Crystalline Mg_2SiO_4 and amorphous Mg-bearing silicate grain formation by coalescence and growth

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Abstract. A novel method for producing MgO and SiO_2 smokes was developed. Mg-bearing silicate grain formation using the coalescence and growth of MgO and SiO_2 grains was carried out in our laboratory. It becomes evident that single and poly crystalline Mg_2SiO_4 (forsterite) and amorphous Mg-bearing silicate grains can be produced by the coalescence and growth of MgO and SiO_2 grains. This result suggests that the observed crystalline Mg_2SiO_4 grains and amorphous Mg-bearing silicate particles in Red Super Giant (RSG), Asymptotic Giant Branch (AGB), post-AGB and planetary nebula (PNe) could be produced by the coalescence and growth of MgO and SiO_2 grains.

Key words. astrochemistry – methods: laboratory – stars: AGB and post-AGB – circumstellar matter – dust, extinction

1. Introduction

IR spectra taken by the Infrared Space Observation (ISO) project of Red Super Giant (RSG), Asymptotic Giant Branch (AGB) stars, post-AGB stars and planetary nebula (PNe) indicated a mixture of amorphous and crystalline silicates (Waelkens et al. 1996; Waters et al. 1996). The observation of crystalline phases changed our view of the silicates. Although Mg-rich crystalline silicates were observed, Fe-rich crystalline silicates were not observed. The direct formation of Mg-bearing crystalline silicates i.e., Mg_2SiO_4 (forsterite) and MgSiO_3 (enstatite) grains was not achieved in condensation experiments in the laboratory (Nuth et al. 1988; Suzuki et al. 2000). On the other hand, experiments based on gas-solid direct condensation from Mg-Fe-SiO- H_2 - O_2 vapor yield various metastable phases (Rietmeijer et al. 1999).

In a previous paper, we demonstrated crystalline Mg_2SiO_4 grain formation due to the coalescence and growth of Mg and SiO smoke grains (Mg-SiO system) in the case of an SiO-grain-rich atmosphere in a Mg-SiO system (Kaito et al. 2003). These Mg_2SiO_4 grains contained silicon crystallites. This was the first time that crystalline Mg_2SiO_4 grain formation had been achieved in the laboratory by coalescence and growth.

In spite of increasing interest in the formation of refractory compound particles in materials science and astrophysics (Henning et al. 2002; Colangeli et al. 2003), the unavailability of a suitable evaporation source for the reaction gas

Fig. 1. Schematic representation of the production of compound grains by mixing two smokes. Boat A is a Mg evaporation source. Boat B is a SiO evaporation source. In the gas mixture of Ar and O_2 , boats A and B were heated to 800 and 1400 °C, respectively. An outline of the two smoke cloud shapes is presented.

remains an unavoidable problem. We recently found that some oxide grains can be produced by the use of a tantalum (Ta) boat in a gas mixture (Atou et al. 2003). In the present grain

Fig. 2. Typical smoke grains of crystalline MgO and amorphous SiO_2 collected under the present experimental conditions.

formation experiments, we adapted this technique, and the coalescence of MgO and SiO_2 smoke grains (MgO- SiO_2 system) was successfully carried out. Spherical crystalline Mg_2SiO_4 grains without silicon crystallites, and amorphous Mg-bearing silicate grains, can be obtained on the basis of the coalescence between MgO and SiO_2 grains. In the present case, the crystalline Mg_2SiO_4 grains formed were both single crystals and polycrystalline.

2. Experimental

The evaporation chamber was a glass cylinder of 17 cm diameter and 30 cm height, covered with stainless steel on top and connected to a high-vacuum exhaust through a valve at its bottom. After evacuation of the chamber, smoke was produced by introducing a gas mixture of O_2 gas at 20 Torr and Ar gas at 80 Torr. In the present experiment, two evaporation sources in V-shaped tantalum boats (50 mm long, 2 mm wide and 1 mm deep) were set as shown schematically in Fig. 1. Boats A and B were charged with Mg and SiO powder, respectively. By heating boats A and B to 800 and 1400 °C, respectively, in the gas mixture, MgO and SiO_2 smokes were produced and mixed as indicated in a previous paper on the Mg-SiO system (Kaito et al. 2003). The smoke grains in the mixed region were collected at a height of 10 cm above the evaporation source. The collected samples were observed using Hitachi H-7100R and H-9000NAR transmission electron microscopes (TEM). The composition of the grains was determined using an energy-dispersive X-ray (EDX) spectrometer (Horiba EMAX-5370) attached to the H-7100R electron microscope. The transmission IR spectra of the collected samples, embedded in KBr pellets, were measured with a Fourier transform

Fig. 3. IR spectrum of the SiO_2 grains produced in our experiment. The spectrum for quartz can be seen.

infrared spectrometer (FTIR, Horiba FT210) in the wavelength region from 2.5 to 25 μm (4000 to 400 cm^{-1}).

3. Results and discussion

Typical MgO and SiO_2 grains produced in a gas mixture of Ar and O_2 are shown in Fig. 2. As is well known, cubic MgO grains are produced by the oxidation of Mg vapor. Spherical amorphous SiO_2 grains were obtained by evaporating SiO powder in the mixture of O_2 and Ar (Kaito et al. 1987). The IR spectrum of the SiO_2 grains is shown in Fig. 3. The IR spectrum can be identified as quartz (Morioka et al. 1998). By evaporating SiO grains in the gas mixture containing O_2 , SiO grains were changed to SiO_2 by oxidation. The grains were

Fig. 4. The grain indicated by an arrow is a single crystal Mg_2SiO_4 grain.

Fig. 5. HREM image of a polycrystalline Mg_2SiO_4 grain. Dotted lines show the boundary seen in the grain. Moiré fringes are also seen in the left enlarged image.

spherical, and the O-Si-O bending peak at $21.1 \mu\text{m}$ is sharper than in other silicate grains.

As was observed in the Mg-SiO system, the Mg_2SiO_4 grains were obtained in the mixed smoke region of the MgO-SiO₂ system. In the case of the MgO-rich side of the smoke, MgO crystals appeared shaped as truncated cubic grains. In the case of the SiO₂-rich side, spherical amorphous SiO₂ grains were obtained.

As shown in Fig. 4, spherical grains with strong contrasts are seen, and these contrasts suggest the formation of crystalline grains. The selected area electron diffraction (ED) pattern of the grain, indicated by an arrow, is shown in the inset in the figure. The ED pattern shows the formation of a single Mg_2SiO_4 crystal.

Figure 5 shows a high-resolution electron microscope (HREM) image of the Mg_2SiO_4 grain. This grain was composed of polycrystalline grains. Enlarged images of the regions

in the dotted squares are also shown. The lattice image of the (011) plane of Mg_2SiO_4 is seen in both enlarged images, but these images are not parallel, that is, polycrystalline growth occurred. The dotted lines indicate the boundaries seen in the grain. Since some parts of the Mg_2SiO_4 crystals in a grain overlap at the boundary, Moiré fringes are also seen.

In addition to the above-mentioned single crystal and polycrystalline Mg_2SiO_4 grains, spherical amorphous grains were produced as shown in Fig. 6 by their halo ED pattern. By means of EDX analysis, the existence of Mg and Si atoms in the spherical grains has been confirmed. The spherical grains indicated in Fig. 2 show the existence of silicon atoms alone. Therefore, it can be concluded that the spherical amorphous Mg-bearing silicate grains were also produced in the present experiment.

In the present experiment with oxygen gas, the oxidation of Mg vapor occurred near the heat source. The temperature of the mixed smoke in the MgO-SiO₂ system reached

Fig. 6. Mg-bearing amorphous silicate grains. The ED pattern for these spherical grains shows a halo.

approximately 1000 °C (Kaito & Shiojiri 1982; Kaito 1984; Kaito & Fujita 1986). The cooling rate of the smoke is of the order of 10^{-3} – 10^{-4} K/s. The difference in cooling rate in the smoke after the coalescence of MgO and SiO_2 grains may determine whether single crystal, poly crystal or amorphous grains are formed. It is concluded that Mg_2SiO_4 crystals can be produced by the coalescence of MgO and SiO_2 grains, e.g. the direct collision of MgO and SiO_2 grains.

With respect to the production process of crystalline Mg_2SiO_4 and amorphous Mg-bearing silicate grains, it is found that these grains have the same spherical shape. The amorphous grains were generally of spherical shape. In the present experiment, crystalline Mg_2SiO_4 grains did not have the characteristic crystalline shape (Uyeda 1987), and were instead spherical grains with no obvious faces. This suggests that amorphous Mg-bearing silicate grains were produced first and subsequently the crystallization of amorphous Mg-bearing silicate to Mg_2SiO_4 occurred due to thermal annealing. The crystallization process for a Mg-bearing silicate by in situ observation techniques using a TEM will be shown elsewhere.

4. Conclusions

Crystalline Mg_2SiO_4 grains and amorphous Mg-bearing silicate particles can be produced by the coalescence and growth of MgO and SiO_2 grains. The structural differences between crystalline and amorphous grains may have occurred due to differences in cooling rate after the formation of the amorphous Mg-bearing silicate grains in the mixed smoke. The crystalline Mg_2SiO_4 grains and amorphous Mg-bearing silicate particles

observed in RSG, AGB, post-AGB and PNe (Waelkens et al. 1996; Waters et al. 1996) may therefore have been produced by the coalescence and growth of MgO and SiO_2 grains or Mg and SiO grains (Kaito et al. 2003).

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