DIFFERENTIAL-FADING OPTICALLY STIMULABLE MATERIALS FOR NUCLEAR SAFEGUARDS

Francesco d'Errico[1,2,3], Danilo O. Junot[4,5], Ivón O. Polo[5], Andrea Chierici[1], Riccardo Ciolini[1,2], Divanizia N. Souza[4], Linda V.E. Caldas[5], <u>Susana O. Souza[4]</u>

[1] Scuola di Ingegneria, Università di Pisa (UNIPI), Pisa, Italy
francesco.derrico@ing.unipi.it

[2] Istituto Nazionale di Fisica Nucleare (INFN), Sezione di Pisa, Pisa, Italy

[3] Yale Center for Emergency Preparedness and Disaster Response (YALE),
New Haven, CT USA

[4] Departamento de Física, Universidade Federal de Sergipe (UFS)
49100-000 São Cristóvão, SE, Brazil
sosouza@ufs.br

[5] Instituto de Pesquisas Energéticas e Nucleares
IPEN/SP,
São Paulo, SP Brazil
lcaldas@ipen.br

ABSTRACT

Safeguards agencies are concerned with the safety of nuclear installations and the security of nuclear materials. Material protection, control, and accountancy are the first steps towards maintaining continuity of knowledge of these materials and preventing illicit trafficking or diversion of these materials for illicit purposes. Related concerns also exist in arms control, where the item chain of custody is important. In order to strengthen and improve the efficiency and effectiveness of existing safeguards measures, tamperproof devices and materials are needed capable of determining elapsed time since the undeclared movement of a source. Our group developed a new approach for surveillance based on passive, solid-state devices. Relying on a non-electronic detection mechanism is highly desirable because complex electronic components and circuits are potentially vulnerable to tampering and snooping. The device is a set of passive optically stimulated luminescent detectors based on calcium sulfate doped with various rare earths. The different doping produces different temporal fading profiles. When a source causes energy deposition in the detectors, the latter accumulate trapped electrons that undergo de-trapping at different rates. Thus, reading them out produces a set of signals that correlates both with the strength of the source and with the time of its passage.

1. INTRODUCTION

Countries worldwide host thousands of radioactive sources used for medical, scientific, and industrial applications. In particular, radioactive sources are encountered at hospitals in large cities, visited by thousands of people daily, and in remote locations, where individuals or small groups use portable devices for a variety of purposes. Some radioactive materials are encapsulated in solid containers and can range from rice-grain sized seeds, used for brachytherapy treatments, to large irradiators weighing several tons, used for industrial sterilization processes. Some of these radioactive sources are located in open facilities with minimal or no physical protection or on-site surveillance.

Due to inadequate chain-of-custody procedures and insufficient regulatory controls, thousands of radioactive sources have gone missing around the planet in recent decades [1]. The

problem does not affect only "developing countries": even in places with effective regulatory controls, high disposal costs and a lack of repositories have led end-users to abandon radioactive sources at the end of their life cycle. Thus, there is a growing recognition of the need for comprehensive security systems on issues such as improving technical measures to detect illicit movement and trafficking in nuclear and other radioactive materials, developing relevant instruments and methods, and applying nuclear forensics to prevent, and respond to, nuclear security events.

The International Atomic Energy Agency (IAEA) has developed a risk-based graded framework to the security of radioactive sources, establishing five categories of sources that require different levels of protection depending on their radioactivity level. The first and second categories pose the highest risk. The first category requires the most stringent controls and includes radioisotope thermoelectric generators (RTGs), irradiators, teletherapy sources, and fixed, multi-beam teletherapy ("gamma knife") sources. The second category includes industrial gamma radiography sources, high-/medium- dose rate brachytherapy sources, and others. If such sources fall into the wrong hands, they can be used to create radiological dispersion devices (RDDs), commonly known as "dirty bombs". If detonated, a dirty bomb could release high doses of radiation in a concentrated area, triggering panic and rendering that area uninhabitable for an extended period of time—resulting in large economic losses and risks of cancer among people who were exposed. That is why radioactive sources require reliable protection, accounting, and control measures, as well as appropriate management after their decommissioning, regardless of where they are located and used.

In order to strengthen and improve the efficiency and effectiveness of existing safeguards measures, tamperproof devices and materials capable of determining the time elapsed since material movement are desirable [2]. In recent years, novel applications for thermoluminescence (TL) have been explored where the "ideal dosimeter" is not necessarily well suited [3]. In this application, the depopulation of each trap is used as a signature of the time-temperature profile when the sensors are embedded in extreme environments such as fires and explosions.

2. MATERIALS AND METHODS

In thermoluminescence and optically stimulated luminescence (OSL) dosimetry, a time- and temperature-dependent loss of signal occurs after irradiation and before the readout. This is inherently related to the release of trapped charges (electrons or holes) at ambient temperature when the trap depth E is small. In the simplest model, with a single trap, the rate of variation of the trap occupancy is described by an Arrhenius expression:

$$dn/dt = - n \; s \; e^{-E/kT}$$

where n is the trap population density, s is a frequency factor, E is the trap depth, k is the Boltzmann constant and T is temperature.

A pronounced fading is typically considered an undesirable characteristic, leading to a limited useful interval for a luminescent material. Conversely, in this work, we exploited the differential fading of a series of OSL materials in order to detect, time-stamp and thus deter the illicit movement and trafficking radioactive sources. The OSL materials were chosen to have the same chemical composition and energy dependence, but significantly different signal fading rates. The main advantages of using OSL materials are a) simplicity of approach, b) passive operation, and c) absence of vulnerabilities associated with electronics tampering. Calcium sulfate produced with different dopants and co-dopants was considered particularly interesting because it presents: (a) the same energy response but different fading rates; (b) a well-established TL and OSL response.

INAC 2019, Santos, SP, Brazil.

A series of calcium sulfate samples were produced using a slow-evaporation synthesis route [4]. To begin, 6 g of calcium carbonate ($CaCO_3$, JT Backer and Neon) were added to 150 ml of sulfuric acid. The solution of $CaCO_3 + H_2SO_4$ resulting from the mixture was deposited in a beaker and kept in a magnetic stirrer at 120 °C until complete homogenization. Subsequently, the solution was heated to 300 °C until all the acid evaporated (in about 8 hours). At this point, various dopants were added in proportions of mol% of $CaCO_3$ mass. A variety of rare earths was tried for the purpose, including thulium, terbium, and europium. These same rare earths were also tried as co-dopant combinations, namely, terbium-europium and terbium-europium-thulium. Finally, the addition of silver co-doping was also tried with thulium and europium. All, these compounds had been previously investigated in the search for dosimetric materials with high sensitivity, luminescent yield, and stability. It was exactly their absence of a stable signal that made them interesting for the present application.

Crystal formation was controlled by means of an appropriate heating profile and the materials that were obtained after evaporation were pulverized with a mortar to produce different granulometries. The crystals were sieved, and grains were grouped in three different diameter ranges: $\emptyset < 45$ μm, 45 μm $< \emptyset < 75$ μm, 75 μm $< \emptyset < 150$ μm, $\emptyset > 150$ μm. Next, grains were formed into pellets. For their production, 50% by weight of calcium sulfate powder and a 50% of Teflon were mixed and pressed with a 2 tonne hydraulic press. Teflon was added because it is an inert binder providing firmness to the compound, it is adequately transparent to the luminescence from calcium sulfate, and it has a high melting temperature thus permitting both optically and thermally stimulated luminescence applications. Teflon was added to the calcined grains with size of 45 μm $< \emptyset < 75$ μm and 75 μm $< \emptyset < 150$ μm. After pressing, pellets were obtained of approximately 6 mm in diameter and 1 mm in thickness.

The initial quality control tests on the grains were performed at the Federal University of Sergipe (UFS) using a DOIN-L001 OSL reader system developed and produced by the Department of Nuclear Energy of the Federal University of Pernambuco (DEN-UFPE). This reader uses a blue LED (emission peak at 470 nm) as a stimulation source and U-340 type detection filter (transmission between 290 nm and 390 nm). The detection system was computationally coupled to the WinLOE software, also developed by DEN-UFPE, with which the reading parameters were selected. Grains of about 75 μm $< \emptyset < 150$ μm and of $\emptyset > 150$ μm were analyzed using a reading time of 20000 ms, for one stimulation based on continuous mode. In each measurement, 15 mg of calcium sulfate grains were irradiated to doses ranging from 0.3 Gy to 2 Gy using a beta source of $^{90}Sr/^{90}Y$ producing an absorbed dose rate of 353 mGy/min.

The subsequent fading studies on the differently-doped and co-doped pellets were performed with a TL/OSL Risø reader at the Nuclear and Energy Research Institute in São Paulo (GMR-IPEN-SP). The device uses continuous wave (CW) blue LED stimulation with peak emission at 470 nm. A Hoya U-340 bandpass filter (transmission between 290 nm and 390 nm) and an EMI 9235QB photomultiplier tube (maximum quantum efficiency at approximately 200 and 380 nm) are instead used for luminescence detection. Once again irradiations were done using a $^{90}Sr/^{90}Y$ beta particle source, in this case, a higher activity one producing a dose rate of 0.1 Gy/s. Data were recorded at different times after the irradiation, either immediately after or at incremental one-day intervals over the course of one week. Three samples were used for each case and, each time, the emission curve was recorded, and the background signal acquired before the specific sample irradiation was subtracted.

3. RESULTS

Doping calcium sulfate with the above-mentioned combinations of elements produced fading characteristics with widely differing temporal profiles. These differences were clearly detectable in the course of 5 days post-irradiation, which is suitable for the envisaged application.

Table 1 reports the OSL data acquired over 5 days post-irradiation along with the respective Type A uncertainties (u).

Table 1: OSL signal data acquired as the mean value of sets of three detectors irradiated on Day 1 and read out on different days in the course of one week.

Doping	Day 1	u	Day 2	u	Day 3	u	Day 4	u	Day 5	u
EuAg	4.03E+5	6.74E+3	1.63E+5	7.83E+3	1.45E+5	8.65E+3	1.43E+5	7.07E+3	1.29E+5	2.91E+3
Tm	3.91E+4	3.24E+3	3.20E+4	3.37E+2	2.21E+4	3.05E+3	1.87E+4	7.65E+1	1.92E+4	5.16E+2
TbEu	2.32E+6	3.99E+4	1.15E+6	4.10E+4	1.13E+6	5.14E+4	1.05E+6	1.57E+5	1.11E+6	1.87E+5
Dy	6.41E+5	1.90E+4	2.09E+5	1.02E+4	1.59E+5	1.55E+4	1.48E+5	1.24E+4	1.33E+5	1.95E+4
Eu	9.37E+4	3.49E+3	3.70E+4	3.67E+2	2.61E+4	5.37E+3	2.10E+4	4.15E+2	1.83E+4	4.46E+2
TmAg	7.20E+6	2.77E+5	4.18E+6	3.77E+5	2.91E+6	1.94E+5	2.86E+6	2.11E+5	3.00E+6	1.30E+5
TbEuTm	1.25E+6	8.40E+4	9.55E+5	3.54E+4	8.91E+5	6.75E+4	8.10E+5	6.18E+4	8.56E+5	2.16E+4

u = Type A uncertainties

Figure 1 shows the data reported in Table 1, normalized to the initial OSL signal, acquired immediately after the irradiation on Day 1, in order to emphasize the relative fading profile of the different compounds.
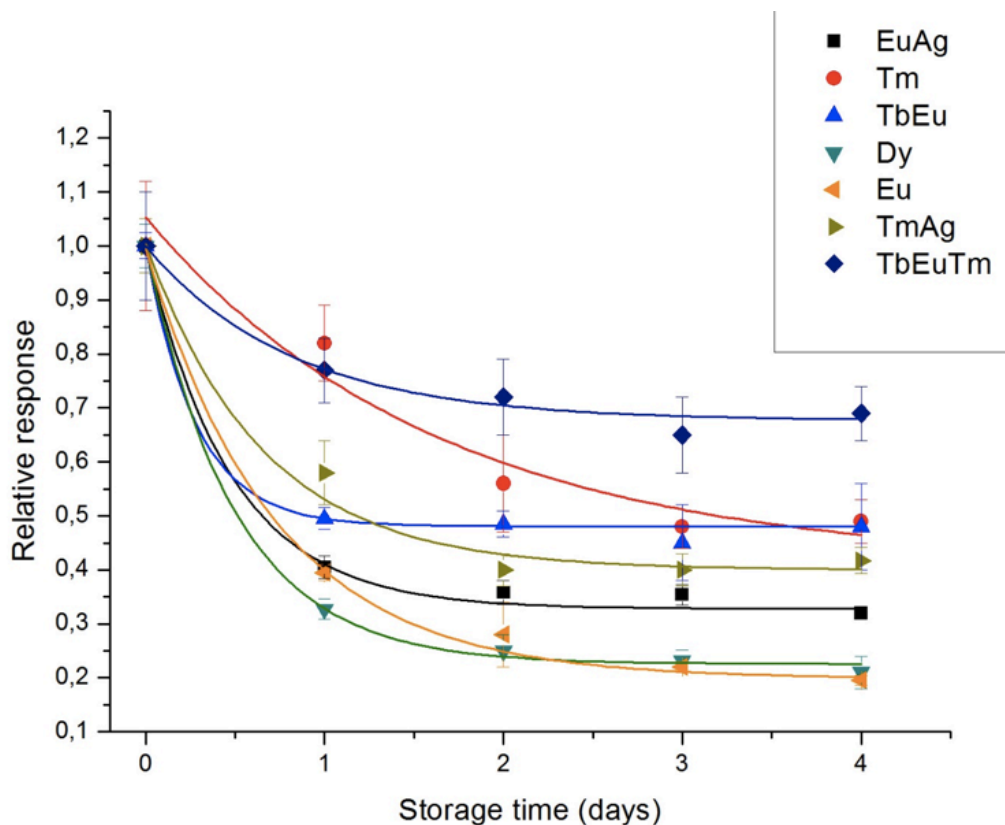

Fig 1. Optically stimulated luminescence of variously doped calcium sulfate pellets acquired at one-day intervals over one-week post-irradiation (results are normalized to the initial OSL signal acquired immediately after the irradiation).

The experiments need to be repeated to achieve greater accuracy and verify the reproducibility of the results. Nevertheless, the time-dependent fading data appear largely consistent with an exponential behavior of the form $y = A_1 * \exp(-x/t_1) + y_0$. The fitting parameters

for the different materials and the respective R^2 regression coefficients are reported in Table 2. The possibility to describe the fading curves with single exponentials greatly facilitates their practical application.

Table 2: Fitting parameters for the exponential equation used to interpolate the experimental results.

Equation $y = A_1*exp(-x/t_1) + y_0$		Value	Standard Error	Adjusted R^2
Eu,Ag	y_0	0.328	0.010	
	A_1	5.5	2.0	0.99045
	t_1	0.477	0.081	
Tm	y_0	0.41	0.10	
	A_1	1.19	0.42	0.87245
	t_1	1.63	0.89	
Tb,Eu	y_0	0.4807	0.0076	
	A_1	19	13	0.99867
	t_1	0.279	0.055	
Dy	y_0	0.2256	0.0075	
	A_1	5.84	0.69	0.99729
	t_1	0.495	0.028	
Eu	y_0	0.1986	0.0071	
	A_1	3.17	0.43	0.99082
	t_1	0.724	0.052	
Tm,Ag	y_0	0.400	0.021	
	A_1	2.8	1.3	0.96900
	t_1	0.65	0.19	
Tb,Eu,Tm	y_0	0.677	0.019	
	A_1	1.10	0.41	0.92876
	t_1	0.82	0.23	

4. CONCLUSIONS

This work provides proof of principle of a novel application of luminescent materials with different fading rates as passive, tamper-indicating systems for the detection of the undeclared movement of radioactive materials. Indeed, if a source transits by the detectors at a time t_0, it appears possible to estimate the elapsed time interval at a time t after t_0 by comparing the ratio of the OSL readings of materials with different fading rates. In principle, just two materials with well-defined intrinsic efficiency would suffice for the purpose, but the use of multiple sensors would provide a useful degree of redundancy. An implementation we envisage for this technology is incorporating these sensors into the tags and seals used by International Atomic Energy Agency inspectors safeguarding materials in storage. Likewise, these sensors could be incorporated into portal monitoring systems for arms control or dismantlement verifications, together with a miniature readout system, to detect unplanned/undeclared exposures within predefined time intervals. Such a device is currently under development at the University of Pisa in close collaboration with the Federal University of Sergipe.

ACKNOWLEDGMENTS

REFERENCES

1. IAEA INCIDENT AND TRAFFICKING DATABASE (ITDB). Incidents of nuclear and other radioactive material out of regulatory control: 2016 Fact Sheet. http://www-ns.iaea.org/security/itdb.asp.

2. K. Mayer, M. Wallenius, K. Lützenkirchen, J. Galy, Z. Varga, N. Erdmann, R. Buda, J-V. Kratz, N. Trautmann and K. Fifield. Nuclear Forensics: A Methodology Applicable to Nuclear Security and to Non-Proliferation. J. Phys. Conf. **312**, (2011) 062003.

3. J.J. Talghader, M.L. Mah, E.G. Yukihara, A.C. Coleman. Thermoluminescent microparticle thermal history sensors. Microsystems & Nanoengineering **2**: 16037 (2016)

4. D.O. Junot, M.A. Couto dos Santos, P.L. Antonio, L.V.E. Caldas, D.N. Souza "Feasibility study of $CaSO_4$:Eu, $CaSO_4$:Eu,Ag and $CaSO_4$:Eu,Ag(NP) as thermoluminescent dosimeters". *Radiat. Meas.,* **71**, 99-103 (2014).