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Spontaneous transformation of water's high-density amorph and a two-stage crystallization to ice VI at 1 GPa: A dielectric study

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Dielectric relaxation spectra of a metastable crystal phase formed on implosive and exothermic transformation of pressure-amorphized hexagonal ice have been measured *in situ* at 0.97 GPa pressure over a range of temperature. The metastable phase showed no relaxation peak at 130 K and 0.97 GPa. When heated at a fixed pressure of 0.97 GPa, it began to transform at ~ 145 K exothermally to a phase whose relaxation rate and equilibrium dielectric permittivity increased. A second, but slower exothermic transformation also occurred at ~ 175 K. After keeping at 213 K, the relaxation rate and equilibrium permittivity reached the known values of these two quantities for ice VI. Thus the metastable phase transformed to ice VI in two stages. It is conjectured that the intermediate phase in this transformation could be ice XII. The rate of transformation is not determined by the reorientational relaxation rate of water molecules in the ices. © 2004 American Institute of Physics. [DOI: 10.1063/1.1747946]

I. INTRODUCTION

Mishima *et al.*'s studies^{1,2} had shown that when hexagonal ice at 77 K is uniaxially compressed to 1.5 GPa, it transforms to an amorphous solid. Since the density of this amorphous solid was found to be higher than that of the vapor-deposited amorphous solid, they named it high-density amorph (HDA). Henceforth we refer to the amorph thus formed (at 77 K and 1.5–1.8 GPa) as HDA. The process of its formation from crystalline ice has become known as pressure amorphization. Mishima *et al.*³ also heated HDA at a nominal pressure of 100 bar at 1 K/min rate inside the vessel. When the temperature of HDA reached 125 K, they found that it transformed exothermally to another amorphous solid whose density was approximately the same as the density of hexagonal ice. It was named low density amorph (LDA).^{2,3} The manner of formation of these two amorphs, their properties and their interrelation have been reviewed by Debenedetti⁴ and by Guillot and Guissani.⁵ Therefore, a brief review of only the ices formed on crystallization of HDA is given here.

Crystallization of HDA to several high-pressure ices was first observed by Bosio *et al.*⁶ in the course of the x-ray diffraction study of the structure factors of HDA and LDA. They had found that the x-ray diffraction spectra of their HDA sample contained spurious Bragg peaks, and they attributed these peaks to “undesirable contamination of the sample by high-pressure crystalline forms of ice.” From a further analysis of the data obtained on several similarly prepared HDA samples, Bizid *et al.*⁷ reported the exact location of these spurious Bragg peaks (see Table I in Ref. 7) and

concluded that the spurious peaks could not be assigned to any known high-pressure phases of ice. Bellissent-Funel *et al.*⁸ also found spurious Bragg peaks in the diffraction studies of their HDA samples, but excluded those peaks from their data processing in favor of establishing the diffraction features of HDA, as Bosio *et al.*⁶ had done.

In 1998, Lobban *et al.*⁹ discovered a new metastable crystalline phase of ice in the stability region of ice V. It had accidentally formed when 1.5 ml of D₂O water at a fixed argon gas pressure of 0.55 GPa, and containing 0.1–0.2 g of silica wool was cooled from 270 to 260 K at the rate of 2.5 K/h—the cooling rate being crucial because a faster rate of 5 K/h produced ice V. They provided its neutron diffraction spectra, determined the unit cell parameters and named it ice XII. Koza *et al.*¹⁰ compared the known Bragg peaks of ice XII reported by Lobban *et al.*⁹ against the spurious Bragg peaks listed by Bizid *et al.*⁷ and concluded that the peaks reported by Bizid *et al.*⁷ corresponded to the Bragg peaks of ice XII. Therefore, ice XII was present in the HDA samples studied by Bizid *et al.*⁷ From their studies of HDA made by amorphizing hexagonal ice by the same procedure as Bosio *et al.*'s⁶ and Bizid *et al.*'s⁷ Koza *et al.*¹⁰ also concluded that “In all our samples, the contaminating crystalline phases can be indexed to ice XII, with no other crystalline modification being formed.” Further studies by Koza *et al.*¹¹ using similar experiments showed that ice XII is produced by compressing ice Ih at 77, 100, 140, and at 160 K to a pressure of 1.8 GPa, and that an increasing amount of ice III/IX also forms with increase in the temperature above 140 K, with successful formation of ice XII limited to a temperature below ~ 150 K. In some of the experimental assemblies used for amorphizing hexagonal ice (ice Ih),^{6–8,10,11} the piston had frequently friction jammed inside the pressure vessel during compression of ice Ih and during decompression of HDA at 77 K. Its

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unpredictable sudden release had caused sharp decreases, and increases, in the pressure, as has been shown in Fig. 2 of Ref. 7. Koza *et al.*¹¹ therefore suggested that a shock wave generated on sudden release of a friction-jammed piston had a role in the production of different high-pressure phases. Johari¹² had already reported that when indium or Teflon was not used to isolate ice Ih from the piston-vessel clearance, as in studies of Refs. 6–8 and 10 and 11, ice Ih had crept in the piston-cylinder clearance, and the resulting friction required an overpressure to displace the piston. The friction became high enough in some studies to sustain an overpressure of up to 0.1–0.15 GPa, and a sudden release of this friction produced a loud-explosion sound and a spike of temperature from 77 to 170 K. Kohl *et al.*¹³ proposed that this spike-type transient local heating could raise the temperature of HDA in to the ice V domain established in the equilibrium phase diagram,² i.e., above 207 K, and could produce ice XII—a domain in which Lobban *et al.*⁹ had originally formed it by cooling water at 0.55 GPa. Since HDA forms at pressures above 0.8 GPa, this seems incompatible with formation of XII by transient heating of HDA to above 207 K, and into the stability domain, 0.35–0.63 GPa,² for ice V during pressure amorphization.

A detailed study of the transformation of HDA by Klotz *et al.*^{14,15} has since shown that ice II, ice V, and ice III/IX, and a mixture of ice IV and ice XII or of ice VI and ice XII form on programmed *in situ* heating of HDA at fixed pressures in the range 0.3–1.2 GPa, with ice III/IX forming at the lowest pressure, before transforming to II. Salzmann *et al.*¹⁶ have also reported that, on heating at the rate of 960 K/h, HDA kept at 0.81 GPa transforms to ice XII beginning at 166 K and ending at 169 K. Since HDA transforms irreversibly to ice XII, we conclude that the temperature rise of up to ~170 K found by Johari¹² could also be partly due to the exothermic effect of HDA's transformation to ice XII and/or to other high-pressure crystalline ices.

It must also be noted that in 1998, Chou *et al.*¹⁷ had reported microscopic observations of the slow growth of a crystal phase of ice in pure water contained in a diamond anvil cell at 0.774 GPa and 280.8 K. The crystal's density was 1.212 g/ml [see Fig. 2F in Ref. 17]. They¹⁷ also studied the high-pressure ice crystal's Raman spectra and found it to be different from the Raman spectra of the known high-pressure phases of ice. They called it a new ice phase, partly because lack of more data prevented them from speculating on its relation with the new phase discovered by Lobban *et al.*⁹ (See note 24 in Ref. 17.) Later studies by Salzmann *et al.*¹⁸ found that the features in the Raman spectra of ice XII, which they produced by heating HDA and identified it by x-ray diffraction using the Bragg peaks reported by Lobban *et al.*,⁹ were the same as the features of the Raman spectra of the new phase reported by Chou *et al.*¹⁷ Salzmann *et al.*¹⁸ concluded that the new phase of Chou *et al.*¹⁷ is in fact ice XII. However, we point out that the density of 1.212 g/ml at 0.774 GPa at 280.8 K of Chou *et al.*'s¹⁷ new ice phase seems to be inconsistent with the density of 1.293 for H₂O ice XII (1.4365 for D₂O ice XII) at 0.5 GPa and 260 K⁹ for the following reason: Even if we ignore the increase in the density expected on increase in pressure by 0.27 GPa, the

density decrease by 0.081 (1.293–1.212) g/ml on increase in temperature by 20.8 (=280.8–260) K leads to a volume thermal expansivity of $3.0 \times 10^{-3} \text{ K}^{-1}$, which seems too high a value for a crystal phase.

Kohl *et al.*¹³ used the volume changes to follow the pressure amorphization of ice Ih, as Mishima *et al.*^{1,3} had done, and identified the solid phases recovered at 77 K and ambient pressure by using x-ray diffraction. They concluded that ice XII does not form on accidental heating of ice Ih. Instead, it forms on accidental heating of HDA. Thus pressure amorphization of ice Ih occurs before ice XII forms. Loerting *et al.*¹⁹ and Salzmann *et al.*²⁰ found that controlled heating of HDA at fixed pressures of 0.81–1 GPa also produces ice IV, and ice VI along with ice XII, depending upon the heating rate.

Thus, Bosio *et al.*'s⁶ report of undesirable contamination of the HDA by high-pressure crystalline ice phases has led ultimately to the discovery that ices III, IX, and XII form during amorphization of ice Ih,¹¹ and that ices IV,^{14,15,21} V,¹⁵ and VI^{14,15,19} form when HDA is heated at a controlled rate. However, ice XII also forms when HDA becomes accidentally heated during the course of ice Ih amorphization,¹³ or is deliberately heated at a fast rate.¹⁸ In some cases, this occurs outside their pressure–temperature regions in the equilibrium phase diagram of the ices. As a result of the discovery of these irreversible transformations, pure ice IV and ice XII can now be prepared in gram amounts²⁰ for study at ~77 K and ambient pressure.

By performing *ex situ* studies of the phases recovered at ambient pressure and 77 K and using x-ray diffraction, Loerting *et al.*¹⁹ have found that ice XII, which they had produced by heating HDA, exists in the 0.7–1.5 GPa and 158–212 K ranges. Moreover, based on Kohl *et al.*'s²² measurements of the enthalpy of (irreversible) transformation of ice XII to cubic ice at ambient pressure and its comparison against the known enthalpy of transformation of ice VI to cubic ice,²³ they discussed the possibility that ice XII has a low-temperature region of stability within the ice VI domain and further outlined a pressure–temperature region (hatched area in Fig. 1 of Ref. 19) for the formation of ice XII. In this region ice VI has been known to be the stable phase (see ice phase diagram in Ref. 2). Since the enthalpy release was more for ice VI than for ice XII at ambient pressure, they concluded that orientationally ordered ice XII can become more stable than ice VI in the 0.7–1.5 GPa and 158–212 K ranges.¹⁹ But Johari's calculations²⁴ showed that when the effect of pressure on the Gibbs energy is taken into account, the energy of ice XII in this pressure range is, instead, higher than that of ice VI. Therefore, ice XII is likely to be less stable than ice VI at high pressures.

We have been investigating the mechanism of pressure amorphization of ice Ih and Ic and crystallization of the amorphs by *in situ* thermal conductivity and dielectric spectroscopy studies performed in real time. In the course of one of such investigations, we have found that when ice Ih at ~130 K is compressed at a slow rate and the pressure reaches 0.8–1 GPa, an implosive transformation occurs and the sample's temperature abruptly increases as a result of the transformation. Thereafter, on heating at a slow rate at that

pressure, the ice phase formed gradually transforms, by a two-stage process, to ice VI. Here we report these studies and discuss their consequences for our understanding of the amorph formed at high temperatures, and of its transformations to different crystalline phases in their thermodynamically nonequilibrium state.

II. EXPERIMENTAL METHODS

A parallel plate capacitor consisting of six plates, each separated by the other by ~ 1.5 mm with polyetheretherketone spacers, was constructed from stainless steel. Its empty capacitance was nominally 32 pF. The capacitor was placed inside a 37 mm internal diameter Teflon container which itself closely fitted inside the high-pressure cylinder of internal diameter 45 mm of a high-pressure assembly. The Teflon cell was filled with ~ 25 ml of water purified by using Milli-Q[®] Ultrapure WaterSystems. It was sealed with a tightly fitting, 5 mm thick Teflon cover and the piston inserted. The whole assembly was placed in a vacuum chamber and load was applied by using a 5 MN hydraulic press. The pressure in the cell was determined from the ratio of load to area to which a correction for friction was applied. This correction had been previously established in a separate experiment by using the pressure dependence of the resistance of a manganin wire. The pressure of the hydraulic oil used to push the piston into the cylinder was computer controlled at the desired rate of increase or decrease. The temperature was varied by cooling the whole pressure vessel by using a built-in helium cryostat equipped with a heater. The temperature and pressure of the sample were computer monitored continuously during the course of the experiment, and the capacitance and conductance of the dielectric capacitor immersed in the ice sample were measured in real time.

The capacitance and conductance were measured at frequencies in the range 1 Hz–1 MHz by means of an impedance analyzer, Solartron 1260, and the dielectric permittivity and dielectric loss of the sample were determined for each frequency. The geometric capacitance of the stainless steel capacitor was determined by using the known dielectric permittivity, ϵ' , of ice Ih of 3.1 ± 0.05 at 1–10 kHz measurement frequency and ambient pressure and low temperatures, as reported by Johari and co-workers.²⁵ (Johari and Whalley²⁶ had also found that for ice Ih, ϵ' at temperatures below 170 K at 10 kHz, was within 0.1% of the limiting high-frequency value of its dielectric permittivity ϵ_∞ and Gough²⁷ have shown that ϵ_∞ decreases from 3.16 at 253 K to 3.093 at 2 K.) Of further relevance to our study are the earlier findings²⁸ that an increase in pressure from ambient to 0.2 GPa reduces the contribution from orientation polarization as the relaxation peak shifts to lower frequencies, increases its optical refractive index, and decrease the contribution from the infrared polarizability. These changes had been determined by measuring the frequency of translational lattice vibrations of ice Ih as a function of both temperature and pressure by Johari *et al.*²⁸ The net effect on ϵ' , which already approaches the value of ϵ_∞ , is thus expected to be less than 1%. After including the measurement errors, we estimate that our ϵ' and dielectric loss data are accurate to better than 3%.

In our experimental procedure, the high-pressure vessel containing water under a pressure of 0.05 GPa was cooled from room temperature to about 100 K at an average rate of 17 K/h. After ice Ih had formed, the temperature was raised and stabilized at 125–130 K, which took a total of 10 h. The pressure was then increased at the rate of 0.1 GPa/h. The heating and cooling rates (near 150 K) used in this study were typically 15 and 10 K/h, respectively. Thus, one set of experiments took a continuous period of several days during which time the pressure and temperature of the sample were continuously monitored. The data are accurate to within ± 0.05 GPa for pressure (at 1 GPa and 100 K), and ± 0.3 K for temperature.

A second experiment was performed in a similar manner by using a concentric electrode dielectric cell made from copper. The change in the geometry of this cell on raising the pressure from ambient to 1 GPa is regarded as insignificant. (Magnitude of this change has been estimated by Johari and Whalley²⁹ for similar dielectric cells made from a 2% Be–Cu alloy, but with the outer electrode itself acting as a pressure vessel which increased the interelectrode distance on pressurizing.) The results obtained by using this concentric electrode cell agreed, within the experimental errors, with the results obtained by using the above-mentioned parallel plate cell whose cell constant had been determined from the ϵ' value of 3.1 for ice Ih as a standard.

III. RESULTS

During the slow pressurization of ice Ih at a fixed temperature of 130 K, the temperature and pressure of the sample were automatically measured at time intervals of 20 s. During the heating and cooling of the samples, the spectra of dielectric permittivity and loss, ϵ' and ϵ'' , were determined at fixed temperature intervals of 5 K. The time taken to measure the spectra was 90 s, and therefore the change in the temperature that occurred during the measurement of the spectra was less than 0.4 K. This change was neglected. When the pressure on ice Ih at 130 K was increased and it reached 0.97 GPa, i.e., a pressure near the end of its transformation range to a high-density amorph at 130 K, an implosion of the sample occurred. As a result, the pressure on the sample instantly decreased to 0.85 GPa and the temperature rose from 130 to about 165 K. The programmed controls restored the pressure to 0.97 GPa in about 3 min and the temperature to 130 K in about 9 min. Since the spectra were collected at 5 K intervals, the spectra at the exact instant of transformations observed here are not available. A comparison of the ϵ' and ϵ'' spectra measured before and after the implosive transformation at 130 K and 0.97 GPa showed no significant change in its shape within the experimental errors. The lack of significant change is likely due to the fact that the value of ϵ' was already low at 3.47, and ϵ'' was less than 0.04, which indicate that contributions to ϵ' and ϵ'' from the relaxation part of the spectra were already minimum and the spectrum was close to that of a dielectrically unrelaxed state. Because of the long electrical leads and the neglected corrections for their length, the measured values at such low magnitudes of ϵ' and ϵ'' were most accurate in the 1–10 kHz range. The values measured at

FIG. 1. (A) The excess temperature measured during heating of the transformed phase at 0.97 GPa. (B) The ϵ' (■) and ϵ'' (○) of the transformed phase measured at a fixed pressure of 0.97 GPa and a frequency of 1 kHz are plotted against the temperature. The inset shows ϵ' in the vicinity of the exothermic transition. The rate of heating was 18 K/h.

1 kHz frequency showed that on transformation, ϵ' increased by 0.03, ϵ'' decreased by 0.02, and $\tan \delta (= \epsilon''/\epsilon')$ decreased from 0.006 to 0.002.

The sample was then heated from 130 to 213 K at the rate of 18 K/h and the spectra were collected in real time at 5 K intervals. When the sample's temperature reached 145 K, an abrupt rise in its temperature and decrease in pressure occurred and continued for a short time. This shows that the sample at 0.97 GPa was transforming to a denser, high-pressure phase exothermally. The rise of the temperature during this transformation appears as the first (sharp) peak in the plot of the excess temperature against the temperature itself in Fig. 1(A) measured *in situ*, in real time. The ϵ' and ϵ'' values of the sample also changed on this transformation. To show the extent of this change, ϵ' and ϵ'' measured for a fixed frequency of 1 kHz are plotted against the temperature in Fig. 1(B). The inset in Fig. 1(B) shows an enlarged scale the manner in which ϵ' at 1 kHz changes on heating. Its value increases in a sigmoid shape manner, approaching a plateau value, but this approach is interrupted by another increase which is only partly shown here, up to a temperature of 187 K.

The ϵ' and ϵ'' spectra measured on heating the sample from 130 to 213 K at 18 K/h are presented in Fig. 2. Since irreversible, kinetically controlled transformations occur

FIG. 2. The ϵ' and ϵ'' spectra of the ice phase formed after transformation at 0.97 GPa and measured at 0.97 GPa in real time during the heating of the sample. The temperature and time in minutes (in parentheses) at which the spectra were measured are indicated. The rate of heating was 18 K/h.

with rates that are both time and temperature dependent, it is necessary to indicate the time at which the spectra were measured. This time was counted in minutes from the instant the impulsive transformation occurred at a fixed pressure of 0.97 GPa at 130 K, and both the temperature of the sample and this time are noted in Fig. 2.

After the sample reached 213 K during the programmed heating, it was kept isothermally for about 5 min and then cooled at an initial rate of about 20 K/h, while its spectra were being measured in real time at 5 K intervals. These spectra are shown in Fig. 3, where the temperature and time of the measurements have also been noted.

IV. DISCUSSION

A. Transformations during amorphization of ice Ih

It has been reported that HDA further densifies gradually when heated at a high pressure and that in some cases high-pressure crystalline ice phases also form during pressure amorphization of ice Ih.¹⁹ Therefore, it is necessary to consider the following questions: (i) did the amorphization at 130 K and 0.97 GPa, produce the same HDA as the amorphization at 77 K? and (ii) did some high-pressure crystalline ices also form during the amorphization?

In order to determine the nature of the high-density amorph formed when ice Ih at 130 K was pressurized to 0.97 GPa, it is necessary to consider the relevance of two recent

FIG. 3. The ϵ' and ϵ'' spectra of the ice phase at 0.97 GPa that had formed on heating [plot in Fig. 1(B)] to 213 K and thereafter keeping for 5 min at 213 K, as measured in real time. The sample was being cooled at 20 K/h from 213 K. The temperature and time in minutes (in parentheses) at which the spectra were measured are indicated.

findings: (i) Loerting *et al.*'s³⁰ finding that when HDA at a pressure in the range of ~ 0.8 – 1.9 GPa is heated from 77 to 165 K it gradually densifies by $\sim 9\%$ to a very high-density amorph (VHDA), and (ii) Johari and Andersson's³¹ finding that instead of there being just two high-density amorphs, HDA and VHDA, there may be a continuity of different amorphs of densities varying between those of VHDA and HDA, which may be obtained by isothermally keeping HDA at a fixed pressure above 0.8 GPa at different temperatures. This seems analogous with Tulk *et al.*'s³² conclusion that a multiplicity of different amorphs are formed when HDA at ambient pressure is kept isothermally at different temperatures and that there is *not* just one HDA but a continuity of amorphs of different densities between those of HDA and LDA.³² This means that there would be a continuity of different amorphs of structures between those of VHDA and LDA, which form under different temperature, time, and pressure conditions.

Of quantitative relevance for our purpose are the plots of volume decrease against pressure provided by Loerting *et al.*^{19,30} From the plot in Fig. 1(B) of their Ref. 30, we estimate that $\sim 60\%$ of the net volume decrease on HDA's conversion to VHDA on heating from 77 to 160 K at a nominal pressure of 1.1 GPa had occurred when the temperature of HDA reached 130 K. Ice Ih in our study reached a pres-

sure of 0.97 GPa at 130 K before implosion, which is comparable to the nominal pressure of 1.1 GPa. If the structure of the amorph formed at 130 K and ~ 1.1 GPa in Ref. 30 was to be independent of the temperature–pressure path (i.e., the state of the amorph was ergodic) then the observations from Fig. 1(B) in Ref. 30, on combining with our results, would mean that the amorph formed in our study at 130 K and 0.97 GPa had already $\sim 60\%$ transformed to VHDA, i.e., instead of HDA, an amorph of a density between those of HDA and VHDA had existed at 130 K and 0.97 GPa. Alternatively, if the structure of the amorph formed at 130 K and ~ 1.1 GPa in Ref. 30 was to depend on the temperature–pressure path (i.e., the state of the amorph was nonergodic), then the structures of the amorph formed here may not be the above-mentioned 60% densified state of HDA. Unfortunately, it is not known what the relaxation times of the various high-density amorphs at the pressure and temperature conditions of their formation are. Also, it is not possible to know how the recently discovered time effect on ice Ih amorphization³¹ effects our view of the densification of HDA during heating at 0.81 GPa observed in Ref. 30. Whether the state of the amorph at 130 K is found to be ergodic or not, we should not regard the thermodynamic and structural states of the amorph at 0.97 GPa and 130 K the same as those of HDA.

We now consider the type of crystalline ices that could also form during the amorphization of ice Ih in our study. From *ex situ* neutron diffraction studies of the ices at ambient pressure, Koza *et al.*¹¹ have observed that when ice Ih at 77 K is pressurized to 1.8 GPa at a rate of 1 GPa/min, or pressurized at 100 K to 1.8 GPa at a rate of 0.5 GPa/min, ice XII is formed. On pressurization at 140 K and higher temperature, ices III and/or IX also formed with ice XII, and almost no XII formed on pressurization at 160 K. Thus they showed¹¹ that fast compression of ice Ih in less than 2 min produced ice XII. But Kohl *et al.*¹³ have reported that ice XII forms from HDA, and not from ice Ih, i.e., HDA forms first and, when its density exceeds 1.1 g/ml, it transforms to ice XII on fast heating. In their study, this heating occurred accidentally as a result of the shock wave produced by the release of the friction-jammed piston in the vessel. Since friction jamming of the piston did not occur in our study, and the implosion was a result of phase transformation, not its cause, none of these ice phases could have formed in the same way here.

B. Crystallization of HDA on heating at high pressures

As mentioned in Sec. I, when HDA is heated at a high pressure, it crystallizes to a number of high-pressure ice phases,^{6,7,10,11,14,15,18–22} depending upon the temperature, pressure, and heating rate. These ice phases are not kinetically and thermodynamically stable in the pressure–temperature conditions of their formation. Briefly, Salzmann *et al.*^{20,21} have concluded that HDA at nominally 0.81 GPa crystallizes to pure ice IV when heated at a rate of 24 K/h (0.4 K/min). But it crystallizes to a mixture of ice IV and ice XII when heated at a rate between 24 and 900 K/h, and crystallizes to pure ice XII when heated at a rate higher than 900 K/h (see Fig. 3 in Ref. 21). Moreover, they showed that

“additional slow heating of ice IV from 162 to 195 K does not lead to the formation of ice XII from ice IV,”²¹ and that ice XII formation from HDA ends when temperature reaches ~ 172 K.²¹ Also, Loerting *et al.*¹⁹ have reported that heating of ice XII at 0.7–1.5 GPa converts it to ice VI when the temperature reaches ~ 212 K.

Klotz *et al.*'s^{14,15} *in situ* neutron diffraction studies had already shown similar crystallization of HDA to mixtures of ice IV and ice XII. They had also found that on heating to 165 K, HDA(D₂O) at pressures of ~ 1 –1.5 GPa crystallized to a mixture of ice VI and ice XII. But, when a mixture of ice XII and HDA was heated in similar conditions, no significant increase in ice XII occurred, and HDA in the mixture transformed to ice VI. This suggests that the preferred transformation of HDA in this case was to ice VI, even when ice XII had been present.

As discussed earlier here, the amorph formed at 130 K is denser than HDA, and therefore its crystallization on heating at a high pressure would not necessarily produce the same ice phases as crystallization of HDA in the above-mentioned studies. There is also a difficulty in comparing our results with those of the earlier studies, because the temperature of a kinetically controlled phase transformation increases with the increase in the heating rate, and that increase can make an ice phase, formed on crystallization of HDA, to appear in the pressure temperature domain of another ice phase. We conclude that the crystalline ices obtained by heating different high-density amorphs at different rates are determined by both the state of the parent amorph and the time–temperature dependence of the transformation rate of (metastable) crystalline ices. There seems to be no accurate way of predicting which ice phase will form.

In an earlier study³³ of the thermal conductivity change during the amorphization of ice Ih, we have reported that the amorph formed at 130 K and ~ 1 GPa abruptly transformed to a higher-density crystalline ice phase. Thermal conductivity of this phase was found to be distinct from those of any known high-pressure ices. The pressure decrease and temperature increase observed on the implosive transformation in that study is similar to that observed on implosive transformation here. Unfortunately, our massive, high-pressure assembly, which is kept under vacuum, neither allows *in situ* studies by diffraction methods nor does it allow rapid cooling of the sample to ~ 77 K at high pressures and subsequently extracting the sample at ambient pressure rapidly enough to avoid heating above 100 K. Therefore, we will discuss the identity of the metastable state and the high-pressure ices in the light of our dielectric and calorimetric studies in Sec. IV E.

In the context of formation of new metastable phases from HDA, Tulk and Klug's³⁴ study of a crystal phase of ice made by grinding HDA in liquid nitrogen at ambient pressure³⁵ should be briefly discussed. In the Raman spectra studies of this phase, they found³⁴ that its O–D stretching band is at 2424 cm^{-1} . They stated “There are a limited number of crystalline phases that may have been formed, and these can be individually ruled out with the exception of ice XII.”³⁴ By comparing the frequency of the Raman bands of their ice phase against the known frequency of Raman bands

of other ices, they ruled out the possibility that ice IV, ice V, or ice VI could have been produced. When they scaled the observed O–D stretching frequency of their crystalline ice phase with the O–O distance according to the known relation, they found that the scaled O–O distances is $2.763\text{ \AA}$, which is consistent with the value of $2.766\text{ \AA}$ reported by Lobban *et al.*⁹ for ice XII. Hence, they concluded that their crystalline phase was ice XII. A further study of its transformation by Raman spectroscopy showed that when the ice sample was annealed at 120 K and ambient pressure, it transformed to LDA and thereafter, on heating above 120 K, to cubic ice. Salzmann *et al.*¹⁸ also measured the Raman spectra of an x-ray characterized ice XII, which they had made by heating HDA at 0.81 GPa to 180 K at a rate of 1500 K/h, and compared its spectra against the Raman spectra of Tulk and Klug's³⁴ crystal. They found that the two spectra differed, and therefore concluded that Tulk and Klug³⁴ had *not* made ice XII.¹⁸ On the basis of these observations, we conclude that the crystal phase produced by Tulk and Klug³⁴ was probably a new crystal phase of ice, which had formed either during the pressure amorphization at 77 K or on mechanical deformation and possible heating during the grinding process of HDA. As already mentioned earlier here, Chou *et al.*¹⁷ had also made a new crystalline ice phase at 280.8 K and 0.774 GPa, which Salzmann *et al.*¹⁸ later identified as ice XII, but its thermal expansion coefficient seems inconsistent with the value usually found for the ices.

C. Dielectric properties of the phases formed

The ϵ' and ϵ'' spectra in Fig. 2 show that as the transformed ice phase is heated, both ϵ' and ϵ'' increase, and a relaxation peak in ϵ'' appears at 158.5 K. Its height increases slowly on heating up to 193.9 K and then rapidly on further heating to 211.7 K. Since the ϵ' and ϵ'' spectra were collected at 5 K intervals, spectra at the maximum temperature of 213 K could not be measured in this programmed heating. With the passage of time, from 2.2 to 5.3 h, and increase in temperature from 158.5 to 211.7 K, the ϵ'' peak shifts to higher frequencies. The low-frequency side of the spectra has become distorted by the dc conductivity and interfacial polarization effects which raise both ϵ' and ϵ'' . Still, the frequency at which the ϵ'' peak appears, f_{max} , and which corresponds to the relaxation rate, can be accurately determined. Its value is plotted against the temperature in Fig. 4(A). Also, the value of ϵ'' at the relaxation peak, ϵ''_{max} , was determined and it is plotted against the temperature in Fig. 4(B). As in most studies of ices, the equilibrium dielectric permittivity ϵ_0 , which is equal to the low frequency plateau value of ϵ' due to orientation polarization, could not be accurately determined because of the contributions from interfacial polarization. This value was estimated by constructing the complex plane plot, as done earlier.²⁹ It is ~ 210 at 211.7 K.

Dielectric properties of all high-pressure ices except for ice IV had been studied by Whalley and co-workers in the 1960s and 1970s. Such properties of ice XII have also not yet been studied. Among the phases that have been known to form on crystallization of HDA, values of f_{max} and ϵ_0 of

FIG. 4. (A) The $f_{\max}$ of the ice phases at 0.97 GPa formed during the heating (■) and thereafter cooling (□) is plotted against the temperature. (B) The corresponding plots of $\epsilon''_{\max}$. The values were determined from the spectra given in Figs. 2 and 3.

only ice V and ice VI are known at such low temperatures as those in our study (ice IX being an antiferroelectric phase, shows no dielectric relaxation³⁶). At 211.7 K, $f_{\max}$ of the ice phase formed here is 800 Hz. The recently published values for $f_{\max}$ and ϵ_0 for ice V are 620 Hz and 140, respectively, at 0.61 GPa and 212 K.³⁷ Clearly, $f_{\max}$ of 800 Hz and ϵ_0 of ~ 210 for the ice phase formed here do not agree with the corresponding values for ice V.

From Johari and Whalley's²⁹ study of ice VI at a pressure of 1.1 ± 0.05 GPa, we estimate $f_{\max} = 960$ Hz from their Fig. 6, and $\epsilon_0 = 215$, from their Fig. 3 at 211.2 K. These values clearly agree with the values of $f_{\max} = 800$ Hz and $\epsilon_0 = 210$ at 211.7 K determined here, even when the small shift in the apparent $f_{\max}$ to a lower frequency and increase in the apparent ϵ_0 as a result of the dc conductivity and interfacial polarization contributions are not taken into account. (Note that ϵ'' of our sample has a larger contribution from dc conductivity than ϵ'' of the ice VI sample in Ref. 29 and this contribution alone would yield a lower apparent value of $f_{\max}$.) We also read the $\epsilon''_{\max}$ value for ice VI from the plots in Fig. 3 of Ref. 29. This value is 93 at 211.2 K at 1.1 ± 0.05 GPa, which agrees with the value of $\epsilon''_{\max}$ of 96 observed here.

The ϵ' and ϵ'' spectra in Fig. 3, which were measured after keeping the sample for 5 min at 213 K and then on cooling, show that both ϵ_0 and $\epsilon''_{\max}$ increase with decrease

in temperature, and that these values are now higher than those measured at the same temperature during heating. The $f_{\max}$ and $\epsilon''_{\max}$ values were determined from the spectra and these are plotted in Figs. 4(A) and 4(B), respectively. The plots show the difference between the $f_{\max}$ as well as that between $\epsilon''_{\max}$ values of the high-pressure ice phase formed on heating and on cooling. The difference demonstrates that on heating from 130 K at 0.97 GPa, the ice phase had been continuously transforming to other phases and that the transformation was complete only when the temperature reached 211.7 K and ice VI had formed. But it is not certain as to which phase had been forming on the initial heating from 130 K at 0.97 GPa.

D. Two-stage crystallization transformation

We now discuss the manner in which the transformation on heating occurs ultimately to ice VI. This may be done by plotting $\epsilon''_{\max}$ of the transforming mixture against the temperature, as shown in Fig. 4(B). (Note that we cannot consider the extent of transformation to ice VI because an intermediate phase is formed.) It is evident from the plot in Fig. 4(B) that $\epsilon''_{\max}$ of the transforming mixture increases slowly initially. It then increases in a stretched sigmoid manner and tends to approach a plateau value at $\epsilon''_{\max}$ of ~ 50 at 185 K. Starting from this approximate plateau value, $\epsilon''_{\max}$ increases again in a stretched sigmoid manner and tends towards a plateau value of $\epsilon''_{\max}$ of ~ 96 at 211.7 K. The manner of the increase in $\epsilon''_{\max}$ indicates that when the metastable phase is heated at 18 K/h rate, it begins to transform at 145 K to a high-pressure ice phase whose ϵ_0 is ~ 105 at 178.7 K. On further heating, this phase transforms gradually to ice VI whose ϵ_0 is ~ 210 at 211.7 K. This shows that two kinetically controlled transformations of the metastable phase occur on its slow heating from 130 K. These two transformations are also evident from the plot in Fig. 1(A), which shows a large exothermic effect (temperature increase) in the 145–151 K range and a slow and small exothermic effect in the 175–185 K range.

The second stage of the transformation, in the 145–212 K range, is undoubtedly to ice VI. Nevertheless, we reiterate that Salzmann *et al.*,²⁰ Loerting *et al.*,¹⁹ and Klotz *et al.*^{14,15} had studied crystallization of a sample of HDA (prepared at 77 K) and that the temperature, pressure, and heating rates in their study were different from those in our study. Therefore, the temperatures of transformation and the stability range of ice VI relative to other high-pressure ice phases observed here cannot be directly compared with their studies. Briefly, crystallization of their samples of HDA had produced pure ice IV or pure ice XII²¹ or a mixture of ice IV and ice XII^{14,15,21} or even a mixture of ice VI and ice XII.¹⁵ Heating of an ice IV and ice XII mixtures by Klotz *et al.*¹⁵ at about 0.65 GPa had ultimately produced pure ice IV and heating of a mixture of ice VI and ice XII by Loerting *et al.*¹⁹ at 1.5 GPa had produced pure ice VI. In our studies we have confirmed only that the ultimate phase formed on heating is ice VI.

Loerting *et al.*¹⁹ have found that ice XII, produced by rapid heating of HDA, exists in the temperature range of

158–212 K and at pressure of 0.7–1.5 GPa. They discussed the possibility that ice XII may become more stable than ice VI, and provided a pressure, temperature region (Fig. 1 in Ref. 19) in which their ice XII existed, although they were aware that in the phase diagram of the ices, only ice VI is stable in that region.² Our study shows that at 0.97 GPa and temperatures above 175 K, ice VI is the stable phase, as deduced earlier²⁴ from the Gibbs energy calculations, and not ice XII. It is conceivable that ice XII brought into the ice VI region by rapid heating of HDA in Loerting *et al.*'s study¹⁹ could transform to ice VI when kept in that region for a longer duration than allowed in their experiments.

E. Nature of the high-pressure ices formed

As explained earlier here, the ice phases formed in our investigation could not be studied by x-ray diffraction, and therefore they remain structurally unidentified. Also, a comparison of these studies against the studies on HDA's transformation would not be meaningful because the amorph formed here is not the same as HDA. Moreover, the nature of the crystallized phase itself and the temperature, pressure, and rate of irreversible crystallization all depend upon: (i) the type and amounts of contaminant crystalline phases in the amorph, which may act as nuclei or seeds and (ii) the rate of molecular diffusion, which also varies with pressure and temperature. Therefore, the question as to whether a new crystalline ice phase, or a mixture of different known high-pressure crystalline ices were formed here is not resolved. We recall that except for ice Ic and ice XII, all stable and metastable phases of ice were discovered by observing changes in their volume, dielectric, and other properties at certain pressures and temperatures, and therefore there is merit in investigations that do not provide structural details.

Implosive transformation of the amorph at 0.97 GPa and 130 K to the metastable phase, as noted earlier here, had raised the sample's temperature to 165 K and lowered the pressure to 0.85 GPa. When this phase was slowly heated after automatic restoring the 0.97 GPa and 130 K, it showed a pronounced exothermic transformation already at ~ 145 K, as seen in Fig. 1(A). Therefore, it seems that rapid temperature change associated with the implosion prohibited the transformation seen at ~ 145 K on slow heating. Earlier studies of crystallization¹⁹ have found that HDA at nominally 1.09 GPa transforms to ice XII rapidly at 160 K when heated at a rate that changed linearly from 6 K/min at 110 K to 1.5 K/min at 240 K, and that this temperature varies with both the pressure and the heating rates.¹⁸ Even though Loerting *et al.*¹⁹ could detect a much weaker endotherm of the glass–liquid transition of glycerol to within ± 2 K¹⁹ at ambient pressure by a thermocouple attached to the outside of the pressure vessel, Salzmann *et al.*^{20,21} did not report a temperature rise at the sudden transformation of HDA at 0.81 GPa pressure to ice XII in their 16 K/min heating experiments. Moreover, the plots in Refs. 16 and 20 show almost no change in the temperature at the abrupt HDA to ice XII transformation. This indicates that neither our high-density amorph is the same as their HDA nor our metastable phase is ice XII.

That the implisively transformed ice phase could be ice XII seems to be ruled out by the following four observations:

(i) The metastable phase here transforms to ice VI in two stages, whereas ice XII had transformed to ice VI in one stage.

(ii) In the two-stage crystallization to ice VI seen in Figs. 2 and 4(B), the dielectric spectra for the first stage of transformation shows that when the metastable phase is heated, its $\epsilon''_{\max}$ increases from a value that has been too low to be measured here at temperature below 149 K. (The concomitant increase in $f_{\max}$ is a result of increase in the temperature.) This means that the transformation is occurring at a phase whose equilibrium permittivity is higher than that of the metastable phase. If both phases were crystalline ices, it would indicate that a less proton-disordered phase is converting to a more proton-disordered phase. But the Raman spectra of ice XII at ambient pressure has shown it to be fully proton disordered,¹⁸ not partially proton ordered.

(iii) Figure 1(A) shows that the (first-stage) transformation of the metastable phase is highly exothermic. This differs from the earlier studies in which no temperature rise during the course of transformation of ice XII to ice VI had been found¹⁹ even when the measurements were sensitive enough to follow the weak glass transition endotherm of glycerol within ± 2 K.¹⁹

(iv) Transformation of the metastable phase occurs here at ~ 145 K, but transformation of ice XII at 0.84 or 1.09 GPa had occurred at a temperature above 212 K when heated linearly from 6 K/min at 110 K to 1.5 K/min at 240 K (Fig. 2 in Ref. 19).

One may also conjecture that the metastable phase in our study may be a mixture of ice IV and XII which has been known to form only when HDA is heated at rates less than 15 K/min.²¹ Also, Koza *et al.*¹¹ had found that a mixture of III and XII had formed on pressurizing ice Ih at a very fast rate at ~ 140 K or higher temperature. They suggested that a shock wave generated during compression had a role in the formation of high-pressure ices. In our procedure, the piston moved without extraordinary large friction and therefore there were no shock waves caused by sudden releases of the piston. However, we test the conjecture that a mixture of high-pressure ice phases exists in the range 150–212 K by determining the change in the shape of ϵ'' spectra at various stages of the transformations as follows.

In a heterogeneous mixture of two ice phases of different relaxation rates, the ϵ'' spectra would show two peaks corresponding to the two phases. These peaks may remain unresolved if the respective relaxation rates as well as the respective contributions to orientation polarization are only slightly different. But, if the relaxation rates differed, the peaks would be well resolved and a detailed shape of the spectra would change as the phase transformation continues and one peak grows at the expense of the other under isothermal conditions. This change would be more clearly seen when contributions to orientation polarization from the two phases are of comparable magnitude and less clearly seen when they differ by a large magnitude. When the transformation is observed by changing the temperature instead of isothermally, the ϵ'' spectra also usually become narrower with the in-

FIG. 5. (A) Normalized loss $\epsilon''/\epsilon''_{\max}$ plotted against normalized frequency at 168.6 and 183.8 K on heating. (B) The corresponding plots at 204 K on heating and 202.7 K on cooling after a 5 min anneal at 213 K. The data correspond to the spectra shown in Figs. 2 and 3.

crease in temperature. But this effect is relatively small when the temperature range is small and can be usually neglected. Thus a change of the spectra with time under isothermal conditions as well as with increase in temperature can indicate if two phases are present. We use this procedure here.

To examine the change in the shape of the ϵ'' spectra we have shown the normalized plots of ϵ'' , i.e., $\epsilon''/\epsilon''_{\max}$ against the normalized frequency, i.e., $f/f_{\max}$, for the low temperature transformation at 168.6 and 183.8 K in Fig. 5(A) and for the high temperature transformation at 204.0 K (heating) and 202.7 K (cooling) in Fig. 5(B). The spectra show differences in their high frequency side of the relaxation peak. To examine it more clearly, we obtained the difference spectra, and have shown it also in Fig. 5 after multiplying it by the factors indicated. It is evident that the difference spectra shows a maximum at high frequencies, i.e., at $f/f_{\max} > 1$ for both cases. Since the change in the ϵ'' spectral width at 202.7 K would be almost the same as at 204.0 K in Fig. 5(B), the maximum in the difference spectra indicates that ice VI is present with another phase in the partially transformed sample. In contrast, the maximum in the difference spectra in Fig. 5(A) arises partly from the presence of a second phase and partly from the difference between the ϵ'' spectral width of the persistent ice phase at 183.8 and 168.6 K. But, as some transformation of the metastable phase has occurred already on heating from 130 to 168.6 K, a two-phase mixture

of the metastable phase and its transformation product is expected. For that reason the maximum in Fig. 5(A) does not indicate whether the sample at a temperature below the exothermic transformation temperature of 145 K in Fig. 1(A) is pure metastable phase or a mixture of ices. Therefore, we investigate this possibility by using results of another study: If a high-pressure ice mixture had formed, and this mixture was to be our (implausibly transformed) metastable phase, its two or multiphase compositions would vary with the pressure and temperature conditions of its formation. Therefore, its thermal conductivity would vary with the conditions of its formation. But thermal conductivity of the metastable phase formed at different temperature and pressure conditions of amorphization has been found to be the same.³³ This reproducibility of thermal conductivity indicates that the metastable phase is not likely to be a mixture of high-pressure ices.

We surmise that in the first stage of transformation over the 145–175 K range in Fig. 4(B), the metastable phase converts to ice XII, and in the second stage of transformation over the 180–212 K range, ice XII converts to ice VI. The latter transformation temperature would seem to be consistent with Loerting *et al.*'s¹⁹ observation that ice XII at 0.84 or 1.09 GPa when heated at 16 K/min transforms at a temperature above 212 K (Fig. 2 in Ref. 19).

Thermodynamically, we may envisage these transformations in terms of the plot of enthalpy against temperature as follows: Enthalpy of the high-density amorph decreases abruptly at 0.97 GPa and 130 K, and the temperature rises instantly to 165 K and pressure decreases to 0.85 GPa. Thus a metastable ice phase forms. When this ice phase at 0.97 GPa is heated from 130 K, its enthalpy decreases slowly but by a relatively large amount, beginning at ~ 145 K and ending at ~ 152 K, and another high-pressure ice phase, possibly ice XII, forms slowly. On further heating, the enthalpy decreases again slowly in the 180–212 K range but by a relatively small amount, and ice VI forms slowly. In this consecutive transformation of type $A \rightarrow B \rightarrow C$, the rates of the transformations differ enough to allow separation of the two stages.

Ice polymorphs are now known to coexist and not to transform to their stable phase of lower energy even when dielectric relaxation time of the transforming phase is short enough for the (irreversible) transformation to continue.^{24,37–39} A remarkable example of this occurrence among the high-pressure ice phases is the coexistence of ice V and ice II in the temperature and pressure domain of ice II.³⁷ Slow transformations of the ice phases when the dielectric relaxation time is less than 1 ms, have also been observed here in Figs. 1(A) and 4(B). In view of these observations, we conclude that the rate of transformation of the ices is not determined by the relaxation rate for reorientation of H_2O molecules in the ices. A further example of such occurrence is in ice Ih, whose dielectric relaxation time is greatly decreased by doping with HF (see detailed discussion in Ref. 2), yet doping with HF is least effective in transforming it to ice XI.⁴⁰

V. CONCLUSIONS

When hexagonal ice at 130 K is pressurized to 0.97 GPa, the high-density amorph formed is different from the usual HDA, i.e., the one that forms on amorphizing ice Ih at 77 K. Sudden, and unpredictable, exothermic transformation of this amorph produces a denser high-pressure phase whose dielectric permittivity is ~ 3.5 and dielectric loss is negligibly small, and these values do not change significantly on heating it to 140 K. Since these dielectric properties and transformation conditions do not correspond to a known high-pressure crystalline ice phase, the transformation has likely occurred to a new metastable ice phase.

Calorimetric and dielectric studies show that on heating at about 0.97 GPa, the metastable ice phase undergoes a two-stage transformation ultimately to ice VI. We conjecture that in the first stage between 130 and 175 K, it transforms to ice XII, and in the second stage this ice XII transforms (undoubtedly) to ice VI. At a pressure of 0.97 GPa and temperatures above 175 K, ice VI is the stable phase.

Despite the very short dielectric relaxation time of the parent ice phases, their transformation to another ice phase remains slow. This means that the relaxation rate for reorientation of the H_2O molecules does not control the rate of their phase transformation.

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