Optically Stimulated Luminescence in $KMgF_3 : Ce^{3+}$ Comparison of Dosimetric Characteristics With $Al_2O_3 : C$

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***Abstract*—Ce^{3+} doped $KMgF_3$ crystals have been investigated as a new material for dosimetry of ionizing radiation. Previous studies have focused on their thermoluminescence (TL) properties. This paper shows that the stored energy in this compound can also be read by visible light. Its sensitivity was found to be one order of magnitude greater than $Al_2O_3 : C$, which can be considered as the standard dosimetric material based on optically stimulated luminescence (OSL). The greater sensitivity was due to a larger wavelength difference between stimulation and emission wavelengths, which results in a better separation of useful signal from scattered light. Time response characteristics were also significantly better than $Al_2O_3 : C$, which allows in principle fast pulsed and multiple readouts. Unfortunately, the high self-dose ($\sim$1.5 μGy/h) due to the natural abundance of ^{40}K isotope is a major drawback for the application of this material in environmental dosimetry. Some features of the mechanism have been studied with different spectroscopic techniques. The luminescent centers have been clearly identified with Ce^{3+} ions. It has been shown that the main trapping centers involved in OSL mechanism are the same as those involved in TL mechanism.**

***Index Terms*—Al_2O_3, $KMgF_3 : Ce$, optically stimulated luminescence (OSL).**

I. Introduction

OPTICALLY stimulated luminescence (OSL) exhibits several potential advantages over thermoluminescence (TL) for application in radiation protection dosimetry. The optical nature of the stimulation is an obvious advantage. Stimulation of materials that melt or decompose at elevated temperatures is possible, especially for materials with a high hydrogen content with a high sensitivity to fast neutrons [1]. Furthermore, thermal quenching of the luminescence is avoided, and no decrease of the sensitivity is expected after repeated uses. In addition to a readout at ambient temperature, one can vary the stimulation parameters such as wavelength, time (pulsed OSL [2]), or power (linear modulation OSL [3]), which provides a powerful tool for the studies of the physics involved.

Despite its early discovery [4], and its early suggestion in the 1950s for radiation dosimetry [5], OSL studies have been less extensively reported than TL studies. The recent availability of cheap and powerful lasers and the discovery of a highly sensitive OSL material, α–$Al_2O_3 : C$, for environmental dosimetry have raised interest in OSL for radiation protection dosimetry [6]. The emission spectrum of the luminescent centers involved in the OSL process of α–$Al_2O_3 : C$ consists of a large band ranging from 350 to 450 nm with a maximum at 410 nm [7]. Few materials with efficient OSL have been proposed for radiation protection since.

One approach to develop OSL materials dedicated to personal dosimetry is to investigate the OSL properties of known TL phosphors. From this perspective, we have investigated a new ultrasensitive TL phosphor $KMgF_3 : Ce^{3+}$ [8]. TL studies on the dosimetric potentials of the fluoroperovskite $KMgF_3$ have been performed with various activators: Yb [9], Eu^{2+} [10], Pb, Cr, Ag [11]. In this paper, we report preliminary results of OSL characteristics for $KMgF_3 : Ce^{3+}$ and compare some of its features with $Al_2O_3 : C$.

II. Experimental

The crystal was obtained from a stoicheometric melt of KF and MgF_2 using the Czochralski method in an Ar atmosphere. The dopant was added to the initial mix of powder before growth. The specified nominal concentration in the melt was 0.5 mol%. Due to segregation phenomena during growth, the dopant concentration in the crystal does not coincide with the one in the melt. The concentration may also vary along the slowly pulled crystal ingot. The real concentration in the crystal is not precisely known. It was cut into a flat ($\sim 5 \times 5$ mm^2) and thin (<1 mm) slab and then polished in order to obtain a good quality surface for optical studies and for a good thermal contact. The weight of the investigated crystal was 34 mg.

$Al_2O_3 : C$ discs of 80 mg were provided by Urals Polytechnical Institute. The samples were annealed at 500 °C for 3 h. The photoluminescence measurement and X-ray induced emission measurements are described elsewhere [12].

The OSL/TL properties were investigated with a Risø reader (TL/OSL-DA-15A/B). Optical stimulation was performed with an OSL unit containing a ring of blue light-emitting diodes (LEDs) with an optical feedback. This configuration of the Risø reader is described elsewhere [13]. The emission of the blue LEDs occurs at 470 nm. Measurements were performed at 100% of their power, which corresponds to an illumination power of 16 mW·cm^{-2} at the sample position, according to the manufacturer specifications. Another stimulation light source was the filtered light (OG515, SWP560, SWP720 filters) from a halogen lamp. The spectrum is a broadband between 515

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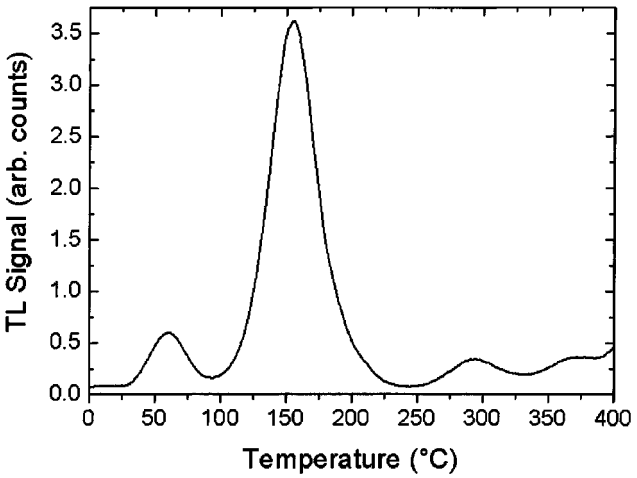

Fig. 1. TL glow curve (heating rate 1 K·s^{-1}) of $KMgF_3 : Ce^{3+}$ after a β-dose of 5 mGy.

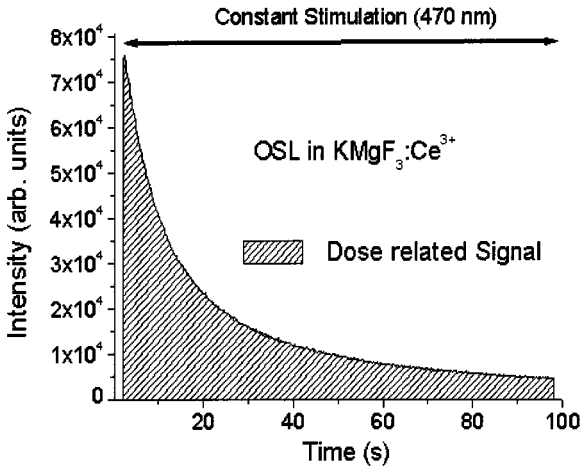

Fig. 2. Typical OSL decay curve of $KMgF_3 : Ce^{3+}$ under continuous stimulation with blue LEDs (470 nm).

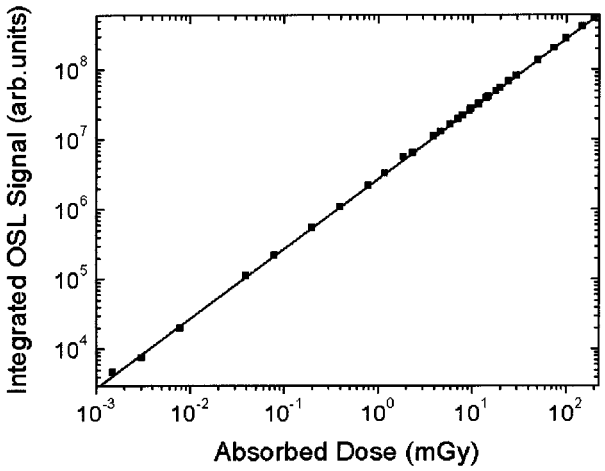

Fig. 3. Integration of the OSL curves as a function of dose. The line is a fit and coincides with the line of linearity.

and 600 nm with a maximum at 545 nm. This stimulation source will be referred to as the yellow-green lamp. The lamp is connected to the OSL unit via a liquid lightguide. The illumination power is 10–20 mW·cm^{-2} at the sample position. The emitted OSL light is separated from the stimulation light either with U-340 (7.5 mm, Hoya) filters for the blue LEDs or with BG 4 (5 mm, Schott) and UG 1 (1 mm, Schott) filters for the yellow-green lamp. OSL is then detected by a photomultiplier tube (PMT) (Product for Research, Inc. model PR1406RF) in a photon counting mode. Irradiation is performed with a $^{90}Sr/^{90}Y$ β-source (either 24.1 MBq or 18.5 kBq) in a built-in holder. TL glow curves were recorded in the same geometry and with the same filters as for OSL measurements with blue LEDs.

The OSL emission spectrum was measured with a spectrometer (Ocean Optics S2000) connected a lightguide of 1 mm diameter equipped with a collimating lens. The lightguide was mounted onto the Risø reader instead of the PMT. The optical stimulation was performed with the blue LEDs, and a 2.5-mm-thick U340 filter was used to attenuate the scattered stimulating light.

III. Results

The TL glow curve recorded immediately after irradiation (Fig. 1) is depicted. It was recorded after a dose of 5 mGy from the $^{90}Sr/^{90}Y$ source. The glow curve structure is similar as found by Kitis [8]. The first peak at 60 °C is fading-sensitive. It disappears completely after 1 h in the dark at room temperature.

This fading induces a high level of phosphorescence, which should be taken into account in OSL experiments. The shape of the intense glow peak at about 160 °C suggests that this peak consists of at least two peaks: a very intense one and an unresolved weak peak on the high-temperature side of the main peak.

A. OSL Characteristics of $KMgF_3 : Ce^{3+}$

The stored information during irradiation can also be efficiently read out by optical means. A typical OSL decay curve under blue LED stimulation is shown (Fig. 2) after a dose of 100 mGy. The OSL readout was carried out at room temperature after having preheated the sample at 60 °C during 3 min in order to reduce the phosphorescence level due to shallow traps.

The decay curve is not modified if the preheat procedure is replaced by 30 min waiting time after the irradiation. The curve shows a first component that can be fitted by a single exponential in the first 20 s and by a second slowly decaying component. Additional OSL experiments have shown that the second component extends over more than 1 h and is reduced to background level only after having heated the samples up to 400 °C.

OSL decay curves were integrated over 100 s and plotted as a function of dose (Fig. 3). The relation is strictly linear from the detection limit ($\sim$1 μGy) up to hundreds of mGy, at which dose-level nonlinearity occurs in the PMT (pileup) due to a high count rate.

The OSL emission spectrum (Fig. 4) was measured after an absorbed dose of 50 Gy from a ^{60}Co source. The emission spectrum of this sample was also measured during X-ray and photoexcitation. All spectra show an asymmetric band peaking at 360 nm. In the case of the OSL emission spectrum, the U-340 filters cut off the longer wavelength part. This emission has been ascribed to transitions from 5d levels to $^2F_{5/2}$ and $^2F_{7/2}$

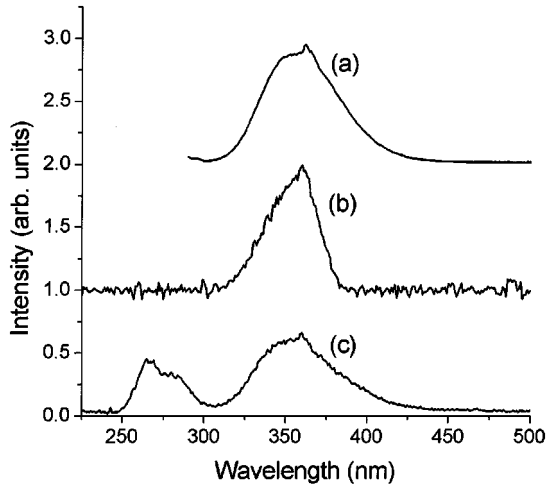

Fig. 4. Emission spectra of $KMgF_3:Ce^{3+}$ induced with different sources: (a) photoluminescence emission excited at 280 nm, (b) OSL emission under 470-nm stimulation, and (c) emission under X-ray excitation.

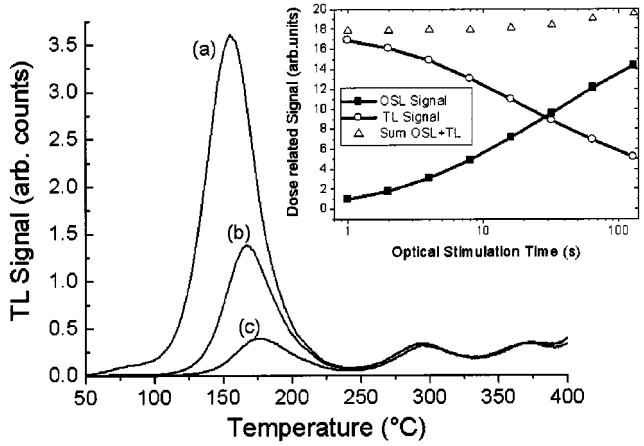

Fig. 5. TL glow curves of a $KMgF_3:Ce^{3+}$ crystal after the same dose and different optical stimulation time with blue LEDs: (a) no stimulation, (b) 2 min, and (c) 10 min.

levels of Ce^{3+} ion in a cationic site (most probably a K^+ site) perturbed by spatially correlated charge-compensating defects [14]. It is clear that the active luminescent centers in the OSL process are the Ce^{3+} ions.

The emission peaks below 300 nm in the X-ray induced emission have been attributed to Ce^{3+} ion in an unperturbed K^+ site [14]. Those emission peaks could not be observed (if present) in the OSL emission spectrum due to the low detection efficiency in that wavelength region.

The correlation between TL and OSL has been investigated as follows. The sample was given a certain dose and preheated at 60 °C during 3 min. The time between the preheat procedure and the TL measurement was kept the same (10 min), but during that time OSL measurements were performed for different periods of time. Then the TL spectrum was recorded at 1 $K{\cdot}s^{-1}$. The three plotted TL glow curves (Fig. 5) were recorded after stimulation periods of 0, 2, and 10 min, respectively.

The observed reduction in the TL intensity confirms that the intense band peaking at about 160 °C involves at least two trapping centers [8]. The efficiency of the optical release of charge

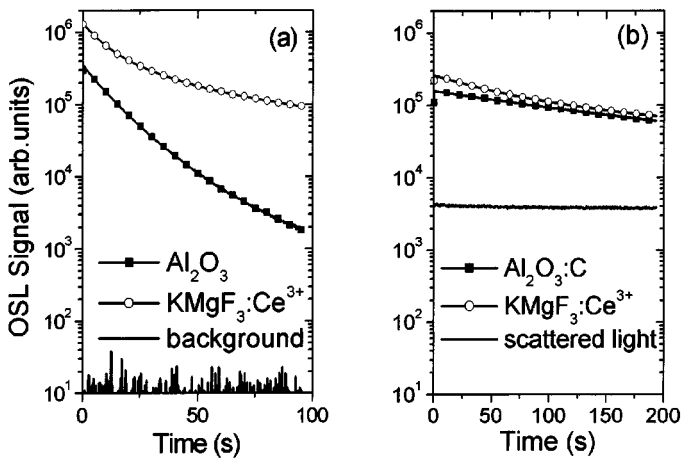

Fig. 6. Comparison between OSL signal of $Al_2O_3:C$ and $KMgF_3:Ce^{3+}$ for (a) blue LEDs stimulation and (b) yellow-green lamp stimulation.

carriers from the deeper traps is weak. Indeed, TL peaks at 300 and 370 °C are also reduced and shifted to higher temperature after long stimulation period (1 h).

Those results suggest that the first component in the OSL-decay curve is due to trapping centers connected with the intense glow peak at 160 °C and the second component due to the deeper traps. The inset shows the decrease of the TL signal and the increase of the OSL signal as a function of the optical stimulation time. Keeping in mind that the luminescent centers and the light detection efficiency are similar for both experiments, we can propose based on this anticorrelation that the transfer efficiency of the charge carriers from the traps to the emission centers is similar for thermal and optical stimulation.

The fading of the stored information has been investigated over two days. No noticeable fading could be observed. This agrees with absence of fading in TL experiments [8] and the observation that in OSL and TL experiments the same trapping centers are involved.

B. Comparison With $Al_2O_3:C$

The comparison of two OSL materials dedicated to dosimetry is not as straightforward as for TL materials. In cwOSL measurements (OSL with a continuous stimulation), an optical filter in front of the PMT must be used in order to attenuate the scattered stimulating light. This filter also attenuates the emitted light and therefore determines to some extent the signal-to-noise ratio. A compromise has to be found between the optimum of light detection and an efficient stimulation. Some of these problems are illustrated in Fig. 6. It shows the decay of both $KMgF_3:Ce^{3+}$ and $Al_2O_3:C$ under blue LEDs and yellow-green stimulation. The filters used with the yellow-green stimulation match $Al_2O_3:C$ emission but the decay is much slower, which increases considerably the time to read out the stored information and thus decreases the signal-to-noise ratio. Increasing the lamp power will speed up the decay but also the scattered light level, which is already quite high for low dose detection, as seen in Fig. 6.

It follows that in an experimental setup, the intensity of the OSL signal is strongly dependent on the choice of filters. Effects of these parameters are included in the quantity "sensitivity."

TABLE I
COMPARISON OF OSL SENSITIVITY S IN COUNTS $mGy^{-1}\cdot mg^{-1}$, DETECTION EFFICIENCY ε IN % AND ITS RATIO S/ε OF $KMgF_3:Ce^{3+}$ AND $Al_2O_3:C$

Stimulation	Yellow-green			BlueLEDs		
	S	ε	S/ε	S	ε	S/ε
$KMgF_3$:Ce	12000	16	750	23000	6	3850
Al_2O_3:C	3200	1	3200	2000	<0.2	>10000

The sensitivity S is defined as the slope of the dose response curve (integrated OSL signal versus dose) and is expressed in number of detected counts per mGy and per mg.

To evaluate the intrinsic efficiency (or a relative measure for it), the effect of the filter and PMT should be taken into account. We calculate the detection efficiency ε defined as

$$\varepsilon = \frac{\int N(\lambda)T(\lambda)Q(\lambda)\,d\lambda}{\int N(\lambda)\,d\lambda} \tag{1}$$

with $N(\lambda)$ the OSL emission spectrum, $T(\lambda)$ the filter transmission, and $Q(\lambda)$ the quantum efficiency of the PMT. The ratio S/ε can be considered as a relative measure for the number of emitted photons per mGy per mg. Indeed, it does not include the geometric efficiency, which is considered to be the same for both samples.

Table I gives the obtained values of the mentioned quantities for $KMgF_3:Ce^{3+}$ and $Al_2O_3:C$ with the two stimulation sources. The detection efficiency of $Al_2O_3:C$ was calculated with the use of the emission spectrum published in [1616]. For $KMgF_3:Ce^{3+}$, the measured Ce^{3+} photoluminescence emission spectrum was used. For the detection efficiency with the blue LED stimulation, only an upper limit could be determined for $Al_2O_3:C$. For a fair comparison, the OSL curves were integrated over the first 20 s.

It appears that the intrinsic efficiency ($\sim S/\varepsilon$) of $Al_2O_3:C$ is three times higher than that of $KMgF_3:Ce^{3+}$. However, the number of detected photons per mGy per mg, i.e., the sensitivity S of $KMgF_3:Ce^{3+}$, is much higher than the sensitivity of $Al_2O_3:C$. This sensitivity is more relevant for comparison for practical application in the continuous stimulation mode. The lower value for $Al_2O_3:C$ is a consequence of the smaller difference between stimulation and emission wavelength ($KMgF_3:Ce^{3+}$ emission maximum 360 nm, $Al_2O_3:C$ emission maximum 410 nm [1616]). The problem of the loss of signal for $Al_2O_3:C$ is well known, and two solutions were proposed to solve it. One proposal was to stimulate with infrared light and to monitor the phototransfer-thermoluminescence [15]. The other proposal is to use pulsed OSL [1616]. In this technique, the stimulation light is pulsed and the emission light only monitored after the pulse. In this case, only an appropriate filtration or synchronized shuttering to avoid damage to the detection system is needed.

For pulsed OSL, the characteristics of the time response to a pulse have to be considered. The time characteristics of the OSL emission in $Al_2O_3:C$ are limited by the radiative lifetime of the emission centers, which have been identified as F-centers with a lifetime of 35 ms [7]. This relatively long lifetime is also the reason of an initial intensity rise during 35 ms in the OSL emission. We performed optical stimulation on $KMgF_3:Ce^{3+}$ with a flashlamp of a few μs pulse duration. The OSL response monitored by an oscilloscope shows a decay of some μs caused by the decay of the lamp itself. It seems that the OSL time response to a pulse is shorter than tenths of μs. Since Ce^{3+} is the luminescent center, we expect a decay time in the order of magnitude of the Ce^{3+} radiative lifetime in this compound (50 ns [14]). For that reason, the time response of $KMgF_3:Ce^{3+}$ to a pulse of light is expected to be very short. This makes the compound very promising for pulsed OSL since a very short decay time will result in a better signal-to-noise ratio.

The much higher sensitivity makes $KMgF_3:Ce^{3+}$ more attractive for radiation dosimetry applications than $Al_2O_3:C$. However, some factors have to be taken into account.

C. Drawbacks

An important property of a dosimeter is the energy response of the material. For γ radiation, it is determined by the effective atomic number Z_{eff}. For environmental and personal dosimetry, a Z_{eff} close to tissue (7.5) is desirable. $KMgF_3:Ce^{3+}$ has a Z_{eff} of 14.7. This means that it will induce an important overresponse below 200 keV. The main contribution to its high Z_{eff} is due to the presence of potassium in its atomic composition. The effective atomic number of $Al_2O_3:C$ ($Z_{eff} = 11.3$) is lower but still high enough to produce an overresponse. Suitable filters can nonetheless flatten the energy response.

Another drawback of this compound is the presence of ^{40}K (β-emitter), a radioactive isotope, with a natural abundance of 0.012%. The ^{40}K decay produces a β dose. Due to the high sensitivity, this self-dose is already observed after 30 min (Fig. 7). From the slope, a self-dose rate of 1.5 $\mu Gy\cdot h^{-1}$ could be deduced. The background due to natural radiation in the Netherlands is 0.08 $\mu Gy\cdot h^{-1}$. The subtraction of the signal due to the self-dose will complicate its application for low-dose-level measurements.

IV. SUMMARY AND CONCLUSION

$KMgF_3:Ce^{3+}$ is not only a sensitive TL material but also a very sensitive OSL material. The main TL peak corresponds to a trap, which can be efficiently stimulated with visible light. Apart from a high sensitivity, it shows a low fading rate, which makes this material a good candidate for radiation dosimetry purposes. Compared to $Al_2O_3:C$, the standard for environmental dosimetry based on OSL, it shows a higher sensitivity because of an easier detection. Since the time characteristics are better, it is expected that with pulsed OSL the sensitivity will be further enhanced. However, low dose measurements are complicated due to a self-dose 10–20 times higher than the background level. Furthermore, with its high Z_{eff} (14.7), its energy response will deviate from the desirable tissue energy response.

Up to now, the fluoroperovskites family doped with rare earth ions has not been extensively studied for storage properties. This study on $KMgF_3:Ce^{3+}$ shows that those compounds have an important potential for applications in dosimetry based on OSL.

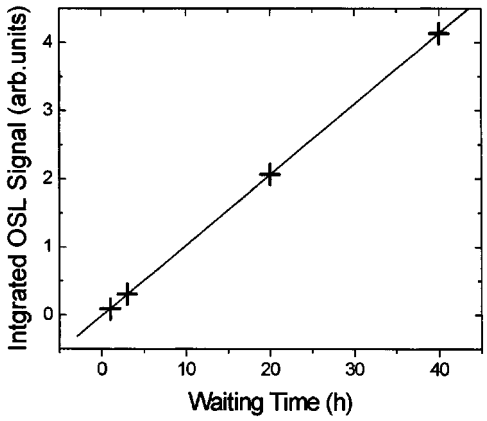

Fig. 7. OSL signal due to self-dose in $KMgF_3:Ce^{3+}$. The points have been obtained by integrating the OSL signal measured without intentional dose for different periods of time.

Variations on this compound may generate a new family of materials for dosimetry.

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