for the confusion in the astronomical literature about spectral properties of SiC grains. We show that, although the conductivity seems to be a common property of many SiC laboratory samples, it is, however, independent on the polytype.

1. Introduction

Thermal emission of solid silicon carbide (SiC) particles has been observed in carbon star outflows (e.g. Little-Marenin 1986, Speck et al. 1997). The identification is based on a broad infrared feature in the 10-13 μm wavelength range, which is ascribed to the fundamental phonon transition of SiC. Attempts have been made to derive the crystal type of the circumstellar SiC grains from a comparison of the observed band profiles to those measured on laboratory analogs (Speck et al. 1997, 1999). Although knowledge about the crystal types (polytypes) of cosmic SiC grains would be very worthwhile, four points must be objected to such a comparison and the conclusions drawn from it:

1. The number of laboratory samples on which the comparison relies is very small and the samples have not been studied sufficiently. In Sect. 3 we

will show laboratory spectra of another set of SiC samples, which fully contradict the conclusions drawn by Speck et al. (1999).

2. The phonon frequencies of the several SiC polytypes are known to be very similar (Mutschke et al. 1999). As we will show in Sect. 2 by calculation of SiC particle spectra, therefore from the theoretical point of view very similar band profiles are expected for the different polytypes.
3. As we have reviewed in another paper in this volume (Henning & Mutschke), absorption and emission by small grains near such strong transitions as the single-phonon band in SiC crystals is entirely determined by surface modes. Therefore, the grain morphology (shape, size and agglomeration) has a huge influence on the spectrum. This will be demonstrated by the calculations in Sect. 2 as well as by measurements (Sect. 4).
4. The β -SiC laboratory spectra used in the comparisons by Speck et al. (1997, 1999) are probably influenced by impurity-induced conductivity, which via plasmon-phonon coupling determines the appearance of the phonon band profile. Unfortunately, such impurity effects are not restricted to one or the other polytype. In Sect. 5 we will discuss this effect by means of a number of new laboratory spectra.

2. Theoretical predictions for SiC particle spectra

SiC is one of the textbook examples for which the dielectric function in the phonon band can be described very exactly by a single Lorentzian oscillator. The oscillator parameters differ slightly from one polytype to another and for the anisotropic polytypes also for the polarizations in the directions of the different principal axes of the crystals. Mutschke et al. (1999) derived average values of the oscillator parameters for the most important polytypes based on an extensive literature study.

We have used these parameters to calculate absorption spectra for particles small compared to the wavelength (Rayleigh limit, see Henning & Mutschke, this volume) for ellipsoidally shaped grains composed of the two most common polytypes. By β -SiC we denote the cubic 3C polytype, by α -SiC the hexagonal 6H type (see Mutschke et al. 1999). The calculated spectra clearly show (Fig. 1) that, first there is no significant difference caused by the crystal type and second the spectrum appears very different depending on the grain shape. In the case of uniform ellipsoidal (or spherical) shapes the extinction is dominated by resonances appearing between the transverse (about $12.6 \mu\text{m}$) and longitudinal (about $10.3 \mu\text{m}$) optical phonon frequencies. These resonances are related to the principal axes of the ellipsoids and are called “surface modes” (compare Bohren & Huffman 1983, chap.12). In the limiting case of infinite elongation of a particle axis (e.g. for extreme needle- or plate-like particles) an additional very strong resonance occurs at the transverse optical frequency corresponding to the volume mode of the material (see Fig. 2).

Infinite plate-like particles have to be equivalent to thin films, which indeed also produce the pure volume mode ($12.6 \mu\text{m}$) in transmission measurements

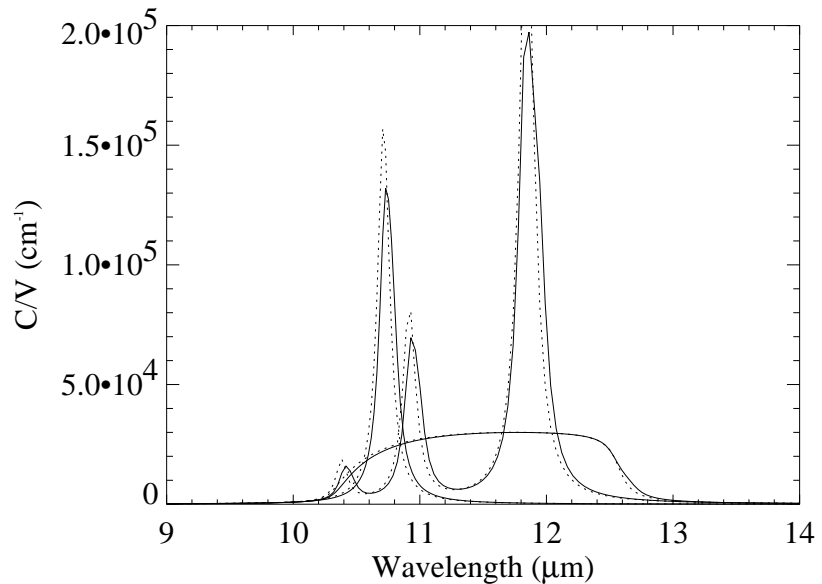


Figure 1. Calculated extinction cross sections of spherical and ellipsoidal α - (solid lines) and β -SiC (dotted lines) submicron particles. The single band with maximum at $10.7 \mu\text{m}$ is produced by spherical grains, the triple structure results from ellipsoidal shapes with an axis-ratio of 1:3:9, and the broad band has been calculated for a continuous distribution of ellipsoidal grains (CDE, after Bohren & Huffman 1983)

normal to the interfaces and a surface mode at the position of the longitudinal optical frequency ($10.3 \mu\text{m}$) for a measurement at grazing incidence and polarization normal to the interfaces. The spectra of “thin films” produced by pressing SiC powder in a diamond anvil cell by Speck et al. (1999) do not show this typical thin-film characteristics but a spectrum quite similar to the CDE (continuous distribution of ellipsoids, Bohren & Huffman 1983) calculation and our measured particle spectra (see next sections). This indicates that forming a continuous thin film in the anvil cell fails in the case of the SiC powders, which together with a basic misunderstanding lead to questions about the influence of the particle-surrounding medium. The comparability of the anvil cell method with single-crystal transmission spectra, which is undoubted if real thin films are formed and only volume modes are measured, should not be intermixed with small-particle extinction measurements where surface modes dominate the spectrum.

Unfortunately, theory at the moment is not able to calculate the extinction for other more realistic grain shapes or distributions of shapes in strong absorption bands. It is quite clear that such a realistic sample will show a more continuous broad band covering more or less the whole wavelength range between the transverse and longitudinal optical phonon frequencies. A possibility for approximating such spectra is the assumption of a distribution of ellipsoidal shapes. A very extreme one with equal probability of all shapes is shown in

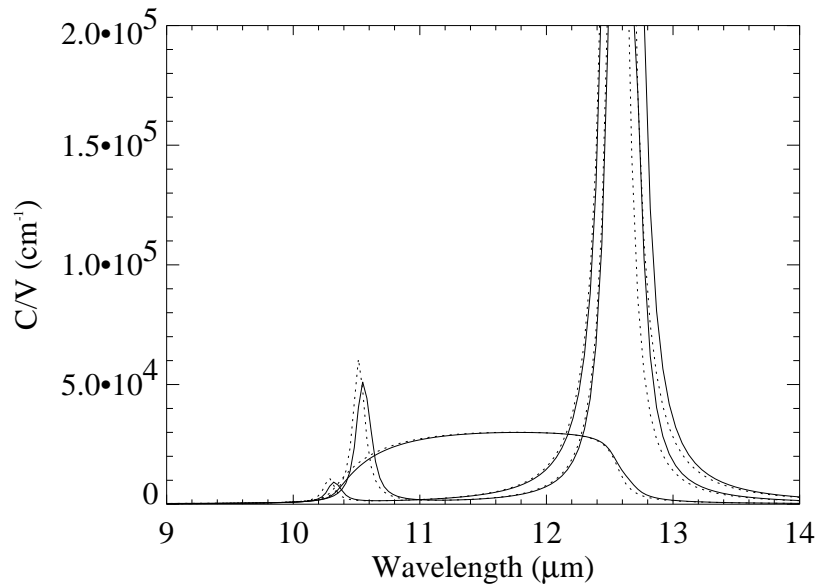


Figure 2. Same as Fig.1 for needle- (resonance at $10.5 \mu\text{m}$) and plate-like particles (resonance at $10.3 \mu\text{m}$). The CDE (broad band) is again shown for comparison. α -SiC .. solid lines, β -SiC .. dotted lines.

Figs. 1 and 2. Although any measured spectrum could be, in principle, translated to such a distribution of ellipsoidal shapes (Papoular et al. 1998), this certainly is not an exact approach especially for irregular, sharp-edged grains and should be handled with care.

3. Measurements on polytypes

As we have seen in the preceding section, from the theoretical point of view, spectra of SiC particles of different polytype should not differ very much - provided that the morphologies are the same. Nevertheless, spectra of the cubic (β -) and hexagonal/rhombohedral (α -) modifications published in the astronomical literature so far, showed band maxima at different positions (11.4 and $11.8 \mu\text{m}$, respectively). These band positions have been taken for characteristics of the polytypes and have been used for deriving the polytype of circumstellar grains.

In order to show that this conclusion is fallacious, we give in Fig. 3 four other spectra of α - and β -SiC laboratory samples. Clearly, all of these spectra show band maxima longward of $11.8 \mu\text{m}$ independent of the polytype. Interestingly, the β -SiC spectra peak at the longest wavelengths, around $12.2 \mu\text{m}$. One of the spectra (dashed line) reveals a big shoulder towards smaller wavelengths, which could indicate a kind of affinity to the β -SiC spectra known from the literature. However, this sample consists of pure α -SiC, which was proved by X-ray scattering.

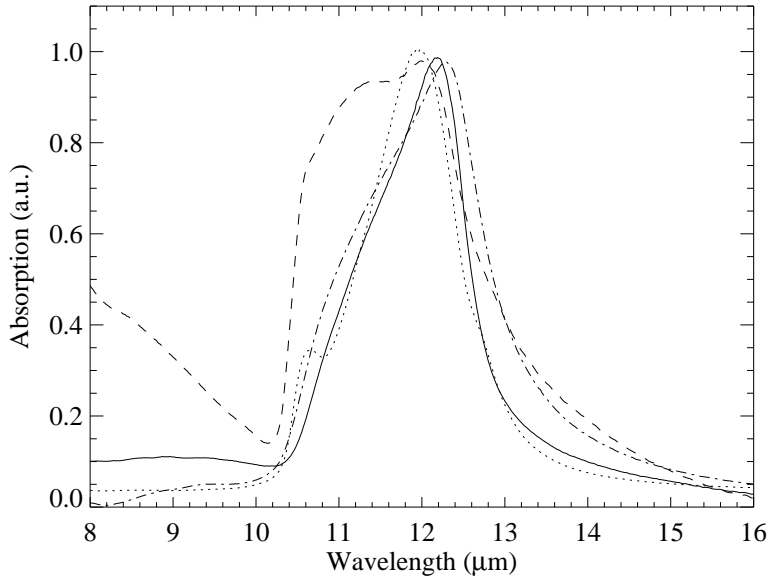


Figure 3. Measured phonon band profiles for two α - (dotted and dashed lines) and two β -SiC (solid and dash-dotted lines) samples.

All of these samples consist of submicron grains, especially the β -SiC samples have typical grain sizes of about 50 nm, well below the Rayleigh limit. We will not deal further with size effects here, since they have been treated in detail by Andersen et al. (1999), Mutschke et al. (1999) and elsewhere in this volume (Henning & Mutschke).

The SiC samples have been measured dispersed in KBr. This is of course not an ideal preparational method since there remains a considerable amount of agglomeration of the grains, which together with the grain shape should determine the actual band profile. However, we are not aware of a better one for a given powder sample. We have to point out that the KBr matrix of course induces an effect on the spectrum in the way discussed by Henning and Mutschke (same volume). For SiC there is a possibility to correct for this in an approximate way by the method proposed by Papoular et al. (1998).

4. Measurements on shape effects

As we have seen in the previous section, there is no clear dependence of the SiC phonon band profile on the polytype, as expected. Nevertheless, the spectra show unsystematic differences in peak position and band shape. Following Sect. 2, a major reason for this behaviour could be different grain shapes.

The problem with discussing grain shape effects arise both from theoretical and experimental side. As pointed out already, there is no theory which clearly can predict what band profiles have to be expected from a sample of the usually irregular, sharp-edged SiC grains. Further, the problem is considerably complicated by the fact that in the measurement the particles are not isolated from

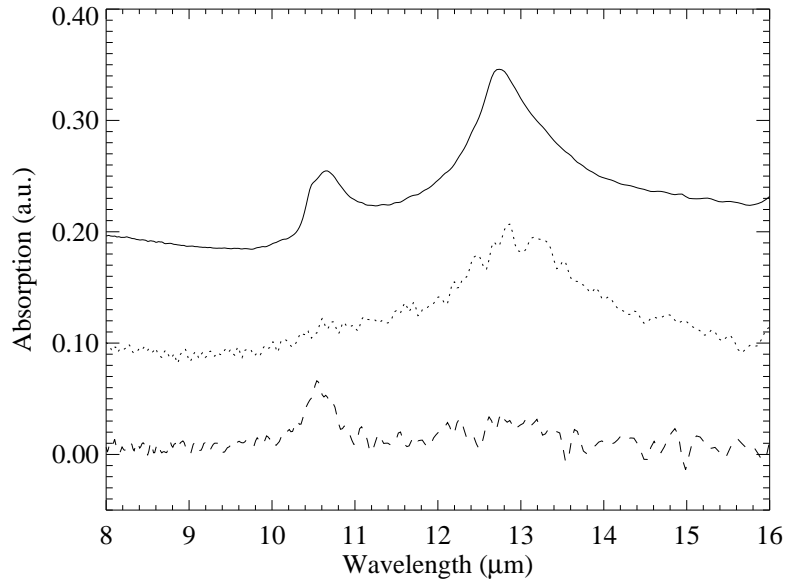


Figure 4. Infrared microscope spectra of β -SiC whiskers prepared on a silicon window. Solid-line: unpolarized light, unaligned whiskers. Dotted line: Radiation polarized parallel to whisker axis, dashed line: perpendicular to whisker axis

each other but form aggregates around the grains of the embedding medium (usually KBr). So far there is no method to deagglomerate submicron powders for a IR measurement. Therefore, we have to expect that the probably very elongated aggregates determine the band profile to a large extent. This could be the reason why we find usually a band maximum quite close to the volume mode. There is no conclusive explanation so far for the small shoulder seen in many commercial SiC powders at about $10.6 \mu\text{m}$ (see the dotted line in Fig. 3, the big bump in the dashed line will be discussed in the next section).

Fortunately, there is a possibility to demonstrate by a measurement at least that shape effects indeed are real. This possibility is provided by commercial β -SiC samples which consist of whiskers with a diameter of $1\text{-}2 \mu\text{m}$ and a length of several ten micrometers. According to Sect. 2, such grains should produce two resonances. One at about $10.5 \mu\text{m}$ should be caused by electric fields normal to the whisker axis, and field components parallel to the whisker axis should produce a resonance close to the volume mode. Fig. 4 shows such measurements carried out with an infrared microscope. The unpolarized spectrum (solid line) indeed reveals both features expected. The IR microscope additionally allowed us to find some whiskers which by chance were aligned in the directions of their axes. Putting a polarizer directly in front of the sample we have been able to measure both resonances separately which proves their origin from the special grain shape.

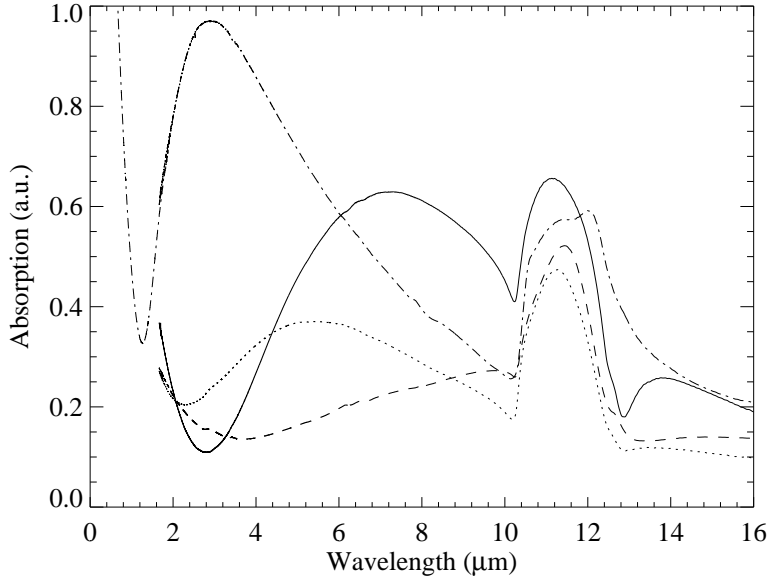


Figure 5. Spectra of different SiC samples showing very broad surface plasmon absorption shortward of the phonon feature. Coupling of plasmon and phonon leads to a modification of the phonon band profile with shift of the band maximum towards shorter wavelengths.

5. Influence of impurities

The calculations and measurements shown in the previous sections should have proven that α - and β -SiC can not be distinguished in the way adopted by Speck et al. (1999). It remains to clarify what is the reason for some β -SiC spectra in the literature to appear with maxima at about 11-11.5 μm in contrast to those we have shown so far.

For this sake Fig. 5 displays four spectra measured on other α - and β -SiC samples. Three of them have their phonon band maxima in the mentioned wavelength range, the fourth (shown already in Fig. 3) a big shoulder at these short wavelengths. Even more striking, all spectra reveal a broad absorption shortward of the phonon band reaching down to the near infrared. The maximum of the very broad absorption varies between 3 and 10 μm . These features point towards highly damped surface plasmon absorption caused by free charge carriers. The resonance frequency of the absorption band depends on the plasma frequency which is proportional to the square root of the carrier density. Similar absorption spectra are known from doped CdO and GaAs small particles. It is also known that the plasmon generally couples to the longitudinal phonon and, therefore, changes the appearance of the former band.

To our experience, such a plasmon absorption is quite common to many commercial and laboratory SiC products. Unfortunately, the nature of the charge carriers is still only partly understood. Mutschke et al. (1999) showed that plasmon absorption can be introduced into SiC particle spectra by doping

the SiC grains with nitrogen. These investigations will be continued because the induced strong mid-infrared absorption should be important for the thermal behaviour of the circumstellar SiC particles. If such doped particles would be present in circumstellar environment they would probably be quite warm, comparable to carbon grains and much warmer than undoped SiC grains. This would also give them an advantage for being observed.

6. Conclusion

In our discussion of the optical properties of different polytypes of SiC we have demonstrated both theoretical and by experimental studies that it is *not* possible to distinguish by IR spectroscopy between α - and β -SiC dust grains. Observed profiles of SiC phonon bands contain information mainly about the morphology (size and shape) of the particles and possibly about the conductivity of the material. The evaluation of these grain properties, however, encounters the very general unsolved problem of calculating band profiles for complicated morphologies.

Therefore, progress in interpretation of observed band profiles in future will mainly rely on laboratory measurements. The first problem which has to be solved in this respect is the preparation of particle samples free from agglomeration and with as little matrix-influence as possible. The second will be the preparation of realistic circumstellar-dust analogues by condensation experiments. Both things have been started already for carbonaceous grains and are our program for the next years also with SiC.

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