Optically stimulated luminescence properties of Tm^{3+} doped $KMgF_3$ fluoroperovskite

Luis Camargo[1], Lituania Pérez-Cruz[2], Epifanio Cruz-Zaragoza[2]
Segundo Agustin Martínez-Ovalle[3], Julián Marcazzó[1,*]

[1]Instituto de Física Arroyo Seco (UNCPBA) and CIFICEN (UNCPBA – CICPBA – CONICET)
Pinto 399, 7000, Tandil, Argentina

[2]Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México
A.P. 70543, 04510 México D.F., México

[3]Grupo de Física Nuclear Aplicada y Simulación
Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia

[*]Email: jmarcass@exa.unicen.edu.ar

Abstract

In this work the optically stimulated luminescence (OSL) properties of undoped and Tm^{3+}-doped $KMgF_3$ fluoroperovskite have been investigated for the first time. OSL efficiency for stimulation with different wavelengths has been analyzed for each compound. The maximum OSL emission was found with blue light stimulation. The radioluminescence (RL) spectra have shown two emission peaks at 455 and 360 nm, which can be ascribed to the $^1D_2$–$^3F_4$ and $^1D_2$–$^3H_6$ transitions of the Tm^{3+} cations. It has been found that doping with Thulium 0.5 mol % renders the most intense OSL emission. Furthermore, several dosimetric properties such as OSL response as a function of dose, reproducibility of the OSL signal after several cycles of irradiation-readout and the minimum detectable dose have been investigated. Finally, the OSL response of $KMgF_3$:Tm^{3+} has been compared to that of commercial Al_2O_3:C and the possible application of this fluoroperovskite to OSL dosimetry has been evaluated.

***Keywords**:* Optically Stimulated Luminescence; Fluoroperovskite; Dosimetry.

1.- INTRODUCTION

Optically stimulated luminescence (OSL) is a good alternative in environmental and personal dosimetry due to several advantages over others dosimetric methods as the thermoluminescence (TL). One of such advantages is that the stimulation method is completely optical, which makes it unnecessary to use a heating system for stimulating irradiated samples. For the same reason no thermal quenching occurs and more robust plastics encased OSL dosimeters can be easily manufactured. Moreover, high sensibility of OSL allows multiple readings because it is no necessary to stimulated all of trapped charge and the readout process can be made very fast by increasing the stimulating light intensity [McKeever, 2001].

In this context, only a few numbers of materials are currently used in OSL dosimetry with different efficiencies. The most widely used is the C-doped alumina (Al_2O_3:C) [Perks et al., 2007] which is considered as the standard material for OSL in practical dosimetry. Another one is the BeO, which has advantage of having a nearly tissue equivalent and high efficiency [Sommer et al., 2008]. However, there is always a constant interest in the search for new materials with improved OSL dosimetry properties.

Previous OSL and TL investigations of this fluoroperovskite doped with others ions showed the potential application of these phosphors in dosimetry [Furetta et al., 1990; Le Masson et al., 2002]. Taking into account this information, the aim of this work was to investigate the OSL dosimetric properties of undoped and Tm^{3+}-doped $KMgF_3$ fluoroperovskite. In particular, best combination of led and filters, OSL response as a function of growing place and of dopant concentration, repeatability of the OSL signal, dose response, minimum detectable dose and fading of the OSL signal were investigated. Finally, OSL efficiency of the investigated compound has been compared to that of commercial Al_2O_3:C dosimeter.

2.- MATERIALS AND METHODS

The $KMgF_3$ compounds were synthesized using the solid state reaction and considering a stoichiometric mixture of the raw materials of pure KF and MgF_2 powders. It was following the phase diagram of the binary system KF-MgF_2, [DeVries and Roy, 1953]. Thulium was added in aqueous solution ($TmCl_3 \cdot 6H_2O$) in stoichiometric proportions in order to obtain the desired concentrations of the Tm^{3+} impurity in the fluoroperovskite material. The dopant concentration varied between 0.2 and 0.5 mol %. Also a reference fluoroperovskite without thulium was prepared.

The mixtures were compressed to improve the contact between the reagents. Two different procedures were employed to achieve the reaction, namely, the compressed powder was put either in an alumina crucible or in a platinum foil and inserted into an oven and increasing the temperature from room temperature (RT) up to 700 °C and it kept constant during 5 hours. The cooling of the product of the reaction was made slowly. The final product in form of powder was washed with boiling water and hot ethanol then it was dried at 200 °C during 2 hours. Finally, samples of $KMgF_3$:Tm with grain size between 75-250 μm was selected to make the measurements.

Samples were irradiated at room temperature with a 10 mCi ophthalmic Sr-90 beta-source rendering a dose rate of 0.022 Gy/min at the sample position.

For optical stimulation three different LEDs were used. A Luxeon V Star green LED with maximum emissions at 530 nm, a Luxeon V Star blue LED with maximum emissions at 470 nm and a Luxeon III Star red LED whit maximum emission at 627 nm. In each case the LED light was filtered by means of two 3mm thick Schott long-pass filters before reaching the sample, namely, OG570, OG530 and GG420 long-pass filters by red, green and blue stimulation, respectively. Each long-pass filter features a maximum transmission of about 0.9 for wavelengths higher than the cutoff wavelength (570, 530 and 420 nm, respectively) and a transmission less than 10^{-6} at shorter wavelengths.

In order to get rid of the stimulation light, two 3mm thick Hoya B-390 or two 3mm thick Hoya U-340 band-pass filters were interposed between the sample and the light detector. The B-390 filter has non-zero transmission between 320 and 500 nm and maximum transmission (0.77) at 390 nm and the U-340 filter has non-zero transmission between 250 and 390 nm and maximum transmission (0.80) at 340 nm.

OSL curves were obtained by means of a photomultiplier tube (PMT) Electron Tube P25PC-02 photon counting head having sensitivity between 180 and 630 nm and maximum response at 350 nm. For all measurements both irradiation and stimulation were applied to the same face of the sample from which the emitted light was detected.

Radioluminescence spectra were recorded by means of an Acton Research SP-2155 0.150m monochromator featuring the same PMT aforementioned. Spectra were measured with in the wavelength range of 300 – 800 nm and at a rate of 60 nm min^{-1}.

3.- RESULTS

3.1. Filters and LEDs

As the OSL dosimetry consists basically in measuring the light emission from a sample previously irradiated while it is being stimulated with light of determined wavelength, knowing the OSL spectrum is crucial in order to determine the optimal combination of filters and LEDs to maximize the collection of emitted light. Because the OSL emission is not stationary, a good alternative is to obtain a radioluminescence (RL) emission spectrum [Cruz-Zaragoza et al., 2017]. In general the emission wavelength depends on the recombination centers and it is expectable that the luminescence centers involved in OSL are the same participating in the RL process.

Figure 1 shows the RL spectra of the $KMgF_3$ fluoroperovskite undoped (blue line) and doped with 0.5 % mol of Thulium (red line). It is possible to see from the figure that samples doped with 0.5 % of Thulium have two broad bands centered at 360 and 455 nm, respectively. On the other hand, undoped sample has an only faint broad band with maximum around 350 nm.

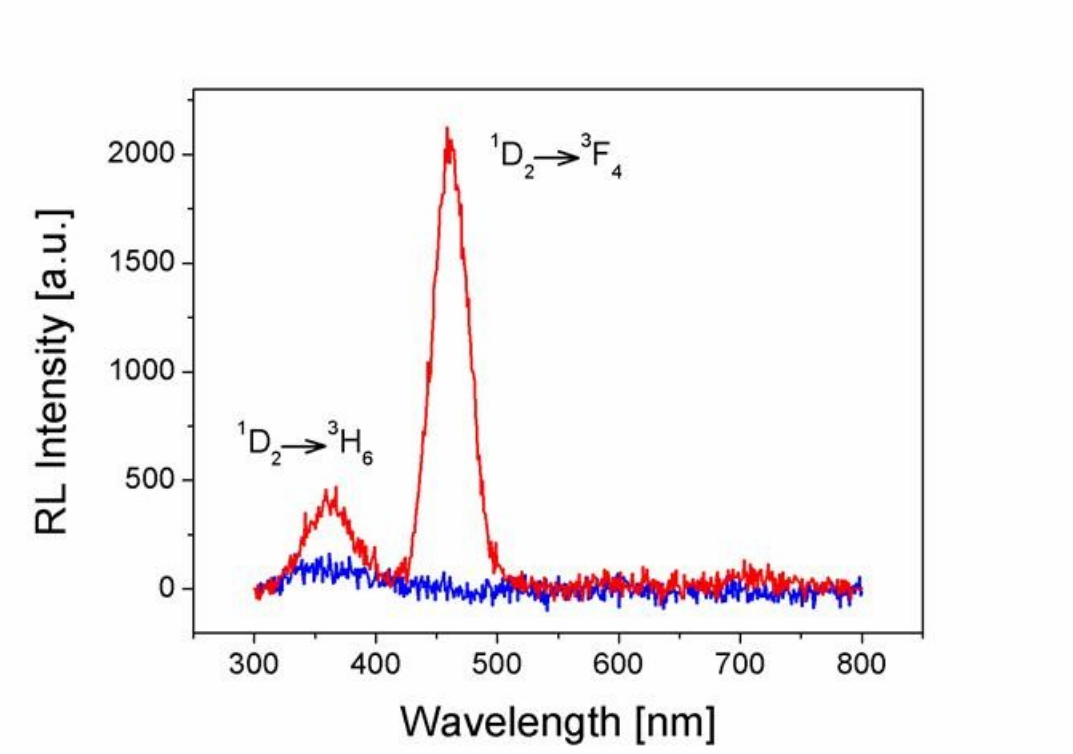

Figure 1. RL spectra of the $KMgF_3$ fluoroperovskite undoped (blue line) and doped with 0.5 % mol of Thulium (red line).

From the spectra of figure 1, two configurations of filters (emission filters) were selected to interpose between the sample and the light detector, i.e., two Hoya B-390 and two Hoya U-340 band-pass filters with transmission between 320 and 500 nm and, 250 and 390 nm, respectively. On the other hand, as it was detailed in the Materials and Methods Section, three

light sources for stimulation were selected; namely, red, green and blue light with maximum emissions at 627, 530 and 470 nm, respectively. When the samples were stimulated with blue light, only the configuration with the Hoya U-340 filters was investigated because of the overlapping of the wavelength.

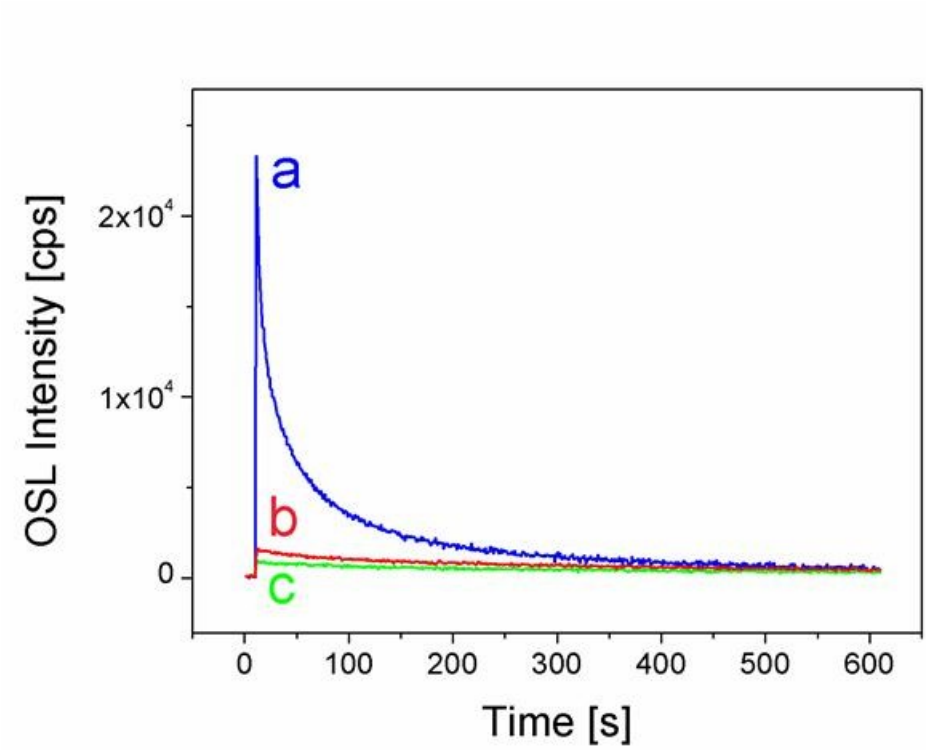

Figure 2. OSL decay curve of $KMgF_3$:Tm (0,5 % mol) under blue (a), red (b) and green (c) light stimulation.

Figure 2 show the effects of red, green and blue stimulation light on the OSL response of KMgF3:Tm (0.5 % mol) after irradiating the sample with a dose of 2.2 Gy of beta radiation. It is evident from the figure that OSL signal is more intense when blue light is employed. By taking into account these results, all OSL measurements will be made with blue stimulation and Hoya U-340 band-pass as emissions filters.

3.2. OSL response as a function of preparation procedure.

As it was afore mentioned, two different procedures were employed to achieve the reaction, namely, the compressed powder was put either in an alumina crucible or in a platinum foil. In figure 3 it is possible to see the OSL decay curves of irradiated $KMgF_3$:Tm (0.5 % mol) and undoped $KMgF_3$ as a function of each preparation procedure. As it is evident from the figure 3, for both $KMgF_3$:Tm (0.5 % mol) and undoped $KMgF_3$, the highest intensity is obtained when samples are prepared in an alumina crucible. In what follows, we will focus on samples prepared by this procedure.

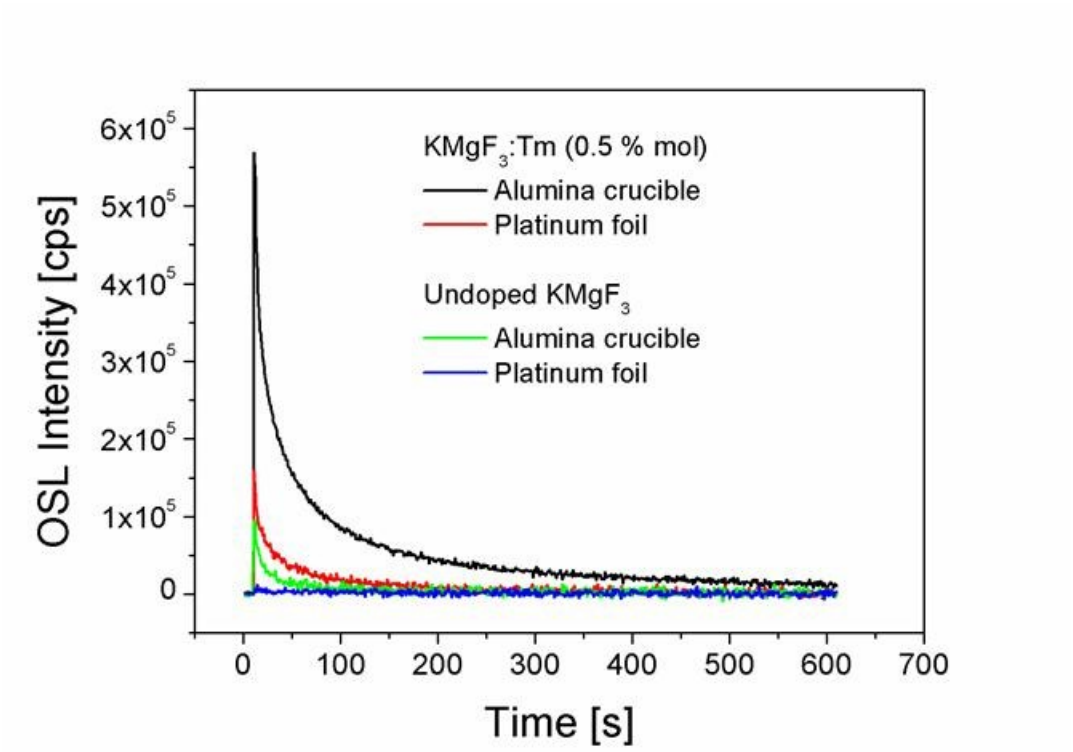

Figure 3. OSL decay curves of irradiated $KMgF_3$:Tm (0.5 % mol) and undoped $KMgF_3$ fluoroperovskite powder as a function of each preparation procedure.

3.3. OSL response as a function of dopant concentration

In order to determine the amount of doping that has the highest OSL efficiency, figure 4 shows the OSL curves of samples of $KMgF_3$ doped with 0.5 and 0.2 % mol of thulium and undoped $KMgF_3$. All samples were irradiated with a same dose of 2.2 Gy and stimulated with blue light. Whereas that undoped $KMgF_3$ sample has lower OSL efficiency (green curve), samples of $KMgF_3$ with 0.2 and 0.5 % mol of Tm present almost the same intensity (red and blue curve, respectively). However, the signal corresponding to the sample doped with 0.5 % mol of Tm (blue curve) shows the most intense OSL peak and highest integrated OSL intensity as well.

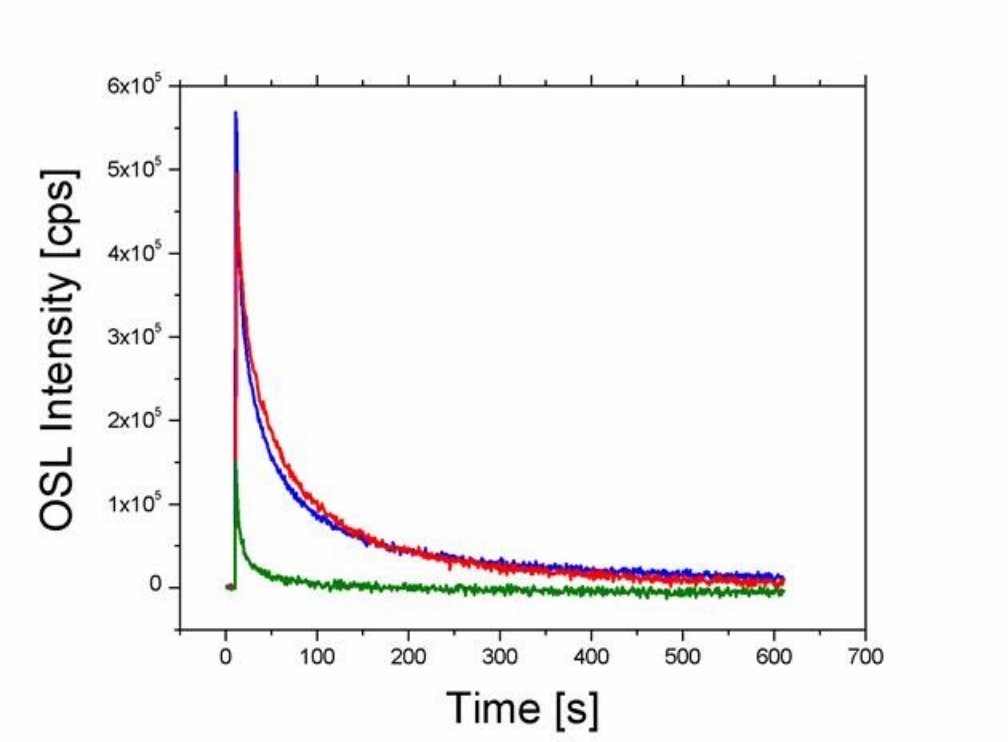

Figure 4. OSL decay curves of irradiated $KMgF_3$:Tm (0.5 % mol) (blue curve), $KMgF_3$:Tm (0.2 % mol) (red curve) and undoped $KMgF_3$ (green curve) fluoroperovskite samples.

3.4 Repeatability of the OSL response

Figure 5 shows the repeatability of the OSL signal of the fluoroperovskite with highest OSL intensity, namely, $KMgF_3$:Tm (0.5 % mol), when it is integrated different section of the OSL curve. It is possible to see a good repeatability of the OSL signal with a percentage standard deviation of 3.8, 2.4 and 6.2 %, when it is integrated the first 10, 20 and 600 seconds of the OSL curve, respectively. In all cases, sample was irradiated with a beta radiation dose of 2.2 Gy. On the other hand, shape of the OSL curves are the same in all the measurements.

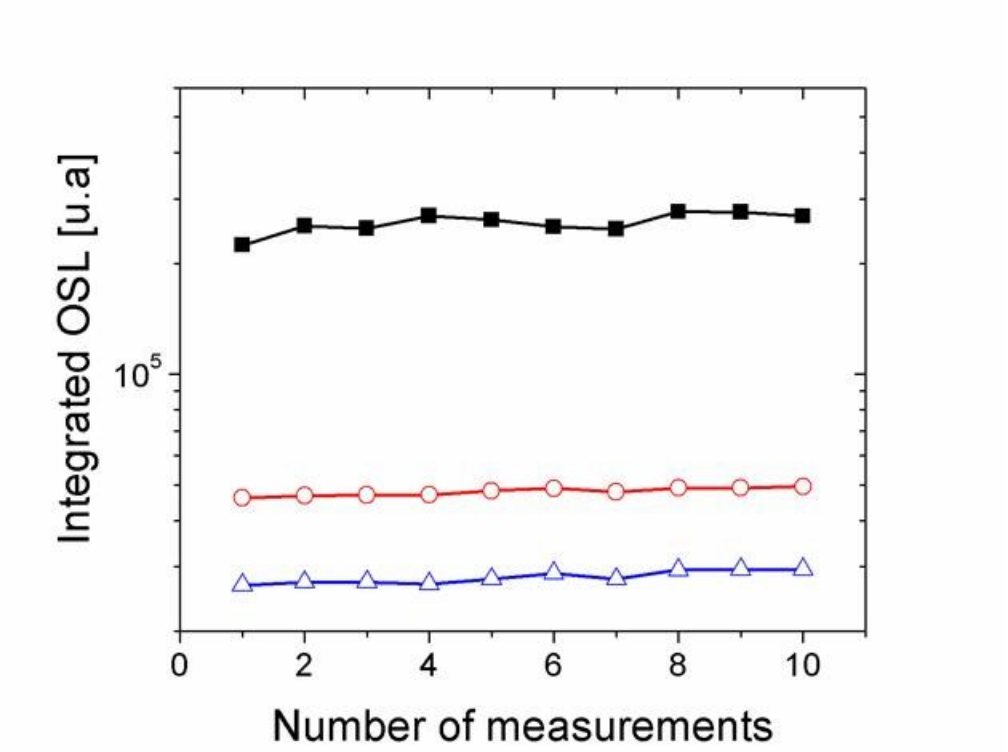

Figure 5. Repeatability of the OSL response when it is integrated the first 10 (hollow blue triangles), 20 (hollow red circles) and 600 seconds (filled black squares) of the OSL curve, respectively.

3.5 Dose response and minimum detectable dose

Figure 6 shows the OSL curves and dose response of KMgF3:Tm (0.5 % mol)

fluoroperovskite. Sample was irradiated with different doses of beta radiation, namely, 0.22, 0.66, 2.2, 6.6, 22 and 90.64 Gy, from bottom to top respectively. In the inset, the dose response when it is integrated the first 20 seconds of the OSL curve is presented. As it can be seen from the figure, a good linearity is observed. It was selected a time of 20 seconds for integration because this time presented the better repeatability (see previous section).

Besides, the minimum detectable dose (MDD) of this fluoroperovskite has been determined by means of MDD=3σ_{BG}, being σ_{BG} the experimental standard derivation of the background signal recorded by using blank detectors. These measurements are carried out by using the same samples except that they are not irradiated [Yukihara and McKeever, 2011]. For $KMgF_3$:Tm (0.5 % mol), a MDD = 0.04 Gy has been found.

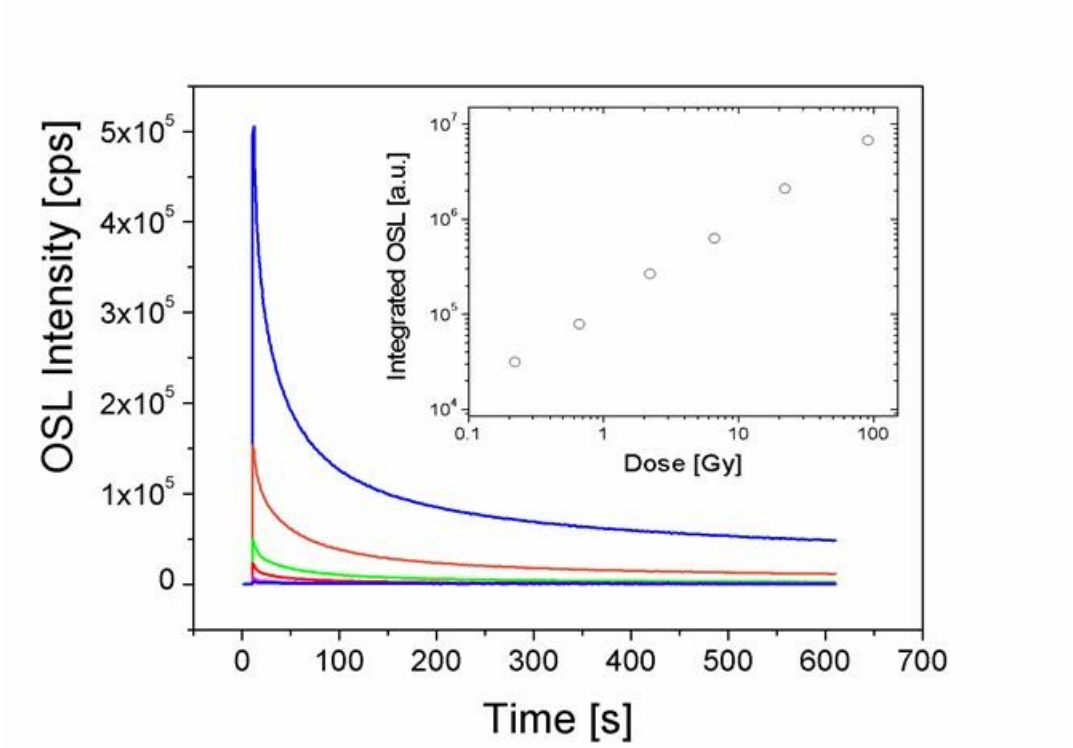

Figure 6. OSL curves of KMgF3:Tm (0.5 % mol) irradiated with different doses, ranging from 0.22 up to 90.64 Gy from bottom to top respectively. In the inset: dose response when it is integrated the first 20 seconds (hollow circles) of the OSL curves.

3.6 Fading of the OSL signal

Figure 7 shows the integrated OSL signal as a function of several storing times, namely, 0.08, 0.16, 0.5, 1.6, 19.2, 72 and 163.5 h. It can be seen from the figure that OSL signal shows an important fading of approximately 75 % after the first 36 hours of storing and then, the response remains almost constant.

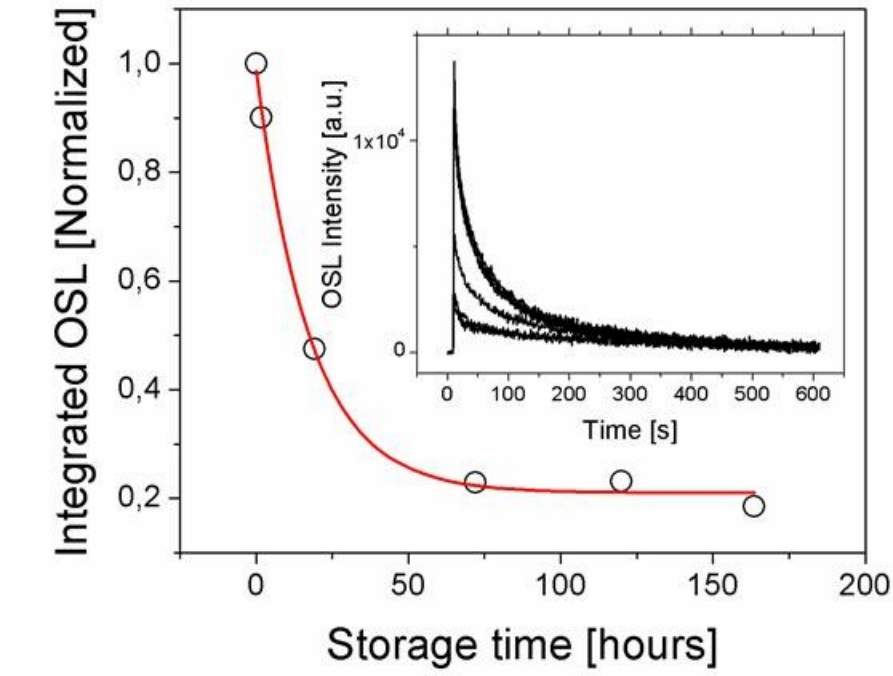

Figure 7. Integrated OSL signal of KMgF3:Tm (0.5 % mol) as a function of the storage time (hollow circles). Continuous line was obtained by fitting by a single exponential. In the inset: the OSL response after 0.08, 0.16, 0.5, 1.6, 19.2, 72 and 163.5 h. of storage, from top to bottom one after another.

3.7 Comparison with Al_2O_3:C

Finally, in figure 8 it is possible to see the OSL efficiency of (b) the KMgF3:Tm (0.5 mol%) compared with (a) the standard commercial Al_2O_3:C dosimeter (Landauer, Inc.). Samples

were irradiated with a beta dose of 2,2 Gy and OSL curves were normalized to the sample weight. As it is evident from the figure, Al_2O_3:C is one order of magnitude greater than KMgF3:Tm (0.5 mol%).

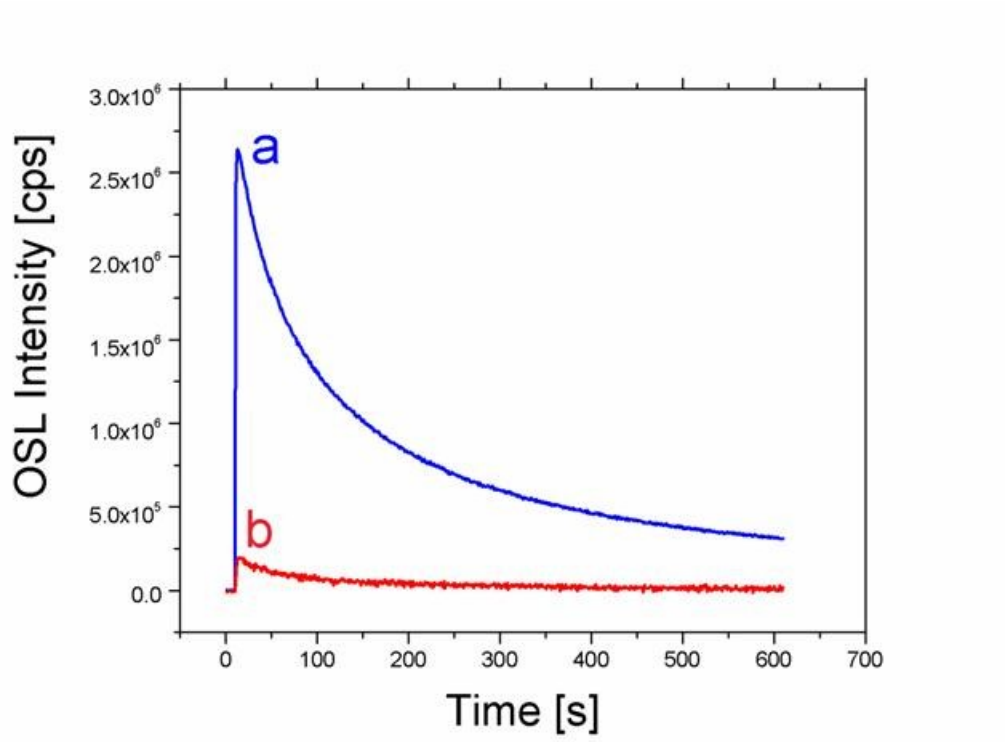

Figure 8. The OSL decay curve of (a) commercial Al_2O_3:C and (b) KMgF3:Tm (0.5 mol%). Both OSL signals have been recorded under the same experimental conditions and normalized to the sample weight.

4.- DISCUSSION

RL spectrum of $KMgF_3$ fluoroperovskite doped with thulium shows two broad bands. The first one is located between 300 and 410 nm and centered at 360 nm and the second one is located between 420 and 500 nm and centered at 455 nm. The two bands centered at 360 and 455 nm can be attributed to the $^1D_2 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3F_4$ transitions of Tm^{3+} ion, respectively [Quintanilla et al, 2011]. On the other hand, undoped sample has an only faint broad band

with maximum around 350 nm. This broad emission band 350 nm was already observed by other authors and it is dominant in the thermoluminescence of KMgF3 host [Furetta et al, 1990]. This peak is attributed to the thermal activation of F centers, created by the material irradiation.

On the three light sources studied for stimulation, namely, red, green and blue light, it was found that OSL signal is more intense when blue light is employed. This result has been observed in previous works regarding the OSL of others rare earth doped $KMgF_3$, i.e., in the OSL of $KMgF_3:Ce^{3+}$ [Le Masson et al., 2002]. When the samples were stimulated with blue light, only the configuration with the Hoya U-340 filters was selected because of the overlapping of the wavelength.

Regarding to the preparation procedure, for both $KMgF_3$:Tm (0.5 % mol) and undoped $KMgF_3$, the highest intensity is obtained when samples are prepared in an alumina crucible. It could be due to the alumina allows migrating ions to the host of the compound when the mass is being melted at the preparation temperature and then, this fact increases its intensity.

Besides, regarding with the doped concentration, the signal corresponding to the sample doped with 0.5 % mol of Tm shows the most intense OSL peak and highest integrated OSL intensity as well when it was compared with $KMgF_3$:Tm (0.2 % mol) and undoped $KMgF_3$.

One of the characteristics to be taken into account when a material is evaluated as a possible dosimeter is the repeatability of its OSL signal. In general, both the shape and the area under the OSL curve are investigated. The best repeatability of the OSL signal was found when it was integrated the first 20 seconds of the OSL curve with a percentage standard deviation of 2.4 %.

The dose response was also studied take into account that it was integrated the first 20 seconds of the OSL curve. A good linearity in the dose range of 0.1 – 100 Gy was obtained

and a regression coefficient equal to 0.995 was found when a linear regression was performed on the experimental data. The minimum detectable dose of this fluoroperovskite has been found to be equal to 0.04 Gy.

From the point of view of the applications of this compound to OSL dosimetry, it is of interest to investigate the fading of the OSL signal as a function of the time elapsed between irradiation and readout. In this context, sample was irradiated with a dose of 2.2 Gy of beta radiation at room temperature (RT) and storage in darkness and a RT for different periods of time. An important fading of approximately 75 % in the first 36 hours of storage is observed and then, the response remains almost constant.

Finally, it was found that the OSL efficiency of the KMgF3:Tm (0.5 mol%) is one order of magnitude lower than commercial Al_2O_3:C dosimeter, which in principle could be considered as a disadvantage. But, this quickly fades out after 100 s of stimulation could make easier to bleach the residual OSL in order to restore the sample between dose measurements. In the case of Al_2O_3:C, the long decay time of its OSL signal could become a drawback if total depletion of traps is necessary before each OSL measurement [Gaza, 2004].

The characterization of this material has been performed by irradiating with a Sr-90 beta source. However, the response of this material to other types of ionizing radiation deserves further research, which will be taken into account in future works.

5.- CONCLUSIONS

The OSL dosimetric properties of the sample of KMgF3 doped with different concentration of thulium have been investigated for the first time. In particular, it was found that samples prepared in an alumina crucible and doped with 0.5 % mol of thulium present the highest OSL efficiency.

RL spectrum of $KMgF_3:Tm^{3+}$ fluoroperovskite shows two broad bands centered at 360 and 455 nm which can be attributed to the $^1D_2 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3F_4$ transitions of Tm^{3+} ion, respectively. On the other hand, undoped sample has an only faint broad band with maximum around 350 nm, which can be attributed to the thermal activation of F centers, created by the material irradiation.

On the light sources studied for stimulation, the blue light (470 nm) stimulation with the Hoya U-340 filters presented the maximum OSL response.

The best repeatability of the OSL signal was found when it was integrated the first 20 seconds of the OSL curve with a percentage standard deviation of 2.4 %. A good linearity in the dose range of 0.1 – 100 Gy was obtained and a minimum detectable dose of 0.04 Gy has been found. An OSL fading of approximately 75 % in the first 36 hours of storage is observed and then, the response remains almost constant.

Although it was found that the OSL efficiency of the KMgF3:Tm (0.5 mol%) is one order of magnitude lower than the OSL response of commercial $Al_2O_3:C$ dosimeter, the quickly fades out after 100 s of stimulation makes easier to bleach the residual OSL in order to restore the sample between dose measurements.

The results of this work show that this fluoroperovskite could be envisaged as new promising OSL dosimeters deserving further investigations.

Acknowledgments

We acknowledge the financial support received from PICT 2015–2647 (ANPCyT, Argentina) and PIP 800/2015 (CONICET, Argentina). Mg. L. Camargo thanks CONICET for granting them doctoral scholarships. Also we acknowledge the partial support of PAPIIT-DGAPA-UNAM under the project number IN112617.

REFERENCES

Cruz-Zaragoza E; Cedillo Del Rosario G; García Hipólito M; Marcazzó J; Hernández A JM; Camarillo E; Murrieta S H. (2017). *Radio-Optically- and thermally stimulated luminescence of $Zn(BO_2)_2:Tb^{3+}$ exposed to ionizing radiation*. J. Nucl. Phys. Mat. Sci. Radiat. And Appl. **5** (1): 169-178.

DeVries RC; Roy R. (1953). *Fluoride Models for Oxide Systems of Dielectric Interest. The systems KF-MgF_2 and AgF-ZnF_2*. J. Am. Chem. Soc. **75:** 2479-2484.

Furetta C; Bacci C; Rispoli B; Sanipoli C; Scacco A. (1990). *Luminescence and Dosimetric Performances of KMgF3 Crystals Doped with Metal Impurity Ions.* Radiat. Prot. Dosim. **33**: 107–110.

Gaza R., (2004). *A fiber-optics, real-time dosimeter based on optically stimulated luminescence of Al2O3:C and KBr:Eu, for potential use in the radiotherapy of cancer,* Doctoral Thesis, Oklahoma State University.

Le Masson NJM; Bos AJJ; Van Eijk CWE; Furetta C; Chaminade JP. (2002). *Optically and thermally stimulated luminescence of KMgF3:Ce3+ and NaMgF3:Ce3+*. Radiat. Prot. Dosim. **100**: 229-234

Le Masson NJM; Vink AP; Dorenbos P; Bos AJJ; Van Eijk CWE; Chaminade JP. (2003). *Ce3+ and Pr3+5d-energy levels in the (pseudo) perovskites KMgF3 and NaMgF3,* J. Lumin., **101:** 175-183.

McKeever SWS. (2001). *Optically stimulated luminescence dosimetry*, Nucl. Instr. Meth. Phys. Res. B **184**: 29-54.

Perks CA; Le Roy G; Prugnaud B. (2007). *Introduction of the In Light monitoring service*, Radiat. Prot. Dosim. **125**: 220-3.

Quintanilla M; Núñez NO; Cantelar E; Ocaña M; Cussó F. (2011). *Tuning from blue to magenta the up-converted emissions of YF3:Tm3+/Yb3+ nanocrystals*. Nanoscale, **3:** 1046-1052.

Sommer M; Jahn A; Henniger J. (2008). *Beryllium oxide as optically stimulated luminescence dosimeter*, Radiat. Meas. **43**: 353-356.

Yukihara EG; McKeever SWS. (2011) *Optically stimulated luminescence: Fundamentals and Applications*. United Kingdom, John Wiley and Sons, Inc. (Third edition, 2011).