

# Is the 21- $\mu\text{m}$ feature observed in some post-AGB stars caused by the interaction between Ti atoms and fullerenes?

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## ABSTRACT

Recent measurements of fullerenes and Ti atoms recorded in our laboratory have demonstrated the presence of an infrared feature near 21  $\mu\text{m}$ . The feature observed has nearly the same shape and position as is observed for one of the most enigmatic features in post-asymptotic giant branch (AGB) stars. In our experimental system large cage carbon particles, such as large fullerenes, were produced from CO gas by the Boudouard reaction. Large-cage carbon particles intermixed with Ti atoms were produced by the evaporation of a Ti metal wrapped carbon electrode in CO gas. The infrared spectra of large fullerenes interacting with Ti atoms show a characteristic feature at 20.3  $\mu\text{m}$  that closely corresponds to the 20.1  $\mu\text{m}$  feature observed in post-AGB stars. Both the laboratory and stellar spectra also show a small but significant peak at 19.0  $\mu\text{m}$ , which is attributed to fullerenes. Here, we propose that the interaction between fullerenes and Ti atoms may be a plausible explanation for the 21- $\mu\text{m}$  feature seen in some post-AGB stars.

*Subject headings:* infrared: stars — methods: laboratory — stars: AGB and post-AGB — stars: carbon — stars: mass loss

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## 1. Introduction

A 21- $\mu\text{m}$ -emission feature has been observed in the shells of carbon-rich post-asymptotic giant branch (AGB) stars (Kwok, Volk & Hrivnak 1989; Volk, Kwok & Hrivnak 1999). As a general rule, the infrared emissions in the circumstellar environments of carbon-rich stars are dominated by the emissions of carbonaceous dust. The carrier of the 21- $\mu\text{m}$  feature remains unidentified, although many candidate materials have been proposed, including nanodiamond (Hill et al. 1997),  $\text{SiS}_2$  (Begemann et al. 1996; Kraus, Nuth & Nelson 1997), a derivative of  $\text{SiC}$  (Speck & Hofmeister 2004; Kimura, Sato & Kaito 2005) and nano-sized  $\text{TiC}$  (von Helden et al. 2000).

In particular,  $\text{TiC}$  grains were extensively discussed after the report by von Helden (2000). Gas-phase  $\text{TiC}$  clusters less than 1 nm in diameter have been suggested as the source of the 21- $\mu\text{m}$  dust feature. The spectrum of  $\text{TiC}$  clusters recorded in the laboratory provides a good fit with the observational data with respect to band position, width and asymmetric profile. On the other hand, the  $\text{TiC}$  spectrum, recorded from infrared reflectance measurements of bulk  $\text{TiC}$ , produced by melting commercial  $\text{TiC}$  powder in an arc furnace, suggests that  $\text{TiC}$  particles characterized by the dielectric function of the bulk material are probably not responsible for the 21- $\mu\text{m}$  dust feature (Henning & Mutschke 2001). Moreover, a recent report of the infrared absorption spectra of synthetic  $\text{TiC}$  grains  $\sim 50$  nm in diameter, which is similar in size to the presolar grains extracted from meteorites (Bernatowicz et al. 1991), and of the spectra of 2-3 nm diameter  $\text{TiC}$  grains, which is close to the size of the  $\text{TiC}$  particles of van Helden, did not show a 21- $\mu\text{m}$  feature (Kimura & Kaito 2003; Kimura et al. 2004). By comparing the flux ratio of the observed 11- and 21- $\mu\text{m}$  emissions from post-AGB stars, it was argued that the origin of 21- $\mu\text{m}$  feature was not due to  $\text{TiC}$  grains (Chigai et al. 2003). Subsequently it was also reported that a physical argument based on the Kramers-Kronig dispersion relations implies that the nano- $\text{TiC}$  model for the 21- $\mu\text{m}$  emissions from post-AGB stars requires more Ti than is observed in the stellar photosphere (Li 2003). Therefore, at the present time, other materials, such as  $\text{SiC}$  have become attractive candidates once again.

Here we show that a significant 21- $\mu\text{m}$  feature arises from large cage carbon particles coordinated with Ti atoms. In particular, this feature seems to be correlated with large fullerenes that were produced during synthesis of  $\text{TiC}$ -core, graphitic-mantle spherules. This study is the first report of a 21- $\mu\text{m}$  spectral feature caused by Ti-atoms with solid C since the discovery by van Helden (2000).

## 2. Experimental procedure

TiC smoke particles and large-cage fullerenes were prepared in our laboratory by a modified gas evaporation method using the Graphitic Smokes Apparatus. Smoke grains were produced at a total pressure of 200 Torr in an atmosphere of CO gas. A carbon electrode, with a thinned section at the middle, was prepared and Ti wire (Alfa Aesar, A Johnson Matthey Company, 0.5 mm $\phi$ , 99.98%) was wound around the thinned section at the carbon electrode, as shown in Fig. 1(a). Upon resistively heating the carbon electrode, the rising vapor and subsequent smoke from the evaporation source is visible. The vapor subsequently cools and condenses to form smoke particles in the gas. This process roughly corresponds to the formation of circumstellar dust particles in a gas outflow from an evolved star. We noticed during the experiment that the Ti wire did not melt in a CO atmosphere, though the wire did melt in inert gas. Therefore, for these experiments TiC grains were produced via two different experimental procedures, as shown in Fig. 1.

## 3. Results and discussion

Figures 2(a) and (b) show typical TEM images of carbon smoke particles produced under 200 Torr of CO gas, (a) using method A and (b) using method B, respectively. The electron diffraction pattern shows the formation of TiC grains. In addition to the carbonaceous grains indicated by arrows, crystalline TiC grains less than  $\sim 15$  nm across are visible as black contrast in Fig. 2(a). Most TiC grains were embedded within carbonaceous grains. The total number density of TiC grains in Fig. 2(a) is much smaller than the total number density of TiC grains seen in Fig. 2(b).

Recently, we found that single-shell, large-cage-structure, carbon particles are produced by the Boudouard reaction, which is the disproportionation of CO molecules into solid carbon and CO<sub>2</sub> gas. A typical high-resolution TEM (HRTEM) image of the large cages produced in CO gas is shown in Fig. 3. In the case of the method A, a small amount of Ti metal and TiC, together with a large quantity of carbon is evaporated from the thinned carbon electrode and Ti-atoms may be sequestered inside of the large-cage carbon particles. Accordingly, TiC grains do not grow as large as the particles produced by Method B. On the other hand, in the case of the method B, since the Ti wire was melted and wrapped around the thinned section of the carbon electrode, the Ti and carbon could have evaporated and formed TiC at the interface. Since the Ti metal coated almost the entire heated carbon surface area, the rate of carbon evaporation using method B decreased. Therefore, TiC grains grew to 20-40 nm using method B, and the relative quantity of carbonaceous cages was greatly decreased.

Mid-infrared spectra (a) and (b) in Fig. 4 were obtained from the specimens shown in Figs. 2(a) and (b), respectively. Both spectra show a characteristic absorption feature that peaks at  $20.3\ \mu\text{m}$ . In particular, the intensity of spectrum (a) is significantly stronger. Although the total mass of TiC grains produced by method A is very small compared with method B, as seen in Fig. 2, the intensity of the  $20.3\ \mu\text{m}$  feature in spectrum (a) is stronger than that in spectrum (b). Namely, the intensity of the  $20.3\text{-}\mu\text{m}$  feature does not appear to depend on the mass of the TiC grains. The infrared spectrum of large carbon cages produced in CO gas without Ti wire does not show the  $20.3\text{-}\mu\text{m}$  feature, as demonstrated by spectrum (c). Similarly, the infrared spectrum of commercial TiC powder also does not show the  $20.3\text{-}\mu\text{m}$  feature, as revealed in spectrum (d). Therefore, we conclude that the  $20.3\text{-}\mu\text{m}$  feature is produced by the interaction between Ti atoms and large, fullerene-like cages. In the case of method B, since Ti atoms are mainly converted to TiC, the amount of distributed Ti atoms in the large-cage carbon particles decreases. Accordingly, the  $20.3\text{-}\mu\text{m}$  spectral feature in the samples produced by method B is weaker. Spectrum (a) also shows a small but significant feature at  $19.0\text{-}\mu\text{m}$ , which corresponds to the strongest absorption feature of buckminsterfullerene,  $\text{C}_{60}$ , in this spectral range (Krätschmer et al. 1990). Since the  $19\text{-}\mu\text{m}$  feature cannot be seen in spectrum (c) of large cages alone, it can be concluded that the formation of  $\text{C}_{60}$  or other fullerenes can be promoted by the catalytic effect of Ti metal. The mean mass absorption coefficient of the sample produced by method A is approximately  $700\ \text{cm}^2/\text{g}$ . It was suggested as a negative argument for TiC that a Ti to Si abundance ratio that is 5 times larger than the solar abundance ratio is required for realizing the observed flux ratio of the  $21\text{-}\mu\text{m}$  feature caused by TiC and a simultaneously observed  $11\text{-}\mu\text{m}$  feature caused by SiC (Chigai et al. 2003). However, the absorption intensity of our sample is 10 times larger than the  $70\ \text{cm}^2/\text{g}$  of the TiC clusters discussed by von Helden. Therefore, the natural abundance of Ti is sufficient to explain the intensity of the observed  $21\text{-}\mu\text{m}$  feature from post-AGB stars.

Five possible coordination sites for Ti atoms can be considered with a fullerene as the origin of the  $21\text{-}\mu\text{m}$  feature. Those are at an indeterminate spot either inside the cage or outside the cage, a Ti atom coordinated with the electrons in an aromatic ring of the fullerene, a Ti atom bonded directly to a carbon atom in the fullerene, and by the substitution of a Ti atom for a carbon atom within the fullerene itself. Ti endohedral metallofullerenes such as  $\text{Ti}_2@\text{C}_{80}$  and  $\text{Ti}@\text{C}_{90}$  have been produced using DC arc discharge of Ti/C composite rods in He gas (Cao 2001). Since our specimens are also produced by the simultaneous evaporation of carbon and Ti and fullerenes are formed, similar Ti endohedral metallofullerenes should be found in the specimens. If Ti atoms are present outside the fullerene, Ti would easily react with oxygen. After the discovery of fullerenes, although a number of studies have been performed to date (Kroto et al. 1985), the substitution of one metallic atom within a

fullerene has not been reported. Since the 21- $\mu\text{m}$  feature is not observed in most planetary nebulae, the feature must be destroyed or obliterated at an evolutionally stage between the protoplanetary nebula and planetary nebula stages. Accordingly, the feature does not require high stability. Therefore, we suggest that the Ti atoms responsible for the 21- $\mu\text{m}$  feature are Ti atoms coordinated with the aromatic electron cloud of an individual ring of the fullerenes. The TiC clusters of von Helden, which were reported to match the original shape and position of the astrophysically observed 21- $\mu\text{m}$  feature, consisted of up to 125 atoms (von Helden et al. 2000). Since their intensity at 21  $\mu\text{m}$  is only one-tenth the strength of our samples, the 21- $\mu\text{m}$  feature observed by von Helden may have been produced by fullerene-like materials in their by-product. Since the 21- $\mu\text{m}$  feature has never been observed in the AGB phase, the feature should be produced in the evolutionary stage of a post-AGB star. The most plausible site for this to occur is in the superwind phase terminating life on the AGB (Renzini 1981). The superwind phase is a high mass-loss phenomenon in the evolved stellar envelope around the AGB star. The Boudouard reaction can occur at temperatures higher than 400°C, although the maximum temperature would depend on the specific catalyst and total pressure (Trimm 1977). Since the Boudouard reaction is accelerated by the catalytic action of metal particles, we predict that the intensity of the 21- $\mu\text{m}$  feature will be stronger in an object that has a C/O elemental abundance ratio larger than, but close to, unity. Such an object would contain a wealth of metallic species in its atmosphere.

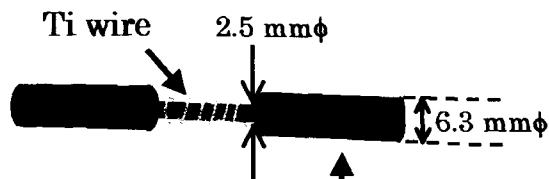
Spectrum (e) shows an emission spectrum from the post-AGB star SAO 96709 (HD 56126), which was observed using the Short Wavelength Spectrometer (SWS) of the Infrared Space Observatory (ISO) (von Helden et al. 2000). The position and width of the 21- $\mu\text{m}$  feature in the infrared spectrum of our large fullerenes with Ti-atoms are a good match to the spectrum of this post-AGB star. In particular, the small fullerene peak at 19.0  $\mu\text{m}$  in spectrum (a) is perfectly coincident with the peak at 19  $\mu\text{m}$  observed in the post-AGB star. Therefore, we believe that the origin of the 21- $\mu\text{m}$  feature is a vibrational interaction between Ti atoms and fullerene cages.

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(a) Method A



(b) Method B

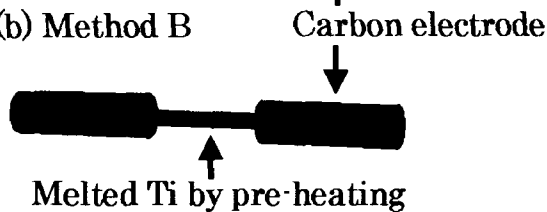


Fig. 1.— Schematic representation of our production methods for TiC grains. (a): Method A, a carbon electrode with a Ti wire was heated in a CO gas atmosphere. In this method, the evaporation of carbon most likely dominated that of TiC. (b): Method B, a Ti wire was first wrapped around the thinned section of carbon electrode, and then melted by pre-heating the carbon electrode in He gas. After the Ti wire was melted onto the carbon electrode, the apparatus was evacuated and filled with CO gas. As a result, the evaporation of carbon was suppressed and the evaporation of Ti or TiC was dominant. A thirty-second run using either method produced about 100 mg of black smoke. Fourteen samples of titanium carbide smoke particles were produced in this set of experiments and using varying ratios of He and CO in the ambient gas mixture.

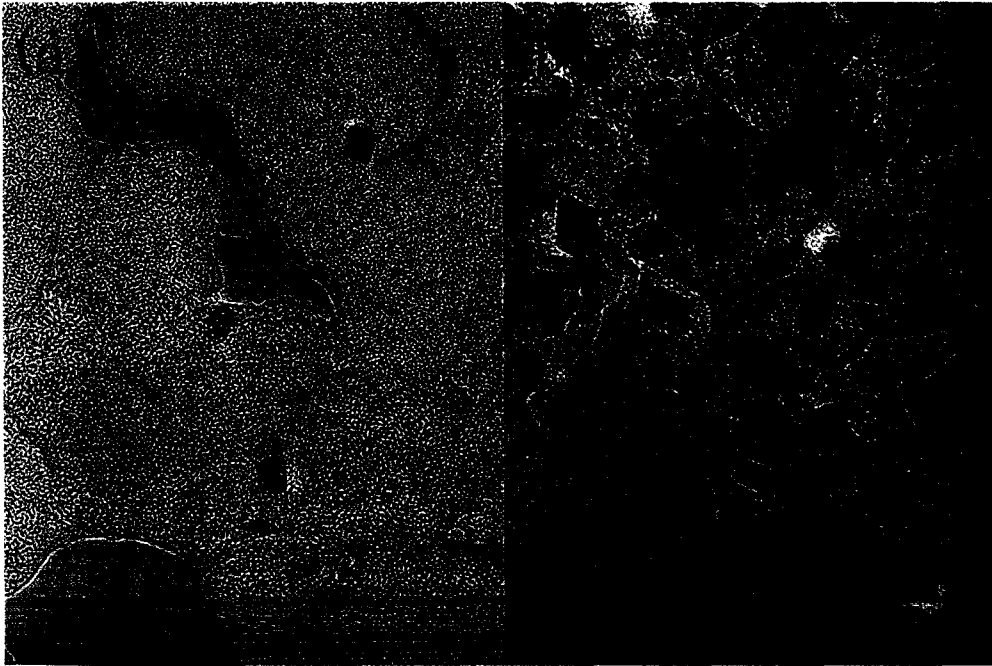


Fig. 2.— Typical TEM images of TiC grains produced by Methods A and B, respectively. The collected smoke samples were mounted on holey amorphous carbon thin films supported by standard 200-mesh Cu TEM grids. TEM observations were carried out using a JEOL 2010 TEM operated at an accelerating voltage of 200 keV at the University of New Mexico, a TOPCON 002B TEM operated at an accelerating voltage of 200 keV and a JEOL 4000EX TEM operated an accelerating voltage of 400 keV at The John M. Cowley Center for High Resolution Microscopy at Arizona State University.





Fig. 3.— A HRTEM image of carbon particles produced in 200 Torr of CO gas. Large cages such as short nanotubes or large fullerenes are visible. The layered structure, which corresponds to the (002) planes of the graphite crystal, was not seen during HRTEM observations of these samples. In addition, the specimen was easily sublimated during vacuum heating, at temperatures similar to those required for the sublimation of fullerenes.

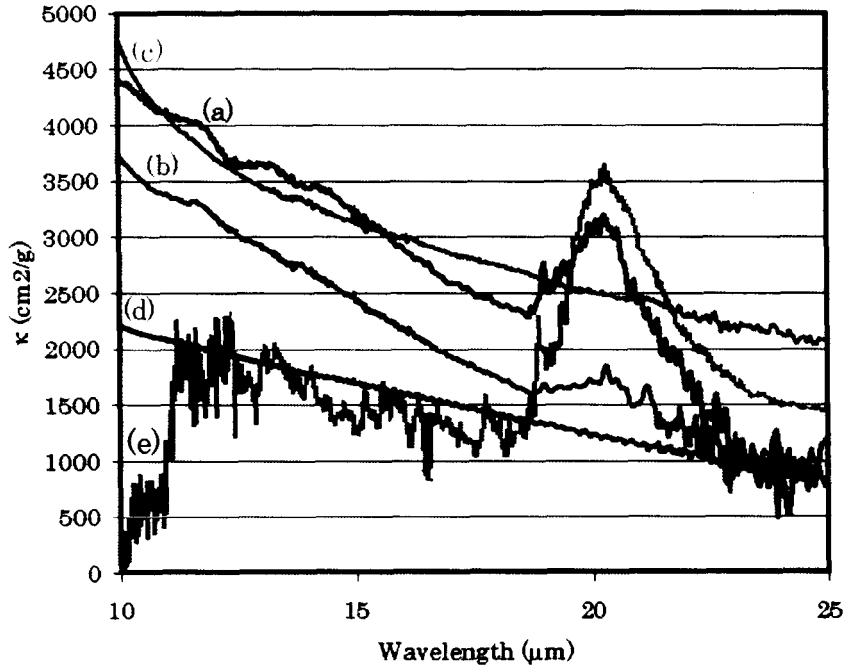


Fig. 4.— Mid-infrared spectra from 10 to 25  $\mu\text{m}$  of laboratory particles embedded in KBr pellets, were measured with a Fourier-transform infrared spectrometer (Mattson Polaris FT-IR spectrometer). The infrared system utilized a KBr beam splitter and deuterated triglyceride sulfate detector. The energy resolution used for this work was  $0.5 \text{ cm}^{-1}$ . (a): corresponding to grains produced by method A, (b): corresponding to grains produced by method B, (c): corresponding to grains produced without Ti wire, (d): corresponding to commercial TiC powder and (e) emission spectrum from the carbon-rich post-AGB star SAO 96709, which was taken from von Helden (2000). The vertical axis for spectrum (e) is flux density with arbitrary unit. The mass absorption coefficient  $\kappa$  ( $\text{cm}^2/\text{g}$ ) at  $20.3 \mu\text{m}$  of samples produced by method A is approximately  $1400 \text{ cm}^2/\text{g}$  and that made by method B is approximately  $590 \text{ cm}^2/\text{g}$ .