Dosimetric and thermoluminescent characteristics of sintered samples based on $Li_2OAl_2O_3nSiO_2$ systems

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Received 30 de junio de 2011; accepted 25 de agosto de 2011

This work describes the thermoluminescent (TL) characteristics of lithium aluminosilicates, $Li_2OAl_2O_3nSiO_2$, for its possible use as TL dosimeter for low doses. The sinterized tablets of $Li_2OAl_2O_3nSiO_2$were characterized by means of X ray diffraction (XRD), and irradiated at different doses using a Theratron 780C-^{60}Co unit in air at room temperature. The Rasheedy's technique was used for the kinetic trap parameters determination. The XRD results show a mixture of two phases of 64% β-spodumene and 36% β-eucryptite in the sinterized tablets. TL analysis indicates that in these systems, recombination processes prevail, and that these systems can be used successfully as TL dosimeters for therapeutic dose ranges.

Keywords: Lithium aluminosilicates; dosimetry; thermoluminescence.

Este trabajo describe las características termoluminiscentes (TL) de aluminosilicatos de litio, $Li_2OAl_2O_3nSiO_2$, para su posible uso como dosímetro TL de baja dosis. Las pastillas sinterizadas de $Li_2OAl_2O_3nSiO_2$ fueron caracterizadas por difracción de rayos X (DRX), e irradiadas a diferentes dosis usando una unidad de ^{60}Co Theratron 780C en aire a temperatura ambiente. El cálculo de los parámetros de atrapamiento se hizo usando el método de Rasheedy. Los resultados de DRX evidencian una mezcla de las fases β-eucriptita ($Li_2OAl_2O_32SiO_2$) y β-espodumena ($Li_2OAl_2O_34SiO_2$) en una proporción de 36% y 64% respectivamente. El análisis de la respuesta TL muestra que en estas matrices predominan los procesos de recombinación y que podrían ser usadas como dosímetros TL en rangos de dosis terapéuticas.

Descriptores: Aluminosilicatos de litio (LAS); dosimetría; termoluminiscencia.

PACS: 87.58.Sp; 87.66.Pm; 87.66.Sq.

1. Introduction

The irradiation process at centers that work with ionizing radiations [1] requires a quality control program. The verification of absorbed dose is an essential part of this program and consists simply in comparing the measured doses (dosimetry) with the prescribed doses, both medical treatments and industrial processes. Although exists several dosimetric techniques, the thermoluminescence dosimetry (TLD) is one of the most employed to develop this kind of studies and is undoubtedly the main practical application of thermoluminescence. In this activity the TL has achieved great development and a high level of acceptation into international scientific community from the first researches of Daniel and coworkers [2]. Although from the beginning, the TL dosimeter most widely used has been the LiF:Mg,Ti (TLD-100), in recent years, have been proposed and tested all type of TL-materials used for this purpose and for fields ranging from medicine to archeology [3-10]. As a part of this search, different natural systems such as quartz or feldspar, or synthetic systems as silicates with compositional variations of quartz, have been analyzed [11-15].

In order to contribute to these studies, this work describe the TL characteristics and the dosimetric properties of lithium aluminosilicates, $Li_2OAl_2O_3nSiO_2$, synthesized by metal-formates gelification technique [16], and evaluates their viability as TL dosimeter for therapeutic dose ranges.

2. Experimental

2.1. Synthesis and processing

Lithium aluminosilicate vitreous powders, obtained by means of the gelification of aluminum and lithium formiates in presence of tetraethoxy-silane [17], were used for the preparation of 6 mm of radius and 3 mm of thickness tablets (particles sized under 20 μm) by means of uniaxial pressing at 72 Mpa. All the samples (each of 100 g) were preannealed for 1 hour at 1250°C in an electric furnace. The molar ratio of the synthesized matrices was oriented towards the proportion $1Li_2O$–$1Al_2O_3$–$nSiO_2$ with n values between 2 (β-eucryptite phase) and 4 (β-spodumene phase), because for these compositions have been reported low (and even negative) thermal expansion coefficients [18], and luminescent activity [19], which are desired properties for thermoluminescent activity.

2.2. Thermoluminescence tests

Irradiations of samples were carried out in air at room temperature using a Theratron 780C-^{60}Co unit at a distance of 80 cm relative to the source, in a radiation field of 10×10 cm^2. The samples were placed between two acrylic plates of 5 mm of thickness, with the purpose of reaching the conditions of electronic equilibrium.

Thermoluminescence measurements were performed using a commercial Harshaw QS 4500 dosimeter manufactured by Bicron®, using a linear heating rate of 10°Cs^{-1}from 50°C up to 400°C. The readings were carried out in a N_2 atmosphere in order to eliminate the infrared contribution due to the heating and to reduce the moisture effects.

In order to reduce the residual signal of the material before each irradiation, allowing their re-utilization, samples were then annealed at 400°C/1h, followed by cooling in air until to reach room temperature.

2.3. Structural and thermoluminescent analysis

Sinterized samples were characterized by means of X-ray diffraction (XRD). The diffractograms were obtained by means of a Rigaku Miniflex diffractometer using a copper source $K_{\alpha 1}\lambda$=1.54 Å to a sweeping rate of 0.5°/min.

Glow curves obtained were analyzed using a decomposition, fitting and simulation technique proposed by Rasheedy [20], for obtaining the trap parameters of the individual glow peaks in a complex glow curve. These parameters include the order of kinetics b, the activation energy E (eV), the pre-exponential factor S'' (s^{-1}) and the initial concentration of trapped electrons n_0(cm^{-3}).

This technique is applicable in TL curves consisting of multiple peaks and determines, by a general equation, the order b based on a set of three data points in an experimental TL glow curve, considering that for general order kinetics, the behavior of TL intensity of a phosphor is governed by the following equation:

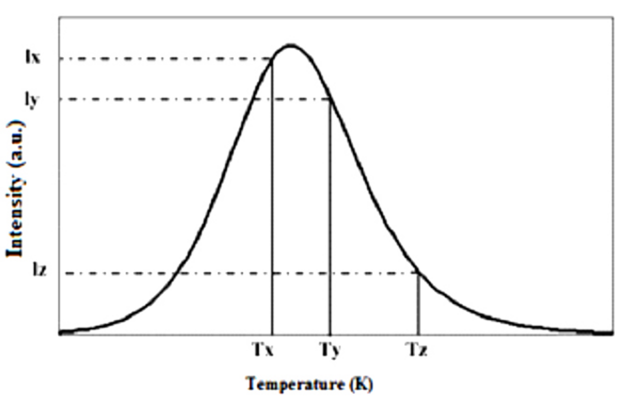

FIGURE 1. Parameters I_x, I_y, I_z, T_x, T_y y T_z, in a isolated TL glow peak.

$$I = -\frac{dn}{dt} = \frac{n^b}{N^{b-1}} S \exp\left(\frac{-E}{kt}\right) \tag{1}$$

Where I (in arbitrary units) is the TL intensity, n (cm^{-3}) the electron concentration trapped at time t (s), N(cm^{-3}) the traps concentration and k (eV/K) is the Boltzmann's constant. The solution of Eq. (1) for b≠1 is given by:

$$I = \frac{n_o s'' \exp(-E/kt)}{[1 + [((b-1)S'')\ \beta] \int\limits_{T_o}^{T} \exp(-E/kt')dT']^{b/(b-1)}} \tag{2}$$

Where β(Ks^{-1}) is the linear heating rate and n_0(cm^{-3}) is the concentration of traps populated at the starting heating temperature T_0(K). The pre-exponential factor S'' (s^{-1}), which is defined as $S'' = S(n_0/N)^{b-1}$is constant for a given dose, but it varies with changing the absorbed dose, *i.e.*, with n_0.

The importance of Eq. (2) is that once the parameters b, E and S'', are obtained, it will be possible to simulate with this expression, the thermoluminescent response in the LAS-type matrices studied in this research.

To determine the kinetic parameters it will be assume that, during the TL run, the concentration of populated traps at a temperatureT_i is proportional to the area A_i, where A_i is the area under the glow peak between theT_i and T_f (final temperature of the glow peak).

Let us consider I_x is the TL intensity at a temperature T_x at any portion of the glow peak (see Fig. 1), Eq. (1), thus, becomes:

$$I_x = \frac{(A_x)^b}{N^{b-1}} * S * \exp\left(\frac{-E}{kT_x}\right) \tag{3}$$

Where T_x(K) is the temperature corresponding to the intensity I_x, and A_x is the area under the glow peak between the T_x and T_f. Also, let us assume that $I_y = I_x/y$ and $I_z = I_x/z$ are the intensities at portions equal to 1/y and 1/z from the intensity I_x, respectively. Then, similar to Eq. (3), the following equations may be written:

$$I_y = \frac{I_x}{y} = \frac{(A_y)^b}{N^{b-1}} * S * \exp\left(\frac{-E}{kT_y}\right) \tag{4}$$

$$I_z = \frac{I_x}{z} = \frac{(A_z)^b}{N^{b-1}} * S * \exp\left(\frac{-E}{kT_z}\right) \tag{5}$$

Where A_y and A_z indicate the areas under the glow peak from the temperatures T_y to T_f and T_z to T_f, respectively. There are not any relations between the intensities at which T_x, T_y and T_z exist. Also, T_x can antecede T_y (and/or T_z) or viceversa.

From (3) and (4) one obtains:

$$E = \{(\ln y) - b\ln[A_x/A_y]\}\left\{\frac{kT_xT_y}{T_x - T_y}\right\} \tag{6}$$

And from equations (3) and (5) one obtains:

$$E = \{(\ln z) - b\ln[A_x/A_z]\}\left\{\frac{kT_xT_z}{T_x - T_z}\right\} \tag{7}$$

Combining the Eqs. (6) and (7) can be obtained an expression for the parameter b:

$$b = \frac{T_y[T_x - T_z]\ln(y) - T_z[T_x - T_y]\ln(z)}{T_y[T_x - T_z]\ln\left[\frac{A_x}{A_y}\right] - T_z[T_x - T_y]\ln\left[\frac{A_x}{A_z}\right]} \tag{8}$$

With the order of kinetics determined, the activation energy of TL process can be determined using Eqs. (6) or (7). Now, with b and E parameters can be obtained pre-exponential factor S'' from Eq. (2):

$$S'' = \frac{\beta E \exp(E/kT_m)}{[bkT_m^2] - (b-1)E\phi\exp(E/kT_m)} \tag{9}$$

Where T_m(K) is the temperature corresponding to the maximum intensity, I_m, of the glow peak and,

$$\phi = \int_{T_o}^{T_m} \exp\left(\frac{-E}{kT'}\right) dT' \tag{9'}$$

Finally, inserting (9) into (2) can be obtained an analytical expression for n_0:

$$n_o = \frac{I_m \exp(E/kT_m)}{S''}\left(\frac{bkT_m^2 S''}{\beta E\exp(E/kT_m)}\right)^{b/(b-1)} \tag{10}$$

In Eq. (10), the parameters b, E, S'' y β are known, and the values of I_m and T_m can be obtained from experimental glow curve.

The quality of Rasheedy's fit has been tested with the figure of merit (FOM) [21], where FOM is given by

$$\text{FOM} = \Sigma_{ji}^{jf}\frac{100|y_j - y(k_j)|}{A} \tag{11}$$

Where FOM = Figure Of Merit (%), j_i = first channel in the region of interest, j_f = last channel in the region of interest, y_j = information content of channel j, $y(k_j)$ = value of the fitting function in channel j, A = integral of the fitted glow-curve in the region of interest.

Glow curves with FOM values in excess of 5%, must be examined by another technique of deconvolution, because in these cases the fit is not as accurate.

3. Results

3.1. Structural analysis

Crystalline phase analysis by means of XRD (Fig. 2) revealed the presence of the β-spodumene (JCPDS 35-0797), and β-eucryptite (JCPDS 17-0533) structures. It was also observed that the crystallization was not complete, amorphous residual phases remain which confer a glass-ceramic nature to the host. Additionally, the XRD analysis of LAS-type matrices revealed a compositional ratio of 64% β-spodumene and 36% β-eucryptite.

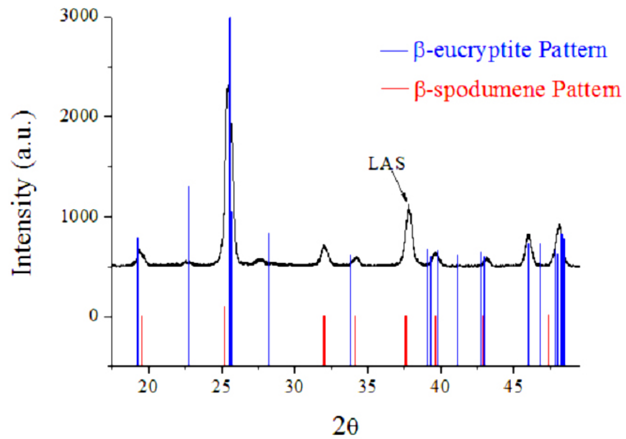

FIGURE 2. XRD patterns of the phases present into LAS composition treated at 1250°C during 30 min.

3.2. Glow curves

Figure 3 shows the glow curve of a LAS-type tablet irradiated at different doses. In the temperature range used, the curve exhibits a single peak around 270±1×C, which can be used for TL dosimetry. Note that the signal intensity increases proportionally with dose.

3.3. Kinetic analysis

Glow curves shown in Fig. 3 were analyzed by the method proposed by Rasheedy described previously. The results are reported in Table I.

Note that into LAS-type matrix as the absorbed dose increases, recombination events (b=1) take precedence over re-trapping processes (b=2).

Also can be observed that, as the absorbed doses increases, the population of initially filled traps (n_o) increases. This increase in "n_o" favors the probability of release the trapped electrons to the conduction band, obtaining, as net effect, an overall reduction in the activation energy of TL pro-

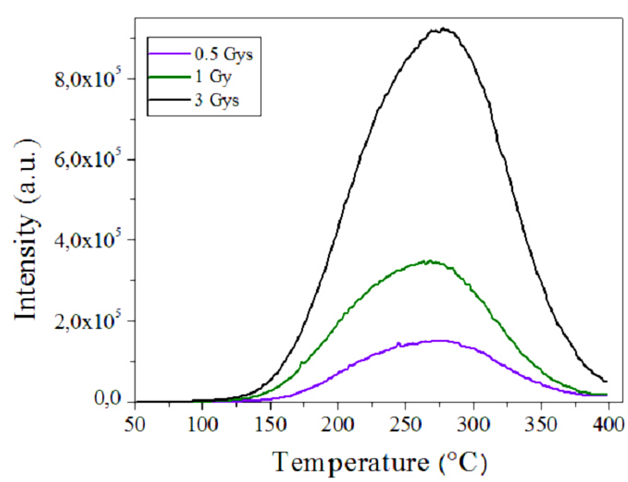

FIGURE 3. Glow curves for the same tablet irradiated at 0.5, 1.0 and 3.0 Gys.

TABLE I. Kinetic parameters of LAS-type matrix irradiated at 0.5, 1.0 and 3.0 Gys.

Kinetic parameters	Dose (Gys)		
	0.5	1.0	3.0
b	1.22	1.17	1.07
E(eV)	0.50	0.48	0.45
S'' (s^{-1})	7.26E+03	6.03E+03	2.05E+03
n_o (a.u.)	2.04E+06	4.57E+06	1.29E+07
FOM (%)	5.7	3.8	3.6

cess. Additionally, this reduction in activation energy, causes a decrease in the value of pre-exponential factor, because the TL process is activated more easily.

On the other hand, the Fig. 4 shows experimental and fitted glow curves, obtained with Eq. (2). For each curve, we observe that the theoretical peak, fitted curve, with the values of the kinetic parameters fits well to the experimental one (Exp curve). Although, at temperature values below T_m, a deviation between experimental and predicted intensities can be seen, the goodness-of-fit (FOM values), exhibits inferior values than 5% for 1.0 and 3.0 Gys (see Table I). For the dose of 0.5 Gys, although the error exceeds 5%, this is not too disproportionate for what eventually this methodolgy could be used for doses below 1 Gy.

3.4. Reproducibility

To study the reproducibility of the TL response, the samples were subjected seven times to the same annealing treatment defined for reuse (400°C/1h) and irradiated at a dose of 50 cGy. From experimental data was obtained an uncertainty of 2.0% associated to mean value of measurements.

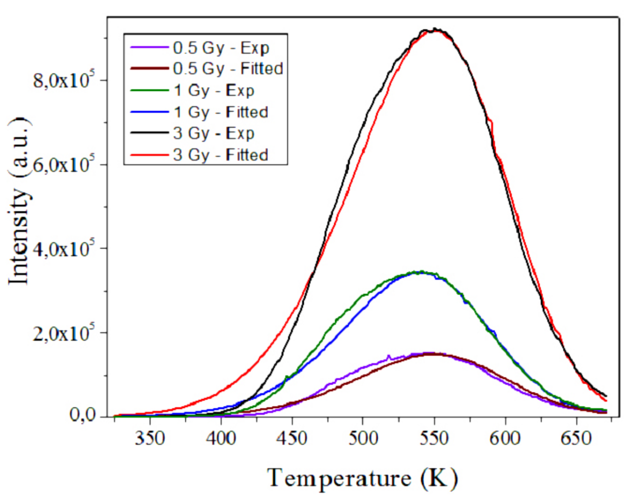

FIGURE 4. Experimental (Exp) and fitted (fitting) glow curves for the same tablet irradiated at 0.5, 1.0 and 3.0 Gys.

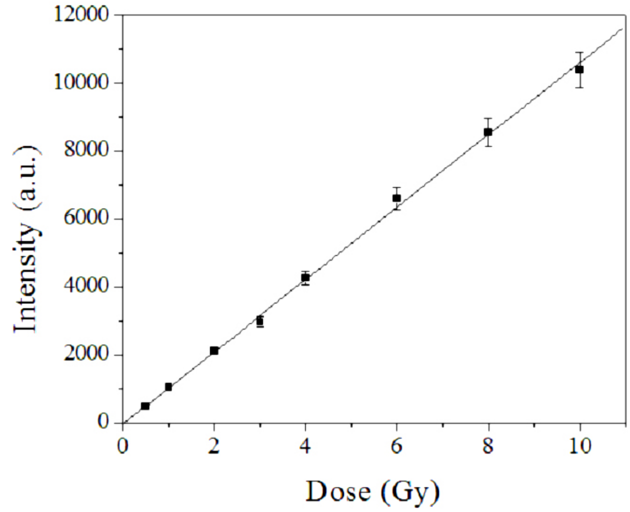

FIGURE 5. Relationship intensity versus dose for LAS-type matrices in the range 0.5-10.0 Gys.

3.5. Relationship intensity versus dose

The sintered tablets were irradiated at different doses from 0.5 up to 10 Gys to study the material response with dose. The results are shown in Fig. 5, where the points represent the mean values of each set of measurements obtained after each irradiation. The error bars correspond to standard deviation of 5% on the average value of each group of measures. The results show a linear correlation of intensity (referred to, in this case, as total intensity of emission) versus dose, obtaining a correlation coefficient R of 0.99918.

3.6. Fading Process

In order to study the signal fading the samples were exposed to 50 cGys (gamma radiation) and stored at room conditions. The tablets were measured during the 30 days after irradiation. After 48 hours, the tablets showed a TL signal fading of 13%, reaching a weakening of 38% during the first 15 days tending to a constant value during the next 15 days.

3.7. Detection Limit

The minimum dose detected by LAS-type tablets was of 2 cGys, after samples were exposed to gamma radiation. This is threshold dose of Theratron 780C-^{60}Co equipment. The observed glow curve showed the same characteristics mentioned previously.

4. Discussion

In the thermoluminescent materials the TL emissions are essentially processes related to the presence of impurities (dopants) that have been naturally or artificially introduced into the lattice of the host matix [22]. These impurities generate specific energy levels or traps in the forbidden energy band situated between the valence band and conduction band, which does not exist in the pure material. These new levels can be occupied by charge carriers, electrons and/or holes, released during irradiation.

By observing the TL curves of these samples (Fig. 3), can be assumed to consist of a superposition of two or more signals TL. Other researchers [23] using a deconvolution analysis of the TL glow curve under general-order kinetics theory, found that these samples show four peaks between 180°C and 300°C, which indicates that the tablets have different types of defects.

The glow curve kinetic analysis (Table I) show that recombination events take precedence over retrapping processes. This is consistent with the other parameters, since the activation energy decreases with increasing absorbed dose favoring recombination processes and this is evidenced by the decrease in pre-exponential factor.

The samples showed an uncertainty of 2.0%, these results can be considered good enough taking into account that commercial dosimeters TLD-100, in which we used the same methodology, showed an uncertainty of 1.1% [24].

The strong fading presented by the samples can be related to storage conditions (relative humidity $\sim$ 70% and average temperature 32 ± 4°C), which even can modify the response of commercial dosimeters widely used as the TLD-100 and may be controlled using appropriate thermal treatments post-irradiation [24].

5. Conclusions

Structural analysis indicates that LAS-type matrices are of glass-ceramic nature, exhibiting, in the crystalline region, a compositional ratio of 64% β-spodumene and 36% β-eucryptite.

The FOM values obtained, allow to state that Rasheedy's method is a valid technique to determine the kinetic parameters of the LAS systems in the range 0.5-3.0 Gys. For higher doses is recommended to carry out additional studies and/or implement deconvolution techniques.

The TL-kinetic analysis shows that in LAS-type matrices, the recombination processes predominate over the retrapping processes. This is consistent with the other parameters, since the activation energy decreases with increasing absorbed dose favoring recombination processes and this is evidenced by the decrease in pre-exponential factor.

The LAS systems exhibit a glow curve with a broad peak whose intensity increases proportionally to doses, showing a linear response in the range 0.5-10.0 Gys. Since the samples exhibit good reproducibility and the fading process can be controlled with appropriate thermal treatments, we can state that these materials could be use in the gamma TL-dosimeters manufacturing for therapeutic dose ranges.

Acknowledgments

The authors acknowledge to Centro de Cancerología de la Sabana (Montería-Colombia) for allowing the use of their instalations.

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