EVOLVING THE 10 μm BAND OF SILICATES NANOPARTICLES DURING HOMOGENEOUS NUCLEATION AND SUBSEQUENT GROWTH. S. Ishizuka[1], Y. Kimura[1], I. Sakon[2], [1]Depatment of Earth and Planetary Science, Tohoku University, Aoba-ku, Sendai, Japan (b3sm6002@s.tohoku.ac.jp), [2]Depatment of Astronomy, University of Tokyo, Hongo, Tokyo, Japan

Introduction: Silicate dust is one of the most abundant minerals in the universe. IR band structures from 8 μm to 12.5 μm in wave length arising from Si-O stretching provide us the information of unrevealed dust evolution processes around evolved stars. The Infrared Space Observatory mission revealed the existence of crystalline silicates around evolved stars based on the 10 μm band structure [1], which shows wide variety from amorphous silicate rich to crystalline rich [2] . In the outflow of asymptotic giant blanch (AGB) stars with high mass loss rate, 10-15 % of crystalline silicates are contained [3] and its formation mechanism is the key process to understand the lifecycle of dust. Numerous laboratory experiments such as direct condensation [e.g. 4] and annealing of amorphous silicates [e.g. 5] showed IR spectra variation due to structure, chemical composition, temperature, size and shape and processes of crystalline silicates formation. Nevertheless the scenario is not fully understood.

One of the reasons is the difficulty of IR measurement technique. When we measure transmittance spectra, samples are usually embedded in KBr media. Then, the spectral profiles like peak wavelength, FWHM and intensities are changed by the medium effect, particles agglomeration and surface pollution by the air [6, 7]. Aerosol technique application only succeeded in IR measurements of free-flying silicates which had elliptical and irregular shapes directly comparable to astronomical observation without KBr embedding effects [8]. However, the dust evolution history based on 10 μm band structure remains unrevealed and the amount of directly comparable spectra data is still insufficient. In this study, we developed a new technique to measure IR spectra of free-flying nanoparticles and investigated homogeneous nucleation processes of silicates from the evaporated gas *in-situ*.

Experimental procedure: Silicates particles were produced in a specially designed vacuum chamber combined with FT-IR (Fourier-transform infrared spectroscopy). The original chamber is made of stainless-steel and the twin windows penetrating optical path of FT-IR are composed of KRS5 whose feature is high transmittance in mid-IR region and no cleavage. The inner diameter of the flange is 9 cm and the height of the top chamber is 20 cm. The cylinder of the bottom chamber is connected to a turbo molecular pump. After evacuating the chamber less than 1×10^{-4} Pa, connecting valve was closed then highly pure O_2 and Ar gases were injected. The evaporation source of V-shaped Ta boat (30 mm in length, 5 mm in width and 0.03 mm in thickness) connected to Cu electrodes was rapidly heated to over 2000°C by electro residence. The source temperature was monitored using a radiation thermometer. Heated Mg and SiO powder on the evaporation source were evaporated and the gas flowed upward due to thermal convection and cooled to occur homogeneous nucleation of nanoparticles, which is visible as a smoke. There were optical path of FT-IR above the evaporation source in order to measure IR spectra of the fresh condensates *in-situ*. The experiments were carried out under the regulated atmosphere at the height of measurement position 3 cm above the source. FT-IR resolution was 2 cm^{-1}. The flowed nanoparticles were attached to a collecting holder fixed at the top of the chamber. The collected particles were picked on an amorphous thin film of carbon mounted on a standard Cu grid for a transmission electron microscope (TEM). The produced particles were observed by TEMs (Hitachi-8100 and JEM-2100F) at acceleration voltage of 200 kV. Resident particles on the collecting board were agitated with KBr powder and prepared a KBr pellets as conventional KBr pellet method.

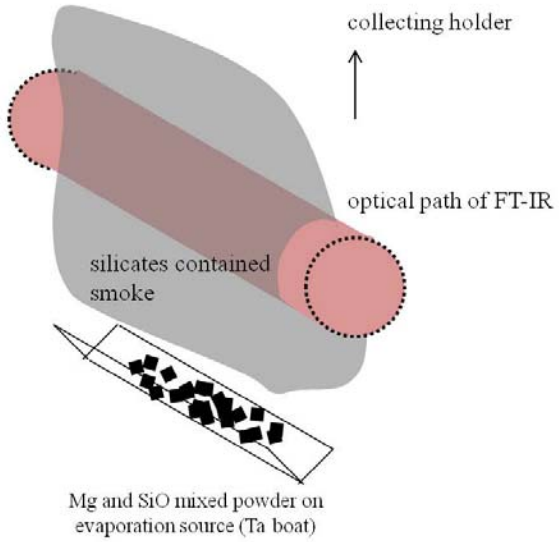

Figure 1 Schematic presentation of the evaporation source for nanoparticles formation and *in-situ* IR measurements of the free-flying nanoparticles.

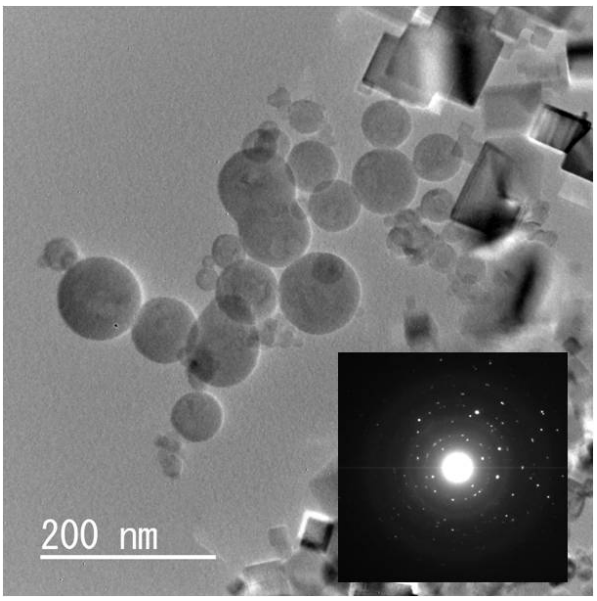

Figure 2 Bright field TEM image and corresponding ED pattern of condensates. Spherical particles containing forsterite single crystal and square shaped MgO were observed.

TEM observation : TEM image and corresponding electron diffraction (ED) pattern in Fig. 2 shows existence of 30-100 nm sized spherical forsterite and square shaped MgO. Particles seem to be the coalescence products (e. g. [9, 10]).

***In-situ* IR measurements of the free-flying nanoparticles :** We measured 10 μm band and analyzed the metamorphosis of Mg-bearing silicates. During the measurement, annealed forsterite at higher temperature (double peaked and longer wave band exceed) shown in Fig. 3 (a) as first condensates, annealed forsterite at lower temperature (double peaked and shorter wave band exceed) shown in Fig. 3 (b) as secondary condensates, and at last silica (peak wavelength at 9.2 μm) and amorphous silicates (broad feature at 9.7 μm) shown in Fig. 3 (c) were observed accordant with Mg/SiO_x ratio changes in precursor gases derived from relative intensity of MgO band at 16.8 μm and silicates band at 10 μm. Relative intensity of the longer and shorter wave bands of forsterite varies depending on the annealing temperature [11]. When Mg/SiO_x ratio was high, forsterite nanoparticles annealed at higher temperature. When Mg/SiO_x ratio is low, amorphous silicates were formed due to annealing at lower temperature. It seems that Mg/SiO_x ratio affects to the annealing temperature. It suggests oxidization heating supplied by MgO or latent heating of crystallization determines annealing temperature and the 10 μm band structure.

10 μm band structure, especially wave length, of free-flying nanoparticles showed different features from KBr measurements (e. g. [10, 12]) and consistent with sphere shaped forsterite calculated from optical constants([7, 11]).

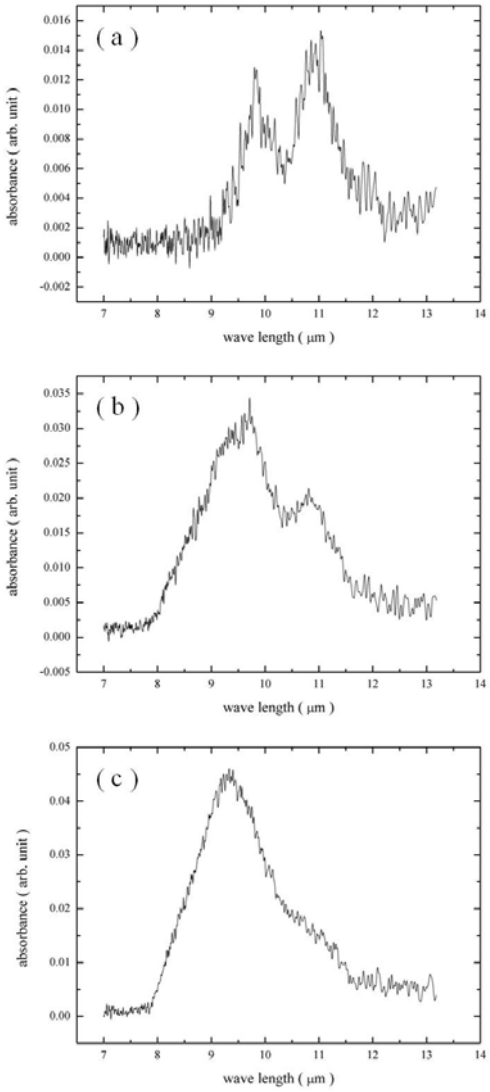

Figure 3 Silicates 10 μm band structure varied gradually according with Mg/SiO_x ratio. Representative IR spectra when Mg/SiO_x ratio was (a) high, (b) medial and (c) low are shown.

References: [1] Waters, L. B. F. M., et al. 1996, A&A, 315, L361, [2] Speck, A. K., et al. 2000, A&A, 146, 437 [3] Molster, F., & Kemper, C. 2005, Space Sci. Rev., 119, 3, [4] Tsuchiyama, A. 1998, Mineralogy journal, 20, 59, [5] Hallenbeck, S. L., et al. 2000, ApJ, 535, 247, [6] Bohren, C. F., & Huffman, D. R. 1983, Absorption and Scattering of Light bySmall Particles (New York: Wiley), [7] Fabian, D., et al. 2001, A&A, 378, 228 , [8]Tamanai, A. & Mutschke, H., et al. 2006, ApJ, 648, L147 [9]Kamitsuji, K., et al. 2005, A&A, 429, 205 [10] Kimura, Y., et al. 2008, ApJ, 684, 1496, [11] Koike, C., et al. 2010, ApJ, 709, 983 [12] Koike, C., et al. 2003, A&A, 399, 1101