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Study of TL and OSL Correlations and Properties of $3Al_2O_3$-$2SiO_2$ Phosphor

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Abstract— *In the present work $3Al_2O_3$-$2SiO_2$ phosphorus doped with Er and Yb, with grain sizes about 0.25 up to 0.50 μm, were synthetized by sol-gel technique. TEM images showed the presence of nanocrystalline structure of erbium silicon, erbium oxide and ytterbium oxide in the samples. The T_{bleach}-T_{max} and R-TL methods were applied successfully in order to investigate the TL and OSL correlation, comparing the R-TL bleaching decay rates and decay values of CW-OSL and LM-OSL individual components.*

Keywords— *TL and OSL environmental dosimetry, 3Al2O3-2SiO2:Er,Yb phosphors, Residual TL technique, CW-OSL/LM-OSL*

1. INTRODUCTION

With the purpose of finding a new luminescent phosphor to be used in environmental and accident retrospective dosimetry, the present work intend to study the TL and OSL properties of the mullite ($3Al_2O_3$-$2SiO_2$) with Zeff = 11.5, which is close to effective atomic number of the sediments. Some few works about TL of mullite can be found in the literature, investigating the TL and radioluminescence emissions of ceramic synthetic mullite (Yang et al, 1998 and 2000) and works of TL emission of mullite porcelain for use in retrospective dosimetry (Oks, 2011; Bailiff, 1995 and 1997). Therefore, the TL and OSL of mullite properties are not understood in detail yet, in order to study the luminescence emission mechanism a study about TL-OSL correlation has been performed. TL peaks are associated to individual components of CW-OSL and LM-OSL using T_{bleach}-T_{max} method for LM-OSL curve and residual TL (R-TL) method, all the experimental data are de-convoluted and the bleaching decay rates for individual R-TL peaks, LM-OSL and CW-OSL components are evaluated and compared. Several phosphors have been successfully studied using these methods (Singh et al, 2012; Dallas et al, 2010; George et al, 2009).

2. SAMPLES AND EXPERIMENTS

Pure polycrystalline $3Al_2O_3$-$2SiO_2$ and Eu (8 mol%) and Yb (8 mol%) doped samples were obtained by the sol-gel process. High purity reagents were used for making the samples, which were aluminum sec-butoxide, TEOS, ammonia and distilled water in stoichiometric amounts. The crystalline morphology of the resulting samples was verified by X-ray diffraction analysis.

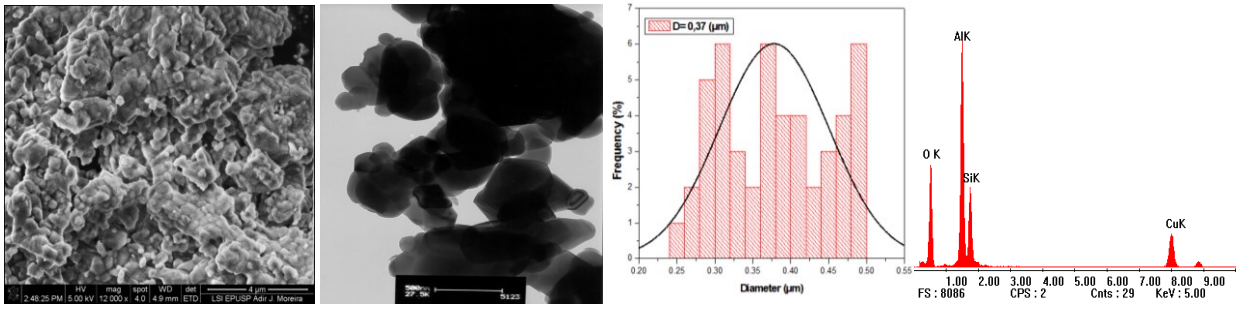
In order to study surface morphology of phosphor Transmission Electronic Microscopy (TEM, Philips, model CM200, with 160 kV aceleration voltage), equipped with Energy Dispersive Spectrometer (EDS) have been carried out. Complementary images were made by Scanning electron microscope (SEM) using a NanoSEM FEI Company model 400.

The TL and OSL measurements were recorded using a Risø TL/OSL automated reader; model TL/OSL-DA-20, for TL glow curve measurements the heating rate used was 5 °C/s and the samples were heated up to 500 °C.

In order to observe the correlation between TL peaks and OSL signals, the samples were initially irradiated with a dose of 10 Gy and the CW-OSL measurements was detected during 250 s and for LM-OSL experiments the detection time was 1000 s.

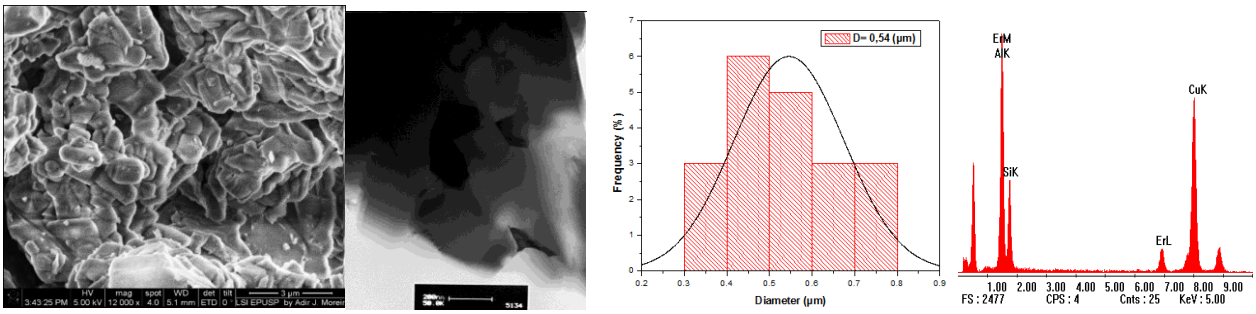
T_{bleach}-T_{max} method was applied to found the quantity of LM-OSL individual components, the samples were beached during 10, 25, 50, 75, 100, 125, 150, 175 and 200 s, T_{bleach} and T_{max} values were obtained and a graphic with the temperatures was plotted, the number of plateaus indicate the quantity of individual components of the LM-OSL curve. Using this result the LM-OSL curve was de-convoluted using general order LM-OSL kinetic equation, taking in account the Figure of Merit (FOM) values, which should be less than 2% (Polymeris et al, 2006; Kitis and Pagonis, 2008; Singh et al, 2012).

In R-TL method TL glow curves were measured with samples previously irradiated with a dose of 10 Gy and optically bleached during 5, 25, 50, 75, 100, 150 and 300 s. The optical bleach was acquired with CW-OSL measurements. The obtained R-TL glow curves were de-convolved theoretically using general order GCD function (Kitis, et al, 1999), the normalized integral of the individual R-TL peaks were plotted against to respective bleaching times, and the bleaching rates of each TL peak were evaluated. These bleaching rates were compared to decay constant of each individual components, which comprise CW-OSL and LM-OSL curves. The decay rates for individual components of CW-OSL curve were



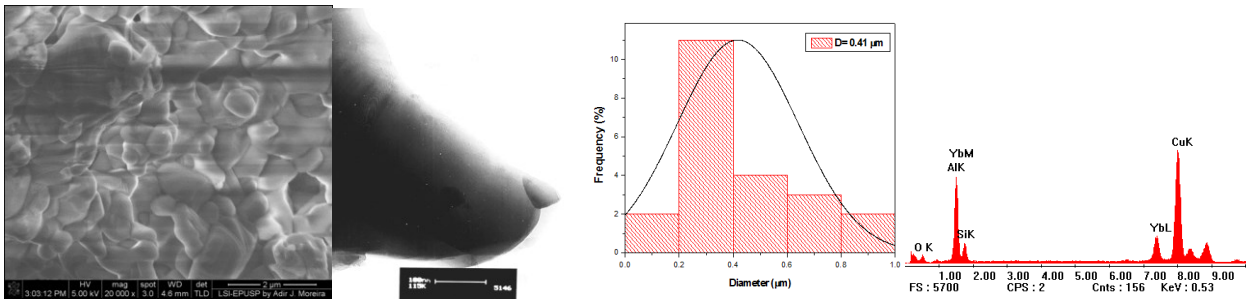
(a) (b) (c) (d)

Fig. 1: (a) SEM image and (c) grain size distribution for undoped sample; (b) TEM image and (d) EDS from undoped sample. Scale Bar, 500 nm.



(a) (b) (c) (d)

Fig. 2: (a) SEM image and (c) grain size distribution for 8 mol% Er doped sample; (b) TEM image and (d) EDS from 8 mol% Er doped sample. Scale Bar, 200 nm.



(a) (b) (c) (d)

Fig. 3: (a) SEM image and (c) grain size distribution for 8 mol% Yb doped sample; (b) TEM image and (d) EDS from 8 mol% Yb doped sample. Nanocrystal with size of 50 nm can be visualized. Scale bar, 100 nm.

evaluated by de-convolution using first order CW-OSL equation, and in the same way the first order LM-OSL equation was used for LM-OSL curve de-convolution, the equations are described in Singh et al, 2012.

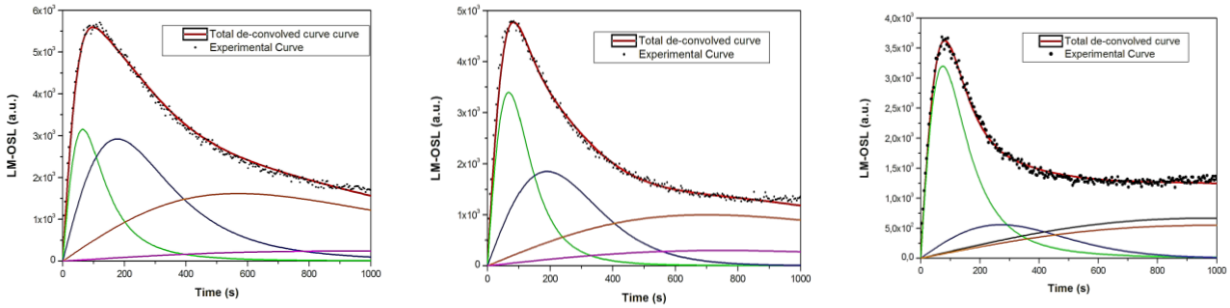
3. RESULTS AND DISCUSSION

3.1 Morphology Analysis

Fig. 1 shows results obtained for undoped sample, SEM image revealed an agglomerated morphology without porous presence (Fig. 1a) and presented a grain size distribution between 0.25 up to 0.50 μm, the average grain size was about 0.37 μm (Fig. 1c).

TEM image showed that the grain does not have porous (Fig. 1b) and the EDS results exhibited the occurrences of *Al, O* and *Si* certificating that the sample did not suffer contamination during the production procedure (Fig. 1d). The signals of *Cu* in Fig. 1d, 2d and 3d resulted from the sample holder.

For sample doped wit 8 mol% of Er the SEM image (Fig. 2a) shows almost the same morphology found in undoped sample, however the grain sizes followed the normal distribution and the average size increases to 0.54 μm (Fig. 2c). According to TEM image (Fig 2b) the sample has nanocrystals, with about 200 nm of size, of erbium silicon and erbium oxide, detected by X-rays diffraction



(a) (b) (c)

Fig. 4: LM-OSL curve recorded of mullite, a) undoped sample, b) doped with 8 mol% of Er and c) doped with 8 mol% Yb. Black points are the experimental curve and red line is the total theoretically fitted curve; green, blue, pink and orange curves represent the individual components of LM-OSL.

measurements, on the matrix grains boundaries. EDS result also exhibited the Er occurrence (Fig. 2d).

For sample doped with 8 mol% of Yb the SEM image (Fig. 3a) shows similar morphology found in other samples and the average size was about 0.41 μm (Fig. 2c). Fig. 3b shows the TEM image of Yb doped sample with ytterbium oxide nanocrystals, also detected by X-rays diffraction, with about 50 nm and the EDS result, for this sample, showed Yb presence (Fig. 3d).

3.2 OSL Analysis

After T_{bleach}-T_{max} experiment it was concluded that there are 4 individual components in LM-OSL curve, Fig. 4 shows the de-convolution results obtained for the three samples. Also the CW-OSL curves are de-convoluted and all the decays rates are listed in the Table 1, with respective FOM values, it can be noted that low values of FOM could be obtained and they ranging from 0.13 to 0.76 %.

Fig. 5 and 6 shows R-TL results provided by the samples, it could see that TL peaks at low temperature decayed faster with the increase of bleaching time, and for undoped sample (Fig. 5a) the peak at high temperature remain, almost in totality, after 300 s of illumination and some additional emission occurred after 400 °C approximately. In the case of the Er doped sample the intensity of the peak at high temperature, after 300 s of bleaching, declined by nearly 50%, and the additional emissions also appeared at temperature above 400 °C (Fig. 6a). The Yb doped sample results are shown in Fig. 6c) this sample supplied better defined TL peaks and the intensity increase at high temperature it was not noted. All the R-TL experimental curves are de-convoluted, some typical examples are shown in Fig. 5 b), and Fig. 6 b) and d). The bleaching decay rates of each R-TL peaks are calculated and are listed in Table 2.

Comparing the decay rates listed in Tables 1 and 2 it can be noted how complex can be the relation between the TL peaks and OSL individual components. The decay results for 280 °C TL peak of undoped samples can be related as b_1=0.097 s^{-1} with f_1=0.0978 s^{-1} and 0.0991 s^{-1}, b_2=0.0050 s^{-1} with f_3=0.0052 s^{-1} and 0.0050 $s^{-1}$and b_3=0.0006 with f_4=0.0006 s^{-1}. The 395°C has only one correlation between b_2=0.0006 s^{-1} and f_4=0.0006 s^{-1}.

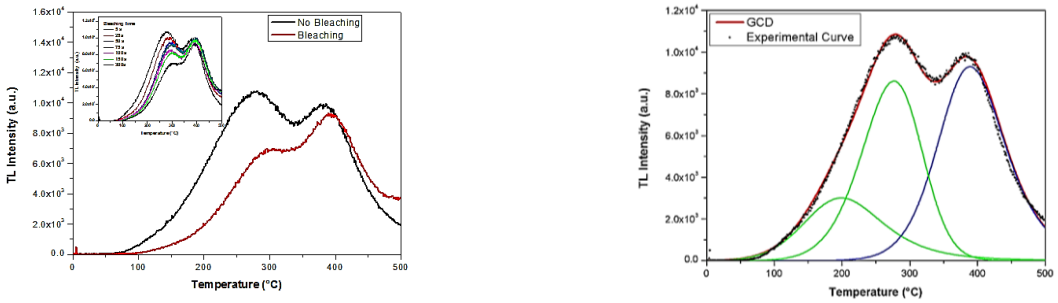
Table 1: Decay rates of CW-OSL and LM-OSL of mullite and respective FOM values.

Mullite dopant	*OSL*	*f_1 (s^{-1})*	*f_2 (s^{-1})*	*f_3 (s^{-1})*	*f_4 (s^{-1})*	*FOM (%)*
Undoped	CW	0.0978	0.0253	0.0052	0.0006	0.13
	LM	0.0991	0.0248	0.0050	0.0006	0.76
Er 8 mol%	CW	0.1250	0.0103	0.0287	0.0004	0.28
	LM	0.1247	0.0048	0.0239	0.0004	0.30
Yb 8 mol%	CW	0.0291	0.0980	0.0049	0.0002	0.37
	LM	0.0244	0.0960	0.0046	0.0003	0.76

Table 2: Calculated bleaching decay rates for R-TL experiment.

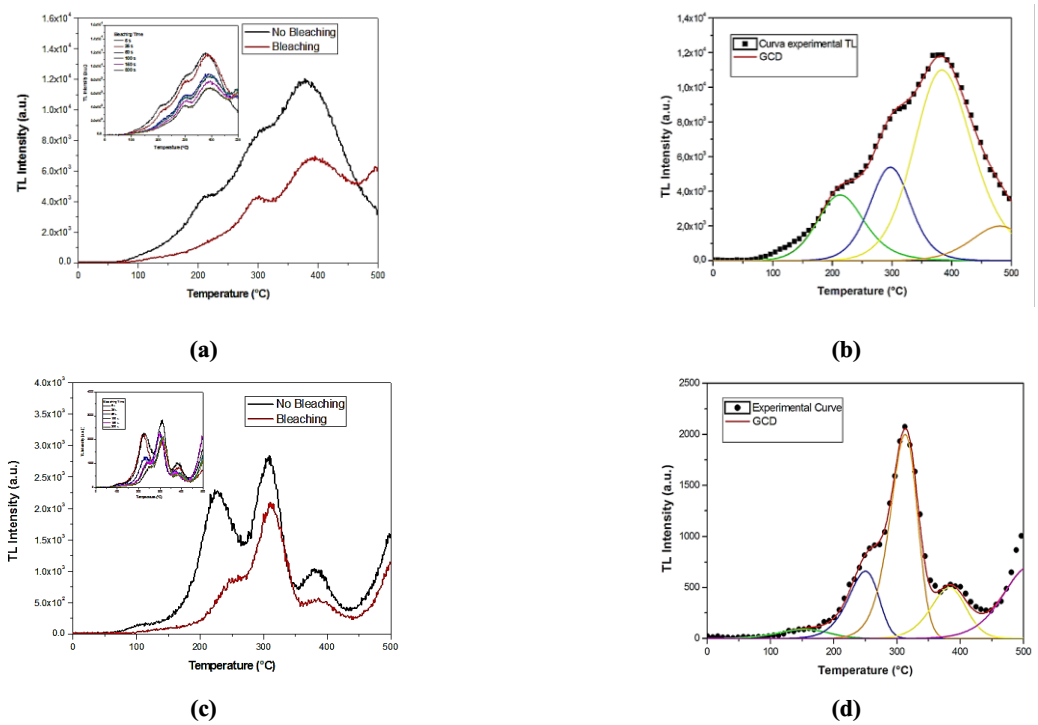
Mullite dopant	*RT-Peak (°C)*	*b_1 (s^{-1})*	*b_2 (s^{-1})*	*b_3 (s^{-1})*
Undoped	280	0.0970	0.0050	0.0006
	395	0.0094	0.0006	$1x10^{-5}$
Er 8 mol%	210	0.1250	0.0100	0.0004
	300	0.0126	0.0250	0.0004
	380	0.0240	0.0013	0.0004
Yb 8 mol%	225	0.0047	0.0212	0.0002
	300	0.0960	0.0003	0.0010
	385	0.0308	0.0017	0.0003

For Er doped sample the bleaching decay rates of 210 °C TL peak, b_1=0.1250 s^{-1}, b_2=0.0100 s^{-1} and b_3= 0.0004 s^{-1} can be related to f_1 (0.1250 and 0.1247 s^{-1}), f_2 (0.0103 s^{-1}) and f_4 (0.0004 s^{-1}) respectively. The results for 300 °C TL peak correlated b_1=0.0126 s^{-1} with f_2= 0.0103 s^{-1}, b_2=0.0250 s^{-1} with f_3=0.0287 s^{-1} and b_3=0.0004 s^{-1} with f_4=0.0004 s^{-1}. In the case of 380 °C it was found that b_1=0.0240 with f_3 = 0.0239 s^{-1} and b_3=0.0004 s^{-1} with



(a) (b)

Fig. 5: TL glow curve after optical bleaching during 5, 25, 50, 75, 100, 150 and 300 s, TL glow curve de-convoluted using general order GCD function (Kitis, et al, 1999), a) and b) undoped mullite.



(a) (b)

(c) (d)

Fig. 6: TL glow curve after optical bleaching during 5, 25, 50, 75, 100, 150 and 300 s, TL glow curve de-convoluted using general order GCD function (Kitis, et al, 1999); a) and b) 8 mol% Er doped mullite and c) and d) 8mol% doped Yb mullite.

f_4=0.0004 s^{-1}. Therefore, the obtained decay values are very close, for this sample only the LM-OSL component with f_2= 0.0048 s^{-1} could not be related to any TL peak.

Finally for Yb doped sample the decay rates for 225 °C peak, we obtained that b_1=0.0047 s^{-1} with f_3=0.0049 s^{-1} and 0.0046 s^{-1}, b_2=0.0212 s^{-1} with f_1=0.0291 s^{-1} and 0.0244 s^{-1} and b_3=0.0002 s^{-1} with f_4=0.0002 s^{-1} and 0.0003 s^{-1}. For 300 °C peak b_1=0.0960 with f_2=0.0980 s^{-1} and 0.0960 s^{-1}; b_2=0.0003 with f_4=0.0002 s^{-1} and 0.0003 s^{-1}. The last peak at 385 °C b_1=0.0308 s^{-1} with f_1=0.0291 s^{-1} and b_3=0.0003 s^{-1} with f_4=0.0002 s^{-1} and 0.0003 s^{-1}.

4. CONCLUSION

Our results indicated that polycrystalline powder of mullite ($3Al_2O_3$-$2SiO_2$) was successfully obtained using sol-gel technique. A second phase formation consisting in nanocrystallites of erbium silicon and erbium oxide, with average diameter size of 200 nm and ytterbium oxide with size of 50 nm, approximately, located at the boundaries of the mullite grains, were observed in the doped samples. The grain sizes of the samples varied from 0.37 to 0.54 μm and no pores was found.

The T_{bleach}-T_{max} and R-TL methods applied to mullite supplied consistent results of TL and OSL correlations.

It was verified for $3Al_2O_3$-$2SiO_2$ that 280 °C TL peak is related to three individual OSL components and 395 °C peak with one component. For Er doped sample TL peak at 210 °C is related to three individual OSL component, 300 °C peak also with three and 380 °C with two components. Finally, for sample doped with Yb, each TL peak at 225, 300 and 385 °C is related to three, two and two OSL components.

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