



Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

The glass transition in high-density amorphous ice

Thomas Loerting^{a,*}, Violeta Fuentes-Landete^a, Philip H. Handle^a, Markus Seidl^a, Katrin Amann-Winkel^a, Catalin Gainaru^b, Roland Böhmer^b^a Institute of Physical Chemistry, University of Innsbruck, Innrain 80-82, A-6020 Innsbruck, Austria^b Fakultät Physik, Technische Universität Dortmund, Otto-Hahn-Straße 4, D-44221 Dortmund, Germany

ARTICLE INFO

Article history:

Received 29 June 2014

Received in revised form 19 August 2014

Available online xxxxx

Keywords:

Glass transition;

High-density amorphous ice;

Dielectric relaxation spectroscopy;

Differential scanning calorimetry;

Polyamorphism

ABSTRACT

There has been a long controversy regarding the glass transition in low-density amorphous ice (LDA). The central question is whether or not it transforms to an ultraviscous liquid state above 136 K at ambient pressure prior to crystallization. Currently, the most widespread interpretation of the experimental findings is in terms of a transformation to a superstrong liquid above 136 K. In the last decade some work has also been devoted to the study of the glass transition in high-density amorphous ice (HDA) which is in the focus of the present review. At ambient pressure HDA is metastable against both ice I and LDA, whereas at >0.2 GPa HDA is no longer metastable against LDA, but merely against high-pressure forms of crystalline ice. The first experimental observation interpreted as the glass transition of HDA was made using in situ methods by Mishima, who reported a glass transition temperature T_g of 160 K at 0.40 GPa. Soon thereafter Andersson and Inaba reported a much lower glass transition temperature of 122 K at 1.0 GPa. Based on the pressure dependence of HDA's T_g measured in Innsbruck, we suggest that they were in fact probing the distinct glass transition of very high-density amorphous ice (VHDA). Very recently the glass transition in HDA was also observed at ambient pressure at 116 K. That is, LDA and HDA show two distinct glass transitions, clearly separated by about 20 K at ambient pressure. In summary, this suggests that three glass transition lines can be defined in the p–T plane for LDA, HDA, and VHDA.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/3.0/>).

1. Introduction

Amorphous ices are the dominant form of water in the universe, even though they do not naturally form on Earth's lithosphere. They may occasionally form at <150 K in the coldest region of Earth's atmosphere, near the mesopause at altitudes of about 80 km [1]. The most widespread occurrence of amorphous ice is on interstellar dust, in comets, and many other astrophysical environments including the Saturnian rings [2]. The conditions of the formation of amorphous ices in nature vary greatly. Crystalline ice may amorphize under the influence of UV- or ion-irradiation [3,4]. On interstellar dust particles, amorphous solid water may form by chemical vapor deposition at 10 K, involving reaction of O, H, O₂, H₂ and OH, or by direct water vapor deposition onto dust particles. Also in the laboratory many routes to amorphous ices exist. Some of them are: a) deposition of water vapor onto cold substrates [5], b) ultrafast cooling of liquid water droplets [6], c) pressure-induced amorphization of crystalline ice [7,8], and d) temperature- or pressure-induced amorphous–amorphous transformations [9–12]. One of the main questions related to amorphous ices is the question

whether or not they are thermodynamically continuously connected with liquid states. If they were, then the amorphous ices would need to be regarded as vitrified liquids, i.e., glassy states. Alternatively the amorphous ices could be regarded as distorted crystalline phases, nano-crystals, or crystal-like states. A thermodynamic connection with the stable liquid at ambient temperature is very difficult to check, if not impossible, because amorphous ices crystallize very rapidly above the crystallization temperature T_x . Depending on pressure T_x is about 140–190 K [13–22]. While the liquid can be supercooled rather easily below the melting temperature it crystallizes very rapidly upon cooling below the homogeneous nucleation temperature T_H . Depending on pressure T_H is about 181–235 K [23]. That is, there is a gap of about 30–40 K width, in which crystal nucleation and growth are very rapid and can hardly be avoided. This gap, in which non-crystalline water cannot be observed on time scales exceeding 1 s, has become known as “no-man's land”. In very recent studies, using ultrafast probing of evaporatively cooled droplets, some unfrozen, liquid droplets could be investigated at temperatures down to 227 K at (sub-)ambient pressure after flight times of a few milliseconds [24]. The crystallization of ice can even be avoided altogether by ultrarapid cooling at rates $\geq 10^7$ K/s, whereas at cooling rates of 10^5 K/s a significant fraction of the droplets crystallizes [25]. After ultrafast cooling the droplets are in a vitrified liquid, glassy state called hyperquenched glassy water (HGW). By

* Corresponding author: Thomas Loerting, Institute of Physical Chemistry, University of Innsbruck, Innrain 80-82, A-6020 Innsbruck, Austria.

E-mail address: thomas.loerting@uibk.ac.at (T. Loerting).

contrast to the very recent study [24], in which in situ probing down to 227 K was possible, the droplets could not be studied in situ upon cooling in the “no-man’s land”, e.g., at 190 K for the hyperquenching experiment. Instead only the deposits typically stored at 77 K could be investigated [25]. Since HGW is produced by cooling stable liquid droplets fast enough to avoid crystallization it seems that there has to be a thermodynamic connection between HGW and stable liquid droplets [6,26,27]. The question whether quantities such as heat capacity show maxima or singularities upon cooling [28–30] is still unresolved, though. For amorphous ices produced via other routes the thermodynamic connection was even completely unclear until recently. This is especially true for amorphous ices which require pressure-induced amorphization of crystalline ices in the course of their preparation, such as high-density amorphous ice (HDA) [7,8]. However, the connection between the liquid and the amorphous state cannot be probed only upon cooling the liquid, but also upon heating the amorphous solid. Ultrafast heating and simultaneous ultrafast probing would be required to beat crystallization and to check for thermodynamic continuity within the no-man’s land. This has been out of reach in research on amorphous ices so far even though calorimetry methods reaching heating rates on the order of 10^5 K/s were employed to study them [31,32]. However, it has been possible to study whether or not a glass transition can be observed upon heating amorphous ice prior to crystallization and/or prior to the transformation to other amorphous ices [20,31–44]. This glass transition would lead to an ultraviscous liquid state which is also called deeply supercooled liquid water. If the glass transition was absent amorphous ice may either be crystal-like or glassy, but does not reach its liquid state prior to transformation. For HDA a crystal-like nature was suggested on the basis of inelastic neutron and X-ray scattering experiments indicating similarity to high-pressure ice polymorphs such as ice VI or ice IX [45–50].

Amorphous ices, glassy water, and (deeply) supercooled liquid water have been subject of several reviews in the last decade [28, 51–55]. These reviews have touched on the question regarding the glass transition in low-density amorphous ices. The present work expands on these reviews by focusing on the recent advances related to the possibility of a glass transition in HDA.

2. Ice polyamorphism

In terms of densities the amorphous ices can be grouped into three categories: low-density amorphous ices (LDAs), high-density amorphous ices (HDAs), and very-high density amorphous ices (VHDAs) [54]. As a function of pressure three linear regimes of amorphous ice bulk densities can be identified at temperatures just below crystallization [54]. The ambient pressure densities (at ~ 80 K) of the three amorphous ices are 0.93 ± 0.02 , 1.15 ± 0.02 , and 1.26 ± 0.02 g/cm³, respectively [56]. Especially after vapor deposition at low temperatures amorphous ices may be microporous [57] and show specific surface areas of up to 2700 m²/g [58]. Before annealing some of these ices may contain a large number of micropores, and show porosities of up to 70%. After annealing at temperatures > 120 K the micropores collapse and compact amorphous ices result [59]. The presence of empty pores reduces the overall densities significantly, while bulk densities are not affected. Amorphous ices of bulk ambient pressure densities < 0.90 g/cm³ and > 1.30 g/cm³ have not been identified so far. Also amorphous ices of densities of 0.96–1.12 g/cm³ are unknown. This gap in densities is a clear indication of what has become known as polyamorphism [60–62] – the occurrence of (at least two) amorphous forms of ice [9]. Furthermore, the polyamorphic ices differ significantly according to structural methods such as X-ray or neutron diffraction. All of them show a hydrogen-bonded network with tetrahedral coordination of water molecules. In particular, the number of interstitial water molecules can be employed to categorize the amorphous ices. LDA does not show any interstitial water molecules, whereas HDA and VHDA show one and two interstitials, respectively [63–65]. These interstitial

molecules are located at OO-distances of 3.0–3.4 Å from a (randomly chosen) central water molecule. They are not bonded to the central water molecule by hydrogen bonds, which are characterized by OO-distances of 2.77–2.85 Å [10], but are instead located in between the first and second coordination shells. Just like any water molecule in amorphous ices the interstitial water molecules themselves are tetrahedrally coordinated so that the Walrafen water pentamer can be regarded as the basic building block of all amorphous ices [66].

The term polyamorphism [60–62] was used in different ways in literature. It has been used not only in the correct sense, but also in flawed ways. “False polyamorphism” involves two (or more) amorphous states differing just in terms of the degree of relaxation. Among these amorphous states there are more stable and less stable ones. The less stable states relax continuously towards the more stable states, whereas a relaxation from the more stable to the less stable state will never be observed. That is, the relaxation is irreversible and only proceeds one way (monotropic). “False polyamorphism” is the same as relaxation. By contrast, “true polyamorphism” is understood to involve changes in topology, e.g., connectivity or the number of interstitial water molecules. “True polyamorphism” also necessitates that conditions can be found at which the polyamorphic states are at metastable equilibrium. That is, there is reversibility and the transitions may proceed in both directions with hysteresis (enantiotropic). For the amorphous ices, it is possible to switch back and forth between the three polyamorphic states by isothermal compression and decompression experiments [12,13,67,68]. In the case of the LDA \rightarrow HDA transition a very sharp transition involving a sudden 25% change in density is observed as a function of pressure, in spite of the low transformation temperature of 130 K [13]. The upstroke and downstroke transitions show hysteresis, with an equilibrium pressure of about 0.20 GPa; below which LDA is the most stable amorphous phase and above which HDA is the most stable amorphous phase [69,70]. Also in the case of HDA \leftrightarrow VHDA isothermal upstroke and downstroke transitions can be observed, with an equilibrium pressure of about 0.75 GPa [12,67]. Below 0.75 GPa HDA is the most stable amorphous phase, and above 0.75 GPa VHDA is the most stable amorphous phase. By contrast to the very sudden and sharp LDA \leftrightarrow HDA transition, the HDA \leftrightarrow VHDA transition is less sharp and involves a 10% density change smeared over a ≈ 0.2 GPa wide pressure interval. While we regard these experimental observations sufficiently meet the criteria for “true” polyamorphism, it was suggested from computer simulations of water models that VHDA may instead be a relaxed form of HDA [71–73].

Recent molecular dynamics simulations on ST2 water and the monatomic Fermi–Jagla potential have paved an experimentally tractable way of distinguishing true from false polyamorphism [74–78]. Both models show (true) polyamorphism in the glassy state and liquid–liquid separation at higher temperatures. The two amorphous states (LDA and HDA) in these models show two distinct glass-to-liquid transition temperatures T_g . That is, the observation of two well separated glass transition temperatures at a specific pressure indicates true polyamorphism. In the pressure–temperature plane two T_g lines, $T_{g,1}$ and $T_{g,2}$, can be defined. One of these lines pertains to the most stable amorphous/liquid state, and the other to an amorphous/liquid state metastable against the other amorphous/liquid state. The T_g line pertaining to the most stable amorphous/liquid state shows a discontinuity at the liquid–liquid coexistence line where there is a switch of the most stable amorphous state, and thus a switch from $T_{g,1}$ to $T_{g,2}$ [79]. By contrast, for other models such as SPC/E water, which do not show (true) polyamorphism the glass transition temperatures for all amorphous states coincide [74]. In such simulations the glass-to-liquid transition can be recognized by a sudden increase in mean-square displacement of oxygen atoms, a step-like increase in heat capacity or thermal expansivity or a kink in volume vs. temperature curves [74,80–83].

Co-existence of two amorphous ices was also found in other simulations [84], in agreement with experiments [85,86]. Instead of reaching two glass transition temperatures, both amorphous ices connect with

Download English Version:

<https://daneshyari.com/en/article/7901742>

Download Persian Version:

<https://daneshyari.com/article/7901742>

[Daneshyari.com](https://daneshyari.com)