Adding memory to pressure-sensitive phosphors

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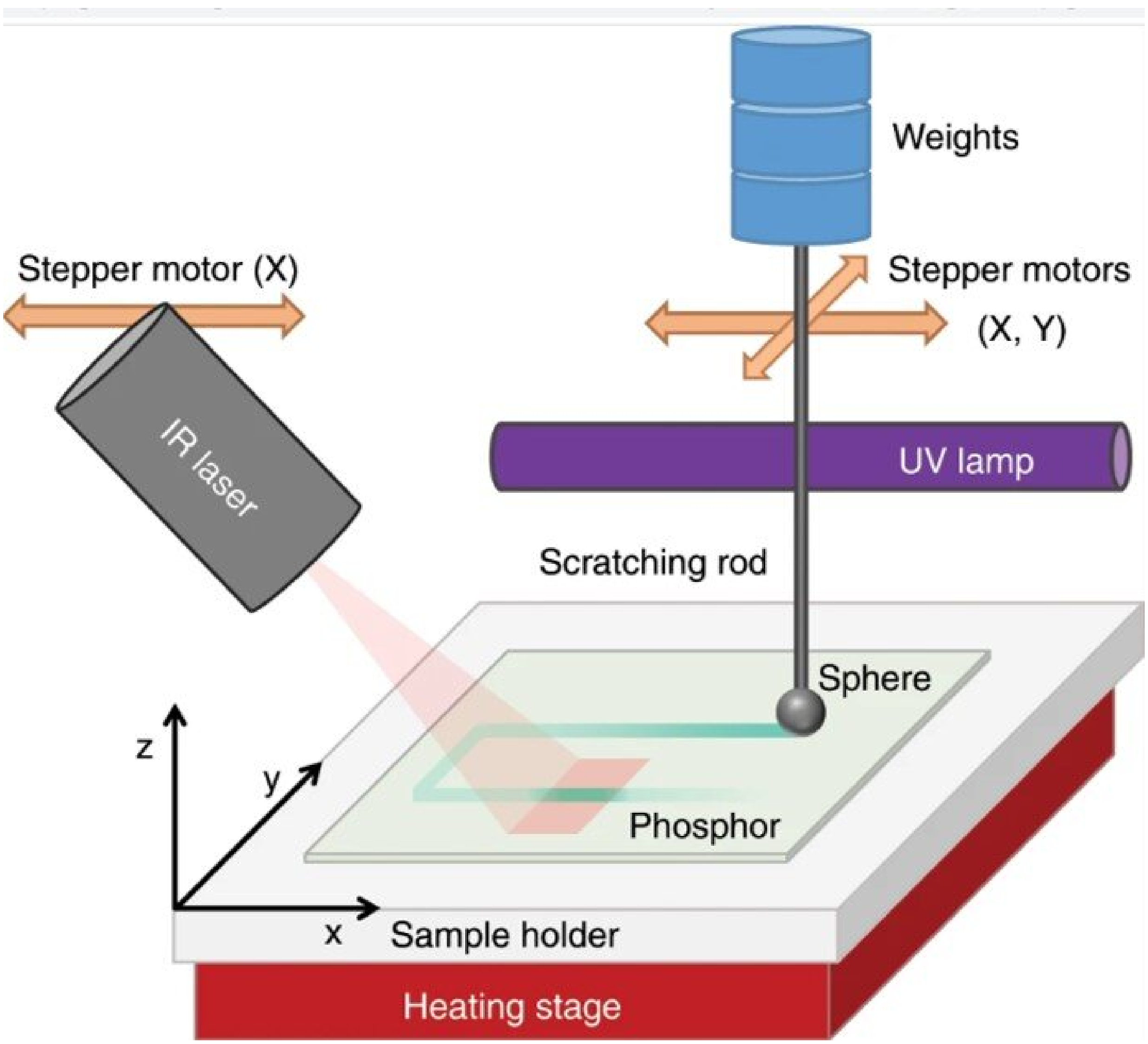
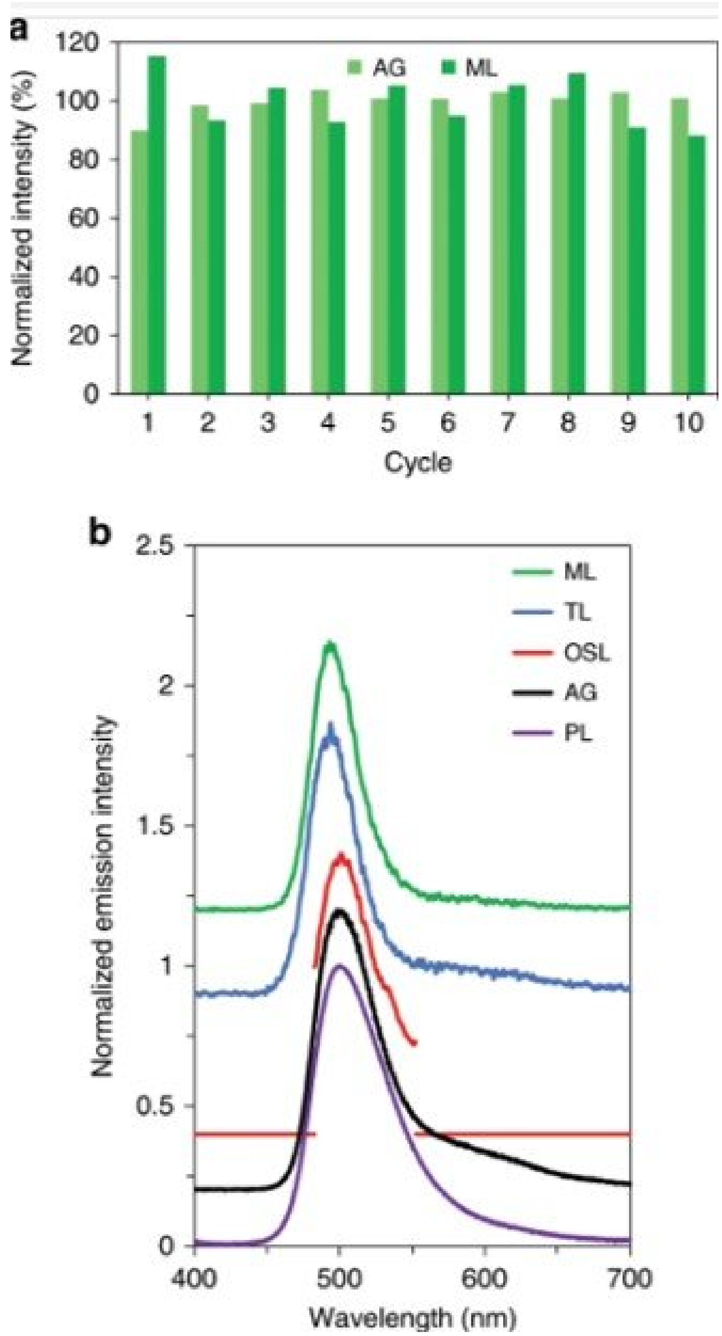


Schematic representation of the experimental setup includes a UV excitation source, a motorized friction stage, an IR laser and a digital camera. The camera, omitted to preserve clarity, is mounted at a slight angle to the phosphor–polymer composite sample. Credit: Light: Science & Applications, doi: 10.1038/s41377-019-0235-x

Mechanoluminescence (ML) is a type of luminescence induced by any mechanical action on a solid, leading to a range of applications in materials research, photonics and optics. For instance, the mechanical action can release energy previously stored in the crystal lattice of phosphor via trapped charge carriers. However, the method has limits when recording ML emissions during a pressure-induced event. In a new study, Robin R. Petit and a research team at the LumiLab, Department of Solid State Sciences at the Ghent University—Belgium devised a new technique to add a memory function to pressure-sensitive phosphors. Using the method, the scientists obtained an optical readout of the location and intensity of a pressure event three days (72 hours) after the event.

The team noted the outcome using Europium-doped barium silicon oxynitride ($BaSiO_2N_2:Eu^{2+}$) phosphor, which contained a broad trap depth distribution or depth of defect distribution—essential for the unique memory function. The excited electrons of phosphor filled the 'traps' (or defects) in the crystal lattice, which could be emptied by applying weight to emit light. The research team merged optically stimulated luminescence (OSL), thermoluminescence (TL) and ML measurements to carefully analyze the influence of light, heat and pressure on trap depth distribution. Based on the memory effect, the materials remembered the location at which pressure had occurred, helping researchers to develop new pressure sensing applications and study charge carrier transitions within energy storage phosphors. The work is now published on *Light: Science & Applications*.

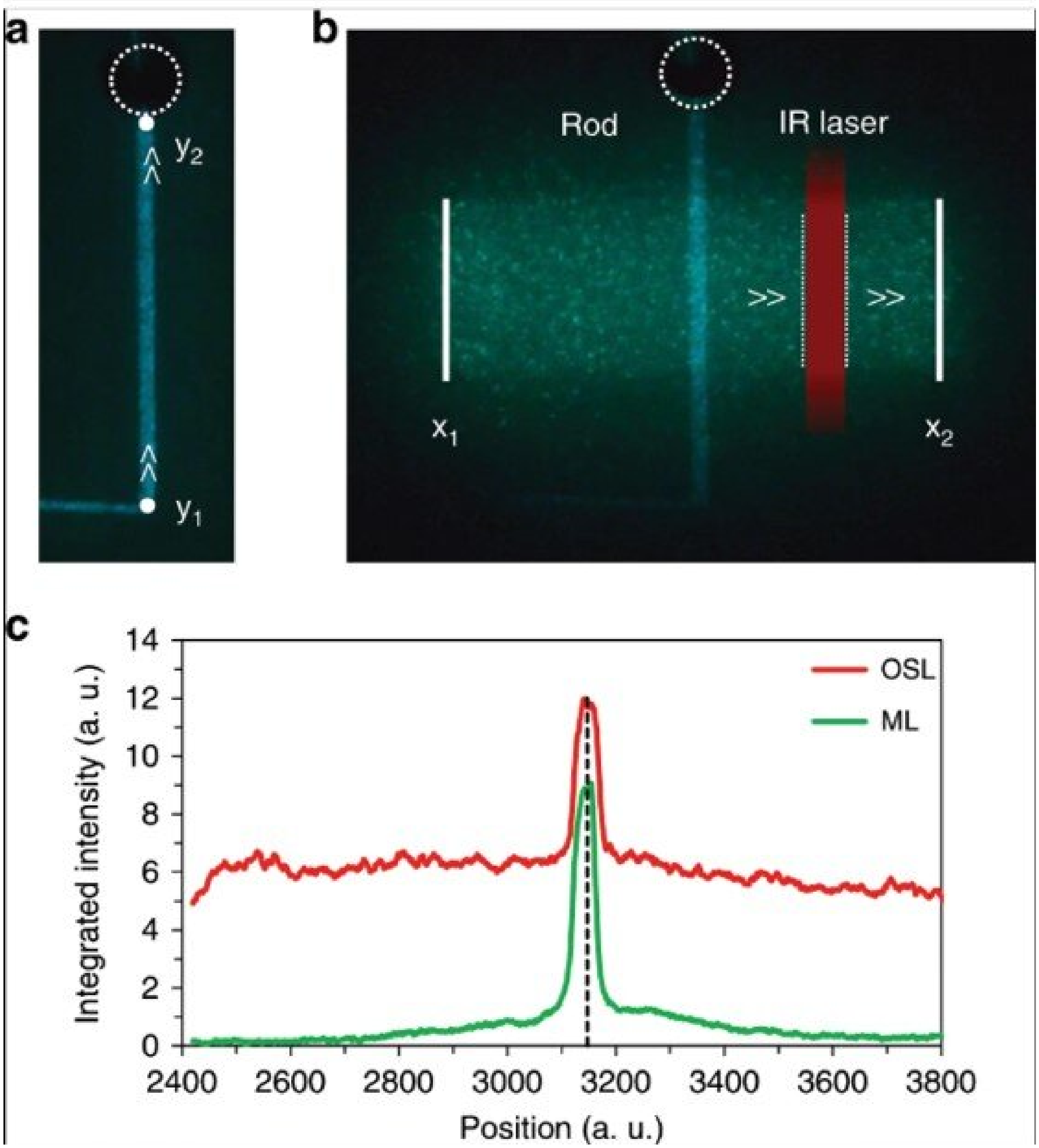
When specific materials are subjected to mechanical action, light emission can be observed as mechanoluminescence (ML). The process can be induced through different types of mechanical stress including friction, fracture, bending, impact of a weight and even ultrasound, crystallization and wind. The phenomenon can be used to identify stress distribution, microcrack propagation and structural damages in solids, while allowing a variety of applications in displays, to visualize ultrasound and even map personalized handwriting. However, the technique is limited by the range of emission colors, restriction of real-time measurements and restricted signal visibility.



Reproducibility and spectral characterization. (a) Variation of the AG and ML intensity throughout 10 cycles of UV excitation (1 min), waiting (3 min) and dragging the rod over the surface of the phosphor–polymer composite sample. Both AG and ML are normalized to their respective averages. (b) Emission spectra under steady-state excitation (PL), during the afterglow (AG), at the maximum of the thermoluminescence glow peak (TL), during mechanical stimulation (ML) and upon infrared laser irradiation (OSL). To block the reflected IR laser emission, a bandpass filter was used, centred on the emission band for BaSi2O2N2:Eu2+. Credit: Light: Science & Applications, doi: 10.1038/s41377-019-0235-x

Using Eu^{2+} doped $BaSiO_2N_2$ phosphor as an example, the scientists first excited the phosphor with ultraviolet (UV) or blue light to bring it into an excited state. When the ion transited back to the ground state, they observed a blue-green emission of color. Researchers had previously shown that thermally assisted detrapping (electron removal from a trap) allowed 'glow-in-the-dark' phosphors for safety signage or bioimaging functions. Applying pressure in the setup similarly induced detrapping for thermal- and pressure-induced detrapping to become competing processes. The scientists avoided the presence of background emission or afterglow in the setup to increase visibility of the signal. In this work, Petit et al. introduced the pressure memory (P-MEM) property, which allowed phosphor particles that were subjected to pressure to remember the process under infrared radiation (IR) more than 72 hours after pressure application.

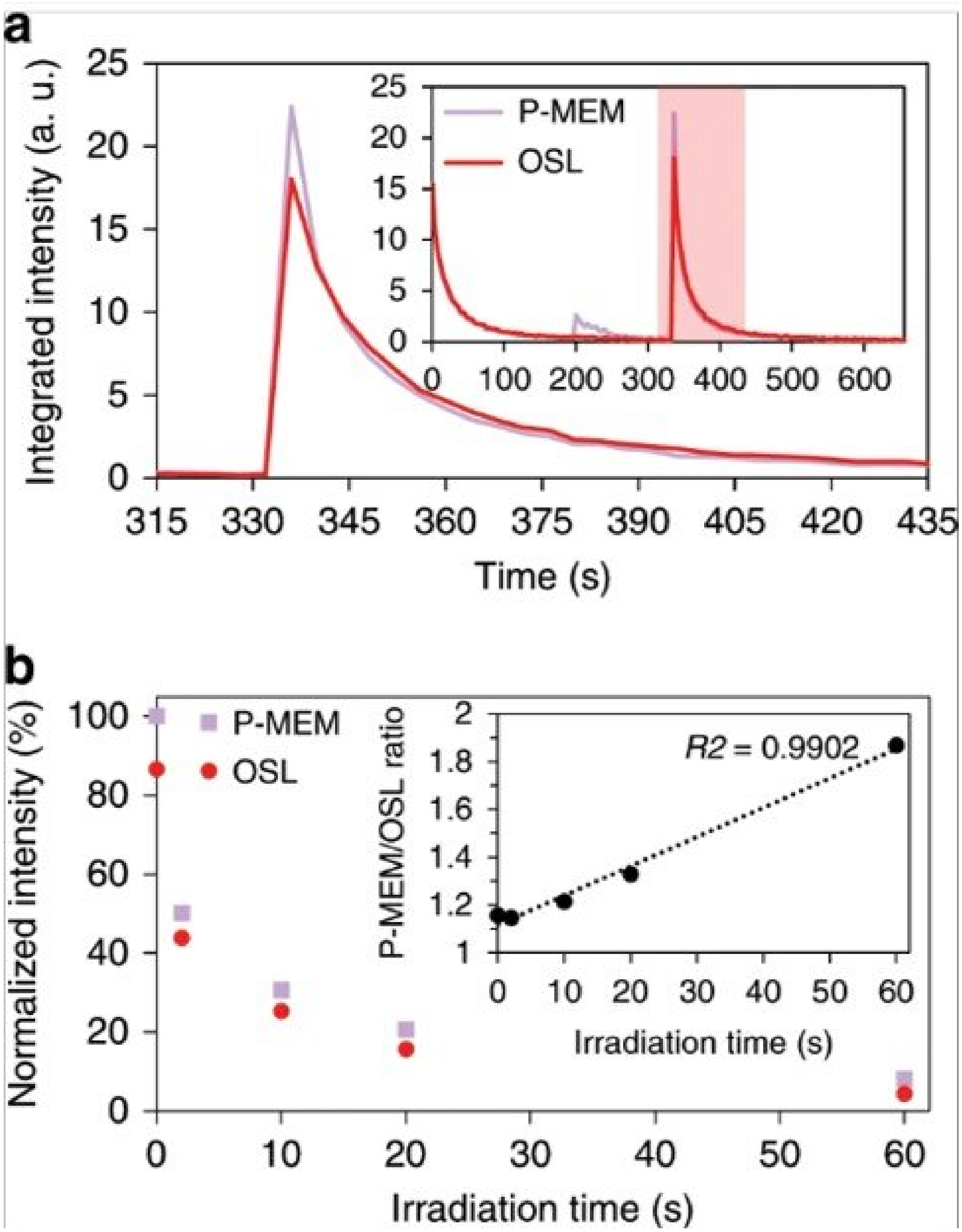
The team investigated the underlying working principles of the P-MEM (pressure-memory) property using a relatively large range of trap depths within the phosphor where different traps responded differently to specific stimuli (pressure, heat, light). When they mechanically induced detrapping some of the charge carriers recombined to yield immediate light emission while others were redistributed across relatively shallow traps or almost permanently stored in deep traps. To release the charges in deep traps they used IR radiation. The work opens new avenues for pressure sensing and facilitates the study of energy storage phosphors by probing subtle interactions between thermal, mechanical and optical detrapping.



The P-MEM property. (a) After UV excitation and a waiting time of 3 min, the rod was dragged back and forth between positions y1 and y2 (approximately 20 mm). Half an hour later, an IR laser was swept from left to right, during which image (b) was taken. Finally, the OSL intensity profile (c) was calculated within the area confined by x1 and x2. For comparison, the ML intensity profile within the same area but measured during the application of pressure is also indicated. Credit: Light: Science & Applications, doi: 10.1038/s41377-019-0235-x

To test reproducibility of the ML tests, the scientists first performed mechanical stimulation by non-destructively dragging a spherical-shaped rod across the surface of the phosphor. They guaranteed reproducibility of the measurements by recovering the initial ML intensity after each UV excitation step. The capacity of active storage traps remained unaltered due to mechanical stimulation, while the dragging process remained non-destructive. To achieve the P-MEM property, the team combined mechanical and optical stimulations in the lab, they used pressure to move the electrons and used optical means to read-out the results.

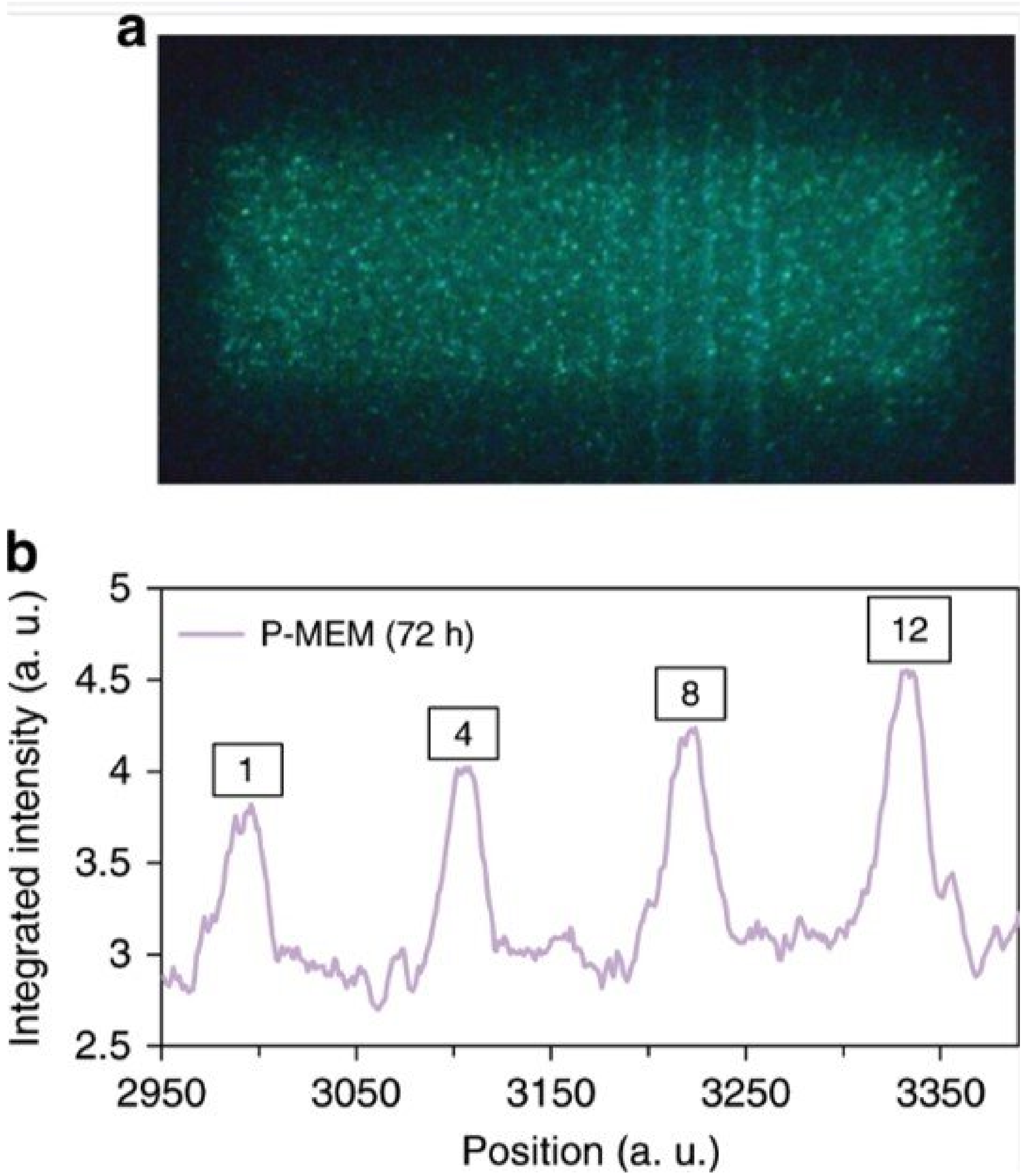
First, they exposed the crystal to UV light followed by ML stimulation by dragging a rod back and forth several times, then irradiated the sample using the IR laser. During IR stimulation, the emission spectrum originated from the Eu^{2+} luminescent center in $BaSiO_2N_2$. The team investigated the relationship between the luminescence intensity and magnitude of the load in the experiment; which increased linearly with the applied load. Applying higher loads for mechanical stimulation emptied more traps in the crystal to release more charge carriers. Some of the released electrons recombined immediately with ionized europium ions to yield the common ML signal.



Increasing P-MEM signal visibility. (a) Temporal behaviour of the P-MEM signal. The inset shows the complete duration of the experiment with periods of afterglow (first ~180 s), mechanical stimulation (~180–250 s) and IR irradiation (~330–600 s). The highlighted area is shown in detail in the main figure. (b) Effect of pre-irradiation on the OSL and P-MEM intensity, leading to an increase in contrast between both signals, as shown in the inset. Credit: Light: Science & Applications, doi: 10.1038/s41377-019-0235-x

After extensively testing the setup, Petit et al. observed the origin of P-MEM using thermoluminescence (TL) to reveal the occupation of traps in phosphors. For this, they divided the TL-glow curves in to three regions containing a shallow (25 degrees C to 45 degrees C), intermediate (45 degrees C to 80 degrees C) and deep trap region (>80 degrees). The results implied that the P-MEM property was based on a reshuffling event to release charge carriers that occupied deep trap levels.

It was equally important for the research team to visualize the P-MEM signal as a function of time. They achieved this by performing a dedicated experiment to test the influence of IR irradiation and observed two effects relative to (1) emptying of deep trap levels, followed by the (2) subsequent decay originating from the gradual depletion of shallow and intermediate trap levels. Due to the stability of deep traps, after optimizing the setup, the team observed the P-MEM signal with sufficient intensity—three days after the application of pressure and IR-irradiation assisted readout.



Exploring the limits of the P-MEM property. (a) Digital picture of the sample during irradiation of the phosphor with IR radiation 72 h after mechanical stimulation, consisting of a sequence of drags. (b) Integrated intensity profile derived from a, showing the P-MEM intensities corresponding to 1, 4, 8 and 12 drags. Credit: Light: Science & Applications, doi: 10.1038/s41377-019-0235-x

In this way, Robin R. Petit and colleagues detailed a specific interaction between mechanical and optical detrapping in $BaSiO_2N_2:Eu^{2+}$, which led to the unique P-MEM property observed in the study. They recovered a pressure-induced ML signal after IR irradiation of the phosphor, based on the detailed interactions. When they conducted optical detrapping with IR irradiation, the deeper traps emptied rapidly to create an increased signal strength at places where pressure had previously occurred, even 72 hours between the pressure stimuli and IR readout. The deep traps played a significant role in obtaining the P-MEM phenomenon and can be extended to even longer hours.

The work opens a new path for information storage and retrieval, while mechanical stimulation provides a unique way to write information. The described P-MEM has great potential within structural health monitoring applications and in biomedicine. The comprehensive results indicate that much remains to be understood on the inner workings of luminescent phenomena relative to detrapping and retrapping routes, warranting further in-depth research.

More information: Robin R. Petit et al. Adding memory to pressure-sensitive phosphors, *Light: Science & Applications* (2019). DOI: 10.1038/s41377-019-0235-x

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