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Thermoluminescence study of the amorphization of hexagonal ice by irradiation at 77 K

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Abstract

We report on a thermoluminescence study of D₂O ice I_h. A sample of hexagonal (I_h) ice is irradiated by a 100 MeV X-ray source at 77 K. The emission spectrum that is measured immediately after the end of the irradiation process has the thermoluminescent behaviour of amorphous ice. We follow the kinetic transition to the stable form, taking place at 85 K. The relaxation time of the transition is of the order of 5 minutes.

We conclude that, due to irradiation, a few outer layers of ice I_h are converted to the low-density amorphous form of ice which then converts to cubic ice.

Although complex to quantify, thermoluminescence appears to be, in the present study, particularly sensitive to the time evolution of irradiated samples.

Keywords: thermoluminescence; water; amorphous ice

1. Introduction

Under irradiation and specific conditions, different solids may become “activated” and present defects which may constitute a certain number of “traps”. Most generally, these traps are metastable and the electrons which they contain are, thus, susceptible to come back to lower energy levels, most often the ground state [1].

The creation of defects into solids can be done by mechanical constraints, electromagnetic fields or irradiation. To investigate these traps, it is frequently resorted to the method of thermally stimulated luminescence, generally called thermoluminescence. The activated solid is progressively heated and, as thermal energy flows in, the trapped electrons

are freed and, as they come back to more stable levels, they release their excess energy under the form of light, hence the name thermoluminescence.

This technique has been in use for a long time to assess the potential exposure of people working near radiation sources and also for the exact determination of the age of buried ceramics which have been exposed to the radionuclides contained in the soil or to the regular flux of cosmic rays over decades or centuries.

Thermoluminescence can provide as well valuable information about the structural evolution of different forms of crystalline and amorphous ices.

In our research we have been using thermoluminescence to study the structure of different types of ices derived from water which have been submitted to several pre-treatments in the liquid state. Our experimental procedure has been already fully described in previous publications [2-3].

More than ten crystalline and amorphous forms of ice are identified in different regions of the phase diagram. Depending on the method of preparation, some of them are metastable. At atmospheric pressure, the situation is particularly complex because of polyamorphism [4]. Depending on the external conditions and technical procedures, several amorphous phases can be identified generating a large field of research where several fundamental problems remain opened [5].

Shortly and within the context of the present work, crystalline ice I_h pressurized to typically 1.5 GPa at 77 K transforms in an unstable high density form of amorphous ice (HDA) which subsists after release of the applied pressure. Upon heating at atmospheric pressure, it transforms at 125 K in the well known low density form of amorphous ice (LDA). This form of amorphous ice can be obtained as well by quenching of small droplets of liquid water or by vapour deposition on a cold substrate. Its structure is similar to that of deeply supercooled water. Several structures of LDA have been identified and characterised by scattering techniques [6]. Here we compare our present results to the LDA form obtained by heating HDA ice. As every glass form, LDA is an unstable phase. Upon heating it crystallises at 150 K in a metastable cubic form of ice, I_c which has a transition to the stable hexagonal form I_h at 200 K [5].

2. Thermoluminescence of irradiated ice samples

In the 2000 publication we did show that the thermo luminescence glow of pure water ice, activated by gamma rays at liquid nitrogen temperature, and slowly warmed up from 77 K to the melting point, was characterized by two main peak areas around 117 K (peak 1) and 168 K (peak 2), as depicted in Fig. 1. A spectrographic analysis of these two emission zones shows that Peak 1 had two main components around 342 nm and 665 nm whilst Peak 2 presents a set of four components of decreasing intensity, respectively at 448 nm, 483 nm, 523 nm, and 575 nm (Fig. 2). As such, Peak 2 displays a very similar “structure” to a border band emission spectrum of the Ewles-Kröger type [7].

Experiments carried with either D₂O or H₂O give the same results with the exception of a slight shift of the peak temperatures which were of 115 K and 162 K for H₂O but with a 50 times smaller light intensity. The origin of the isotopic effect on the intensity is not yet understood. For that particular reason our experiences have been essentially carried with deuterated water.

We did investigate other forms of crystalline and amorphous ice at atmospheric pressure. In particular, we measured the thermoluminescence glow of high density (HDA) and low density (LDA) forms of amorphous ices and of crystalline ice Ic within their temperature domain of metastability [8].

The thermo-luminescence glows of these different amorphous and crystalline ices proved to be substantially different from the ones of hexagonal ice (Fig. 3). Particularly in the case of LDA, the peak 1 is very intense and appears at a lower temperature (101 - 102 K) than for other forms of ice. We conclude that the differences in position and magnitude of this peak can be associated to each of the amorphous or crystalline forms of ice, without ambiguity. The energy spectrum of peak 1 yields also results significantly different for each form of ice: it is centred at 390 nm (instead of 342 nm for hexagonal ice) for HDA, and LDA (Fig. 4). Finally, for the crystalline form Ih obtained after successive transformations from HDA or from LDA, the peak around 162 K (peak 2) is virtually absent, in contrast with non pressurised crystalline ice (curve labelled IH in figure 4).

In all preceding experiments the activation of the ice samples at 77 K was done by gamma rays courtesy of the Marcoule AREVA Celestin Reactor, and since the thermoluminescence measurements were performed in a remote laboratory, several hours elapsed before the resulting curves could be recorded. To improve the efficiency of our research we made then the acquisition of a 5 kW, 100 MeV X-ray unit allowing us to carry the irradiation on site. Basically, we found the same patterns that we had seen before. This was also the case when irradiation was performed with an electron-beam (Aerial 2.2 MeV accelerator). These results demonstrate that the thermoluminescence glow of the samples doesn't depend substantially on the nature of the radiation generating the defects.

3. Kinetic effects and interpretation

More recently, with X-rays we did proceed to the thermoluminescence analysis of ice I_h almost immediately after irradiation. In this manner, we observed that, surprisingly, when the recording was done within a few minutes after the end of irradiation, a new low temperature peak did show up (Fig. 5). We repeated these experiments with the electron-beam and obtained the same result.

That emission (that we call peak 0) appeared to be very sharp and quite transient since it disappeared totally within 2 hours after irradiation (Fig 5). Recording the emitted light at a fixed temperature of 77 K we could see that it follows a very clean-cut kinetic mechanism, i.e. the intensity has an exponential decay with a relaxation time equal to 5.3 minutes. We did, therefore, concentrate our experiments at a fixed time of 3 minutes after the end of irradiation both under X-rays or e-beam. Our numerous recordings did deliver the following results:

- Peak 0 occurs abruptly in a narrow temperature range between 83 and 87 K for a constant warming rate of 2.90 K/min and lasts for no more than 3 minutes.

- Its emission spectrum is identical to those of HDA, LDA, and I_c ices and centred at 390 nm (Fig 6). Its shape is quite similar to the sharp light emission recorded when LDA transits into ice I_c (Fig 3).

- There are no changes in the position and patterns of peak 1 and peak 2.

The occurrence of Peak 0 is, thus, a very peculiar issue which can only be witnessed immediately after the end of irradiation.

The more likely interpretation of the results is that, at 77 K, the radiant energy (whatever X-rays or e-beam) provokes an amorphization of the surface layer of the frozen ice sample, probably on a very small depth. This effect of radiation is known and has been studied in detail by infra-red spectroscopy both in the region of the intra-molecular stretching band [9] and in the intermolecular far infrared region [10]. In these studies, the fraction of amorphized ice depends strongly on the temperature of irradiation. Our study is performed at a fixed temperature (77 K) but shows a kinetic effect which may correspond to a gradual transition of the amorphous phase to the stable phase.

Under irradiation, a few layers of the original hexagonal ice are transformed into a low density form of amorphous ice, probably the LDA form. This amorphous layer is fairly unstable because it is in contact with the stable form Ih. As soon as the irradiation ends, it starts to relax into cubic ice giving thus a sharp emission at 390 nm, i.e. in the same domain as pure LDA. That cubic ice will later on transform in hexagonal ice in the course of rewarming but without any noticeable light emission as we already saw in our previous experiments. [1]

The kinetics of the phase transformation is relatively slow as it lasts for several minutes. A more complete study will establish a possible relation between the intensity of radiation, the penetration depth and the observed relaxation time.

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Figure captions

Figure 1: Thermoluminescence glow of pure water ice (D_2O) activated by gamma rays (1.3 kGy) at 77 K and warmed up to the melting point. There are two peak areas at 115 K (peak 1) and 162 K (peak 2).

Figure 2: Spectral analysis of the two main emission zones. Same conditions as in figure 1.

Figure 3: Thermoluminescence glow of different phases of D_2O irradiated at 77 K (10 kGy) after compression at 1.7 GPa at 77 K and subsequent thermal treatments in the sequence HDA-LDA- I_c - I_h). The curve labelled IH refers to hexagonal ice that has not been compressed.

Figure 4: Emission spectra of peak 1 of different forms of D_2O after irradiation at 77 K.

Figure 5: Thermoluminescence glow of crystalline ice I_h measured after 3 minutes and after 2 hours after the end of the irradiation (1.3 kGy at 77 K).

Figure 6: Emission spectrum of peak 0 of D_2O ice I_h compared to those of amorphous forms after irradiation at 77 K. The right hand scale corresponds to peak 0 and the left hand scale to the amorphous ices HDA and LDA measured in bulk form.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

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