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Thermoluminescence of deuterated amorphous and crystalline ices

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Abstract

Low-temperature thermoluminescence has been used to assess the structure of solids. When applied to frozen liquids it can also provide interesting information on the initial product in the liquid state. We have shown, in previous publications (C.R. Phys. 1 (2000) 107, Physica A 323 (2003a) 67) that two major light emission peak areas were displayed in the case of deuterated ice, one of them linked to the crystal network and, most probably to the pre-existing hydrogen bonding in the original water. In the present research we have investigated the thermoluminescence glow of several types of deuterated ices obtained by compression at 77 K including amorphous solids. We observed, in this latter case, an almost complete disappearance of the peak area that we attributed to crystal lattice and hydrogen bond systems. This confirms that high pressures, when applied to hexagonal ice at 77 K, can induce ''melting'' in the solid state and give rise to an unstructured ''liquid''.

1. Introduction

Luminescence can be generated by the release of trapped electrons created into solid imperfections by ionizing radiant energy. It might also result from annealing of lattice strains or polymorphic transitions in metastable materials. In most cases, with the exception of triboluminescence and chemiluminescence light is emitted in the course of heating of the ''activated'' solid and this process is, consequently, called thermoluminescence (Johnson and Farrington, 1961). As such, it is one among other thermally stimulated processes as differential thermal analysis (DTA), thermally stimulated conductivity, thermogravimetry … and has been studied in depth by several authors, notably, McKeever (1985) and Chen and McKeever (1997). Generally, the initial ''activation'' of the solid is done by ionizing radiations (Cobalt 60 gamma rays, electron beams, X-rays) but it might also result from the action of cosmic rays and natural radioelements. In that latter case, it is often used to date geological sediments, such are volcanic layers (Hütt and Smirnov, 1983), mainly feldspars (Visocekas, 1993; Zink and Visocekas, 1997) and is, today, an acknowledged technique in museums and public auctions to discriminate and date archaeological samples such as antique China (Aitken, 1984).

In all cases, the shape, intensity and temperature range of thermoluminescence diagrams are representative of the material under investigation and equally depend upon activation and recording conditions (radiant source, dose received and dose rate, temperature of irradiation and subsequent heating mode, etc.). Thus, every singular sample presents a specific glow showing a characteristic photometric/temperature profile as well as given emission spectra over a wide range of wave length from near infra-red to ultra-violet which might give interesting information on the structure of the original solid.

Since we have been involved for a long time into the effect of low temperatures on living material and

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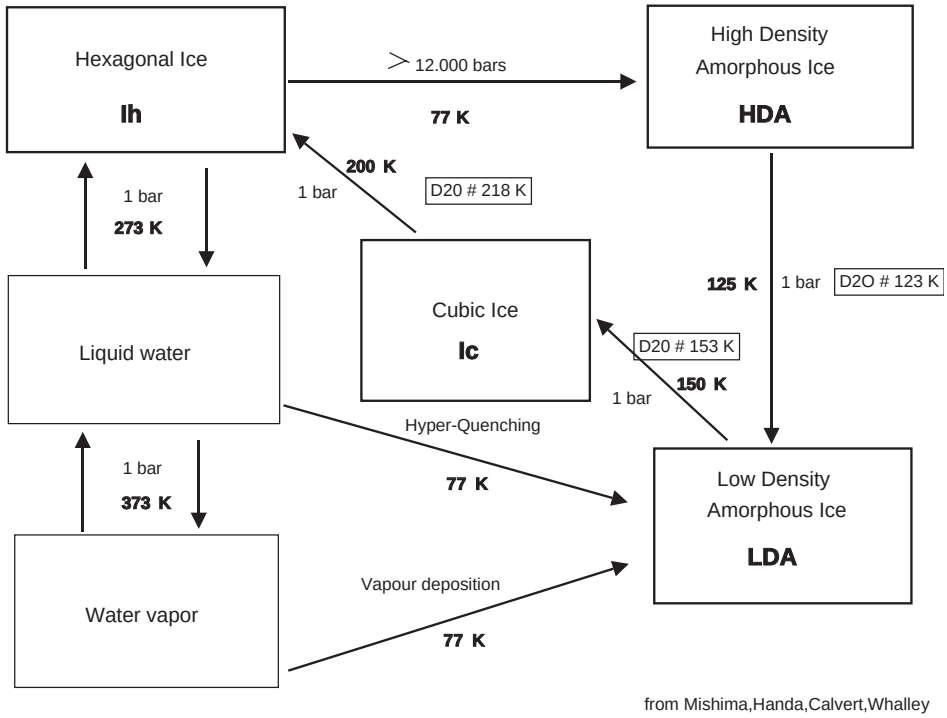

Fig. 1. A schematic outline of amorphous and crystalline ices—the boxed D_2O temperatures are those identified in the present paper.

biological fluids (Rey, 1957, 1959) and into freeze-drying (Rey, 1977, 2003b) in which water plays a determinant role, we have focused our research on water itself in its solid form, namely ice. In recent publications, we have given the results of our experiments on the thermoluminescence of pure ice (both hydrogen and deuterium oxide ice (Rey, 2000)) as well as of different other aqueous based systems in which the initial solutions have been turned into solid by low temperature freezing (Rey, 1988, 2003a).

Water, indeed, has been the central focus of a large number of publications in the last decennias (Velikov et al., 2001; Bosio et al., 1986; Teixeira, 2001; Bellissent-Funel et al., 1987; Mishima et al., 1984; Mishima, 1994; Johari et al., 1996) which have shown that ice can present very different structures at low temperature, depending upon the environmental conditions (thermal history, pressure …) which prevail during freezing and observation. On that basis it has been even proposed by Mishima and Stanley (1998) that this unique and ubiquitous substance can demonstrate all kinds of different states ranging from crystalline structures to polyamorphic metastable phases where glassy "solids" appear as ultra-viscous "liquids". In this most challenging and pioneering area, the different states under which water does appear as "solid" ice, are under more or less constant revision but can, at first glance, be summarized as shown on Fig. 1.

It is, on that basis, that we did attempt to follow the thermoluminescence of ice, starting at 77 K from its high-density amorphous state (HDA) until, in the course of rewarming, it comes back to its original hexagonal crystalline form (Ih). To that end, we have been using the same methodology that we resorted to in our preceding research, namely, the initial "activation" of ice by irradiation with Cobalt 60 gamma rays in liquid nitrogen. In this research work, we are reporting, here, the results of the experiments done with deuterium oxide (D_2O) ice since, as we have shown previously, it gives a much stronger and more reliable signal than H_2O though its evolution is basically identical (Rey, 2000).

2. Experimental

2.1. Material

High-purity D_2O has been kindly provided for this research by COGEMA (Celestin Reactor in Marcoule).

2.2. Preparation of the HDA starting sample

D_2O of 0.5 cm^3 is deposited into the central cylindrical cavity ($\odot$ 6 mm) of a precooled (−20°C, 253 K) metallic

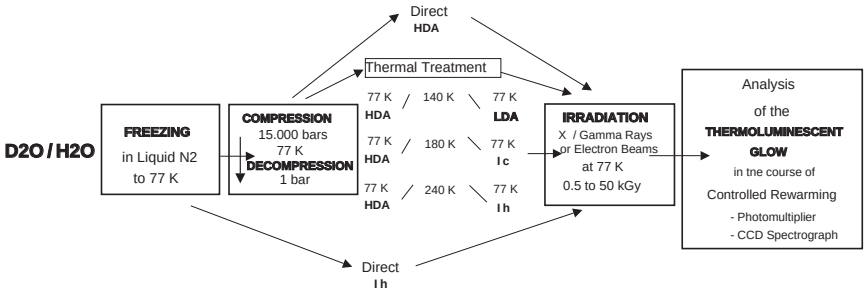

Fig. 2. Experimental set-up for the preparation of the samples.

block made of hardened stainless steel and let to freeze. A cylindrical piston (needle-bearing special steel) is then deposited on the frozen ice and the whole transferred into a liquid nitrogen bath where it is kept for 30 min. The block with its protruding piston is then adjusted on a solid stainless-steel support positioned at the bottom of an insulated teflon container filled with liquid nitrogen, itself placed under the head of a hydraulic press, the pre-cooled piston of which comes in close contact with the cylindrical piston of the block. Compression is then done progressively to avoid strain heating and carried over a 2 min lapse time to 15.000 bars/cm^2 (1.5 GPa). During compression, the ice creaks and, suddently, over 12.000 bars (1.2 GPa) collapses. Compression is raised to 15.000 bars (1.5 GPa), maintained for 5 min and then released.

The block holding the sample with its protruding piston is further placed, still under liquid nitrogen, on an annular stainless-steel ring holding in its center an aluminium capsule ($\odot$ 20 mm) and, making use of the same press, the crushed ''ice'' is expelled by the piston into the capsule. The sample, which corresponds, at that time, to HDA Ice appears as a fluffy white powder and is placed directly into a special container filled with liquid nitrogen or transferred, as an intermediate step, to a thermal treatment set-up.

In that particular case and provided it is maintained below 110 K HDA is fairly stable and can be kept for months in its metastable state. It will only evolve further into a second kind of amorphous ice low density amorphous (LDA) Ice by a polyamorphic transition (Mishima and Stanley, 1998) if rewarmed over 125 K. Despite our own samples have been processed within a few hours after the preparation of HDA, we have seen that frozen HDA, kept at 77 K, was still in its original state more than 6 months later. This confirms the observations made by Bellissent-Funel and Teixeira (Personal communication) who carried neutron scattering studies at the Laboratoire Leon Brillouin in Saclay on samples of HDA prepared weeks before by Russian Scientists in Moscow and carried under liquid nitrogen.

2.3. Preparation of ''annealed'' thermally treated samples

The capsules holding the HDA powder are placed in a cryostat, set at 77 K and then, depending upon the type of ice which has to be prepared, progressively warmed up (4 K/min) through the transition level, then cooled back to 77 K and placed into the container. Fig. 2 shows the experimental set-up for the preparation of LDA ice, cubic ice (Ic) and hexagonal ice (Ih).

Under those conditions, up to 20 samples of ''each type'' can be prepared and stored at 77 K.

2.4. Irradiation

To perform gamma irradiation the container is transferred to the Celestin reactor in Marcoule. There, the samples are placed in a Dewar flask, positioned into a tight aluminium container, which is driven into the center of a ''basket'' holding eight Cobalt 60 cartridges (containing each three pencils), placed at the bottom of a 6 m deep water pool. Irradiation starts at the time the canister enters the basket. Depending upon the position of the cartridges and upon their activity, dose rates of 5–100 kGy/h can be achieved. Dosimetry is done beforehand, in the same canister, and also during the experimental run thanks to a set of Alanine, Harwell Red and Amber, and F.W.T. dosimeters (with due correction for those dosimeters which are at low temperature). In the present experiments, and in view of our preceding results (Rey, 2000), we gave 10 kGy to the samples.

2.5. Recordings

2.5.1. Differential thermal analysis (DTA)

Some HDA samples were used, first, for DTA following the technique that we have described earlier (Rey, 1960, 1999). Since they are of small size, our instrument has been ''miniaturized'', using needle point thermocouples instead of the conventional Pt 100.

2.5.2. Thermoluminescence

Each capsule holding its specific samples is placed in a controlled temperature cryostat, set at 77 K, and progressively warmed up (4 K/min). During rewarming the thermoluminescence glow is recorded continuously by a photomultiplier (Philips) as a function of temperature. It is also possible to send the emitted light thanks to a silica optical fiber, to an Acton Spectrograph (300 i) connected to a CCD camera (cooled with liquid nitrogen) (Princeton Instruments). However, in this particular case, and due to the very low level of incoming light, we cannot follow the emission on a continuous way but only "average" the thermoluminescence glow during a given time (ranging from 2–10 min) to cover the "peak areas" recorded with the P.M.

3. Results

3.1. Thermoluminescence of irradiated HDA

In a first set of experiments we studied HDA samples which had been irradiated by gamma rays at 77 K (10 kGy) and have been rewarmed directly without any further treatment. First, we performed a DTA to verify that the phase changes did occur as forecasted and we ran, in parallel, a thermoluminescence experiment. Fig. 3 gives the results.

As could be expected from the work of Handa et al. (1986) we detected the three major transitions which show up, on the DTA diagram, as exothermic events.

HDA → LDA near 123 K
LDA → Ic near 153 K
Ic → Ih near 218 K

By far the most spectacular event is the passage from LDA to Ic and the less significant, the transition from Ic to Ih, a very modest exothermic phenomenon as already underlined by Handa et al. (1986). The temperatures that we observed are well in line with those noticed by these authors taking into account that, in order to get a reliable signal, we rewarmed the sample at a substantially higher rate than that they have been using.

As far as thermoluminescence is concerned we discovered that HDA gave a very important and wide glow starting near l05 K, peaking at 112 K and fading away at around 135 K. It is not unlikely that this emission is correlated with the structural relaxations observed in frozen aqueous systems by thermally stimulated current techniques (Johari and Jones, 1975; Onsager et al., 1978). Quite remarkable also is the fact that no special luminescence signal appears when HDA evolves into LDA.

To the contrary, the transition from LDA to Ic near 150 K gives a very fast strong and sharp light emission which coincides almost exactly with the transition and is accompanied by a spectacular evolution of the sample which, sometimes, burst out. (We have been compelled, in some experiments, to cover, at the onset of the analysis, the fluffy amorphous powder with a small glass disk to prevent the material to be blown away.)

The last transition, which is quite weak, thermally, does not show any specific light emission, the thermoluminescence glow being almost nil since 170 K.

As such, the thermoluminescence of high-density amorphous D_2O ice is substantially different from the one of normal D_2O (Rey, 2000) since peak 2 (around 168 K) has totally disappeared. This, indeed, falls in line with our previous hypothesis that this particular luminescence period could be closely linked to the ice

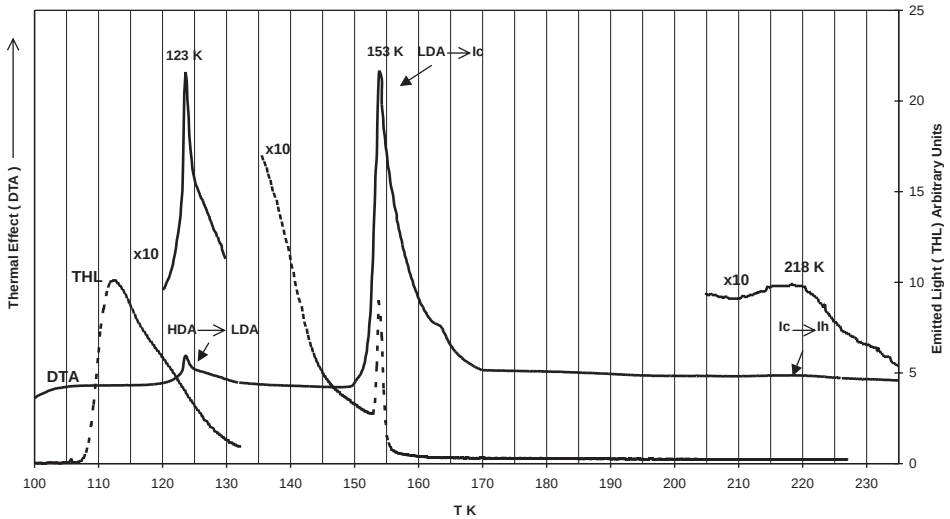

Fig. 3. DTA and THL of a sample of high density amorphous Ice after gamma irradiation at 77 K (10 kGy).

lattice which, apparently, does not exist any longer after the transformation by low-temperature compression of hexagonal ice into an amorphous material.

As could be expected, the phase transition from LDA into Ic, corresponding to the rupture of a metastable state, does not always occur at the same temperature and, in different experiments, we noticed that the "flash luminescence" which is linked to it, could appear at temperature ranging from 123 to 165 K. In all cases, however, it presents exactly the same pattern, a very sharp peak, occurring in less than 15 s and centered, most often, around 150 K.

3.2. Thermoluminescence of thermally treated HDA

In order to investigate the particular behaviour of the different ice types generated from HDA we prepared these ices first by an appropriate thermal treatment before irradiation at 77 K. To that end, we followed the experiment set-up delineated in Fig. 2, each sample

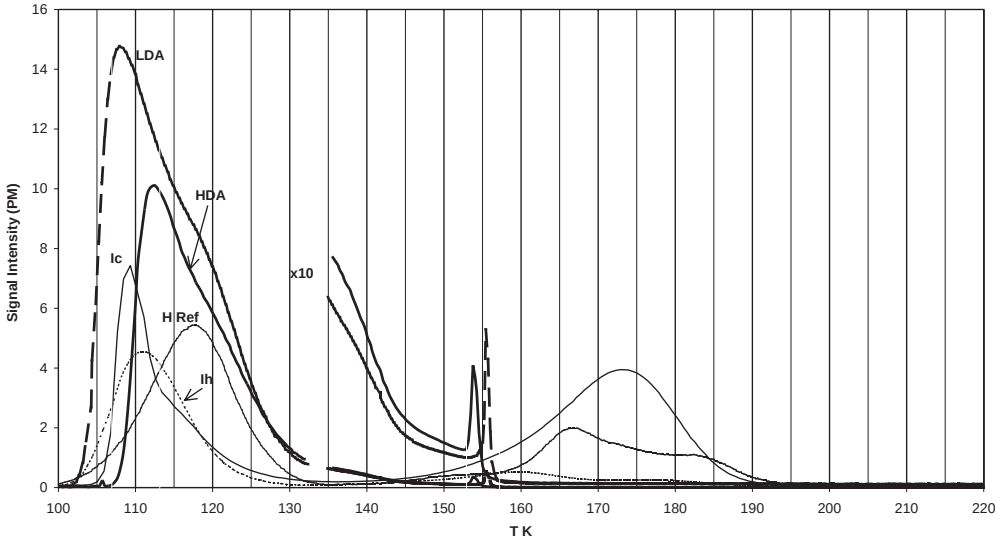

Fig. 4. Thermoluminescence curves of different ice types prepared by thermal treatment of an initial HDA ice then cooled back to 77 K and irradiated by gamma rays (10 kGy)—LDA low-density amorphous Ice—Ic cubic Ice—Ih hexagonal ice—comparison is made with H Ref a sample of Ih prepared by direct cooling.

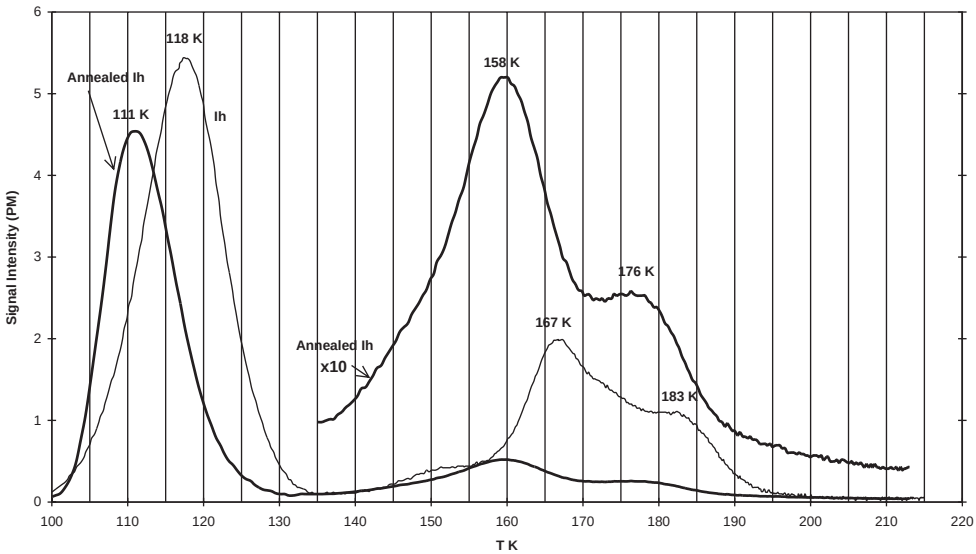

Fig. 5. Comparison of the thermoluminescent glows of Ih prepared by direct cooling and Ih processed by annealing HDA at 240 K.

being cooled back to 77 K after transition and before exposition to gamma rays. Fig. 4 gives the results.

HDA and LDA, as could be expected, gave very similar luminescence curves:

- A rather high and wide peak between 100 and 130 K. LDA emission is stronger and occurs at somewhat lower temperatures (108 K instead of 112 K for HDA).
- Both show also the sharp emission linked to the phase transition of LDA to Ic (154 K for HDA, 155 K for LDA).
- Then, the thermoluminescence is almost null beyond 170 K. The behaviour of both amorphous states can then be considered as almost equivalent.

3.2.1. Ic

Conversely, when LDA has been converted into Ic and that latter type is activated by gamma Rays at 77 K it shows a totally different evolution:

- At low temperature, there is a rather sharp peak near 110 K but its height and width are substantially smaller than for the amorphous types.

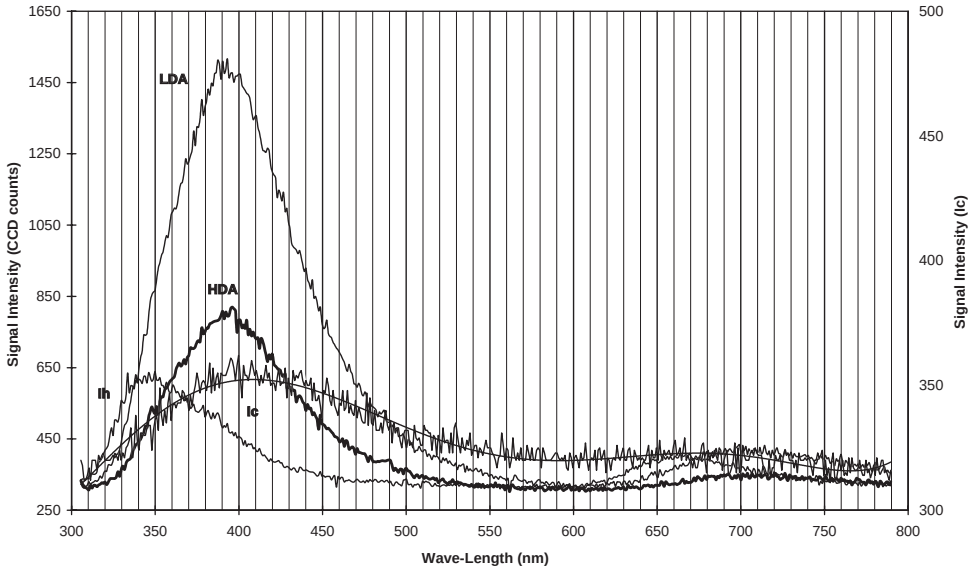

Fig. 6. Light emission spectra of different ices in the Peak 1 area. The thermoluminescent glow has been averaged from 100 to 130 K.

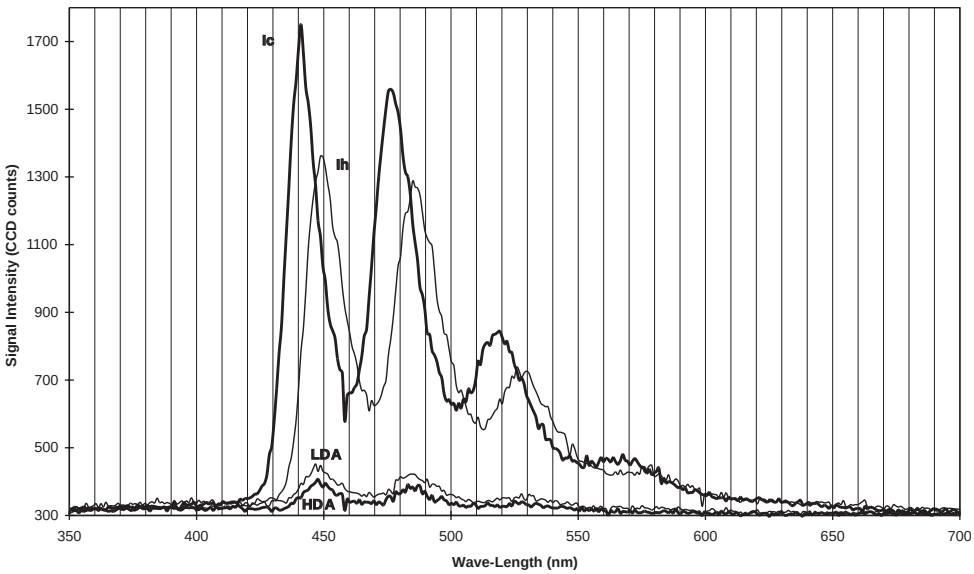

Fig. 7. Light emission spectra of different ices in the Peak 2 area. The thermoluminescent glow has been averaged from 140 to 190 K.

- The phase transition luminescence at 154 K has, of course, totally disappeared and a large peak shows up in the 170 K area.

We can assume that, with the restoration of a lattice in the newly formed Ic we come back to the luminescence conditions shown for "classical" hexagonal ice. The peak, however, summits at a slightly higher temperature 174 K instead of 168 K for Ih.

3.2.2. *Ih*

Finally, when Ih has been generated by thermally treating HDA up to 240 K it gives a thermoluminescence glow, after irradiation at 77 K, which is very similar to the one of "uncompressed" Ih (Fig. 5). However, the two peak areas, 1 and 2, are not exactly positioned in the same way, 111 and 158 K for "annealed "(thermally treated) Ih and 118 and 167 K for "conventional" Ih.

It, thus, appears that all types of ice which result (directly or after subsequent processing) from HDA by low-temperature compression of hexagonal ice, have, at least for thermoluminescence, quite different patterns.

The spectral analysis of the emitted light gives confirmation of that point (Figs. 6 and 7). In Fig. 6 we see that peak area 1 displays two main emission bands—a rather important one in the blue-violet zone and a smaller one in the red. LDA, HDA, and Ic are ranked as they appear in the photometer recording. However, the peak is now shifted around 400 nm whilst it is positioned at 348 nm for casual Ih.

In peak 2 area (Fig. 7) it is not surprising to see that neither HDA nor LDA do show any significant level of emission since they were irradiated in the "amorphous" state. Conversely, Ic has a very strong emission but it is located at slightly lower wave lengths, when compared to uncompressed hexagonal ice. All types, nevertheless, display the four successive rays that we have identified previously for D_2O ice (Rey, 2000) presenting, thus, the characters of a Ewles–Kröger type of spectrum.

It would be of interest to investigate further that issue and see whether thermoluminescence could help to assess the relationship between the two identified polyamorphic phases and the liquid, supercooled and glassy states of water as discussed by Mishima and Stanley (1998).

References

Aitken, M.J., 1984. Thermoluminescence Dating. Academic Press, London.

Bellissent-Funel, M.C., Bosio, L., Teixeira, J., 1987. Structure of high-density amorphous water. II. Neutron scattering study. J. Chem. Phys. 87, 2221–2223.

Bosio, L., Johari, G.P., Teixeira, J., 1986. X-ray study of high-density amporphous water. Phys. Rev. Lett. 56, 460–463.

Chen, R., McKeever, S.W.S., 1997. Theory of thermoluminescence and related phenomena. World Scientific, Singapore.

Handa, Y.P., Mishima, O., Whalley, E., 1986. High density amorphous ice. III. Thermal properties. J. Chem. Phys. 84, 2766–2770.

Hütt, G., Smirnov, A., 1983. Thermoluminescence dating of sediments by means of quartz and feldspar inclusion methods. PACT 9, 463–471.

Johari, G.P., Jones, S.J., 1975. Study of the low-temperature "transition" in ice Ih by thermally stimulated depolarization measurements. J. Chem. Phys. 62, 4213–4223.

Johari, G.P., Hallbrucker, A., Mayer, E., 1996. Two calorimetrically distinct states of liquid water below 150 K. Science 273, 90–92.

Johnson, N.M., Farrington, D., 1961. Luminescence during annealing and phase change in crystals. J. Chem. Phys. 34, 1434–1439.

McKeever, S.W.S., 1985. Thermoluminescence of Solids. Cambridge University Press, Cambridge, pp. 1–378.

Mishima, O., Calbert, L.D., Whalley, E., 1984. Melting ice at 77 K and 10 kbar: a new method of making amorphous solids. Nature 310, 393–396.

Mishima, O., 1994. Reversible first-order transitions between two H_2O amorphs at $\sim$0.2 GPa and $\sim$135 K. Chem. Phys. 100, 5910–5912.

Mishima, O., Stanley, H.E., 1998. The relationship between liquid supercooled and glassy water. Nature 396, 329–335.

Onsager, L., Staebler, D.L., Mascarenhas, S., 1978. Electrical effects during condensation and phase transitions of ice. J. Chem. Phys. 68, 3823–3829.

Rey, L., 1957. Studies on the action of liquid nitrogen on cultures in vitro of fibroblasts. Proc. Roy. Soc. B. 147, 460–466.

Rey, L., 1959. Study of the freezing and drying of tissues at very low temperatures. In: Parkes, A.S. (Ed.), Recent Researches in Freezing and Drying. Institute of Biology, London, pp. 40–62.

Rey, L., 1960. Thermal analysis of eutectics in freezing solutions. Ann. NY Acad. Sci. 85, 513–534.

Rey, L., 1977. Glimpses into the fundamental aspects of freeze-drying. In: Freeze Drying of Biological Products. Biological Standardization Series, Vol. 36. Kargel, S., Basel, pp. 19–27.

Rey, L., 1988. Low temperature thermoluminescence. Nature. 391, 418.

Rey, L., 1999. Glimpses into the realm of freeze-drying: classical issues and new ventures. In: Rey, L., May, J. (Eds.), Freeze-Drying/Lyophilization of Pharmaceuticals and Biological Products. Marcel Dekker, New York, pp. 1–30.

Rey, L., 2000. Thermoluminescence de la glace. C. R. Phys. 1, 107–110.

Rey, L., 2003a. Thermoluminescence of ultra-high dilutions of lithium chloride and sodium chloride. Physica A 323, 67–74.

Rey, L., 2003b. Some leading edge prospects in freeze-drying. Amer. Pharm. Rev. 6, 32–44.

Teixeira, J., 2001. L'étrange comportement de l'eau ultra-froide. Pour Sci. 285, 84–91.

Velikov, V., Borick, S., Angell, C.A., 2001. The glass transition of water based on hyperquenching experiments. Science. 294, 2335–2338.

Visocekas, R., 1993. Tunnelling radiation recombination in K-feldspar sanidine. Nucl. Tracks Radiat. Meas. 21, 175–178.

Zink, A.J.C., Visocekas, R., 1997. Datability of sanidin feldspars using near infra-red TL emission. Nucl. Tracks Radiat. Meas. 27, 251–261.