Thermoluminescence and F centers of manganese doped NaCl and NaCl-KCl crystals exposed to gamma radiation

L. Somera[1,2], E. Cruz-Zaragoza[1], J. Roman Lopez[1], J.M. Hernández A.[3], H. Murrieta S.[3]

[1] Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México
A.P. 70-543, 04510 México D.F., México
ecruz@nucleares.unam.mx

[2] Posgrado en Ciencia e Ingeniería de Materiales, Instituto de Investigaciones en Materiales UNAM,
A.P. 70-360, 04510 México D.F., México

[3]Instituto de Física, Universidad Nacional Autónoma de México
A.P. 20-364, 01000 México D.F., México

Abstract

Alkali halides crystals doped with rare earths or transition metals have been widely studied due to the luminescence properties. In particular, NaCl and KCl single crystals present thermally stimulated luminescence (TL) after gamma irradiation. The NaCl and the NaCl-KCl mixed crystal doped with manganese ($MnCl_2$) impurity were grown by using the Czochralski method. The emission characteristic of Mn^{2+} was observed at 543 nm. The crystals were exposed between 0.02 and 10 kGy gamma dose from ^{60}Co irradiator. Optical absorption at room temperature shows the peaked band at 452 nm corresponding to the manganese impurity. The F bands, was ascribed to the electron trapped in the anion vacancy in the lattice, were obtained at 452 nm and 455 nm belonging to NaCl:Mn and NaCl-KCl:Mn, respectively. The F band increases as the doses increase and it was bleaching by the UV light at 470 nm. The glow curves of the samples show the first glow peak between 92-103 °C, while the second main peak was observed at 183 °C for the undoped NaCl and at 148 and 165 °C for the NaCl:Mn and NaCl-KCl:Mn, respectively. The main peak was slowly bleaching when the irradiated sample was illuminated with F (470 nm) light. Optical bleaching confirms that the F center has an important participation in the thermoluminescent response. The glow curves structure from the thermal bleaching suggests the participation of different kind of traps. Also, the kinetics parameters such as activation energy (E), frequency factor (s) and the kinetic order (b) were investigated.

Keywords: Thermoluminescence, optical property, F centers, sodium chloride crystal

1.- INTRODUCTION

The luminescence thermally stimulated phenomena is known since the late nineteenth century when Wiedemann used the term “thermoluminescence” by first time in 1889. The research of the thermoluminescent property for a variety of materials has had a large development, especially with the alkali halides, which are often used as prototypes of other materials. In 1972 Austin and Alvarez Rivas proposed a successful model to describe the TL process in alkali halides. They suggest that during irradiation, a halide atom of the crystal leaves its lattice position and occupying an interstitial position and subsequently forming an F centre. When the crystal is heated the interstitial atoms acquire enough energy to leave its trap and wander through the lattice until reach the F centre. At this stage an electron-hole and vacancy-impurity pairs take place the recombination and results in a luminescence emission.

The TL emission is related with the band structure of solids, therefore this process can be described in terms of the valence band, the conduction band and the band gap, where the traps are housed [McKeever, 1988]. From a theoretical point of view the thermoluminescent process can be described by certain meaningful parameters for each trap involved such as characteristic activation energy (E), a frequency factor (s) and a kinetic order (b) of the defects recombination to generated the glow curves. A first kinetic order (b=1) corresponds with a case where the probability of recombination dominates, while a second order (b=2) indicates that the probabilities of recombination or retrapping are the same. The values between 1 and 2 indicate the participation of non radiative processes occurred in the lattice.

The thermoluminescent properties of alkali halides crystals can be modified by adding an extrinsic impurity (activator) as rare earths or metal transition ions. Impurity ions can shift the absorption bands generated by the electrons trapped in anion vacancies or generate extra absorption bands. Particularly for the Mn^{2+} impurity inside a NaCl host lattice has been reported the formation of two extra absorption bands attributed to the valence change of the manganese impurity [López *et al.*, 1987; Delgado and Alvarez Rivas, 1982]. The glow curves for the NaCl:Mn crystal shows an improve of the TL response due to the metastable states generated by manganese impurity inside the band gap, which act as recombination centers giving rise to an increase of luminescence [López *et al.*, 1979; Hernández *et al.*, 2001].

The aim of this work was to investigate the F center leading to the TL emission by means of the absorption and emission spectra of the NaCl, NaCl-KCl:Mn and NaCl:Mn crystals, as well as the study of its thermal bleaching of the glow curves after exposure to gamma radiation. The kinetics parameters of the glow curves were obtained by a first approximation using the Initial Rise Method [Furetta, 2003; Kitis *et al*., 1998] and also more accurate values by means of the CGCD deconvolution considering the general order kinetics.

2.- MATERIALS AND METHODS

Crystalline samples about 5 x 3 x 1 mm^3 of NaCl and NaCl-KCl doped with Manganese ($MnCl_2$) were grown by Czochralski method and provided by the Institute of Physics-UNAM. The samples were irradiated at room temperature (RT) in a ^{60}Co Gammabeam 651PT irradiator at 14 Gy min^{-1} dose rate in the Nuclear Sciences Institute-UNAM. The optical absorption spectra were measured with a Cary 5000 spectrophotometer in a wavelength range between 200 and 800 nm. Emission spectra were obtained with a Perkin-Elmer LS 55 spectrometer with an excitation wavelength at 230 nm. Thermoluminescence (TL) measurements were carried out in a Harshaw TLD 3500 at a heating rate of 2 °C s^{-1}. Thermal bleaching was achieved by irradiated samples with 500 Gy. The samples were heated at temperatures between 50 and 450 °C and then cooled over a metal block at room temperature. Also the samples were gamma irradiated and exposed to 470 nm UV light (nearly F light for NaCl) or Sun light at different periods of time to perform optical bleaching. A fading test was performed by kept the irradiated samples at 500 Gy at RT during the period times between 2 hours and 30 days. The reproducibility of TL signals of single crystals was obtained by measuring the TL response of the samples after being gamma irradiated and repeating the procedure by several times. In order to obtain kinetic parameters *E*, *b* and *s*, the Initial Rise Method (IR) was used to the glow curves of the samples after being irradiated at 60 Gy. Glow curves were cleaned by the thermal bleaching using a suitable temperature according to each maximum. The values obtained by the IR method were compared with those values obtained by a computerized glow curve deconvolution method based on the General Order Kinetics (GOK).

3.- RESULTS

The as-grown samples of NaCl, NaCl-KCl:Mn and NaCl:Mn were exposed to gamma radiation dose from 0.05 to 10 kGy at room temperature to acquire the optical absorption spectra and the glow curves too. The optical absorption spectra are shown in Figure 1. The pure NaCl sample shows two bands, the main band at 466 nm related to the F center and a second band at 223 nm were observed. The F band of the NaCl:Mn doped sample was approximately at 452 nm and an extra band at 270 nm is also shown that was related to the Mn^{+} ion band. The NaCl-KCl:Mn mixed crystal shows the F band at 455 nm and two bands at about 229 and 272 nm similar to the NaCl:Mn sample case. Another band at 319 nm was observed at high doses that could be related to the Mn^{0} band.

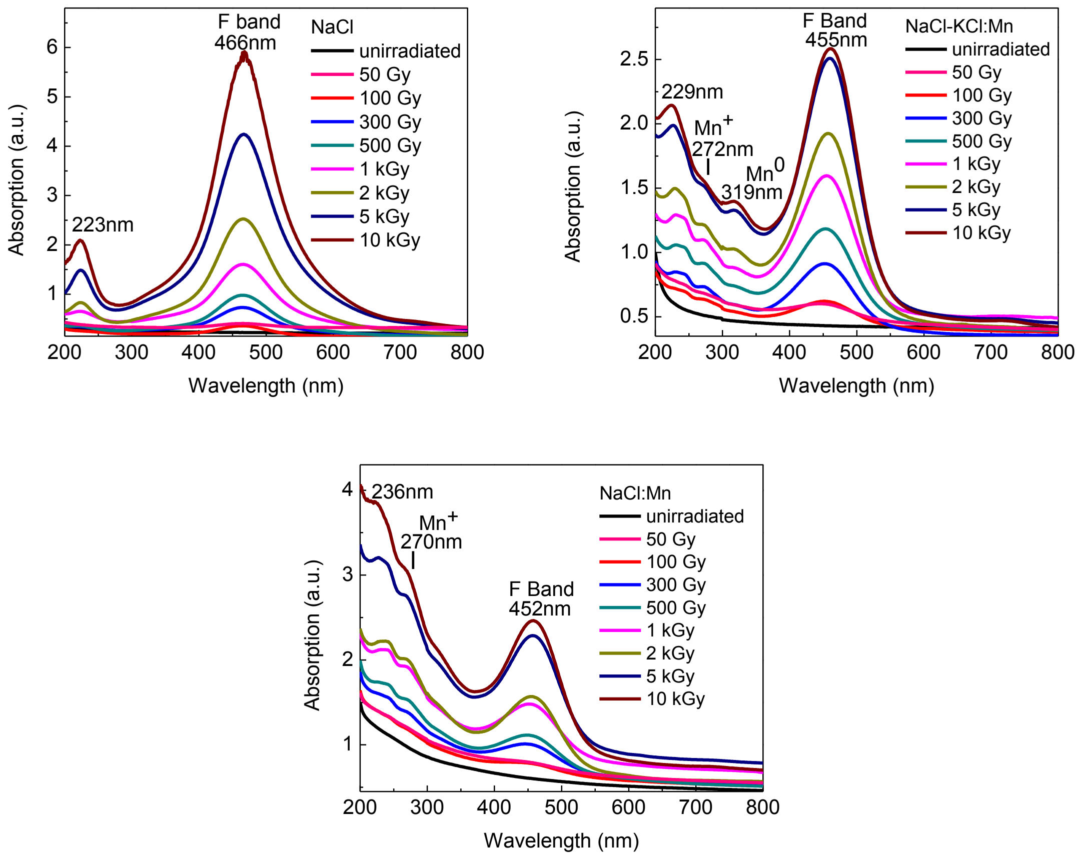

Figure 1. Optical absorption spectra of NaCl, NaCl-KCl:Mn and NaCl:Mn crystals after being irradiated to ^{60}Co gamma radiation.

The emission spectrum of doped samples is shown in Figure 2. The electronic transition responsible for this spectrum is the double excitation $^6A_1(S) + {}^6A_1(S) \rightarrow ({}^4A_1(G), {}^4E(G))$ which produces a red and a green emission bands [Mejía-Uriarte *et al.*, 2015]. Three bands (611 nm, 535 nm, 488 nm) were observed for the NaCl-KCl:Mn mixed crystal sample. The broader red emission band at 611 nm corresponds to the six-fold coordination state and was related with the manganese aggregates.

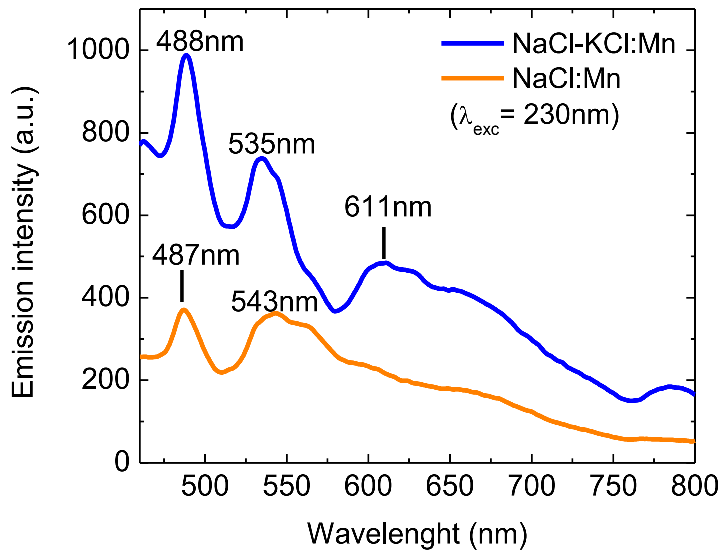

Figure 2. Emission spectra of NaCl-KCl:Mn and NaCl:Mn.

The glow curves of NaCl, NaCl-KCl:Mn and NaCl:Mn crystals after being irradiated at different doses (50 Gy- 10 kGy) are shown in Figure 3. The TL intensity improves with dose up to 1 kGy, where a saturation stage appears.

In the NaCl-KCl:Mn and NaCl:Mn samples the TL intensity of the first peak increases compared with the glow curve of the pure sample. In particular, the TL response of the NaCl-KCl:Mn mixed sample it reached almost the double of the TL signals (Fig. 4). The glow curve for the mixed sample shows a second glow peak approximately at 165 °C which shifts a few grades after being irradiated with 5 and 10 kGy. Two shoulders are also observed at higher temperatures side of the glow curves. The second peak of the NaCl:Mn sample was located at 148 °C and its TL intensity increases until reach at 5 kGy dose.

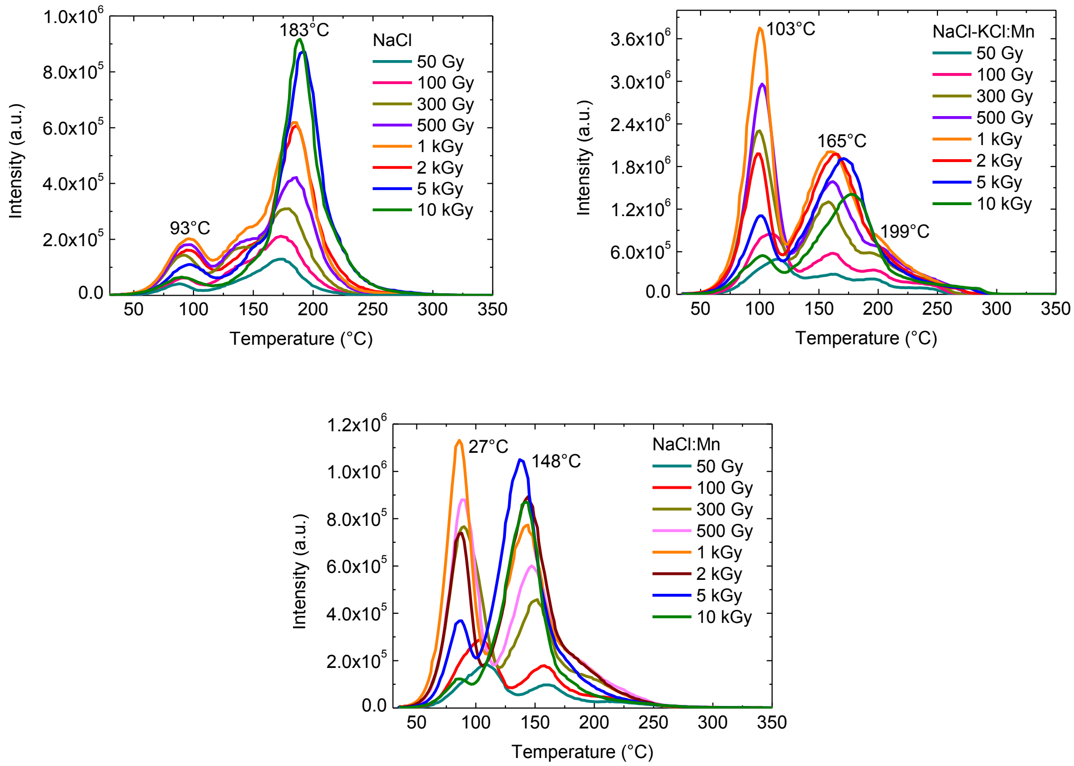

Figure 3. Glow curves of NaCl, NaCl-KCl:Mn and NaCl:Mn crystals after being exposed to different doses of gamma radiation.

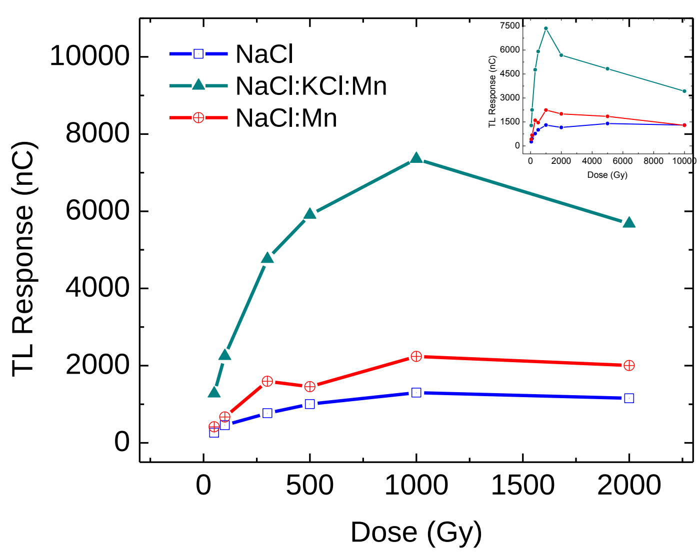

Figure 4. Comparison of TL response of NaCl, NaCl-KCl:Mn and NaCl:Mn crystals after being exposed to different doses of gamma radiation. After 14 measurements of the TL

response, the calculated standard deviation was 0.04. The inset figure shows the behavior of the TL response up to 10 kGy.

The optical bleaching was achieved by exposing samples to blue light (470 nm) or sunlight after gamma irradiation with 500 Gy. Results are shown in figure 5 and figure 6 for blue light and sunlight, respectively. The wavelength of the light (470 nm) used was chosen according to the F band in order to investigate the influence of colour centers in the glow curves (Fig. 5). The sunlight bleaching directly to the sample was carried out with a larger wavelength range (200 to 2000 nm approx.). Figure 6 shows a decrease in the TL intensity, however does not disappear completely at the end of the UV illumination. The presence of extra bands which had not been observed previously was also observed, it is an evidence of the complex glow curves of the Mn doped samples.

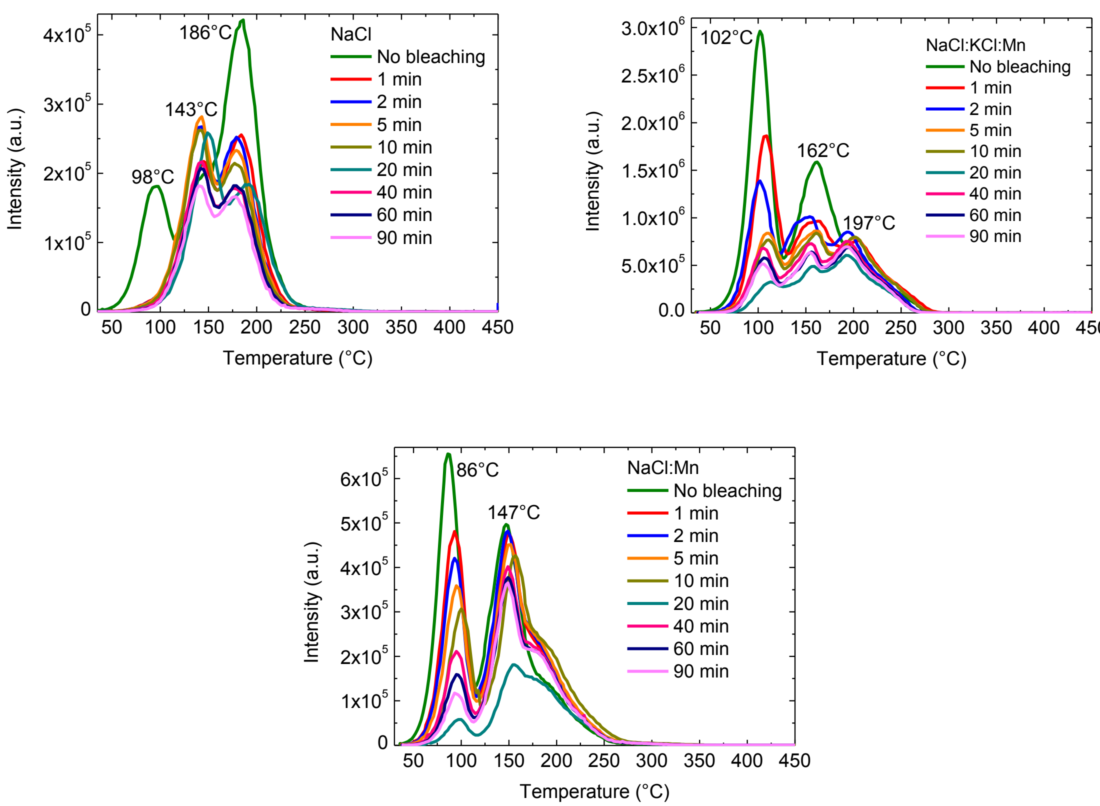

Figure 5. Optical bleaching of NaCl, NaCl-KCl:Mn and NaCl:Mn crystals. The samples were exposed to blue light (470 nm) after being irradiated at 500 Gy.

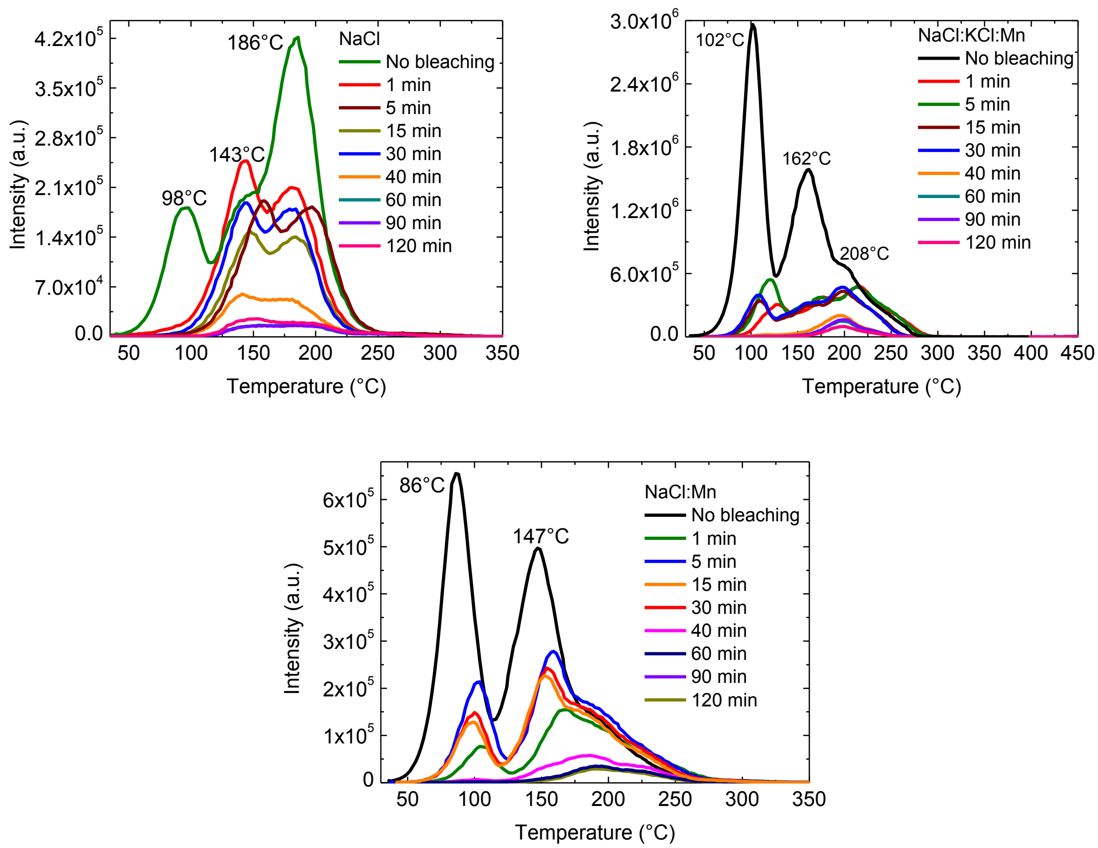

Figure 6. Optical bleaching of NaCl, NaCl-KCl:Mn and NaCl:Mn crystals. The samples were irradiated at 500 Gy and then were exposed directly to the sunlight.

The thermal bleaching was carried out in order to observe the complex glow curves shape and their overlapped glow peaks. Figure 7 shows glow curves of the samples after thermal bleaching. The samples were irradiated and exposed to different temperatures in oven. It is possible to observe the structure of the glow curve below the envelope curve as bleaching temperature increases up to 450 °C. After being heated to 350°C the TL response of the crystals fast decreased and the peak at about 96, 100 and 90 °C for NaCl, NaCl-KCl:Mn and NaCl:Mn samples, respectively, was disappeared completely.

Fading of the samples was tested because it is an important characteristic of the TL material. The crystalline samples were irradiated with 500 Gy and kept them at room temperature (RT) during different periods of time (0-30 days). The TL response of fading in nC is shown in Figure 8.

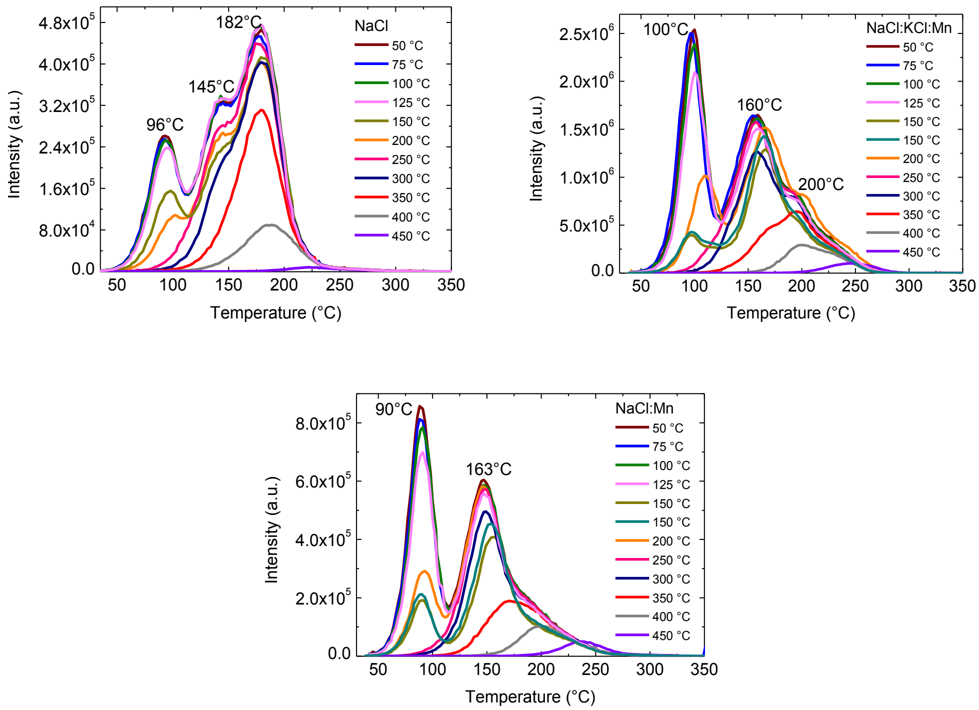

Figure 7. Thermal bleaching of NaCl, NaCl-KCl:Mn and NaCl:Mn crystals. The samples were irradiated at 500 Gy and then were exposed to different temperatures.

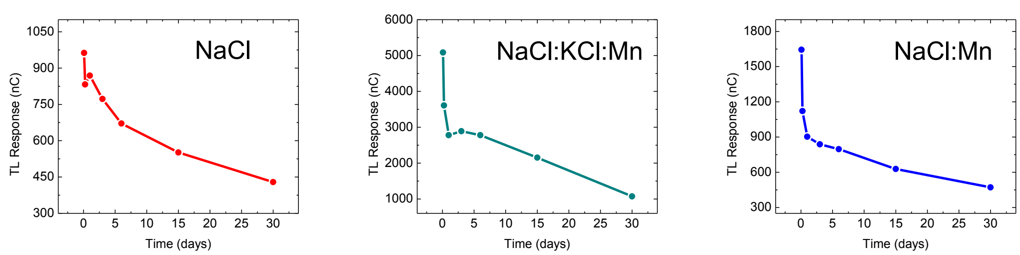

Figure 8. Fading of NaCl, NaCl-KCl:Mn and NaCl:Mn crystals. The samples were irradiated at 500 Gy and then stored in darkness at RT.

The glow curves of the samples irradiated at 50 Gy were used to calculate the activation energy (*E*) by the Initial Rise Method. Because the complex structure of the glow curves shape obtained, the thermal bleaching results were used to get the bleached glow curves to calculate more accurately the activation energy values for each one of them. The computerized glow curve deconvolution (CGCD) procedure based on the General Order Kinetics (GOK) [Furetta and Kitis, 2004] was performed. Results of kinetic parameters obtained by the CGCD deconvolution fitting are presented in Tables 1, 2 and 3, where *E* is the activation energy, *b* is the kinetic order, I_m is the maximum intensity of the glow peak, T_m is the temperature at the maximum of the glow peak, *s* is the factor frequency, *n0* is the initial number of trapped electrons at time t_0 and the *figure of merit* (FOM) [Balian and Eddy, 1977] is the value which indicates the accuracy of the fit, a FOM value lower than 5% is acceptable. Figure 9 shows the deconvolution of the experimental glow curves after being irradiated at 50 Gy gamma dose. Three glow peaks was found for the glow curve of the NaCl pure, while four peaks were well described to the glow curve of NaCl:Mn and for NaCl-KCl:Mn crystals.

Table 1. Kinetic parameters obtained for NaCl crystal by CGCD-GOK computarized deconvolution method.

NaCl pure			
Kinetic Parameters	Glow Peak 1	Glow Peak 2	Glow Peak 3
E (eV)	1.12	1.13	1.15
b	1.24	1.54	1.81
I_m	80080.44	68322.54	129475.92
T_m (°C)	97.08	145.03	174.91
s (seg^{-1})	7.08E+15	1.42E+14	2.53E+13
n0	48762	58732.56	137740.35
FOM	0.385		

Table 2. Results of computerized deconvolution for NaCl-KCl:Mn mixed crystal.

NaCl-KCl:Mn				
Kinetic Parameters	Glow Peak 1	Glow Peak 2	Glow Peak 3	Glow Peak 4
E (eV)	0.95	0.97	1.38	1.4
b	1.34	1.11	1	1.64
I_m	202856.32	119003.45	171759.59	52995.03
T_m (°C)	105.26	148.66	186.45	217.92
s (seg^{-1})	1.85E+13	1.07E+12	5.69E+15	6.96E+14
n0	155506.96	100701.06	116267.64	52837.6
FOM	0.355			

Table 3. Kinetic parameters obtained for NaCl:Mn using CGCD-GOK.

NaCl:Mn				
Kinetic Parameters	Glow Peak 1	Glow Peak 2	Glow Peak 3	Glow Peak 4
E (eV)	0.89	1.24	1.47	1.48
b	1.26	1.93	1.07	2.1
I_m	113838.46	68453.78	32029.45	23518.64
T_m (°C)	105.34	153.53	183.03	223.19
s (seg^{-1})	2.88E+12	1.68E+15	6.42E+16	3.41E+15
n0	89687.98	63998.1	20891.63	26314.96
FOM	0.0651			

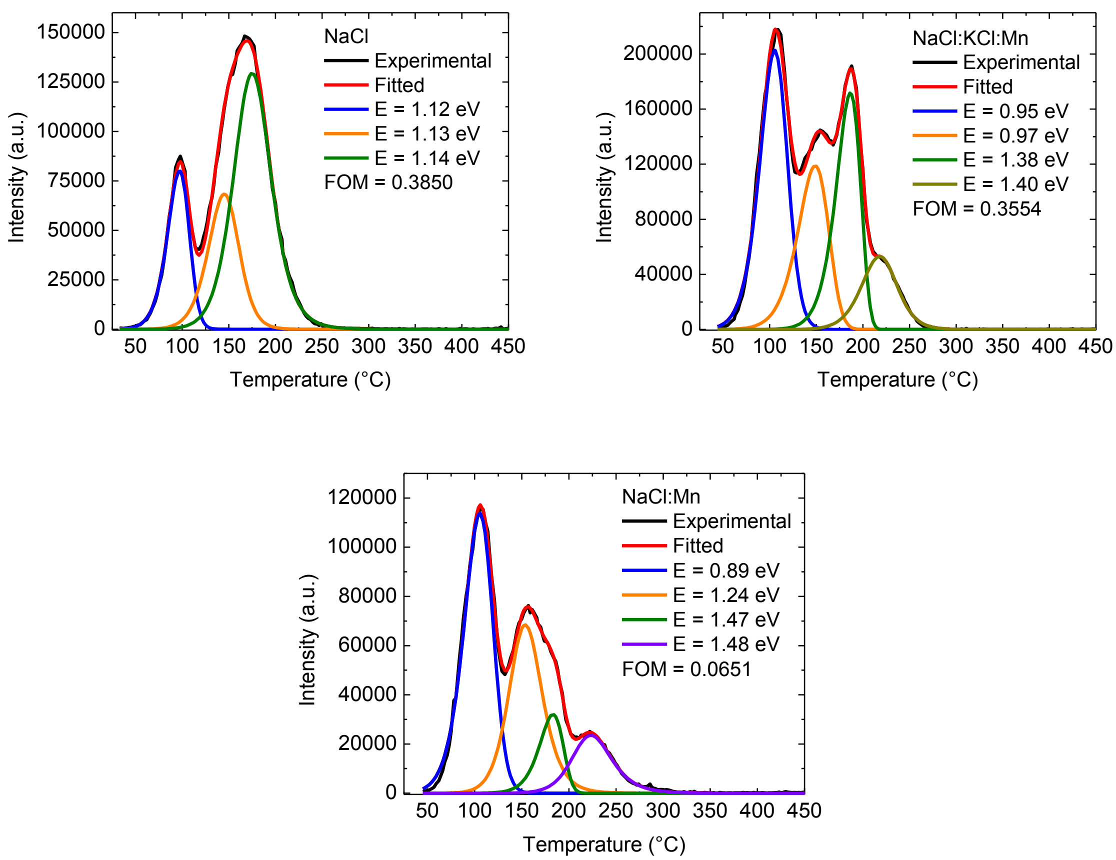

Figure 9. Deconvolution of the experimental glow curves from the NaCl, NaCl-KCl:Mn and NaCl:Mn samples.

The values of the activation energy (Table 4) were obtained by the Initial Rise Method (E_{IR}) and by CGCD computerized deconvolution method of the glow curve (E_{CD}), $T_{m'}$ is the experimental temperature of the maximum.

Table 4. Activation energy (E_{IR} and E_{CD}) obtained by IR and computerized deconvolution methods of the glow curves.

Crystal	$T_{m'}$ [°C]	E_{IR} [eV]	E_{CD} [eV]
NaCl	98	0.95±0.03	1.12
	172	1.06±0.02	1.13
	211	0.49±0.10	1.15
NaCl-KCl:Mn	109	1.21±0.01	0.95
	188	1.27±0.02	0.97
	192	1.34±0.02	1.38
	220	1.40±0.03	1.40
NaCl:Mn	116	1.05±0.02	0.89
	161	1.01±0.02	1.24
	190	1.43±0.02	1.47
	225	1.24±0.04	1.48

4.- DISCUSSION

The F band at 466 nm in NaCl pure crystal observed in the optical absorption spectra was in accordance to those crystal doped [Cruz-Zaragoza *et al.*, 2009; Choudhary *et al.*, 1990), and the second band at 222 nm was ascribed to the V band, i.e., V-type centers that could be forming as a consequence of the interstitial trapping in the lattice. The NaCl:Mn doped sample shows the F band at 452 nm that was shifted attributed to the manganese impurity and an extra band at 270 nm was associated to the Mn^{+} monovalent ion [Delgado and

Alvarez Rivas, 1982; López *et al.*, 1979]. A broad V band at 236 nm was obtained and it is possible was affected by UV background. The shift observed in the F band (455 nm) of the NaCl-KCl:Mn mixed sample, in comparing with previous samples, it was ascribed to the change in the NaCl lattice by the potassium. Another band at 319 nm appeared at high doses and previously has been related with the Mn0-D centers by López *et al* (1979) due to aggregate state of the Mn impurity. The Mn^{+} monovalent ion band and the V band are observed at 272 nm and 229 nm, respectively. The shift in these two bands was attributed to the mixed lattice of this alkali halide.

The divalent nature of the manganese generates additional anion vacancies in order to preserve electrical neutrality of the lattice; in consequence the impurity-vacancy pairs (I-V) are formed. Therefore more F centers are produced during irradiation process and after the thermal stimulation of doped samples, this results in an increase of TL intensity and response, which is observed in the glow curves for NaCl-KCl:Mn and NaCl:Mn crystals. Then the thermoluminescence property can be produced by the recombination of the interstitial halogen ions with vacancy centers in the gap.

In Figure 3 the TL intensity of the second peaks improves while the first glow peak is reduced. This is attributed to a charge transfer produced when the charges trapped at low energy levels are released and then re-trapped by deeper traps during irradiation at high dose, increasing the F centers concentration and therefore the TL response of the crystals.

The aim of the blue light bleaching experiment was to investigate the relation between the F centers and the TL response. The decrease in TL intensity confirms this hypothesis, however a recovery of the TL signal was observed after 20 minutes of light exposure (Figure 5), possibly due to the excitation and charge transfer from the shallowest traps by the absorption of light. The TL glow curves was not bleached completely in these cases, this may be related with the UV component which continues filling the traps.The decreased in the TL intensity as well as the removal of some glow peaks after thermal bleaching, was attributed to the low amount of interstitials remaining available to recombine with F centers after the recombination of some centers that occurs during the heating of the crystalline samples. This bleaching and the fading test allowed determine the amount of glow peaks overlapped under the glow curve for each case. The computerized deconvolution of glow curves, using the values proportionate by the IR method, has been satisfactory as it can observe in Figure 9, and the kinetic parameters values are in good agreement with the experimental data. The deconvolution method shows four glow peaks that well fitted to the experimental glow curves. However, it seems by the optical bleaching that the fraction of the glow curves from 160 to 250 °C may be is ascribed to the quasi continuous traps distribution, that fraction hidden the other glow peaks and make not possible to identify individually with the deconvolution method.

5.- CONCLUSIONS

Optical bleaching with 470 nm light confirms successfully the F centers participation in the TL process of Mn doped sodium chloride crystals, nevertheless is not the only mechanism involve as demonstrated by the UV Solar light and blue light bleaching. The existence of multiple traps generated by the manganese impurity is supported by the thermal bleaching and deconvolution of the glow curves. The relative concentration of F centers on the function of the gamma dose also increasing the TL intensity and the dose response up to approximately at 1 kGy and followed a saturation stage occurred.

Acknowledgements

The author L. Somera would like to thank CONACYT México for scholarship granted during this project. We also thank Benjamín Leal and Francisco García their assistance in carrying out the irradiation, and Maria Cristina Flores (IFUNAM) for assistance in the optical property measurements. This work was supported by PAPIIT-DGAPA UNAM through the project number IN115814.

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