Observation of Phase Change of Methane Hydrate Using THz Waves

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I. Introduction

There has been significant research attention in recent years on gas hydrates, which consist of hydrogen bonding on water molecules. In particular, the creation of methane hydrate, consisting of water and methane gas, has been confirmed in various parts of the world and is expected to provide a next-generation energy resource; the properties of gas hydrates mean they can also be used to store and separate gases. However, the phase change processes of gas hydrates are still not completely understood.

Among the phase change processes, there is a phenomenon called the “self-preservation effect” in methane hydrate, whereby methane hydrate can exist stably for a long time, even though temperature and pressure conditions are outside the region of equilibrium (Fig. 1). Although the critical factor has not been elucidated, there is a hypothesis that supercooled water is involved in the mechanism by which decomposition is suppressed in the self-preservation effect [1]. Several methods have been used to elucidate this decomposition mechanism, but it has not yet been successfully verified.

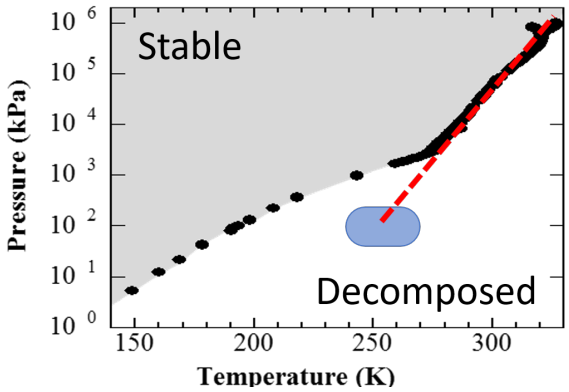

Fig. 1. The self-preservation effect appears under the conditions indicated in the blue area in the figure.

In our previous work, we confirmed the phenomenon, which is regarded as sublimation of methane hydrate in a certain temperature zone. Many studies and analyses have been conducted for ice with a structure very similar to gas hydrate; furthermore, in recent years, the observation results of the pseudo-liquid layer at that time have also been studied, and it has been reported that there is a close relationship between the sublimation and the pseudo-liquid layer [2]. However, there have been few reports on the sublimation of gas hydrates.

II. Result

In this study, we conduct research on methane hydrate using THz Time-Domain Spectroscopy (THz-TDS) as a novel method for observing a phase change.

Figure 2 shows the time-domain waveforms when measuring methane hydrate at 260 K held at atmospheric pressure for about 160 minutes. Time-domain waveform acquisition was performed nine times in total about every 20 minutes, and the time-domain waveform shifted to the left. When decomposition of methane hydrate occurs, it is considered that it changes to ice, with an increase in the refractive index and a shift in the the time-domain waveform to the right, so the shift to the left can be attributed to a change in thickness, i.e. sublimation. Similar measurements were performed between 210 K and 250 K. A left shift of the time-domain waveform was observed at temperatures of 240 K and above, and the degree of the shift increased with increasing temperature. In addition, there is an increase in absorption in this temperature zone, which may be due to the presence of liquid water.

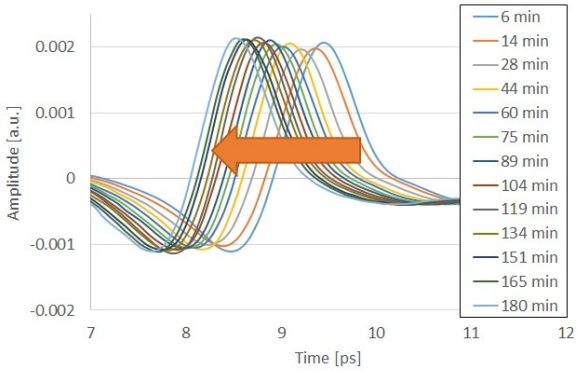

Fig. 2. When the time waveform was acquired while holding at 260 K, it was observed that the sample waveform shifted to the left as time elapsed.

III. Summary

We observed a phenomenon that is likely to be sublimation of methane hydrate using the THz-TDS system. There have been few reports on the sublimation of gas hydrates in the past, and this result represents a significant contribution to elucidating the decomposition process of methane hydrate, which is still poorly understood.

References

[1] K. Takeya, K. Nango, T. Sugahara, K. Ohgaki, A. Tani, *J. Phys. Chem. B* 109 (2005) 21086
[2] K. Murata, H. Asakawa, K. Nagashima, Y. Furukawa, G. Sazaki, *Proc. Natl Acad. Sci. USA* 113 (2016) E6741-E6748