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## Infrared spectra during the growth of free-flying nanoparticles and its application to unidentified infrared bands

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Condensation of refractory materials is the first step of material evolution accompanying with stellar life. Though metals composed of refractory materials are not abundant elements in universe, it becomes relatively dominant at the region close to photosphere at high temperature and condensed to be a dust of refractory material. The first condensate becomes substrates for heterogeneous nucleations of subsequently condensed materials, such as magnesium silicate, at lower temperature. Therefore column density and size of first condensate decide subsequent dust evolution around late type giants. Oxygen rich M-type Asymptotic Giant Branch (AGB) stars are often observed with a 13 micron meter feature caused by a refractory material (e.g. DePew et al., 2006). The origin of the 13 micron meter feature has been theoretically explained by morphological effect of corundum (?-Al2O3). However, the 13 micron meter feature has not been demonstrated experimentally and has been remained as an unidentified infrared band so far. Understanding of the formation process of the origin of the 13 micron meter feature may give us the starting point of material evolution.

Infrared (IR) spectra of mineral samples have usually been measured after embedded into a KBr pellet. Then, the peak positions of a sample are shifted to the longer wavelength by medium effects of surrounding KBr (e.g. Tamanai et al., 2009). Our direct measurement method of free-frying nanoparticles is able to solve this problem and also is avoidable agglomeration of the samples, which dilute characteristic features caused by morphological effect, and contamination of the fresh surfaces of synthesized samples by exposure to air. Bulk crystal forms dangling bonds on their surface in vacuum. However, the dangling bonds changes when it will be in a KBr pellet. In case of nanoparticles, its surface area per volume becomes extremely large compared to that of bulk. It means that the contribution of a dangling bond on the surface of nanoparticles is not able to neglect to features in IR spectra. In these reasons, we started a new project, production of free-frying nanoparticles and observation of its infrared spectra. Here, we will describe the method and focus on the origin of the 13 micron meter feature.

Free-flying nanoparticles of Al2O3 and TiO2 were produced by the gas evaporation method, and condensation processes of the refractory materials were examined using our new technique, free flying nanoparticles method with Fourier-transform infrared spectrometer. Condensed materials were analyzed by transmission electron microscopy (TEM) equipped with energy dispersive X-ray spectroscopy (EDS). In-situ measurement of IR spectra during condensation revealed the difference of the features in the IR spectra between primal condensates and adequately cooled samples as nanoparticles flow. Their IR spectra have a tendency of that primal condensates showed broader feature and the nanoparticles far from the evaporation source showed sharper feature. It may be a result of secondly nucleation from amorphous or molten particles formed by homogeneous nucleation from vapor phase.

As astromineralogical implication, TiO2 nanoparticles with rounded edges have been proposed as a possible candidate for the 13?micron meter feature theoretically (Posche et al., 2003). The spectrum of TiO2 nanoparticles showed the accordance of peak position with the theoretically predicted spectra.