

Possible existence of a higher-pressure liquid state in SnI₄

Kazuhiro FUCHIZAKI¹, Nozomu HAMAYA², Takaki HASE³, and Takumi KIKEGAWA⁴

¹Department of Physics, Ehime University, Matsuyama 790-8577, Japan

²Department of Physics, Ochanomizu University, Tokyo 112-8610, Japan

³Altekna Co. Ltd, Nagoya 451-6004, Japan

⁴Institute of Materials Structure Science, KEK, Tsukuba 305-0801, Japan

We have performed in situ synchrotron x-ray diffraction measurements on tin tetraiodide, which consists of SnI₄ tetrahedral molecules at ambient pressure, and established that the liquid forms existing above and below 1.5 GPa, referred to as the break pressure, where the slope of the melting curve of the crystalline phase changes abruptly, have different structures [1]. Our finding that a high-temperature region (up to ~ 1300 K) below the break pressure is occupied by the molecular liquid phase suggests a possible location of the second critical point close to the break point [2]. This anticipation prompted us to explain the whole aspect of polyamorphic transitions, including those between the two amorphous states [3], hitherto observed in SnI₄ according to a critical-point scenario [4]. This was indeed accomplished within mean-field treatments of the scenario [1,2].

With the aid of molecular dynamics simulations, we showed that once the crystalline state, in which the nearest molecules are facing each other, melts down, and the molecules can rotate, they frequently take the vertex-to-face orientation that makes the *intermolecular* I – I distance shorter than the *intramolecular* distance [1]. That is, the melting helps to undergo polymerization. If the molecules are in the face-to-face orientation as in the crystalline state, much pressure is needed for them to come close within the former distance. This is why a solid-state amorphization to a denser state occurs at ~ 15 GPa, almost ten times as large as the pressure that can induce a transition to the denser liquid phase.

The high-density amorphous state was shown to be a transient state towards the highest-density crystalline state [3,5]. This is brought about by molecular dissociation, and the transition completes at 61 GPa [3]. That the liquid can take the higher-pressure structure in advance can be expected to happen also in a higher-pressure region; a new liquid phase attained by molecular dissociation will realize under much lower pressures. Indeed, our recent in situ synchrotron x-ray diffraction measurements showed that the structure factor of the liquids under 4 through ~ 6 GPa has a tendency to resemble that of the high-density amorphous state undergoing molecular dissociation [5].

We conclude from a series of our findings regarding polyamorphs of SnI₄ that the liquid “foresees” the higher-pressure structure which is realized in the solid state under much higher pressures.

[1] K. Fuchizaki *et al.*, J. Chem. Phys. **130**, 121101 (2009).

[2] K. Fuchizaki, T. Hase, N. Hamaya, and Y. Katayama, “Possible scenario for the liquid - liquid phase transition in SnI₄”, in preparation.

[3] N. Hamaya *et al.*, Phys. Rev. Lett. **79**, 4597 (1997).

[4] K. Stokely *et al.*, Proc. Natl. Acad. Sci. USA **107**, 1301 (2010).

[5] A. Ohmura *et al.*, Phys. Rev. B **80**, 054201 (2009).