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Phys. Status Solidi C **10**, No. 2, 176–179 (2013) / **DOI** 10.1002/pssc.201200509

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Thermoluminescence of NaF:Eu^{3+} phosphors exposed to beta particle irradiation

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Received 21 July 2012, revised 7 September 2012, accepted 9 October 2012
Published online 21 December 2012

Keywords thermoluminescence, dosimetry, NaF, sintering, beta radiation

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Pellet-shaped NaF:Eu^{3+} phosphors were synthesized by sintering. When a 5 K/s heating rate was used, the characteristic glow curves of beta particle irradiated samples exhibited two thermoluminescence (TL) maxima located at 401 K and 498 K, being the higher temperature maximum the most intense. A peak located between 473 and 523 K is considered to have a position very suitable to assure good thermal stability of the stored TL, so this phosphor is attractive for radiation dosimetry. Beta particle irradiated samples displayed a TL response that increases as the radiation dose increased in the 0.08 to 42.5 Gy dose range, with a linear behavior below 10 Gy followed by a sublinear one for higher doses. Under storage after irradiation, the TL maximum at 498 K displayed a remarkable stability, and the TL fading revealed that the maximum at 401 K is not a single peak.

1 Introduction The thermally stimulated luminescence technique, commonly known as Thermoluminescence (TL), may provide some valuable defect information when used in combination with other experimental methods, but the more widely spread and successful application of the TL is in the field of radiation dosimetry. Since the pioneering work by Daniels and his group, the increased use of the TL was accompanied by a growing interest in the development of new phosphor materials with properties suitable to be used as detectors of ionizing radiation [1-4].

It is typical of powder particles to sinter bond together when heated to relatively high temperatures (usually around one-half of their absolute melting temperature). In this firing treatment known as sintering, it occurs the transformation of powder particles into a solid form consisting of bonded particles. Formally, sintering is a thermal treatment for bonding particles together into a coherent, predominantly solid structure via mass transport events that occur largely at the atomic level. Such bonding improves the strength and other engineering properties of the compacted particles. During sintering there are significant changes in the structure and, additionally, many properties can undergo dramatic improvements during sintering. Essentially, it can be considered as a microwelding process of particles that is applicable to all materials, so it is a very important option in designing and manufacturing new materials [5]. Moreover, sintering is a route rather easier and cheaper than other commonly used to grow crystalline materials.

The remarkable TL efficiency of LiF it is well known since the pioneering work of Daniels in 1953 [1], and it has been the widest investigated material, in order to understand, to control, to improve its luminescence properties, and to study how these are modified by the introduction of impurity atoms in the host material. Together with LiF, other alkali halides phosphors display remarkable TL features, particularly when they are doped with rare earth

atoms [2, 3]. Among the ionic crystals, NaF is one of the less investigated concerning to its dosimetric capabilities.

Although dosimeters are available in different forms and shapes, solid easy to handle phosphors are preferred rather than powdered ones. Sintering allows to obtain dosimeters with any shape and size if a suitable mold is used. Recently, we reported the usefulness of sintering processes to manufacture new insulator and semiconductor TL phosphors. The characterization of these materials indicated that they are very suitable for dosimetry applications [6-8].

Following with the development of new efficient TL phosphors by easy and cheap methods, in this article we report the fabrication of pellet-shaped NaF:Eu^{3+} phosphors, as well as their TL properties when exposed to β particle irradiation in the 0.08-42.5 Gy dose range. The whole glow curve looks simple, and the integrated TL response as a function of dose displays a good linear behavior for doses below 10 Gy, and the glow curves show an intensity maximum centered at 498 K when a 5 K/s heating rate is used. It is considered that such peak position assures a very good thermal stability of the TL signal of previously irradiated phosphors if stored at standard environmental conditions. The sensitivity of the synthesized NaF:Eu phosphor is 44% of that of the commercially available dosimeter TLD-100. Computarized glow curve deconvolution (CGCD) reveals that the whole thermogram is composed of five second order individual peaks. Activation energies were computed by the initial rise method [9, 10].

2 Experimental This Pellet-shaped NaF:Eu^{3+} phosphor materials were prepared as follow: NaF (Mallinkrodt, 99 %) and $EuCl_3{\cdot}XH_2O$ (Alfa Aesar, 99.99 %) were weighted (1.5 mol % of $EuCl_3{\cdot}XH_2O$) and mixed in deionized water at room temperature with magnetic stirring during 3 h. Next, temperature was gradually increased up to 363 K to obtain powder, which was mechanically mixed in an agate mortar. Samples containing 0.0836 g of this powder were placed on a 7 mm diameter cylindrical mold, followed by application of a pressure of 0.5 ton during 2 min using a hydraulic press. The obtained pellets were then sintered during 5 h at 1023 K under air atmosphere, in a Thermolyne model 1400 furnace.

A Risø TL/OSL model TL/OSL-DA-15 unit equipped with a ^{90}Sr source was used to perform β irradiations and the TL measurements. All irradiations were accomplished using a 5 Gy/min dose rate at room temperature (≈ 295 K). The TL measurements were carried out from room temperature up to 723 K under N_2 atmosphere using heating rates of 5 K/s or 1 K/s, depending on the purpose of the experiments, as will be explained in the next section.

3 Results and discussion Figure 1 shows the glow curves of NaF:Eu^{3+} samples exposed to different doses of β particle irradiation, for doses in the 0.16-21.3 Gy dose range. A 5 K/s heating rate was used. The TL intensity increases for increasing doses. The TL maximum is centered at around 498 K; for dosimetry, TL peaks located between 473 and 523 K are very suitable for TL dosimetry, because they are very stable under standard storage conditions, and avoid interference of TL with black body radiation [2].

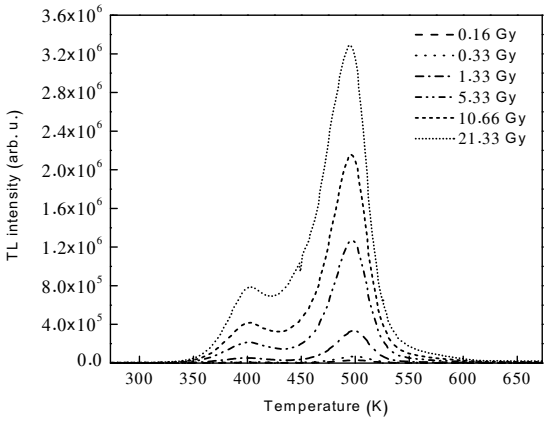

Figure 1 Thermoluminescence glow curves of pellet-shaped sintered NaF:Eu^{3+} samples after being exposed to β particle irradiation in the dose range from 0.16 to 21.33 Gy.

Figure 2 shows the integrated TL as a function of dose, for doses in the range from 0.08 to 42.5 Gy. It displays a linear response in the investigated dose interval, with no indication of response saturation. Figure 3 shows the glow curves as obtained when TL readouts were carried out after different elapsed time intervals between the irradiation at 2.6 Gy and the corresponding TL readout. Because the individual peaks overlapping, the vanishing of low temperature TL peaks leads to a decreasing of the higher temperature TL maximum, and the lower temperature maximum shifts to higher temperature as the elapsed time between irradiation and TL readout increases. The TL maximum at 498 K does no exhibits shift.

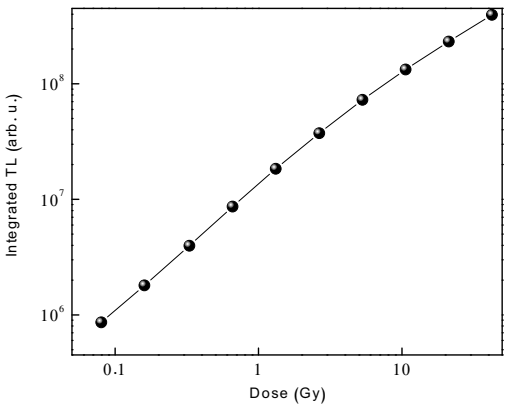

Figure 2 Integrated thermoluminescence as a function of dose, of NaF:Eu^{3+} pellets, exposed to β particle irradiation in the 0.08-42.0 Gy dose range.

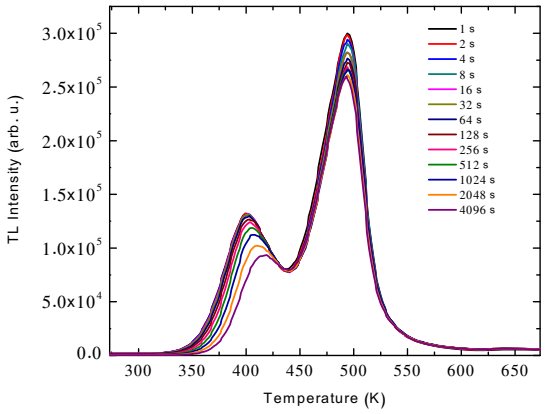

Figure 3 Thermoluminescence glow curves of 2.6 Gy beta irradiated NaF:Eu^{3+}, obtained after different elapsed time intervals between irradiation and the corresponding thermoluminescence readout.

Figure 4 shows the integrated TL as a function of the time interval elapsed between the irradiation and the corresponding TL readout. In all cases, samples were exposed to 2.6 Gy of β particle irradiation. The integrated TL fades fast into the first five minutes, after which it tends to remain constant as the elapsed time between irradiation and the corresponding TL readout increases.

The relative sensitivity of NaF:Eu with respect to that of the TLD-100 dosimeter is 0.13 when exposed to 2.6 Gy. According with this, NaF:Eu exhibits a TL sensitivity of the order of the TLD-100. However, if the mass correction is not taken into account, the sensitivity of the NaF:Eu sintered pellets is 44% of that of TLD-100. For practical use, the mass correction could not be important, since one reads the light emitted by the phosphor, not the relative emission of light per unit mass.

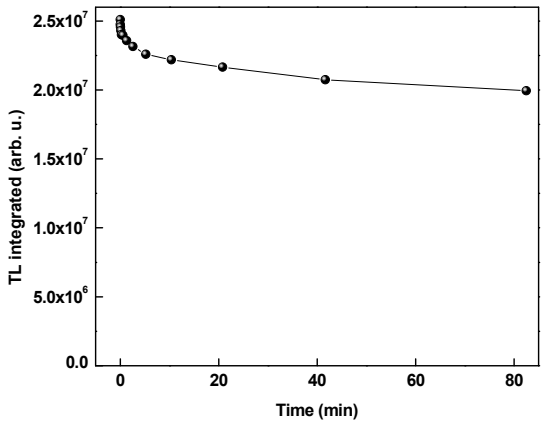

Figure 4 Integrated TL as a function of the time interval elapsed between the irradiation and the corresponding TL readout.

The experimental data for CGCD of the glow curve were collected according to the McKeever method: a TL readout up to a specific temperature T_{stop} is followed by a new readout of the sample up to 673 K in order to obtain the residual glow curve [2, 11, 12]. All the latter glow curves were those treated in the present work. Experimental TL data for the CGCD were collected using a 1 K/s heating rate. The results arisen from these glow curves were the peak maximum temperature, T_m, of each peak, as well as the activation energy, E.

The glow curve deconvolution (GCD) was performed using a general order kinetics expression [11]:

$$I(T) = I_m b^{b/(b-1)} \exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right)\left[Z_m + (b-1)(1-\Delta)\frac{T^2}{T_m^2}\exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right)\right]^{\frac{b}{1-b}}$$

with $Z_m=1+(b\text{-}1)\Delta_m$, $\Delta=2kT/E$ and $\Delta_m=2kT_m/E$. The curve fitting was performed using the MINUIT program [12], whereas the goodness of the fit was tested by the Figure of Merit (FOM) of Balian and Eddy [13], given by:

$$FOM = \sum_i \frac{\left|Y_{Exper} - Y_{Fit}\right|}{A}$$

where Y_{Exper} is the experimental glow-curve, Y_{Fit} is the fitted glow-curve and A is the area of the fitted glow-curve. In the final results given below, the kinetics order is b= 1.95 +/- 0.04, i.e., b = 2 = second order kinetics.

Figure 5 shows an experimental TL glow curve (circles) of a β particle irradiated NaF:Eu sample, together with the individual peaks obtained by CGCD analysis. It can be seen that the glow curve can be resolved in five second order kinetics TL peaks. Table 1 summarizes the peak maximum temperatures and activation energies. According to Figs. 3 and 5, the first peak fades producing the TL fading below 423 K. However, the TL signal at 439 K

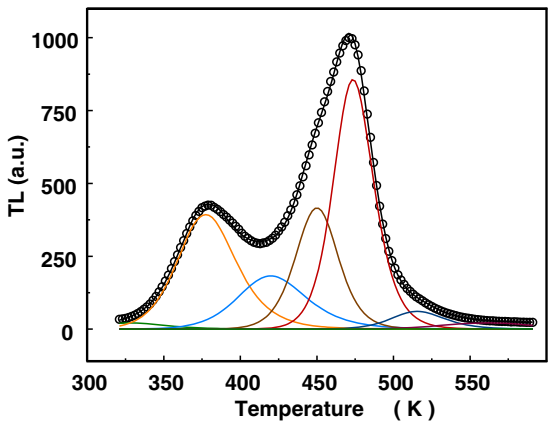

Figure 5 Glow curve of NaF:Eu resolved into individual glow peaks by a computerized glow curve deconvolution (CGCD) analysis.

Table 1 Peak maximum temperatures and activation energies of the glow curve of NaF:Eu, as obtained from the CGCD analysis.

Peak	T_m (K)	E (eV)
1	380±6	0.95±0.05
2	418±4	1.12±0.12
3	449.5±1	1.61±0.08
4	473.3±0.5	2.01±0.08
5	513.5±2	1.99±0.16

does not display any decrease as long as the main maxima firstly decrease, and then tend to remain unchanged, which could be due to the carrier transfer from the third peak to the first one. Also, since a second order kinetics is involved, it could be that de-trapped carriers from the third peak to be re-trapped in the traps associated with the second peak. Anyway, the initial decrease of maximum in spite of the temperature at which is observed is a very interesting point to be investigated.

It is worth mentioning that 30 samples were used for TL repeatability testing. A variability less than 3% was found for the experimental results.

4 Conclusions In this work, we present the thermoluminescence characterization of pellet-shaped NaF:Eu phosphors synthesized by sintering. Sintering is a low cost versatile fabrication technique easier than other available methods. The experimental results show that NaF:Eu exhibits good enough thermoluminescence features, as to be considered for the development of detectors and dosimeters of ionizing radiation. As attractive characteristics, it can be noted the simple form of the whole TL curve, and a maximum intensity at around 498 K when β irradiated samples are heated at a 5 K/s heating rate, and a linear dependence of the TL as a function of dose in the dose range investigated (from 0.08 to 42.5 Gy). The sensitivity of the synthesized NaF:Eu is 44% of that of the TLD-100 dosimeter. Computerized glow curve deconvolution reveals that the glow curve is composed by five individual second order peaks.

Acknowledgements The authors gratefully acknowledge the financial support for this work from Universidad de Sonora, Grant PI 05/DCEN02.

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