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Thermoluminescence of ultra-high dilutions of lithium chloride and sodium chloride

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Abstract

Ultra-high dilutions of lithium chloride and sodium chloride ($10^{-30} \text{ g cm}^{-3}$) have been irradiated by X- and γ -rays at 77 K, then progressively rewarmed to room temperature. During that phase, their thermoluminescence has been studied and it was found that, despite their dilution beyond the Avogadro number, the emitted light was specific of the original salts dissolved initially.

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1. Introduction

Thermally stimulated luminescence—often called thermoluminescence—is a well-known phenomenon amongst the thermally stimulated processes (thermally stimulated conductivity—thermally stimulated electron emission—thermogravimetry—differential thermal analysis and differential scanning calorimetry, etc.). Its theory and applications have been fully developed inter alia by McKeever [1], Chen [2] and Visocekas [3] and it proved to be a most interesting tool to study the structure of solids, mainly ordered crystals. To that end, the studied material is “activated” at low-temperature, usually by radiant energy (UV, X-rays, gamma rays, electron beams, α -particles or neutrons) which most generally creates electrons–holes pairs which become separately “trapped” at different energy levels. Then, when the irradiated material is warmed up, the heating serves as a trigger to release the initially accumulated energy and the trapped electrons and holes move and recombine. A characteristic glow is emitted most often under the shape of different successive peaks according to the depths of the initial traps. As a general rule this phenomenon is observed in ordered crystals though it can be equally

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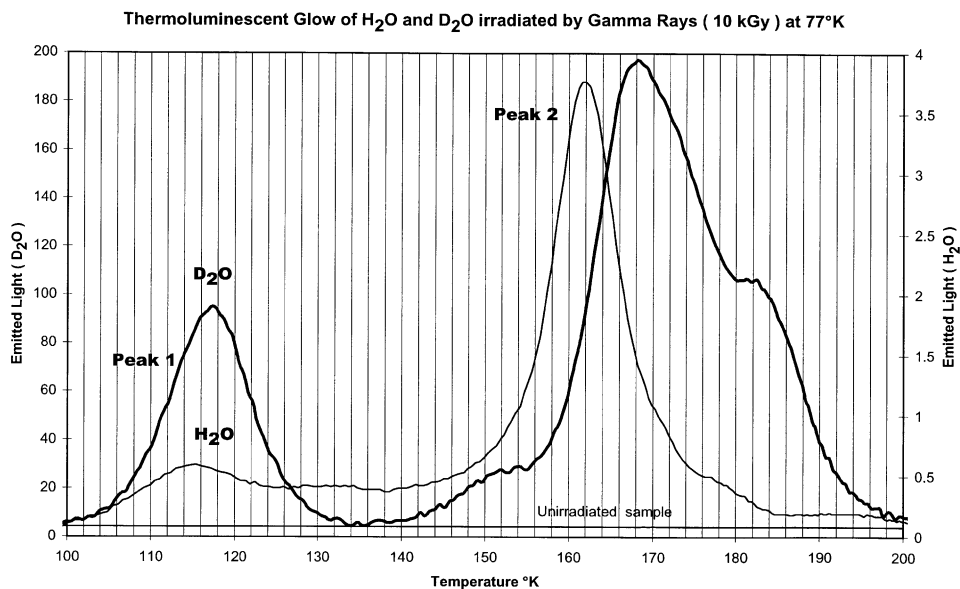


Fig. 1. Thermoluminescent glow of H₂O and D₂O irradiated by gamma rays (10 kGy) at 77°K.

seen in disordered materials such as glasses [2]. In that mechanism, imperfections in the lattice play a major role and are considered to be the place where luminescent centres appear. Thus, thermoluminescence is a good tool to study these imperfections and understand how they appear in the crystal.

This is exactly along those lines that we have carried our first investigations, starting, this time, from liquids which were turned into stable solids by low-temperature cooling. Working essentially with water—mainly deuterium oxide—we have shown [4,5] that the thermoluminescent glow of irradiated hexagonal ice consisted in two major peak areas—Peak 1 near 120 K and Peak 2 near 166 K—(Fig. 1) having well-defined emission spectra (Fig. 2), the D₂O samples giving a much higher signal than the H₂O ones. In both cases, unirradiated samples gave no signals whatsoever. For both D₂O and H₂O we equally showed that the relative intensity of the thermoluminescence glow was a function of the irradiation dose and, that at least for Peak 2, it did show a maximum between 1 and 10 kGy (Fig. 3).

As a first hypothesis on the nature of the emission itself it has been suggested by Teixeira [6] that Peak 2 could be connected to the hydrogen-bond network within the ice which, in turn, could result from the structure of the original liquid sample, whilst Peak 1 looked to be closely related to the molecule. Actually, for a totally different substance, such as formamide which is known to present strong hydrogen bonds, our experiments show a similar glow in the Peak 2 region (Fig. 4). This strengthens our views on the involvement of hydrogen bonds in this mechanism.

To develop this concept further we did select to study the effect of lithium chloride on the thermoluminescence of irradiated D₂O ice since this particular substance is known

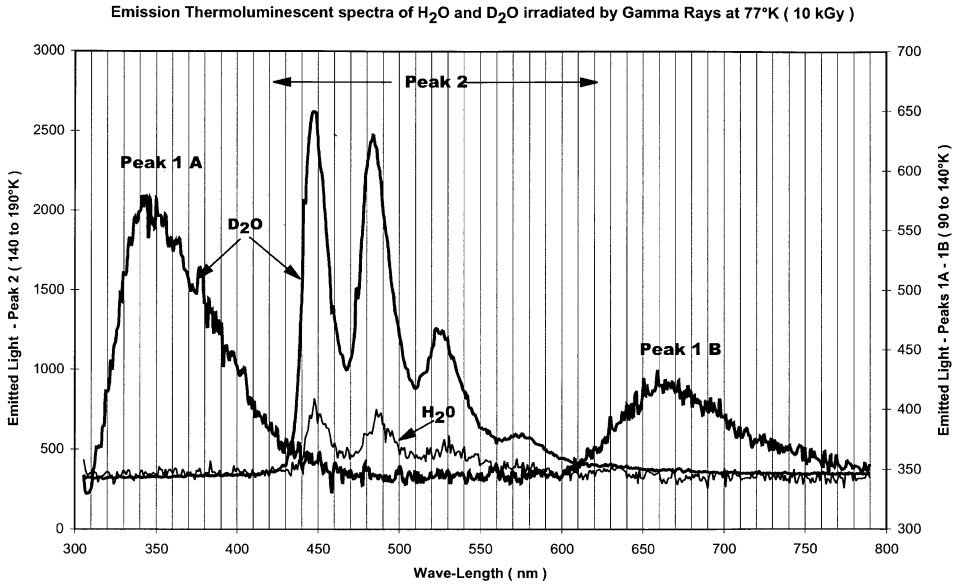


Fig. 2. Emission thermoluminescent spectra of H₂O and D₂O irradiated by gamma rays at 77°K (10 kGy).

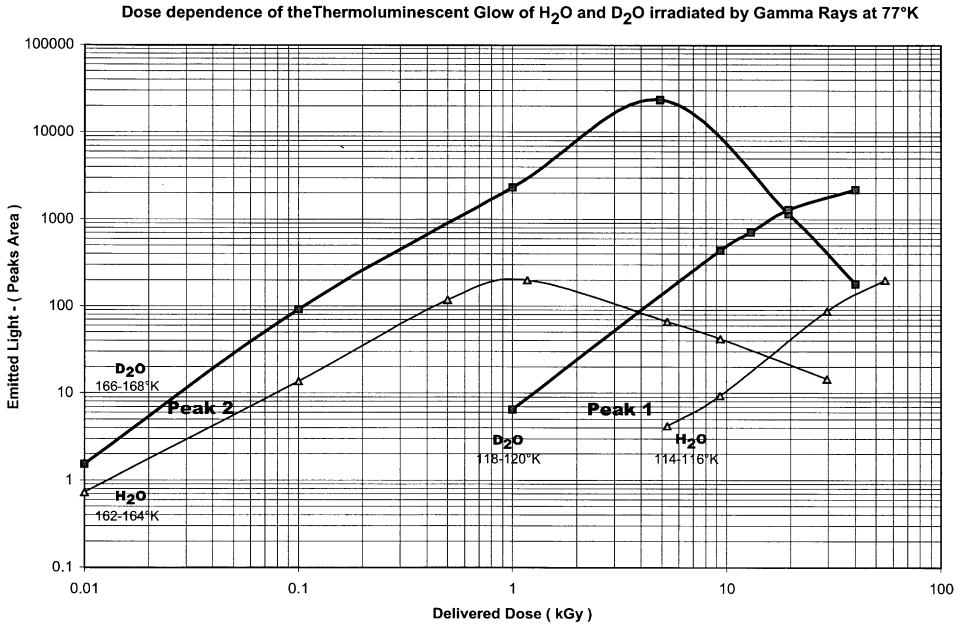


Fig. 3. Dose dependence of the thermoluminescent glow of H₂O and D₂O irradiated by gamma rays at 77°K.

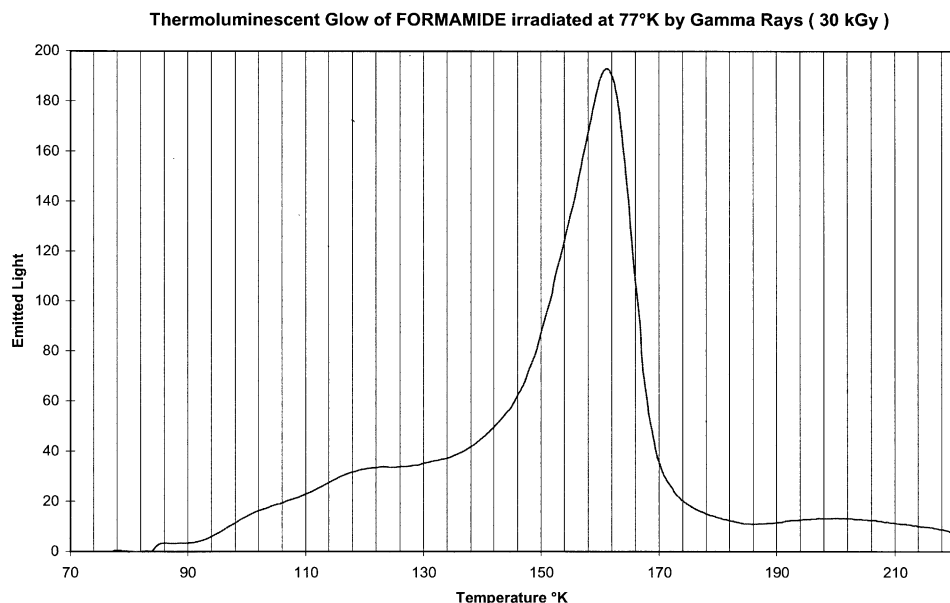


Fig. 4. Thermoluminescent glow of FORMAMIDE irradiated at 77°K by gamma rays (30 kGy).

to suppress hydrogen bonds. The result, indeed, is spectacular and, at the relatively low concentration of 0.1 M Peak 2 is totally erased (Fig. 5) whereas the basic emission of Peak 1 remains almost unchanged.

At that point we thought that it would be of interest to challenge the theory according which pre-existent “structures” in the original fluid, developed around some added chemicals, could survive a great number of successive dilutions when done under vigorous mechanical stirring.

To that end we did prepare ourselves, courtesy of the BOIRON LABORATORIES, ultra-high dilutions of lithium chloride and sodium chloride by successive dilutions to the hundredths, all done under vigorous mechanical stirring (initially 1 g in 100 cm³, then 1 cm³ of this solution in 99 cm³ of pure D₂O ... and so on) until we reached— theoretically—at the 15th dilution, a “concentration” of 10⁻³⁰ g cm⁻³. A reference sample of D₂O alone was also prepared according to this technique, still keeping vigorous agitation (150 strokes/7.5 s at each successive “dilution” step).

We did proceed, then, to the “activation” of these materials by irradiation according the following experimental protocol.

2. Experimental

One cubic centimeter of each solution is placed in aluminium test cavities of 20 mm diameter and 2 mm depth and frozen to -20°C on a cold metallic block. The frozen

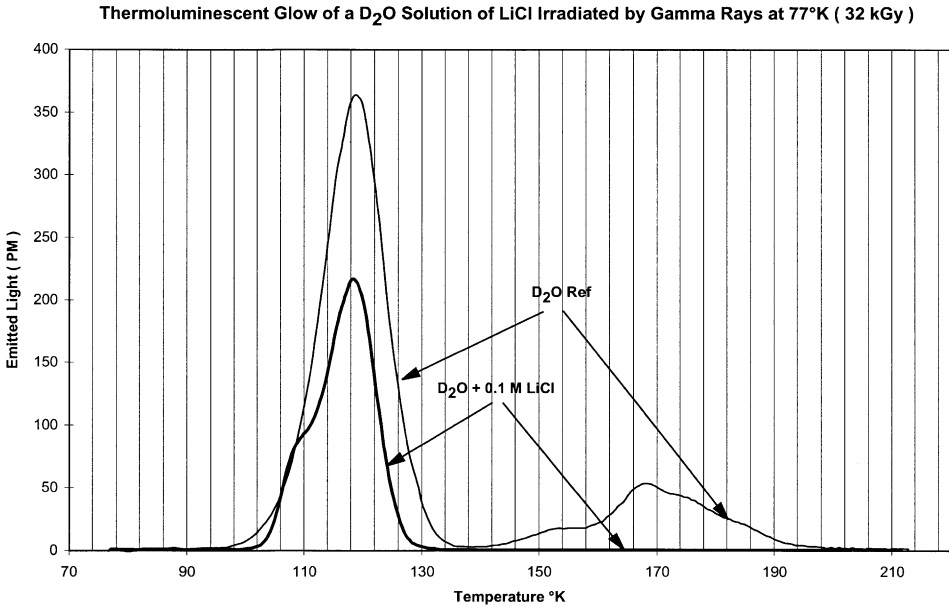


Fig. 5. Thermoluminescent glow of a D₂O solution of LiCl irradiated by gamma rays at 77°K (32 kGy).

systems are kept 24 h at -20°C to achieve stability into their crystallization pattern and they are finally immersed into liquid nitrogen and kept at -196°C for 24 h.

In a first set of experiments the frozen ice disks are irradiated at 77 K with 100 kV X-rays to achieve a dose of 0.4 kGy (30 min). Previous determinations were done to check that the disks having identical positions in the field did receive the same dose (dosimetry has been done using Harwell, FWT, and alanine dosimeters). After irradiation, all the “activated” samples are transferred into a liquid nitrogen container and kept, there, for a week-time, to even out whatever small differences could exist between them.

Finally, all samples are placed in the thermoluminescence equipment and their respective glow recorded—with both a photo-multiplier and a CCD camera connected to a spectrograph—in the course of rewarming ($3^{\circ}/\text{min}$) between 77 and 213 K, as has been done in our previous published experiments.

3. Results

Much to our surprise, the experimental results do show—without any ambiguity—that for an X-ray dose of 0.4 kGy the thermoluminescence glows of the three systems were substantially different (Fig. 6). These findings did prove to be reproducible in the course of many different identical experiments.

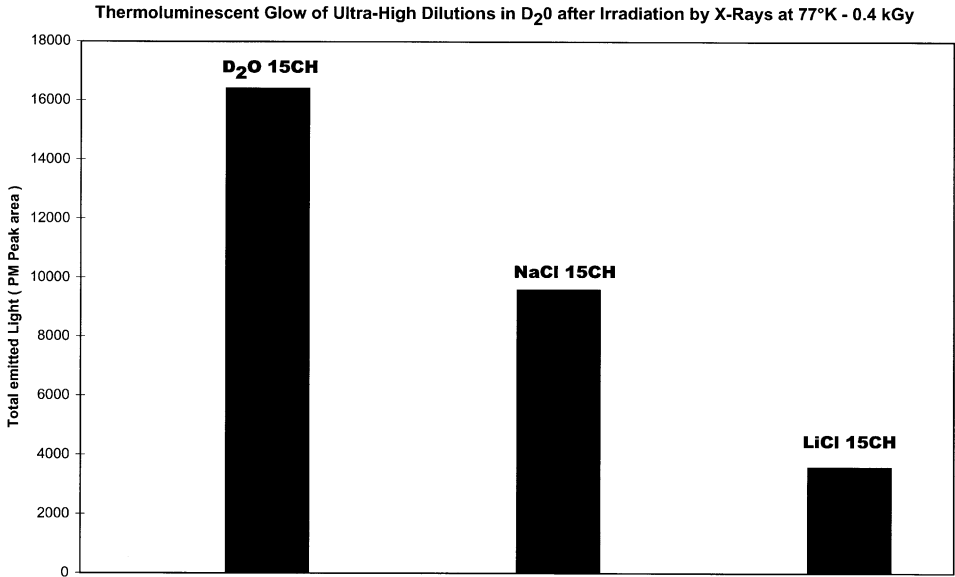


Fig. 6. Thermoluminescent glow of ultra-high dilutions in D₂O after irradiation by X-rays at 77°K (0.4 kGy).

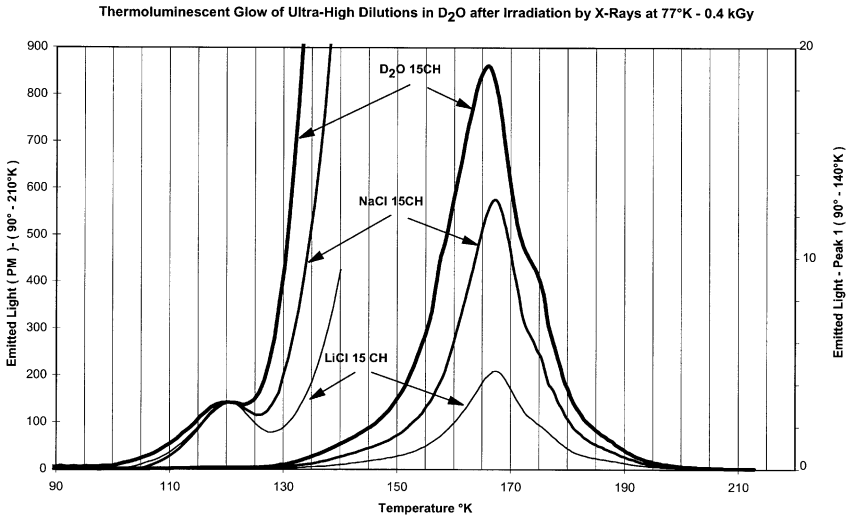


Fig. 7. Thermoluminescent glow of ultra-high dilutions in D₂O after irradiation by X-rays at 77°K (0.4 kGy).

To compare the curves between them we normalised the emitted light readings taking Peak 1 as the reference. In doing so, we obtain for Peak 2 the different curves presented in Fig. 7 which show quite clearly that the initial addition of a solute (NaCl and LiCl) in the original D₂O leaves a permanent effect even when, by successive dilutions made

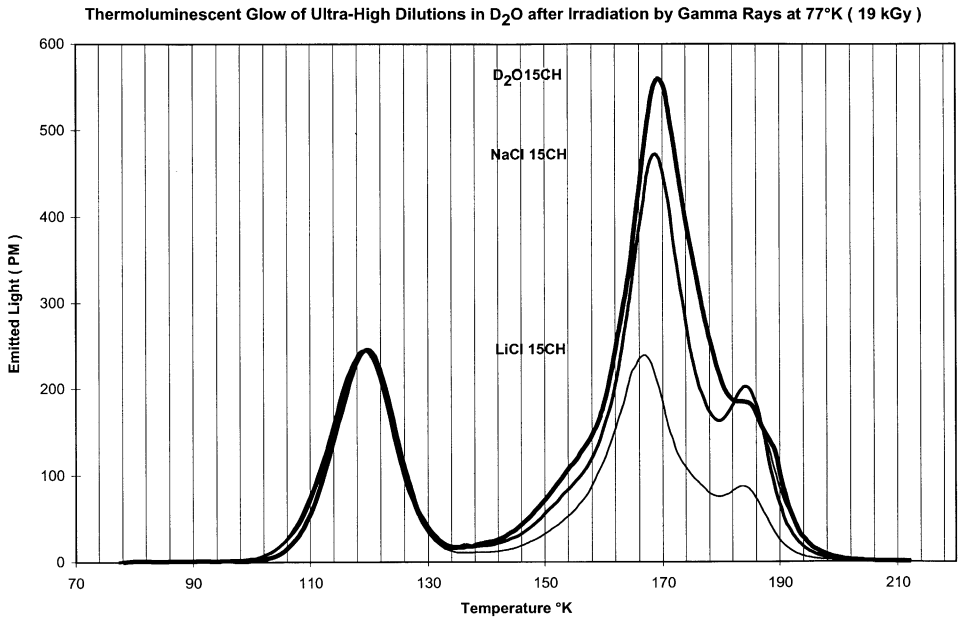


Fig. 8. Thermoluminescent glow of ultra-high dilutions in D₂O after irradiation by gamma rays at 77°K (19 kGy).

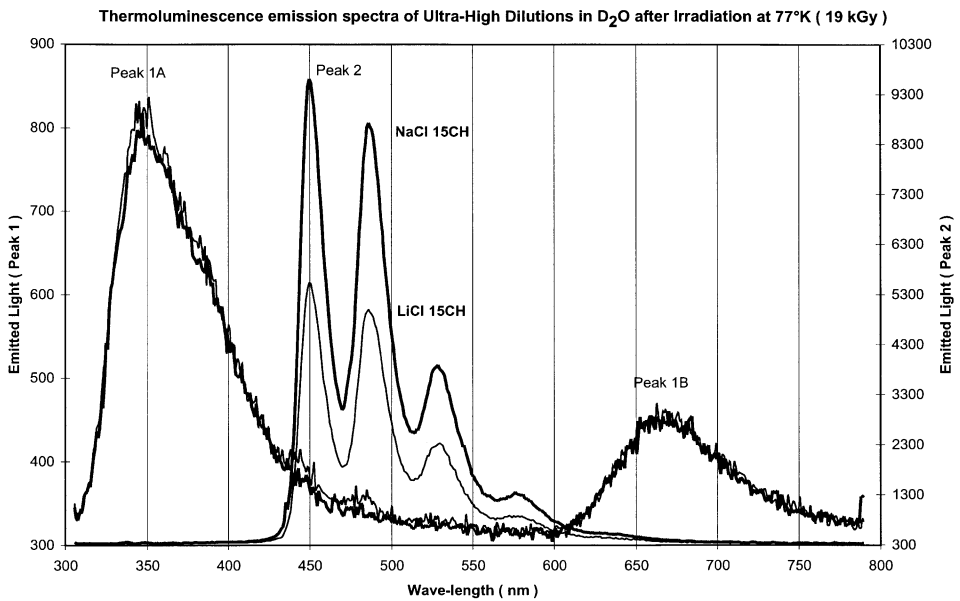


Fig. 9. Thermoluminescence emission spectra of ultra-high dilutions in D₂O after irradiation at 77°K (19 kGy).

under strong vibration, all traces of solute have disappeared. More remarkable to our eyes is the fact that, by far, lithium chloride demonstrates a stronger hydrogen bond suppressing “ghost” effect which could be related to the larger size of the lithium ion.

A second set of experiments done with gamma rays (courtesy of CELESTIN Reactor, COGEMA, Marcoule), at a higher dose (19 kGy) did confirm these findings (Figs. 8 and 9).

It appears, therefore, that the structural state of a solution made in D₂O can be modified by the addition of selected solutes like LiCl and NaCl. This modification remains even when the initial molecules have disappeared and the effect is the same at different irradiation doses (0.4–19 kGy) and for different radiant sources (X-rays, gamma rays). As a working hypothesis, we believe that this phenomenon results from a marked structural change in the hydrogen bond network initiated at the onset by the presence of the dissolved ions and maintained in the course of the dilution process, probably thanks to the successive vigorous mechanical stirrings.

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