Laboratory production of magnesium sulfide grains and their characteristic infrared spectra due to shape

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Received 24 January 2005 / Accepted 13 May 2005

ABSTRACT

Nanosized MgS grains, which have been considered the origin of the 30 μm emission feature of carbon-rich evolved objects, were produced from the gas phase using an advanced gas evaporation method. The far-infrared spectrum of cubic MgS grains showed a characteristic absorption peak at 311 cm^{-1} (32.1 μm) with three shoulders at 460, 400 and 262 cm^{-1} (21.7, 25.0 and 38.2 μm). On the other hand, when the grains were roundish or network-like, the absorption peak at 250 cm^{-1} became predominant. The cubic MgS grains were produced by direct nucleation from the gas phase. In the case of production via a gas-solid reaction, the MgS grains were network-like. Therefore, the formation environments of MgS grains around carbon-rich evolved objects may be predicted from the intensity of 310 and 250 cm^{-1} bands. We suggest that the origins of the absorption band at 310 and 250 cm^{-1} are (100), (110) and/or (111) surfaces of MgS grains, respectively.

Key words. methods: laboratory – stars: AGB and post-AGB – infrared: ISM – infrared: stars

1. Introduction

Infrared observations of carbon stars and some planetary nebulae (e.g., Forrest et al. 1981) have revealed a strong emission feature beginning from 24 μm and extending beyond 30 μm . Condensation calculations for carbon-rich systems (Lattimer et al. 1978) predicted the formation of iron carbide and various metal sulfides, such as MgS and FeS, as the gas cools. Later, it was simultaneously reported that the infrared spectra of metallic sulfides were measured in the laboratory for commercial materials (Nuth et al. 1985) and the first identification of the 30 μm band with MgS was based on the laboratory measurements by Nuth (Goebel & Moseley 1985). Recently, contribution of oxygen atoms in the form of hydroxyl groups (OH) in carbonaceous materials has been reported as a candidate source of the 30 μm feature (Papoular 2000). Then, in addition to the 30 μm feature, the oxygen atoms also contribute to 20 and 26 μm features, which are simultaneously seen at stellar evolutionary stages between the end of the asymptotic giant branch and the planetary nebulae.

Important factors in the determination of spectral features are the size, shape and structure of grains. In particular, it is known that the absorption cross section of MgS

and MgO around 30 μm is very sensitive to grain shape. Begemann et al. (1994) have confirmed the identification of the 30 μm band based on new optical constants of $\text{Mg}_x\text{Fe}_{(1-x)}\text{S}$. The optical constants have given reasonable fits for several sources (Jiang et al. 1999; Szczerba 1999). Absorption cross sections for various grain shapes and shape distributions in the Rayleigh limit were calculated in more detail using the refractive index of $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{S}$ by Begemann et al. (1994) (Hony et al. 2002). When the shape was altered from spherical to ellipsoidal, the feature broadens and the peak position shifts to longer wavelengths from ~ 28 to ~ 39 μm . Similarly, peak shifts based on temperature effects were also calculated. However, since experimental studies in laboratory are lacking, the correlation between the morphology of MgS grains and their infrared spectra has yet to be demonstrated. The shape alteration of grains with the same structure is very difficult to determine in a laboratory approach. A shift of an absorption peak of cubic and spherical MgO grains has been reported, which was coincident with the theoretical calculation by Bohren & Huffman (1983) (Kimura et al. 1997). We have systematically studied the correlation between the infrared spectra, size and structure of TiC grains using a transmission electron microscope (TEM) in the nanoregion (Kimura & Kaito 2003; Kimura et al. 2004). The spectrum of TiC nanoparticles is influenced by slight structural changes and the presence of defects in the

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Fig. 1. Schematic representations of production methods of MgS grains: A, typical gas evaporation method; B, two boats method; C, flash evaporation method.

nanoregion. In the present paper, we will investigate spectral changes for MgS grains condensed from the gas phase. We demonstrate that these infrared spectral features showed a significant dependence on the shape and/or surface of grains.

2. Experimental methods

In the present experiment, three gas evaporation methods were attempted, as shown in Fig. 1. Method A is a typical gas evaporation method (Kaito 1978), and Methods B and C are advanced gas evaporation methods called the two boats method (Kaito et al. 1989) and the flash evaporation method (Tanigaki et al. 2002), respectively. The details will be described in Sect. 3. The evaporation chamber was a glass cylinder 17 cm in diameter and 30 cm in height, covered with a stainless-steel plate on top and connected to a high-vacuum exhaust through a valve at the bottom. After MgS or Mg and S commercial powders were placed on the v-shaped tungsten boats, as indicated in Fig. 1, the chamber was evacuated at 10^{-3} Pa. Ar gas was then introduced at 10 kPa. The samples were evaporated by heating the boats. During heating, smoke rising from the evaporation source can be observed. The vapor subsequently cools and condenses in the gas atmosphere, and solid grains are obtained directly from the gas cloud. The motion of grains follows convection currents produced by heating, and looks like that of smoke. These smoke grains were collected on a glass funnel 10 cm above the evaporation source.

These collected specimens were mounted on an amorphous carbon film supported by a standard TEM grid. The specimens were observed using a Hitachi H-7100R TEM equipped with an energy-dispersion X-ray (EDX) analysis system (Horiba Xerophy), and also using a Hitachi H-9000NAR high-resolution TEM (HRTEM). The far-infrared spectra, ranging from 650 to 50 cm^{-1} (15.4 – $200\text{ }\mu\text{m}$), of samples embedded in polyethylene pellets at a concentration of less than 1% were measured with a Nicolet Nexus 670 FT-IR spectrometer. The wavelength resolution was 0.5 cm^{-1} . This mixture was then heated to $140\text{ }^{\circ}\text{C}$ in air to melt polyethylene. To confirm the alteration of samples due to heating in air, the infrared spectra of the same specimens sandwiched between polyethylene sheets were also observed. As a result, the influences of heating in air on the spectral feature were found to be negligible throughout the present experiment.

3. Procedures and products of each method

In the case of method A, a typical gas evaporation method, MgS commercial powder, which was placed onto the v-shaped tungsten boat, was evaporated by heating the boat in Ar gas, as shown in Fig. 1A. As a result of a TEM analysis of collected grains, MgS grains were produced in small amounts, although sulfur atoms were sufficiently obtained as shown by the EDX spectrum. Since the temperature of the boat was gradually increased during the heating, MgS commercial powder was decomposed before its evaporation. As a result, Mg and S are evaporated individually. Therefore, MgS grains were not the main product.

In the case of method B, the two boats method, Mg and S commercial powders were placed onto the v-shaped tungsten boats P and Q, respectively. Boat Q was set 15 mm below boat P. By controlling the heating temperature of boats P and Q at about 600 and $350\text{ }^{\circ}\text{C}$, respectively, Mg and S simultaneously evaporated at a vapor pressure of 100 Pa order. The evaporated S powder rose above boat P by riding the convection flow produced by the heating of the two boats. As a result, MgS grains were produced at the confluence around boat P. The collected grains were composed of Mg, MgO crystallites, crystalline MgS and amorphous MgS. Using the two boats method, the control of grain production was difficult throughout the experiments, i.e., MgS grains were not the main product.

In the case of method C, the flash evaporation method, MgS commercial powder was dropped into the heated boat, as shown in Fig. 1C. The MgS commercial powder evaporates before it comes into contact with the heated boat. Therefore, even when MgS was decomposed, the evaporated amounts of Mg and S were maintained throughout the experiment. Therefore, MgS grains could be mostly produced. Using the flash evaporation method nanosized grains of an evaporant sample are easily obtained.

4. TEM observation and infrared spectra of produced MgS grains

Figure 2 shows a TEM image and the corresponding ED pattern of commercial MgS powder (Kojundo Chemical Lab. Co., Ltd., Japan, 99.9%). The commercial MgS powder was roundish cubic and the size was 50 – 150 nm , which was assembled as seen in the TEM image of Fig. 2. In addition to the ED rings of MgS,

Fig. 2. Typical TEM image and corresponding ED pattern of commercial MgS powder (Kojundo Chemical Lab. Co., Ltd., Japan, 99.9%).

Fig. 3. Infrared spectra of commercial powder ranging from 650 to 50 cm^{-1} . **a)** corresponding to commercial MgS powder as shown in Fig. 2; **b)** commercial MgO powder; **c)** commercial $\text{Mg}(\text{OH})_2$ powder. **d)** commercial S powder.

two broad ED rings corresponding to (200) and (220) of MgO can be also observed. The size of MgO crystallites was approximately 1 nm, which was estimated from the diffuseness of the diffraction ring. Since MgS oxidizes in air, the measurement of reliable data of pure MgS is difficult (Begemann et al. 1994). Note that the TEM observation and measurement of the infrared spectrum were carried out immediately after the purchase of the commercial MgS powder. The infrared spectrum of the commercial MgS powder showed the characteristic features, which are composed of a markedly strong peak at 248 cm^{-1} ($40.3\text{ }\mu\text{m}$) with three shoulders at 324, 370 and 400 cm^{-1} (30.9 , 27.0 and $25.0\text{ }\mu\text{m}$) and a small bump at 538 cm^{-1} ($18.6\text{ }\mu\text{m}$) within our measurement limit (650 to 50 cm^{-1} (15.4 – $200\text{ }\mu\text{m}$)), as indicated in Fig. 3a. The infrared spectra of commercial MgO, $\text{Mg}(\text{OH})_2$ and S powders are also displayed in Figs. 3b–d for the comparison to MgS spectra. The small bump at 538 cm^{-1} ($18.6\text{ }\mu\text{m}$) of the spectrum of commercial MgS powder may be attributed to the surface oxide (MgO crystallites) of MgS powder.

Figures 4a and 4b show the typical TEM images and the corresponding ED patterns of grains produced by method A and B, respectively. These TEM observations were immediately carried out within 15 min after the production of grains.

Fig. 4. **a)** and **b)** show the typical TEM images and ED patterns of the collected MgS grains produced by methods A and B, respectively. Many nanocrystallites of MgO were produced in both types of specimen, since diffuse ED rings attributed to MgO are visible.

The grains produced by both methods did not show the characteristic crystal habit of NaCl-type structure. The shape is network-like. Many voids, which are visible as white spherical contrasts, are formed in the grains produced by both methods. Generally, these voids are generated by reactions on grain surfaces, such as the oxidation of metallic particles (Kaito et al. 1973). Therefore, both types of specimen will be produced via the solid-vapor reaction, i.e., the reaction between Mg solid and S vapor. Their infrared spectra are shown in Figs. 5a and 5b, respectively. The infrared spectrum of commercial MgS powder is also displayed in Fig. 5d. The spectrum in Fig. 5a exhibits the characteristic three peaks at 376 , 427 and 580 cm^{-1} (26.6 , 23.4 and $17.2\text{ }\mu\text{m}$), which are mainly attributed to MgO. It is well coincident with the strongly diffused rings in the ED pattern, indicating that the specimen is composed of MgO nanocrystallites. On the other hand, the spectrum in Fig. 5b exhibits peaks at 250 and 309 cm^{-1} (40.0 and $32.4\text{ }\mu\text{m}$) attributed to MgS in addition to the two peaks at 402 and 580 cm^{-1} (24.9 and $17.2\text{ }\mu\text{m}$) attributed to MgO.

Fig. 5. Infrared spectra of produced MgS grains ranging from 650 to 50 cm^{-1} are shown in **a)–c)**. **a)** corresponding to MgS grains as shown in Fig. 4a which were produced by method A. The characteristic three peaks are seen at 376, 427 and 580 cm^{-1} (26.6, 23.4 and 17.2 μm). **b)** corresponding to MgS grains as shown in Fig. 4b, which were produced by method B. The characteristic four peaks are seen at 250, 309, 402 and 580 cm^{-1} (40.0, 32.4, 24.9 and 17.2 μm). **c)** corresponding to MgS grains as shown in Fig. 6 which were produced by method C. The characteristic four peaks are seen at 460, 400, 311 and 262 cm^{-1} (21.7, 25.0, 32.1 and 38.2 μm). The infrared spectrum corresponding to the commercial MgS powder is also indicated in **d)**.

Fig. 6. Typical TEM image and ED pattern of collected MgS grains produced by method C. The ED pattern clearly shows the formation of MgS grains.

The TEM image and corresponding ED pattern of typical grains produced by method C are shown in Fig. 6. The ED pattern clearly shows the production of MgS grains. The grains are 10–100 nm in diameter and the majority are 10–30 nm in size. The produced MgS grains were typically cubic indicating the NaCl-type structure. In contrast to the commercial MgS powder, ED rings corresponding to MgO were rarely observed. A HRTEM image of typical MgS grains approximately 35 nm in size is shown in Fig. 7. The lattice planes of 0.260 nm corresponding to (200) of MgS are clearly observed through a grain. Although the ED pattern of MgO was not detected, MgO nanocrystallites less than 5 nm in size are observed on the

surfaces of MgS grains, as indicated by circles. Moiré fringes in MgS grains, as indicated by dotted circles in Fig. 7, correspond to interference between the (200) lattice planes of MgS grain and MgO surface crystallites.

The infrared spectrum of these MgS grains is shown in Fig. 5c. Four characteristic peaks can be seen at 460, 400, 311 and 262 cm^{-1} (21.7, 25.0, 32.1 and 38.2 μm). The remarkable difference between the spectrum of the commercial MgS powder shown in Fig. 5d and that of produced MgS grains shown in Fig. 5c is in the intensity of 310 and 250 cm^{-1} bands. The 310 cm^{-1} band of the produced MgS grains became significantly more intense in contrast to the 250 cm^{-1} band, which dominates in the spectrum shown in Fig. 5d. The origins of these two bands at 310 and 250 cm^{-1} can be attributed to the shape and/or surface of the grains. Generally, peak shifts are demonstrated by the grain shape. It was calculated that for spherical MgS grains the peak is shifted from $\sim 370 \text{ cm}^{-1}$ ($\sim 27 \mu\text{m}$) to $\sim 260 \text{ cm}^{-1}$ ($\sim 38 \mu\text{m}$) for needle-shaped grains (Hony et al. 2002). It has also been calculated that the main resonances of cubic MgO particles are between those of spherical and needle-shaped particles (Bohren & Huffman 1983). Since MgS is of the same structure as MgO, the character of the absorption should be similar, i.e., the absorption of cubic MgS grains will be located between those of spherical and needle-shaped grains in the calculation. Indeed, in the present study, cubic MgS grains show the absorption peak at 311 cm^{-1} (32.1 μm) which is between $\sim 370 \text{ cm}^{-1}$ of spherical and $\sim 260 \text{ cm}^{-1}$ of needle-shaped grains, as shown in Fig. 5c. However, roundish cubic MgS grains show a main peak at 248 cm^{-1} which is different from the $\sim 370 \text{ cm}^{-1}$ of the calculation by Hony et al. (2002). Therefore, we will suggest other possibilities regarding the origin of the two peaks.

In our previous study, we demonstrated using nanosized TiC grains with different geometries and sizes that the absorption features at 12.5 and 14.3 μm originate from the surface rather than the grain size, i.e., the (100) surface of carbon-rich TiC grains and (111) surface composed of Ti atoms, respectively (Kimura et al. 2004). In this study, the surface of roundish cubic commercial MgS powder is surrounded by (111) and (110) in addition to (100). On the other hand, the surface of produced cubic MgS grains is mostly surrounded by (100). Therefore, it can be concluded that the origin of 310 cm^{-1} is (100) and that of 250 cm^{-1} is (110) and/or (111). This hypothesis is coincident with the spectrum shown in Fig. 5b. The spectrum (Fig. 5b) from a network-like grain shown in Fig. 4b with various surfaces including (100), (110) and (111) shows similar intensity between two peaks at 310 and 250 cm^{-1} which hardly shifted in position.

Another possibility explaining the strong 250 cm^{-1} from roundish cubic MgS grains can be considerable the coagulation of the grains. Although it has been reported that the infrared spectrum of particles is affected by the agglomeration (Clément et al. 2003), the correlation between the state of agglomeration and spectral changes is not sufficiently known. The agglomeration effects have not been seen or noticed in the nanoparticles produced by the gas-evaporation methods. However, in the case of the commercial MgS particles, the particles are heavily agglomerated and coalesced compared with

Fig. 7. Typical HRTEM image of produced MgS grains. The formation of MgO crystallites can be observed as indicated by circles, although it was observed immediately after MgS grain production. Dotted circles indicate the Moiré fringes corresponding to the correlation between the (200) lattice planes of MgS grains and surface MgO crystallites.

gas-evaporated particles. Accordingly, the agglomeration effect may not be negligible. Here, the agglomeration effect can be considered a surface effect. When the coalescence among the MgS grains occurs, (100) surfaces are predominantly coalesced due to their NaCl-type structure. As a result, the absorption intensity at 310 cm^{-1} is more suppressed by the decrease of (100) surfaces. Therefore, it can be concluded that the absorption intensity at 250 cm^{-1} becomes strong in comparison with 310 cm^{-1} . We suggest that the surface effect is more plausible than the geometrical effect, i.e., cubic or round shape as the origin of the 310 and 250 cm^{-1} bands in the nanoregion.

5. Summary

Although the measurement of completely oxideless MgS grains could not be carried out, we demonstrated that the spectrum of MgS grains produced from the gas phase shows the characteristic feature at 311 cm^{-1} ($32.1\text{ }\mu\text{m}$). When MgS grains are produced directly from the gas phase in the ejected gas from objects, the grains become cubic. The infrared spectrum then shows the 310 cm^{-1} band, although it should

depend on temperature. On the other hand, when MgS grains are produced via a gas-solid reaction, the 250 cm^{-1} band becomes more intense than the 310 cm^{-1} band. We conclude that, according to the band profile, it can be decided whether grains in cosmic environments have formed via direct gas-phase condensation or a gas-solid reaction.

Acknowledgements. This work was partially supported by grants from JSPS Research Fellowships for Young Scientists from April 2002 to March 2004 and Postdoctoral Fellowships for Research Abroad from April 2004 to March 2006.

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