The Investigation of the Thermoluminescence Emission Bands of LiF:Mg,Ti (TLD-100) by a Simple Developed Model

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Abstract

In this study, a new simple model based on the classical treatment of lattice vibrations and the Franck-Condon principle is developed to describe the shape of thermoluminescence (TL) emission bands of crystalline solids. According to developed model, shape of the emission band has a Gaussian form and depends on just two physical parameters: peak energy E_0 and broadening of emission spectra U. In order to demonstrate the success of the developed model, the emission spectra of dosimetric material LiF:Mg,Ti (TLD-100) was also measured. Then, a computerised best-fit program including the developed model was used to analyse the emission spectra. The number of individual bands and their kinetic parameters were also obtained by this program. Two emission bands were observed for all glow peaks with peak energies at around 3.0 eV and 2.75 eV.

Key Words: Thermoluminescence, LiF.Mg,Ti, TLD-100, Emission Band

1. Introduction

During the last fourty years, many investigations have been done to understand the structure of certain defects present in the TLD-100 responsible for the complex behaviour of the thermoluminescence glow peaks of this material [1]. In these studies, many techniques (i.e. optical absorption, dielectric loss, ionic conductivity, electron spin resonance and TL) have been employed to understand the nature of centers in this material. Especially, TL and optical absorption techniques are very sensitive techniques to obtain the properties of defects in solids. Despite an overwhelming amount of data on this subject, a satisfactory description is still lacking due to inadequacy of the used models in these

techniques to determine the nature of the defects [1]. The fundamentals of emission and also absorption band models are derived from the theory of molecular spectra [2]. A precise calculation of shape and location of emission band was done by considering the mutual influence of lattice ions and their electrons with luminescence (recombination) centers (LC). Huang and Rhys [3] were primarily interested in computing the shape of the emission band and in determining the probability that an excited electron would return to the ground state by luminescent or by non-radiative transitions after completely neglecting short-range interactions between luminescent center and neighbouring ions. However, Pekar [4-5], for the same system as that used by Huang and Rhys [3], calculated the wave functions of the system starting with a Hamiltonian expression. In his calculation, he utilised the adiabatic approximation and the Condon approximation and assumed that the coupling between the LC and the lattice was only via the single optical mode of frequency ω_l. Later calculations have been performed by Meyer [6], O'Rourke [7] and Lax [2] based upon the same models as Pekar [4-5] and Huang and Rhys [3]. Although a number of theoretical calculations was made on the shape of emission bands, the shape of TL emission spectra of some TL materials (i.e., LiF:Mg,Ti) is not successfully explained with the developed models [8-9].

Probably, the last attempt on this subject was made by Yazıcı et al. [10] and they came to conclusion that the luminescence mechanism of this material could be very well explained by an associated pair-trap defect model [11]. According to this trap model, the trap and LC are the same center. During the heating process of the sample, the electrons in the ground state of the trap raise to the excited state of the centers from which they may either be re-trapped or, alternatively, emit a photon by returning to the ground state of the centers. At the same time, it is clear that the LC can be thought as a trap in associated pair-trap defect model and the emission spectra of this type defect model can be well explained by the developed model than the previous model.

In this study, a new simple model based on classical treatment of the lattice vibration and the Franck-Condon principle is developed to describe the shape of TL emission band of crystalline solids. In order to demonstrate the success of the developed model, the emission spectra of LiF:Mg,Ti (TLD-100) was measured and then analysed by this model using a computer best-fit program.

2. Theory

The simplest band model in crystalline solids for the TL emission is shown in Figure 1. According to this model there are at least two distinct localised energy levels; one of which acts as a trap (T) and the other as a recombination (luminescent) center (R) [12]. The electrons in the traps must be excited to the conduction band (CB) (transitions 1 and 2) to observe TL. These electrons then migrate in the CB (3) and recombine with holes in the luminescent centers by the emission of photons (transition 4 and 5). In some crystals, the electrons in the CB do not recombine directly with the holes in the ground state of luminescent centers. According to this situation, the creation of recombination can be explained in two steps. In transition 4, the excess energy of the electron transfers

to the lattice via phonons. This process is called multi-phonon emission. According to this process, there is a strong coupling between the electron and the lattice vibration. If an electron approaches to the luminescent center, it settles down to this center due to the vibration of the lattice around the luminescent center. The electron is still in the excited state of luminescent center after transition 4. The second recombination process is the transition of electrons from the excited state to the ground state of luminescent center via emitting photons.
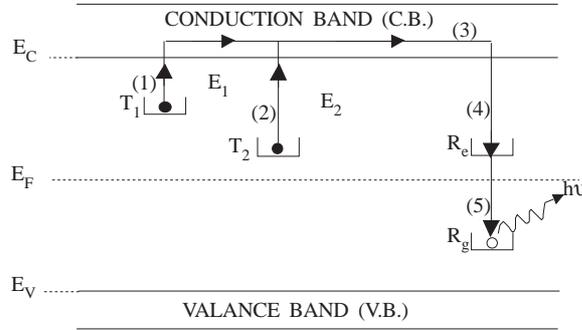
Figure 1. Simple band model for TL emission. T_1 and T_2 electron traps, R_e and R_g is the excited and ground state of a recombination (luminescent) center, E_1 and E_2 is the energy difference between the band edge of the conduction band and electron trap T_1 and T_2, respectively. Allowed transitions: (1) and (2) thermal release, (3) migration, (4) non-radiative recombination, (5) radiative recombination.

Let us consider the interactions between LC and the ions around the LC which is at a great distance from each other and LC. In other words, we shall discuss the determination of the form of the energy levels when the distance between the ions and LC (inter-nuclear distance) is very large as in the ionic crystals (i.e., alkali halide crystals- LiF:Mg,Ti). A basic premise of this study is that the wave function of the LC falls into product of an electron wave function (depending on the distance between ions and LC as a parameter) and a wave function for the motion of the LC. A simple schematic representation of the effect of electron wave function is shown in Figure 2. In this figure, the big and small circles around the LC represent the approximate effect of the electron wave functions in the excited state and ground state of the LC, respectively. The excited state configuration of the luminescent center is shown in Figure 2a, when an electron approaches this center. Figure 2b represents ground state configuration of the luminescent center after the transition of an electron from the excited state to the ground state via emitting a photon. The differences between the excited state and ground state depend on the strong electron-lattice interaction. The potential energy of both states of the luminescent center is influenced by the configuration of the lattice around the luminescent center and expressed as a function of the configuration co-ordinate (CC) diagram. The distance Q

between the luminescent center and its nearest neighbour (ligand) ions is often used to characterise the CC diagram.
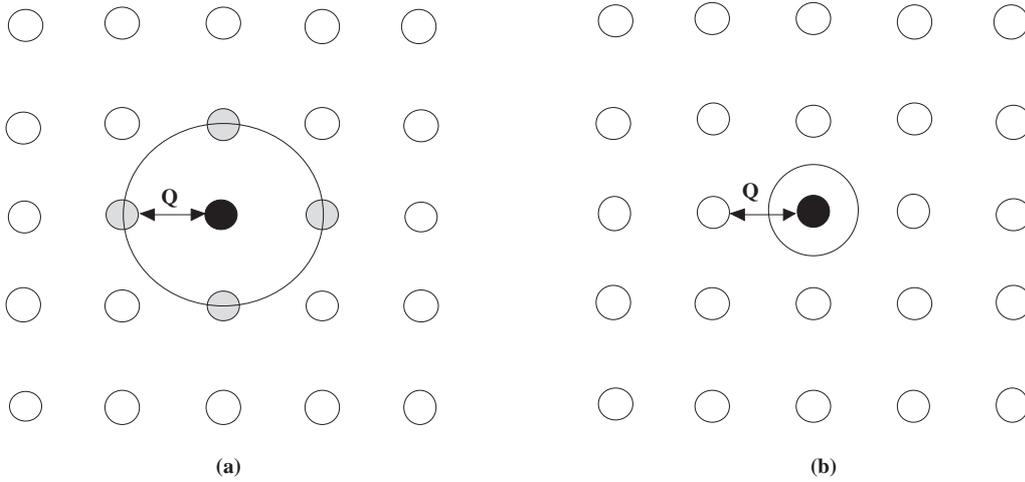

Figure 2. The excited and ground state configuration of a luminescent center in crystalline solid for one-dimension. (a) in the excited state, (b) in the ground state.

The shape of an emission band of a luminescent center in the crystalline solid can be explained by the use of a CC diagram. The CC representation is also used to depict the coupling between the vibration lattice energy and the electron lattice interaction energy. A CC scheme is represented in Figure 3. The horizontal axis shows the CC distance (Q) and vertical axis shows the total energy of the luminescent center, i.e., the electronic (E_e) plus the vibration excitation energy (E_m). In this model each energy state of a center is represented by a wavefunction that consists of the product of an electronic wavefunction and a vibrational wavefunction. The electronic wavefunction is expressed in terms of electron in the center, whereas the vibrational wavefunction is the wavefunction of the center in a potential due to the presence of the ligand ion.

It is well known that the shape of emission band of a luminescent center has a Gaussian line shape and depends on the distribution of the number of emitted photons $N(E)$ with different emitted photon energies E_f from excited state to ground state. The number of emitted photons at a given photon energy E_f according to our model is given by the relation

$$N(E_f) = \frac{1}{2U\sqrt{\pi}} Exp(-\frac{(E_f - E_0)^2}{U^2}),$$
(1)

where E_f is the emitted photon energy at a certain co-ordinate Q, E_0 is the photon at the maximum of emission peak, and U is the full-width at half maximum (FWHM).
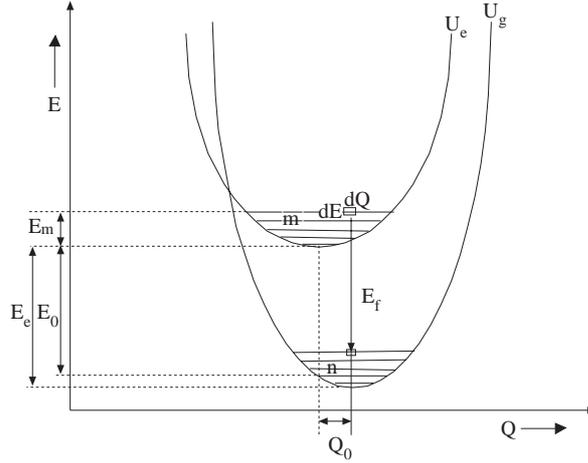
Figure 3. The Configuration Coordinate diagram of a luminescent center in the solid.

The emission band is generally measured in terms of emitted light intensity as a function of emitted photon wavelength (or energy). The intensity is related to the total number of emitted photons per unit volume of the sample. The expression of a TL emission band (distribution of intensity of the line as a function of energy) according to our model is given as

$$I(E_f) = \frac{I_0(E_0)}{2U\sqrt{\pi}} Exp(-\frac{(E_f - E_0)^2}{U^2}).$$ (2)

According to Eq. (2), the shape of the emission band has Gaussian form and depends on two physical parameters: E_0 and U. The details of the derivation of equation 1 and 2 are given in the work of Yazici [10]. This developed TL emission band model (eq.2) was used to fit the emission spectra of the TLD-100.

3. Experimental Procedure

TL samples used in this study were LiF:Mg,Ti (TLD-100) single crystalline chips with dimensions of 3x3x0.9 mm^3 obtained from Harshaw Chemical Company, Ohio, USA. The samples were annealed at 400°C for 1 hour after through the experiments to erase any residual information before the subsequent irradiation and then cooled in air at approximately 75°C/min to room temperature. All annealing treatments were carried out with a specially designed microprocessor- controlled electrical oven. The temperature sensitivity of the oven was estimated to be ± 1°C.

The samples were irradiated with beta rays from a ^{90}Sr-^{90}Y source at room temperature immediately after quenching. The irradiation durations were adjusted to 3 minutes throughout the experiments. The irradiation equipment is an additional part of the 9010 Optical Dating System that purchased from Little More Scientific Engineering, UK.

The glow curves were recorded using a Harshaw QS 3500 model TL apparatus inter-

faced to a PC where the glow curves analysed. Glow curve readout was carried out on a platinum planchet at a linear heating rate 1°C/sec up to 400 °C. The time duration between the irradiation and TL readout was always kept constant at about 1 min. During the experiments, each sample was readout twice. The second reading with the same profile is considered to be the background of the reader plus chip and was subtracted from the first one.

In this study, the employed optical filters between the samples and photomultiplier tube were purchased from Barr Associates, Inc. Westford, USA. The peak wavelength of employed optical filters were between 300 and 1000 nm. Also it was measured that the FWHM of the employed optical filters were always less than 10 nm by using a Jasko 7800 Model UV/VIS double beam spectrophotometer. The glow curve measurements were performed five times for each optical filters.

4. Results

The glow curves obtained from LiF:Mg,Ti at different wavelengths are shown in Figure 4. The usual peak numbers are labelled on this figure. It is obvious that relative TL peak intensities are highly changed with employed optical filters. The most intense glow curve is obtained when the optical filter with a peak wavelength of 420 nm was used. The peak temperatures obtained from this glow curve are: peak 2 at 113°C; peak 3 at 151°C; peak 4 at 190°C; peak 5 at 217°C; and peak 6 at 282°C.
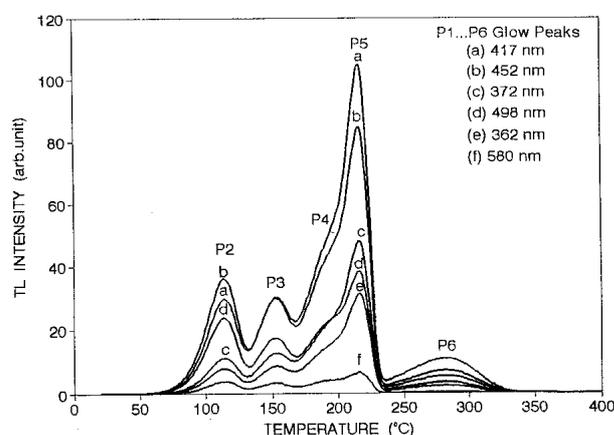
Figure 4. The glow curves from LiF:Mg,Ti at different wavelengths.

The emission spectrum of all glow peaks are obtained from the glow curves which were previously recorded after analysing them by Randall-Wilkins model [13] using a computer glow curve deconvolution method [14] (Figure 5). During these operations, the glow peak intensity values were always chosen as a reference relative intensity value for emission spectras. The main emission peak was seen at ≈420 nm, which is in good agreement with the similar spectras recorded by previous authors [15-18]. It is clear that there are, in fact, several emission components in the spectras as seen from the shape

of the curves. All of these emission spectras were also resolved by using the developed simple expression (eq.2). The separation procedures were also performed by means of a computerised curve-fitting program. This program was obtained from Bos and Piters [19] and modified by us according to our developed expression. The previously recorded emission band around 620 nm [8-9, 12, 20], however, was not observed in this study. One reason for this is that this band seems to appear at the emission spectra of TLD-100 that have been exposed to higher irradiation dose levels ($>10^3$). The emission spectrum of whole glow peaks were successfully fitted with two emission bands. But there is a small systematic shift in the central photon energy and relative intensity of emission band as the peak temperature increases. At 113°C (peak 2) the 2.7 eV component is dominant. As the temperature increases, this band broadens and its intensity decreases. Therefore,

Table 1. Kinetic parameters of TL emission spectrum of LiF:Mg,Ti (TLD-100).

Authors	Peak No	Band No	E_0 (eV)	U (eV)	C_1 (eV)	C_2 (eV)	C (eV)
Fairchild and et al.[a]	5	1	3.01	0.90*	3.07	0.04	-
		2	2.90	0.72*	2.94	0.04	-
		3	2.71	0.96*	2.75	0.04	-
Delgado and et al.[b]	5	1	3.01	-	-	-	-
		2	2.88	-	-	-	-
		3	2.70	-	-	-	-
Yazıcı[3]	2	1	2.98	0.51**	-	-	1.95
		2	2.70	0.38**	-	-	1.08
	3	1	3.00	0.44**	-	-	1.76
		2	2.71	0.43**	-	-	1.27
	4	1	3.01	0.43**	-	-	1.16
		2	2.74	0.45**	-	-	1.27
	5	1	3.02	0.40**	-	-	0.95
		2	2.77	0.46**	-	-	1.21

[a]Ref.[8]
[b]Ref.[21]
[c]This work
*U=FWHM
**FWHM=$2\sqrt{\ln(2)}U$

at 217°C (peak 5) the 3.02 eV is the main component. Similar behaviour was also observed by some previous studies [21-22]. It is observed that the emission maxima of the glow peaks from 2 to 5 appear at about 450, 434, 426, 419, and 410 nm, respectively. The

kinetic parameters of emission bands obtained from the emission spectrum of glow peak 2, 3, 4 and peak 5 are given in Table 1, which also contains selected results of previous publications.
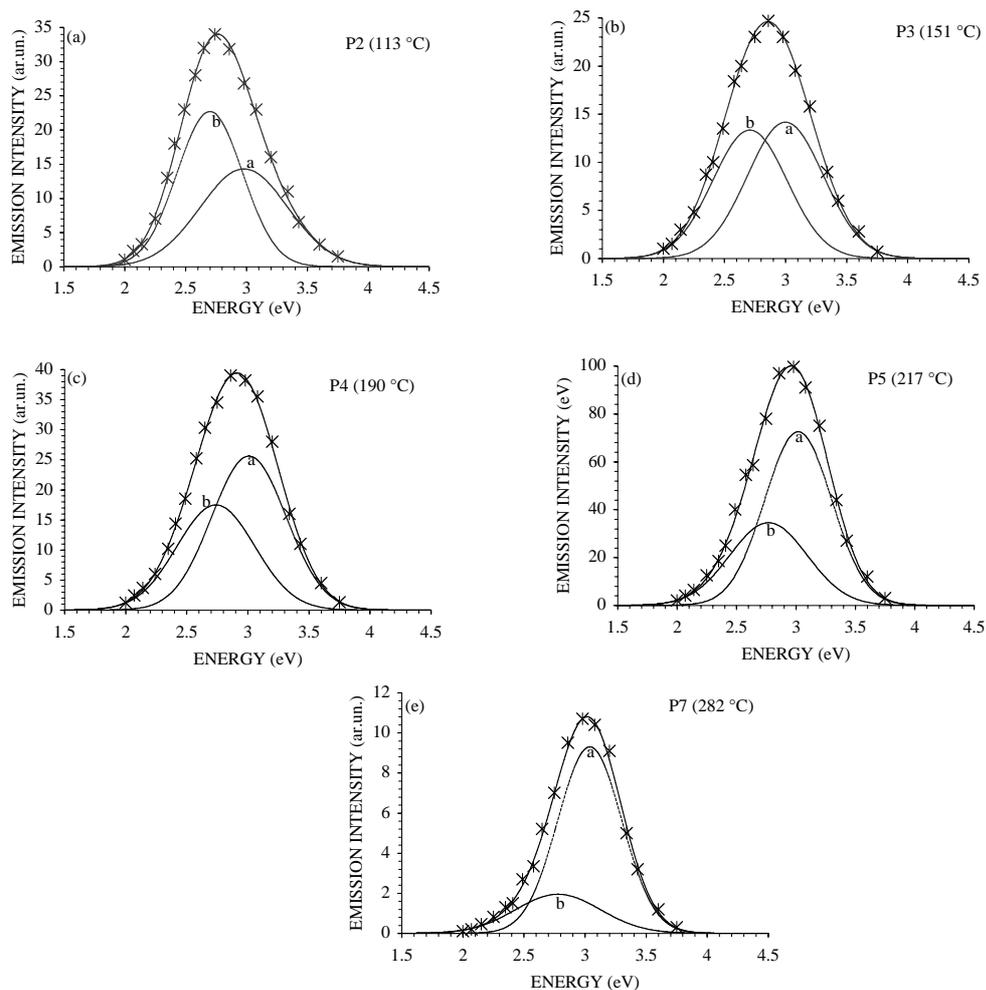
Figure 5. TL emission spectra measured at the maxima of different glow peaks from LiF:Mg,Ti. In this figure, * are measured experimental data, the smooth lines are fitted curve. (a) Glow peak 2, (b) Glow peak 3, (c) Glow peak 4, (d) Glow peak 5, (e) Glow peak 6.

5. Discussion

Earlier investigations about the emission spectra of LiF:Mg,Ti have been done by several authors [23-24]. Especially, four emission band regions have been observed at

approximately 300, 420, 520, and 620 nm. In all works a broad line emission at approximately 420 nm was observed. Additionally, Townsend et al. [22] have observed a gradual shift in the emission maxima to the lower wavelength with increasing peak temperature. The experimental measurements at low temperatures represented that the principal emission is also in the region of 400-420 nm [25]. The other peculiar properties such as the effect of the ageing period duration and heating rate on the emission bands have been previously investigated [20-21]. Delgado and Delgado [21] showed that there were no changes on the emission spectrum, but Piters and Bos [20] observed only very small changes with heating rate. However, in most of these studies, the emission spectra were recorded at large dose levels in the order of 10^3 Gy. It is well known that at high dose levels, the shape of glow curve of LiF:Mg,Ti alters and some new peaks appear at the high temperature side of peak 5 [1]. In all these studies, the TL emission spectra of LiF:Mg,Ti around 420 nm were described by three emission bands with central photon energies E_0 of $\approx$3.0 eV, $\approx$2.90 eV and $\approx$2.70 eV by using the expression given in the paper of Fairchild et al. [8]. According to this expression, the emission band maxima should decrease slowly and monotonically with increasing temperature and the full-width at half maximum should increase monotonically with increasing temperature. However some authors [1, 26] strongly criticised that the emission spectrum of some materials can not be accurately resolved with this equation. Therefore, the number of bands in the emission spectra of LiF:Mg,Ti was also criticised by many authors [1, 9]. In this study we also assert that two bands are more plausible than three bands.

The number of emission bands is not a free fitting parameter during the deconvolution of measured spectrum into individual emission bands. If the number of bands is not known it can be found by fitting the spectrum several times with a different number of bands. Therefore, in this study, it is tried to resolve the experimental results with three emission bands according to the developed model to obtain the best-fit result. However, it was seen that third band always drifted away from the region of experimental points or the computer program indicated that its intensity was minor importance when compared with the intensities of the other two bands. Second, the emission spectras were tried to fit with one band. However, there were large differences between experimental and computed spectra in this case. When the experimental results were fit with two bands instead of one or three bands, a best-fit is always obtained.

When the emission spectra comprises more than one emission band, the total spectrum is formed by a summation of different bands. One of the most important evidence of multi-component emission spectra is the shifting of peak emission energy to the higher or lower energy sides with increasing temperature; and the other evidence is, if the relative intensity of individual emission bands correlate with impurity concentrations one would conclude that the multiple-band model is correct. In this study, as in the previous studies [20-22], it has been observed that the emission spectrum of LiF:Mg,Ti varied markedly with temperature. Additionally, the measurements of TL emission spectra of a LiF:Mg,Ti sample with different impurity concentrations have been represented that the relative intensities of emission bands are highly depend on the impurity concentrations. These mean that the emission spectrum of LiF:Mg,Ti is the sum of the variation of at least two

or probably three emission bands.

Although there is controversy in the number of fitting bands between this work and previous results, there is a good agreement in the parameters of the most intense band (see Table 1). It is thought that these incompatibles are probably due to the different behaviour of the temperature dependency of E_0 and U, or different irradiation dose levels, or high overlap of the emission bands or many other experimental parameters, but not due to the lack of the developed model.

In conclusion, the developed model in this study strongly claims that the best fit for the emission spectra of LiF:Mg,Ti can be obtained by two bands instead of three bands. Also, it is suggested that the emission spectra of LiF:Mg,Ti can be better explained by an associated pair-trap model.

Acknowledgements

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