A preliminary determination of the kinetics parameters of doped NaCl: Ca, Mn single crystals during fading stage

Alejandro Ortíz Morales[1, 2], **Claudio Furetta**[2]
[1]*Unidad Interdisciplinaria de Ingeniería y Tecnologías Avanzadas, Departamento de Ciencias Básicas, IPN, Av. Instituto Politécnico Nacional 2580, Colonia La Laguna Ticomán, C.P. 07340, México D.F., México.*
[2]*Unidad de Irradiación y Seguridad Radiológica, Instituto de Ciencias Nucleares, Universidad Nacional, Autónoma de México, A.P. 70-543, 04510 México D.F., México.*

E-mail: alortiz@unam.mx

(Received 14 February 2014, accepted 20 June 2014)

Abstract

Thermoluminescent (TL) kinetics parameters of NaCl single crystals doped with Ca and Mn as impurity ions at two concentration: $CaCl_2$ (1%) $MnCl_2$ (0.1%) and $CaCl_2$ (1%) $MnCl_2$ (0.3%), are analyzed. The crystals were exposed to gamma photons of ^{60}Co source, and the fading at room temperature was monitoring during 120 days. The kinetic parameters, activation energy *E* and the frequency factors *s*, of the TL glow curves were determined using the computerized glow curve deconvolution program (CGCD) using general order. The results show that the activation energy increases as the elapsed time from irradiation increases too, indicating a trap distribution occurred in the double doped sodium chloride crystals

Keywords*:* Thermoluminescence, kinetics parameters, sodium chloride.

Resumen

Se analizaron los parámetros termoluminiscentes cinéticos (TL) de NaCl monocristales dopados con Ca y Mn como iones impuros en dos concentraciones: $CaCl_2$ (1%) $MnCl_2$ (0,1%) y CaCl2 (1%) MnCl2 (0,3%). Los cristales fueron expuestos a fotones gamma de una fuente de ^{60}Co y el desvanecimiento a temperatura ambiente fue monitoreado durante 120 días. Los parámetros cinéticos, la energía de activación E y los factores de frecuencia s, de las curvas de resplandor TL se determinaron utilizando el programa computarizado de resplandor de curva deconvolucionada (CGCD) usando orden general. Los resultados muestran que la activación de la energía aumenta conforme incrementa demasiado el tiempo transcurrido desde la irradiación, lo que indica que ocurrió una distribución atrapada en los cristales de cloruro de sodio dopados dobles.

Palabras clave*:* Termoluminiscencia, parámetros cinéticos, cloruro de sodio.

PACS: 78.55.Fv; 78.60.Kn; 76.30.Mi; 76.30.Lh **ISSN 1870-9095**

I. INTRODUCTION

The main dosimetric and optical characteristics of NaCl doped with $CaCl_2$ and $MnCl_2$ have been recently reported [1].This double doped phosphor has been considered for this study due to the effective atomic number, Z_{eff}, equal to 15.71 for A and 15.74 for B preparations respectively, the which is similar to the atomic number of bones; because its atomic number, this phosphor could be used in clinical applications, i.e. radiotherapy and radiodiagnostic. In previous work [1] it was observed that the TL signal decay at room temperature was about 20% and 30%, respectively for preparations A and B, at the end of the monitored period, *i.e.* 120 days.

To get more information about the fading mechanism, a study about the kinetics parameters has been carried out during the fading period to investigate the behavior of the trapping centres using the Computerized Glow Curve Deconvolution (CGCD) applied at various periods of time during fading experiment at room temperature.

The determination of the kinetics parameters during fading allows to check if the TL emission is due to a distribution of trapping levels or to a single level: *i.e.* if the activation energy remains quite constant during the fading period, it means that only one trap centre is responsible of the corresponding TL emission. On the contrary, if the activation energy increases as the elapsed time from irradiation increases too, this is an indication of a trap distribution are present [2, 3].The aim of this paper is the determination of the kinetics parameters, *E* [*eV*] and *s*[s^{-1}] during fading stage and verifies if the TL emission is due to a distribution of trapping levels or to a single level.

II. MATERIALS AND METHODS

Single crystals of NaCl, double doped with calcium (1%) and manganese in different concentrations (0.1% and 0.3%), were growth using the Czochralsky method at the Crystal Growth Laboratory of the Physics Institute of UNAM. Two different double doped preparations for NaCl single crystals were obtained: $CaCl_2$(1%)$MnCl_2$(0.1%) and $CaCl_2$(1%)$MnCl_2$(0.3%), indicated in this paper as preparations A and B, respectively. The final concentrations in each preparation were determined by atomic absorption spectrophotometry.

The obtained samples were totally transparent, having size dimensions of about 4x4x0.3 mm. The composition of the co-doped NaCl samples is given in Table I. In the same table are also given the values of the effective atomic number (Z_{eff}). Before irradiation the samples were annealed at 770 K during 1 hour. After cooling down to room temperature (RT) the samples, inserted in black bags to avoid any light effect, were irradiated to a test dose of 5 Gy at, t=0, 30, 60 and 120 days.

The samples were exposed to gamma photons from ^{60}Co of a Gammacell 200 irradiator with a dose rate of 0.66 Gy/min. All the samples were read out in only one session at the end of the experimental period. The TL reader system was a Harshaw TLD model 3500; a constant heating rate of 2 °C/sec was used and nitrogen gas was allowed to flux into the reading chamber during the read out to eliminate any spurious signals. The TL emission was integrated from room temperature (25°C) up to 400°C.

TABLE I. Composition of the co-doped NaCl samples and atomic effective number (Z_{eff}).

Dopants	Sample A	Sample B
Na[ppm]	3.88 E-01	3.87 E-01
Cl[ppm]	6.07 E-01	6.07 E-01
Ca[ppm]	3.60 E-03	3.60 E-03
Mn[ppm]	4.30 E-04	1.30 E-04
Z_{eff}	15.71	15.73

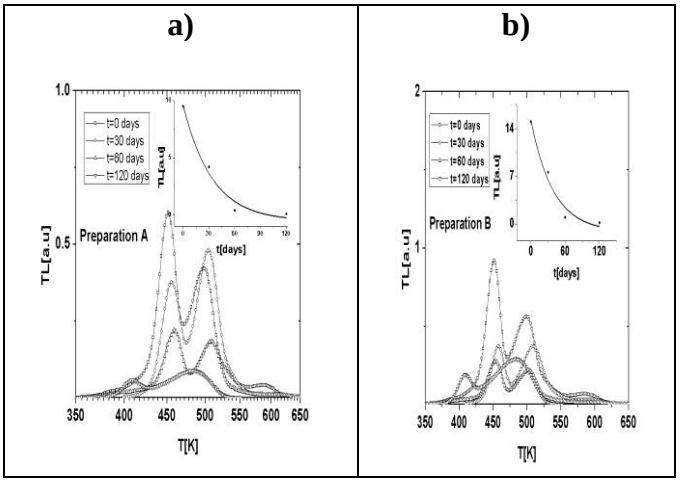


FIGURE 1. Glow curves of fading from NaCl, a) preparation A, and b) preparation B, the inset shows for both curves the fading of signal TL as a function of time.

The glow curves for sodium chloride crystals double doped are shown in Figure I (a,b); the reference glow curves for each preparation have been obtained immediately after irradiation (t = 0 days). The TL glow curves for both preparations are roughly similar. The glow curve of preparation A shows two well resolved peaks, at 459 K and 509 K respectively. On the ascending part of the first peak a small shoulder appears at about 399 K. On the descending tail of the second peak a shoulder appears at about 615 K.

The glow curve of preparation B is quite similar to the previous one: the first peak appears at 455 K and the second at 505 K. As before, two shoulders appear in the low and high temperature regions. In both cases the first peak is always much higher than the second one.

The kinetic parameters, *i.e*., the activation energy (E) of the traps involved in TL emission, the order of the kinetics (b) and the frequency factor (s) have been obtained using the Computerized Glow Curve Deconvolution (CGCD) program. The algorithm of the deconvolution program is based on the generalized-order kinetics equation (1) [4, 5].

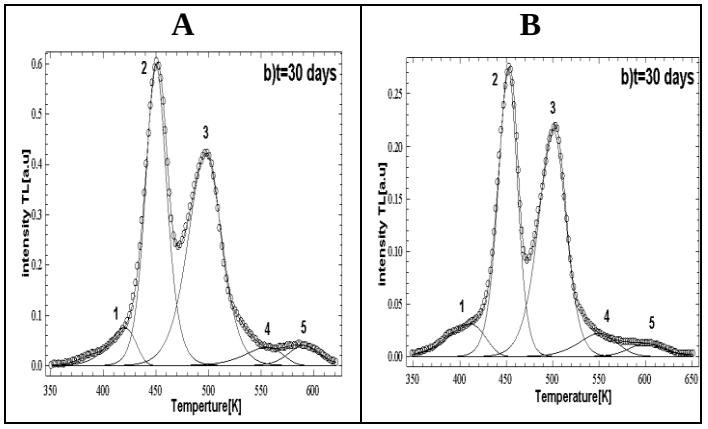
$$I(T) = I_M (b)^{\frac{b}{b-1}} \exp\left(\frac{E}{kT}\frac{T-T_M}{T_M}\right)\left[(b-1)(1-\Delta)\frac{T^2}{T_M^2}\exp\left(\frac{E}{kT}\frac{T-T_M}{T_M}\right)+Z_M\right]^{\frac{-b}{b-1}} \quad (1)$$

Where I_M and T_M are the TL peak maximum intensity and peak maximum temperature, respectively, $E(eV)$ the activation energy, b the kinetic order, and

$$\Delta_M = \frac{2kT_M}{E}\,,\ \Delta = \frac{2kT}{E} \text{ and } Z_M = 1+(b-1)\Delta_M\ ,$$

with the pre-exponential factor given by

$$s = \frac{\beta E}{kT_M^2}\frac{1}{Z_M}\exp\left(\frac{E}{kT_M}\right).$$



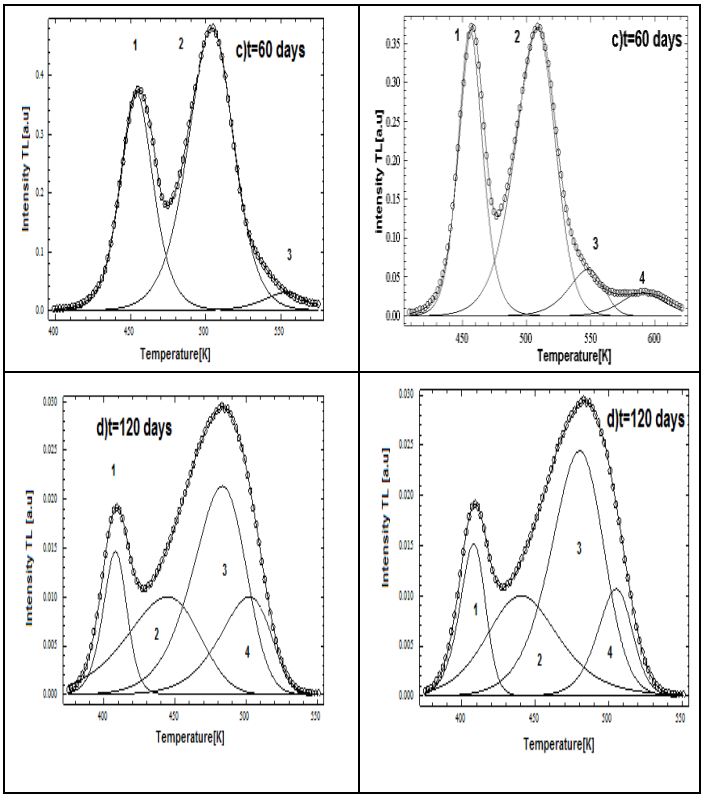


FIGURE II. Deconvolution of glow curves as continuous lines, the experimental curves are indicate as open circles. NaCl:Ca,Mn (preparations A in left column, and B in right column) exposed to 5 Gy and 0.66 Gy/min dose rate.

The curve fitting procedure was performed using the goodness of the fit was tested with the figure of merit (FOM) [6] given by:

$$FOM = \sum \frac{\left|Y_{Exp} - Y_{Fit}\right|}{A}. \qquad (2)$$

Where Y_{Exp} , Y_{Fit} are the experimental and fitted data of the glow curve, respectively, and A is the integral of the fitted glow curve. A FOM equal or less than 5 % means a very good fit [6].

III. DISCUSSION

The behavior of the TL signals as a function of the elapsed time from irradiation, for preparations A and B, is regular: both first and second peak decrease as a function of the elapsed time from irradiation. The second peak for preparation A seems to increase after 30 days from irradiation. Always for the same preparation, after 120 days of storage, the two main peaks disappear and only one large peak is present with a very little peak on the low temperature side. A similar behavior can be observed for preparation B. Furthermore, in both preparations the peak temperatures at the maximum are not stable and a little shift may be observed.

TABLE II. Kinetics parameter of NaCl: Ca, Mn (preparation A) exposed at 5 Gy, and 0.66 Gy/min dose rate.

Peak	T_M[K]	E[eV]	s[s^{-1}]	b
Fading t = 0 days, FOM = 0.05				
1	410	0.73	8.65E+07	**1.01**
2	452	2.20	8.83E+23	**1.62**
3	500	1.82	3.93E+17	1.54
4	550	1.46	2.41E+12	1.32
5	600	2.41	2.81E+19	1.99
Fading t = 30 days, FOM = 0.04				
1	420	1.06	7.55E+11	**1.01**
2	450	2.62	6.66E+28	**1.92**
3	498	1.56	7.96E+14	1.37
4	540	2.84	6.78E+25	1.99
5	585	2.68	1.97E+22	1.99
Fading t = 60 days, FOM = 0.03				
1	453.75	2.35	3.38 E+25	**1.99**
2	504	1.85	5.46 E+17	**1.61**
3	554	2.11	2.52 E+18	1.16
Fading t = 120 days, FOM= 0.02				
1	408	2.11	4.15E+25	**1.58**
2	444	0.78	7.50E+07	**1.36**
3	483	1.17	2.38E+11	1.10
4	507	2.99	1.74E+29	1.98

TABLE III. Kinetics parameter of NaCl: Ca, Mn (preparation B) exposed at 5 Gy, and 0.66 Gy/min dose rate

Peak	T_M[K]	E[eV]	s[s^{-1}]	b
Fading t = 0 days, FOM = 0.05				
1	410	0.73	8.65E+07	**1.01**
2	452	2.20	8.83E+23	**1.62**
3	500	1.82	3.93E+17	1.54
4	550	1.46	2.41E+12	1.32
5	600	2.41	2.81E+19	1.99
Fading t = 30 days, FOM = 0.04				
1	420	1.06	7.55E+11	**1.01**
2	450	2.62	6.66E+28	**1.92**

3	498	1.56	7.96E+14	1.37
4	540	2.84	6.78E+25	1.99
5	585	2.68	1.97E+22	1.99
Fading t = 60 days, FOM = 0.04				
1	456	2.50	1.16E+27	**1.75**
2	508	1.65	3.60E+15	**1.34**
3	548	2.15	1.08E+19	1.21
4	590	2.49	2.78E+20	1.99
Fading t = 120 days, FOM =0.02				
1	408	1.99	1.21E+24	**1.42**
2	440	0.95	9.38E+09	**1.98**
3	480	1.26	2.40E+12	1.32
4	505	2.24	5.35E+21	1.43

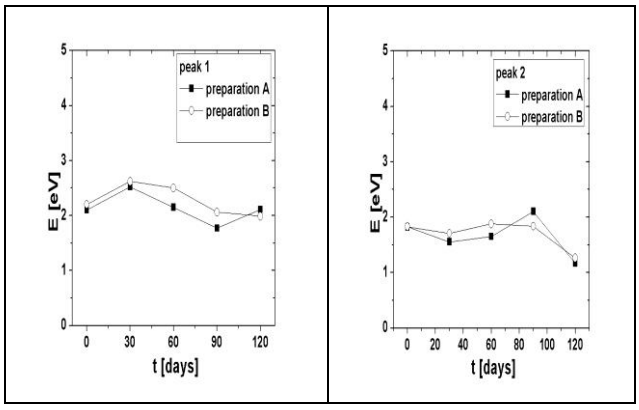


FIGURE III. Activation energy for preparations A and B as a function of the elapsed time from irradiation; t = 0, 30, 60, 90, 120 days.

A. Fading theoretical model

Kitis *et al*.[7] developed some useful expressions for fading correction in practical situations, for our experimental purpose was initial and instantaneous irradiation followed by fading at room temperature, give that;

$$\Phi(t) = \Phi_o \exp[-\lambda t]. \qquad (3)$$

Where Φ is the total area of the peak[u²], and λ *is* the escape probability per unit of time.
Using the previous equation one obtains:

$$\lambda_A = 24.96E-03d^{-1},$$
$$\lambda_B = 21.99E-03d^{-1}.$$

Which means a lost percent per day of 2.49 and 2.19 respectively for both samples.

TABLE IV. Fading parameters of preparation A and B.

Preparation	A	B
Φ_0 [u²]	9.04±0.28	15.76±2.02
λ[months^{-1}]	0.03±0.02	-0.03±0.08

The variation of the activation energy values when the elapsed time from irradiation increases may indicate a trap distribution in the doped NaCl single crystals. Activation energies and temperatures at the maximum of the peak 1 and peak 2 for samples A and B respectively during fading at RT are reported in Table II and III.

VI. CONCLUSIONS

The more evident result of this study is the variation of the activation energy during the storage of the samples at room temperature. The variation is not very large but, any way, it could indicate a more complex structure of the trapping centres and a possible distribution of traps, *i.e*. a continuous or quasi-continuous trapping distribution could be supposed. Furthermore, it seems that in both preparations, in the time interval from 60 to 120 days, there is a transfer of trapped charges from the first peak, *i.e*. E increases, to the second peak, *i.e*. E decreases; in other words, an increase of the activation energy means that the trapping levels are far from the conduction band and a decrease of the E value means trapping levels more closed to the conduction band. All the previous effects need a more accurate fading experiment, using for instance different temperatures of storage. The Fading model is the simplest case, which represents the usual problem of fading correction during storage of previously irradiated, and is useful just to predict the loss of TL signal as function of elapsed time in some experimental situations.

ACKNOWLEDGEMENTS

The authors wish to thank to Benjamin Leal Acevedo and Francisco Garcia for their technical assistance in irradiation samples.

REFERENCES

[1] Ortiz Morales, A., Furetta, C., Kitis, G., Negrón Mendoza, A., Cruz Zaragoza, E., *Thermoluminescent properties of NaCl monocrystal double doped with $CaCl_2$ and $CdCl_2$*. Radiation Effects & Defects in Solids **161**, 383-393 (2006).
[2] Furetta, C., Kitis, G., Weng, P. S., Chu, T. C., *Thermoluminescence characteristics of Mg_4BO_7: Dy,Na.*

Nuclear Instruments and Methods, In: Physics Research **A 420**, 444-445 (1999).

[3] Furetta, C., *A fading based method for checking the presence of closely overlapping peaks in thermoluminescent (TL) materials*, Radiation Effects & Defects in Solids **162**, 319–323 (2007).

[4] May, C. E., Partridge, J. A., *Thermoluminescent kinetics of alpha-irradiated alkali halides*, Journal of Chemical Physics **40**, 1401-140 (1964).

[5] Kitis, G., Gomez Ros, J., Tuyn M., *Thermoluminescence glow-curve deconvolution functions for first, second and general orders of kinetics*, Journal Physics Applied Physics **31,** 2636-2641 (1998).

[6] Balian, H. G., Eddy, N. W., *An improved criterion over the normalized Chi-squared test for assessing goodness of fit of gamma ray spectral peaks*, Nucl. Instrum. Methods **145**, 389–395 (1977).

[7] Kitis, G., Furetta, C., *Simulation of competing irradiation and fading effects in thermoluminescence dosimetry*, Radiation Effects & Defects in Solids **160**, 285-296 (2005).