

STRUCTURAL MODIFICATION IN AMORPHOUS MgSiO_3 WITH HEAT TREATMENTS. J. Matsuno¹, A. Tsuchiyama¹, C. Koike¹, H. Chihara¹, Y. Imai², K. Murata², R. Takahashi¹, S. Kohara³, Y. Kitajima⁴, A. Yoshiasa⁵ and Y. Seto⁶. ¹Dep. of Geology and Mineralogy, Kyoto Univ., Kitashirakawa, Oiwake, Sakyou, Kyoto, 606-8502, JAPAN (jmatsuno@kueps.kyoto-u.ac.jp), ²Dep. of Earth and Space Sci., 1-1 Machikaneyama, Toyonaka, Osaka, 560-0043, JAPAN, ³Japan Synchrotron Radiation Research Institute (SPring-8/JASRI), 1-1-1 Kouto, Sayo, 679-5198, JAPAN, ⁴Photon Factory, High Energy Accelerator Research Organization, 1-1, Oho, Tsukuba, 305-0801, JAPAN, ⁵Dep't Earth Sci., Kumamoto Univ., 2-39-1, Kurokami, Chuoh, Kumamoto, 860-8555, JAPAN, ⁶Dep. of Earth and Planetary Sci., Kobe Univ., 1-1, Rokko-dai, Nada, Kobe, 657-8501, JAPAN.

Introduction: It has been well known that infrared (IR) spectra of astronomical observations and that of laboratory measurements revealed the presence of crystalline silicate dust (e.g., enstatite, MgSiO_3 and forsterite, Mg_2SiO_4) as well as amorphous silicate dust in circumstellar environments (e.g., [1]). In contrast, the interstellar dust is almost amorphous [2]. They were incorporated into the circumstellar disk of young stars, and crystalline silicates could form by heating. In order to understand the formation and evolution of the circumstellar dust, crystallization of amorphous silicates have been performed (e.g., [3-6]).

Imai [5] carried out heating experiments of amorphous MgSiO_3 prepared by an induction thermal plasma (ITP) technique and obtained the activation energy and frequency factor for the crystallization of enstatite. In powder X-ray diffraction (XRD) profile of the run product heated for 3 hr. at 800 °C, three broad and weak peaks at around 9°, 35° and 60° in 2θ appeared in addition to an original halo peak of the starting amorphous material at around 26° (Fig. 1a,b). After 6 hr. heating, weak peaks disappeared (Fig. 1c), and after \geq 12 hr. heating, enstatite crystallized (Fig. 1d). An IR absorption feature of the amorphous silicate was observed at around 18 μm , which originates from O-Si-O bending vibration in the starting material (Fig. 1h). After 3 hr. heating at 800 °C, a 22 μm shoulder peak grew and intensity of the peak at around 18 μm decreased (Fig. 1i). In the spectrum of heating for 6 hr., the 18 μm feature grew again while the 22 μm shoulder peak became unclear, and after \geq 12 hr. heating, enstatite crystallized (Fig. 1j,k). These evolutions of both XRD pattern and IR spectrum onset enstatite crystallization were also observed at different temperatures (780 °C and 820 °C). Previous heating experiments of amorphous Mg-silicates synthesized by sol-gel method showed the similar weak and broad peaks in their starting materials by XRD and these peaks disappeared after heating [3,4,6,7].

These XRD and IR features may be caused by structural changes of SiO_4 network and/or Mg^{2+} site in the amorphous silicates. The 18-22 μm features of the IR spectra may also affect the estimation of silicate dust species around the circumstellar regions. There-

fore, it is important to elucidate the reason of appearance and disappearance of the XRD and IR features. Thus, we measured high energy X-ray diffraction (HEXRD) data and extended absorption fine structure (EXAFS) spectrum of the amorphous samples to investigate bond distance and coordination numbers. It should be also noted that the amorphous silicates prepared by the sol-gel method may contain H_2O or OH residue due to insufficient dehydration of the gel although there was no evidence. Thus, we examined the effect of hydration to the XRD and IR features too.

Experimental: The heating experiments were performed using two amorphous MgSiO_3 . One was synthesized by ITP technique and the other was by sol-gel method. Nanometer-sized spherules (typically 70 nm in diameter) were produced by ITP technique [5]. By spraying slurry composed of $\text{Mg}(\text{OH})_2$ and SiO_2 in ethanol with the Mg/Si ratio of 1 into an ITP chamber together with Ar and O_2 gas at one atmosphere. They evaporated at about 10000 K and amorphous nanospheres condensed from the gas by rapid quenching (10^4 - 10^5 K/sec). For the sample preparation by the sol-gel method, Mg ribbons were dissolved into ~10% nitric acid solution and mixed with tetraethyl orthosilicate and the mixture started to gel. Thereafter, ~15% ammonia solution was gradually added. Finally, the gel was dried at 400 °C over a night [3]. Both amorphous MgSiO_3 were heated in air at a constant temperature ranging from 780 to 850 °C for different durations from 0.5 to 240 hr [3,5].

The phases of the samples were determined using XRD (SmartLab, Rigaku). The samples were mounted on a reflection-free sample holder of silicon and exposed to $\text{CuK}\alpha$ radiation. For the IR spectroscopic measurement, the samples were dispersed and embedded in KBr for mid-IR and in polyethylene for far-IR measurements. The spectra were obtained with a Fourier transform IR spectrometer (Nexus 670, Nicolet).

The HEXRD measurements were performed with a synchrotron X-ray at BL04B2 of SPring-8 and the incident photon energy was 61.6 keV [8]. The EXAFS measurements were performed in a high-vacuum chamber at a soft X-ray spectroscopy station BL11A and 11B of the Photon Factory, the Institute of Materi-

als Structure Science of the High Energy Accelerator Research Organization. Powder samples were diffused on carbon adhesive tapes on a brass sample holder. X-ray absorption spectra were recorded by total electron yield [9].

In order to investigate the effect of hydration, we performed a hydrothermal alteration experiment using the amorphous MgSiO_3 prepared by ITP at 150°C for 3 weeks with a water/rock ratio of 0.1 by weight under saturated water vapor pressure in a Teflon vessel sealed by a stainless jacket.

Results and discussion: In the HEXRD analysis, structural information was obtained by the Fourier transformation of the total structure factor $S(Q)$ obtained by normalizing the raw data after several corrections [8], where Q is a scattered angle and inversely proportional to the diffraction angle, to a total correlation function, $T(r)$, where r is a real space distance. Both the $T(r)$ of the starting material and that of the run products of the heating experiments show that the Si-O correlation peak at $\sim 1.62 \text{ \AA}$ (Fig. 2). This means that the Si-O bond of the SiO_4 structure did not change. In contrast, Mg-O distance of the run product of heating for 3 hr. is slightly longer ($\sim 2.05 \text{ \AA}$) than that of the starting material and heating for 6 hr. ($\sim 2.00 \text{ \AA}$). This feature is also supported by the EXAFS data, suggesting the XRD and IR features are related to the changes of the Mg-O distance.

The XRD pattern of the run product on the hydrothermal experiment has three broad and weak peaks at around 9° , 35° and 60° in 2θ in addition to an original halo peak of the starting material at around 26° (Fig. 1g). This is similar to that of the sample heated at 800°C for 3 hr. (Fig. 1b). The peaks of the hydrothermal run product correspond to hydrous phyllosilicates (e.g., talc and serpentine) although it is difficult to definitely identify a specific phase by XRD alone because of their orientation rotation and/or swelling. The features observed in the XRD pattern of the run products at 800°C for 3 hr. should also correspond to hydrous phyllosilicates. The peak positions of the amorphous silicate produced by the sol-gel method [3,4,6,7] are also similar to that of phyllosilicates. The shift of $18\text{--}22 \mu\text{m}$ of IR absorption probably results from phyllosilicates too. In the ITP method, H_2O or OH molecules (or H and O separately), which were originated by decomposition of $\text{Mg}(\text{OH})_2$, should be incorporated into the amorphous MgSiO_3 during the rapid condensation. In this case, a possible scenario is follows: (1) phyllosilicate minerals crystallized from the O and H bearing amorphous silicate by heating for 3 hr., (2) they were dehydrated and became amorphous for 6 hr., and finally (3) anhydrous silicate (enstatite)

crystallized by heating for 12 hr. Although the exact amount of the phyllosilicate is unknown, the weak XRD peaks suggest that the amount should be small.

The present results suggest that H_2O (or H and O) should be included in amorphous silicates condensed in circumstellar regions and hydrous silicates may form by mild heating, such as at $\sim 1000 \text{ K}$ for a few hours. They may be observed around the circumstellar region of evolved stars on $22 \mu\text{m}$ IR absorption, although more kinetic experiments are needed.

References: [1] Tielens et al. (1997) *Ap&SS*, 255, 415-426 [2] Kemper et al. (2004) *ApJ*, 609, 826-837 [3] Murata et al. (2009) *ApJ*, 697, 836-842 [4] Matsuno et al. (2012) *ApJ*, 753, 141-147 [5] Imai (2012) PhD thesis [6] Thompson et al. (2012) *A&A*, 545, A60 [7] Douy et al. (2002) *Sol-Gel Sci. & Tec.*, 24, 221-228 [8] Kohara et al. (2007) *J. Phys.: Condens. Matter*, 19, 565101 [9] Kitajima et al. (1998) *J. Synchrotron Rad.*, 5, 729-731

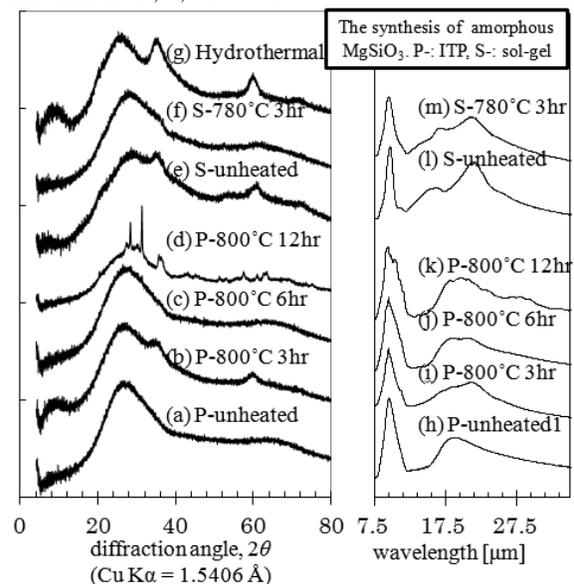


Figure 1: XRD and IR spectra (absorption unit) of MgSiO_3 amorphous silicates prepared by ITP method (P) or sol-gel method (S) and their heating or hydrothermal run products.

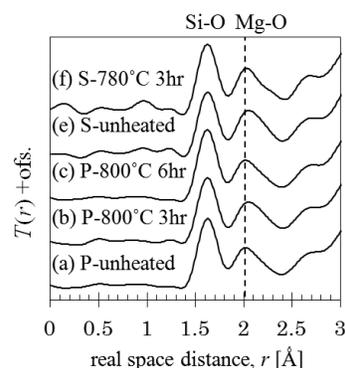


Figure 2: The total correlation functions, $T(r)$, obtained by HEXRD measurements. Peaks around 1.6 \AA and 2.0 \AA corresponds to the bond length of Si-O and Mg-O, respectively.