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Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

THERMOLUMINESCENCE AND OPTICAL PROPERTIES OF SOME DOSIMETRIC MATERIALS

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Abstract

Thermoluminescence and optical properties of LiF:Mg,Cu,P; $BaSO_4$:Dy; $BaSO_4$; Eu and α-Al_2O_3:C were investigated as a part of a broader research project on TL mechanisms in various materials. The effects of ionizing radiation on these phosphors are determined in this work by means of thermoluminescence and optical absorption experiments with the aim of identifying new defects formed in these systems and of testing dosimetric characteristics.

Keywords: dosimetric characteristics, optical absorption, thermoluminescence

Introduction

The aim of this paper is to study the thermoluminescence and optical characteristics of several materials developed in our laboratory and of that commercially available α-Al_2O_3:C.

Thermoluminescence, namely thermally stimulated luminescence after the end of excitation process, is a case of phosphorescence observed under steadily increasing temperature. In the usual TL experiments, the system undergoes irradiation with ionizing or not ionizing radiations at a temperature where the phosphorescence is low (usually at room temperature), and later heated through a temperature range where the phosphorescence is bright, up to a temperature where all charges have been thermally excited out of their metastable levels and then the luminescence completely disappears. Efficient TL materials have high concentration of traps, provided by structural defects and impurities.

Not all of the numerous known TL materials are suitable for dosimetry. For dosimetric purposes, a TL material is expected to show, among others, the following characteristics: a glow curve with its main peak up to 200°C; high sensitivity and stability; high resistance against environmental factors; negligible dependence of the TL emission on the radiation energy and good linearity of the TL signal in the specific useful range of radiation dosimetry.

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Only few materials have been found up to now matching all the above features; however, the search in this area is in constant progress and in the near future new appropriate TL materials are expected to join those already used.

The presently available TL materials are usually divided into two main groups: those materials tissue equivalent, which in general show poor sensitivity to ionizing radiation and those highly sensitive but with high effective atomic number and consequently poor equivalence to tissue [1]. In recent years a new LiF:Mg,Cu,P TL phosphor has been developed which seems to combine together tissue equivalence and high sensitivity properties [2].

Experimental procedures

Materials studied were LiF:Mg,Cu,P; $BaSO_4$:Dy; $BaSO_4$:Eu which were prepared in our laboratory [3] and that commercially available α-Al_2O_3:C.

The preparation of the LiF:Mg,Cu,P was carried out by adding to the undoped LiF, just synthesized, the dopants $MgCl_2$, CuF_2 and $(NH_4)_2HPO_4$ in aqueous solutions until the required concentration was reached. The samples were crystals with about 2 mm of thickness and 5 mm in diameter.

The preparation of $BaSO_4$:Dy and $BaSO_4$:Eu was carried out by dissolving $BaSO_4$ in concentrated H_2SO_4 together with Dy_2O_3 or Eu_2O_3. Crystals are formed after evaporation of the acid and then dried at 400°C for several hours.

Previous to the experiments each TL material was submitted to the thermal annealing specified in Table 1. All samples were handled in the dark and kept in plastic holders to prevent any exposition to light.

Table 1 Thermal treatment annealing at which each TL material was submitted

TL material	Temperature/°C	Time/min
LiF:Mg,Cu,P	240	10
$BaSO_4$:Dy	300	30
$BaSO_4$:Eu	400	60
α-Al_2O_3:C	800	30

Irradiations with gamma radiation were performed using a ^{60}Co Vickrad Irradiator (5.9TBq) at a dose rate of 235 Gy h^{-1}, and a ^{137}Cs Victoreen irradiator (2.3 GBq) at a dose rate of 2.26 mGy h^{-1}. X-ray irradiations were made by using two X-ray generators: a Philips CT50 and a Philips RT1000 obtaining the effective energy by measuring the half-value layer of Al or Cu [4].

TL readings were made using a Harshaw 4000 TL analyser coupled with a PC to process the glow curves. Both TL and temperature signals were digitized by means of two channels of an RS 232C interface. The software was designed to perform the following tasks: display the glow curve and produce hard copies

on a printer, store data on floppy disks, enlarge a part of glow curves, substract the background from initial signal to obtain the net TL emission and compute integrals of preselected fractions of the glow curve. The TL signals were integrated from room temperature (293 K) up to 573 K, except in the case of LiF:Mg,Cu,P which was heated up to 513 K. All samples were read at a heating rate of 10 K s^{-1}, in nitrogen atmosphere to prevent any spurious lumnescence.

The basic electronic equipment for detecting the TL emission spectrum at a particular temperature was the same described elsewhere [5]. To record the spectrum, a 0.45 m Pacific grating monocromator possessing a scanning motor drive attachment and a Hamamatsu R943-03 photomultiplier tube were employed. The output of the phototube was processed by a Pacific photometer model 162 and then it was presented in a strip chart recorder.

Room temperature optical absorption spectra were measured in the wavelength region 190–900 nm with a double beam spectrophotometer Perkin-Elmer λ-5.

Dosimetric characteristic studied were: glow curve, sensitivity, reproducibility, linearity and fading. Each experimental data point represents the average of at least five measurements.

Relative sensitivity, given by the ratio of sensitivity of the material to the sensitivity of TLD-100, was determined by irradiating samples of the materials studied jointly with TLD-100 samples at 100 mGy of ^{60}Co gamma radiation. A given set of detectors was irradiated repeatedly at an absorbed dose of 100 mGy to determine the reproducibility of a given detector. This characteristic depends both on the TL material and on the reader quality. To determine the linearity, samples were irradiated with gamma radiation at different doses in the range from 10^{-5} to 10^{2} Gy. Fading was determined by irradiating samples with gamma radiation and storing them in the dark at room temperature for various periods of time.

TL parameters of LiF:Mg,Cu,P and $BaSO_4$:Dy were determined by the deconvolution method [6]. Meanwhile those of $BaSO_4$:Eu and α-Al_2O_3:C were determined by the glow curve shape method (width method) [7]. This method extracts information from a glow peak utilizing the peak temperature (T_m) and two temperatures (T_1 and T_2) on either side of T_m corresponding to half peak intensity as well as the half width parameters and symmetry properties. These relevant parameters are: the total half intensity width, $\omega=T_2-T_1$; the high temperature half width, $\delta=T_2-T_m$; the low temperature half width, $\tau=T_m-T_1$ and the symmetry factor, $\mu_g=\delta/\omega$.

The following formulas were used to determine E and s values by the glow curve shape method:

$$E_\delta = [0.976 + 7.3(\mu_g - 0.42)]kT_m^2/\delta$$

$$E_\tau = \{[1.51 + 3.0(\mu_g - 0.42)]kT_m^2/\tau\} - [1.58 + 4.2(\mu_g - 0.42)]2kT_m$$

$$E_\omega = \{[2.52 + 10.2(\mu_g - 0.42)]\ kT_m^2/\omega\} - 2kT_m$$

$$s = \frac{\beta E}{kT_m^2} e^{(E/KT_m)}[1 + (b - 1)\, 2kT_m/E]^{-1}$$

where b is the order of the kinetics.

Data were fitted by the least squares method considering an uncertainty equal to $\pm\sigma$.

Results and discussion

Previous to irradiation, the materials studied were characterized by optical absorption. All unirradiated crystals did not show any optical absorption band in the wavelength region 190–900 nm.

The optical absorption spectra of the gamma irradiated materials studied are portrayed in Fig. 1. From these spectra it can be observed that; LiF:Mg,Cu,P exhibited two absorption bands at 225 and 310 nm which could be attributed to Mg° and Mg^{+} ions respectively giving an indication that the Mg^{2+} is transformed in Mg° and Mg^{+} during the irradiation. $BaSO_4$:Dy showed absorption bands at about 370, 450, 545, 576, 622, 650 and 670 nm. The band at 370 is believed to be due to SO_4^- radical, that at 576 nm could be attributed to SO_3^- absorption; absorptions at 622 and 650 could correspond to O^-. Meanwhile, the peaks at 450, 545 and 670 nm of the absorption bands are very similar to those corresponding to the Dy^{2+} ion. This suggests that during irradiation of $BaSO_4$:Dy some of the

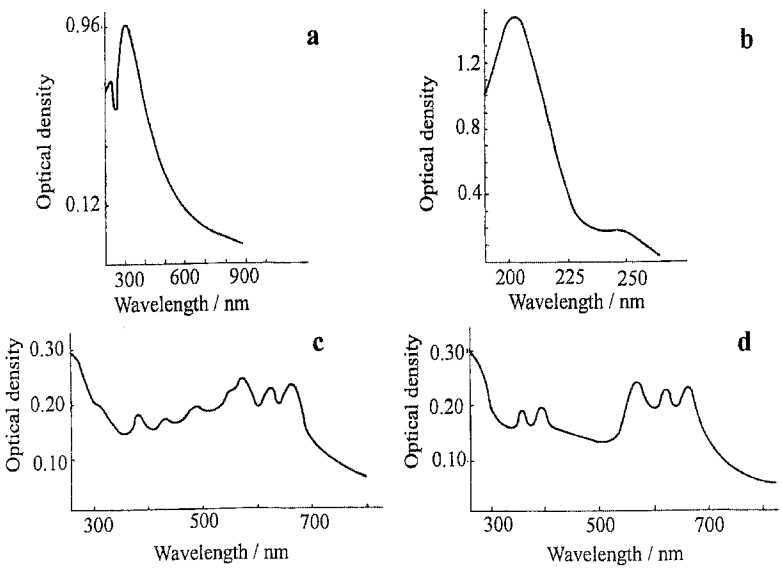

Fig. 1 Optical absorption spectra of the materials studied irradiated with gamma radiation. a) LiF:Mg,Cu,P; b) α-Al_2O_3:C; c) $BaSO_4$:Dy and d) $BaSO_4$:Eu

Dy^{3+} ions transform into Dy^{2+}. Absorption bands exhibited by $BaSO_4$:Eu at about 370 and 575 nm, are associated with SO_4^- and SO_3^- radicals respectively; those at 625 and 650 could be attributed to O^-. Meanwhile, that at 380 nm is characteristic of the Eu^{2+} ion. This suggest that the recombination of the F centers with the SO_4^-, SO_3^- and O^- radicals occurs simultaneously with the recuperation of the Eu^{2+} ions. The intense absorption band showed in the optical absorption spectrum of α-Al_2O_3:C is associated with F centers; while the less intense bands appeared at 230 and 255 nm are typical of the F^+ centers. Then, it is possible to suppose that the F^+ centers are formed to compensate the charge of the impurity C^{2+}; and, consequently that the luminescence of α-Al_2O_3:C is mainly due to the F centers influenced by V-type centers.

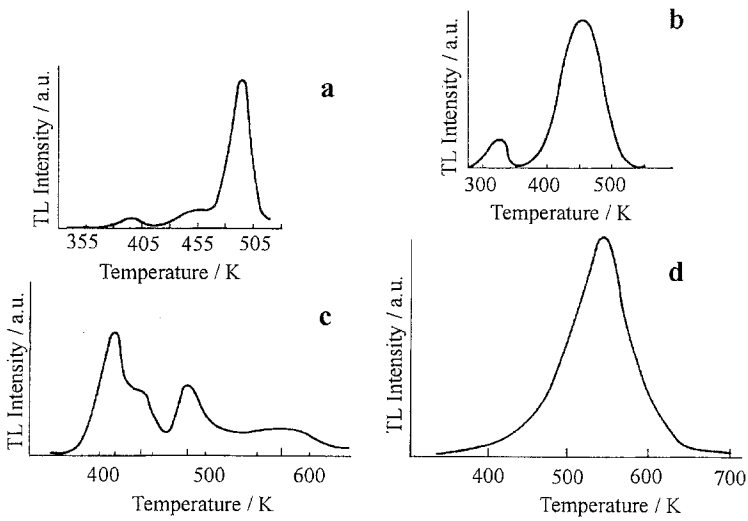

Fig. 2 Glow curves of the TL materials studied which were irradiated with gamma radiation. a) LiF:Mg,Cu,P; b) α-Al_2O_3:C; c) $BaSO_4$:Dy and d) $BaSO_4$:Eu

Figure 2 shows the glow curves of the materials studied, irradiated with gamma radiation. The glow curve of LiF:Mg,Cu,P exhibits three peaks at about 396, 455 and 494 K, which were labelled as peaks 1, 2 and 3 respectively. Peaks 1 and 3 are well defined but peak 2 can be observed as a shoulder at the left hand side of peak 3. Three different kinds of traps are formed by ionizing radiation in LiF:Mg,Cu,P with different and presumably competitive kinetic processes. A reasonable interpretation can be attempted by indicating intrinsic color centers as the defects responsible of the 494 K glow peak, and complex defects originated by association of simple color centers with the impurities as those emitting at the other temperatures. The glow curve of $BaSO_4$:Dy exhibited a four-peak pattern. The four peaks appeared at 415, 440, 493 and 565 K. Hence, it is proposed that the radicals SO_4^-, SO_3^- and O^-, produced by gamma irradiation, form

stable trapping sites of various activation energies in the $BaSO_4$ lattice, which are responsible for the complex multipeak TL glow curve of this material. Glow curve obtained for $BaSO_4$:Eu irradiated with gamma radiation exhibited essentially a single glow peak at about 540 K which is characteristic of this material. The glow curve of α-Al_2O_3:C irradiated with gamma radiation showed two peaks at 336 and 460 K. The low temperature peak, observed immediately upon irradiation, decays at room temperature in a few hours after irradiation.

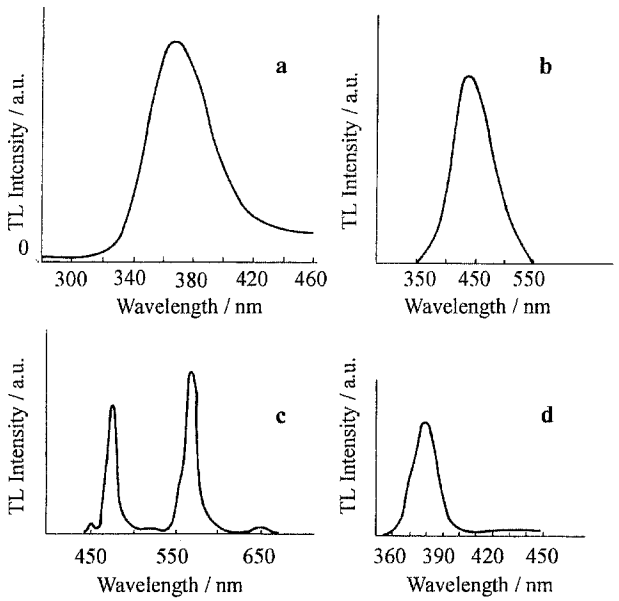

Fig. 3 TL emission spectra of the gamma-irradiated TL materials studied. a) LiF:Mg,Cu,P; b) α-Al_2O_3:C; c) $BaSO_4$:Dy and d) $BaSO_4$:Eu

The emission spectra of the materials studied are shown in Fig. 3. The spectral character of the emission recorded during the TL of LiF:Mg,Cu,P was found to be the same for all peaks and consisted of a broad band at about 370 nm associated with the characteristic emission of the Cu^+ ion. This suggests that Cu^{2+} ion is reduced to Cu^+ during irradiation. The emission spectrum of $BaSO_4$:Dy consisted of three bands peaking at about 473, 573 and 660 nm. The wavelength peak positions of these emission could be ascribed to the characteristic emissions of Dy^{3+}. Emission spectrum of $BaSO_4$:Eu exhibited a maximum at 380 nm which corresponds to the characteristic emission of Eu^{2+} ion and suggests that, apparently, the Eu intervene as Eu^{2+} in this material. Emission spectrum of α-Al_2O_3:C consists of a broad band peaking at about 425 nm which gives an indication that F^+ centers are formed to compensate the charge of the impurity C^{2+} and, consequently that the TL of α-Al_2O_3:C is due mainly to F centers.

Trapping parameters of the individual glow peaks evaluated by the glow curve shape and by deconvolution methods are given in Table 2. Normally it is not expected as shallower trap to release charge carriers at a higher temperature and a deeper trap to release them at a lower temperature as occurred in the case of $BaSO_4$:Dy. This apparent anomaly in the value of the trap depth (1.92 eV) of the 487 K glow peak could be due to overlap of the glow peaks in the glow curve of

Table 2 Trapping parameters of the TL materials studied which were determined by deconvolution and glow curve shape methods

Material	T_{peak}/K	Order of kinetics	Trap depth/eV
LiF:Mg,Cu,P	396	1	1.56
	455	1	1.63
	494	1	2.55
$BaSO_4$:Dy	407	1	2.35
	420	1	2.43
	442	2	3.36
	487	1	1.92
$BaSO_4$:Eu			E_δ=1.15
	540	1	E_τ=1.10
			E_ω=1.12
α-Al_2O_3:C			E_δ=0.67
	336	1	E_τ=0.68
			E_ω=0.67
			E_δ=0.96
	460	1	E_τ=0.94
			E_ω=0.95

Table 3 Main dosimetric characteristics of the TL materials studied which were determined irradiating them with gamma radiation

Material	Sensitivity*	Repeatability	Linearity range (Gy)	Fading**
LiF:Mg,Cu,P	25	2%	10^{-4}–10^{2}	3%
$BaSO_4$:Dy	15	7%	10^{-2}–10	14%
$BaSO_4$:Eu	100	4%	5×10^{-3}–50	10%
α-Al_2O_3:C	20	5%	2×10^{-5}–4.5	10%

*Relative to TLD-100

**During one month in the dark at room temperature (20°C)

$BaSO_4$:Dy. Table 3 shows the main dosimetric characteristics of the materials studied.

Conclusions

The models for TL production in the materials studied most consistent with the spectroscopic data described above are the following:

In the case of LiF:Mg,Cu,P TL could be attributed to the reduction of both the Mg^{2+} ions to Mg^{+} and Mg^{0}, and the Cu^{2+} ions to Cu^{+} and Cu^{0}, influenced by the P. In the case of $BaSO_4$:Dy, some of the released electrons are captured by the Dy^{3+} ions, reducing these to Dy^{2+}. Meanwhile the released holes are captured in the sulphate sites, forming trapped-hole centers of the type SO_4^-, SO_3^-, etc. The emission of light takes place when a thermally released hole recombines with reduced ions reconverting them to Mg^{2+}, Cu^{2+} or Dy^{3+} ions in an excited condition respectively.

The origin of TL in $BaSO_4$:Eu could be due to the oxidation of Eu^{2+} ion to Eu^{3+} during the irradiation and the subsequently recombination of the thermals released electron with the Eu^{3+} ion reconverting it to Eu^{2+} in an excited state.

In α-Al_2O_3:C the TL could be attributed mainly to the F centers due that it could be supposed that F^+ centers are formed to compensate the charge of the impurity C^{2+}.

All the materials studied presented dosimetric characteristics which make them appropriate for radiation dosimetry. In order to establish firmly this possibility, experiments are now in progress in our laboratory with the aim to analysing some other dosimetric characteristics such as threshold dose, neutron and charged particle response and sensitivity to UV and visible light.

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