This paper presents the thermo luminescence (TL) analysis of natural salt (NaCl:Cu,Mg,O,As,Mn) obtained from the salty water bodies from Mizoram, India. The aim of the present work was to investigate the potential of selection of natural salt for possible dosimetry applications. Natural salt obtained by evaporating salty water was analyzed using XRD and was irradiated with 0.5 Gy gamma rays by Theratron780C machine and analyzed by quenching using a commercial based TLD reader TL1009I at the heating rate 5 C/Sec. Analysis of the glow curves by different methods confirms that the sample exhibits thermal quenching. The study is useful to study the above said phenomena in other similar samples.

Keywords: Thermo luminescence, natural salt, kinetic parameters, thermal quenching
INTRODUCTION

Thermo luminescence (TL) is the thermally stimulated emission of light following the previous absorption of energy from radiation\(^1\). The output of a TL is a glow curve plotted between TL intensity and stimulating temperature.

With the increase of heating rate, the peak temperature of the glow curve shifts to higher temperature side with decrease in intensity. This effect is due to thermal quenching\(^2\) and it is present in several important TL materials\(^3,4\), such as quartz and Al\(_2\)O\(_3\)\(^3,4\). Thermal quenching is the process such that the luminescence efficiency decreases with temperature due to the increase probability of non-radiative transitions due to killer centre\(^5\). Under the influence of thermal quenching the activation energy \(E\) is underestimated by initial rise and peak shape methods. Recently, thermal quenching effect on TL glow curves of Al\(_2\)O\(_3\):C and quartz had been widely studied by some researchers\(^2,6\).

Several studies had been done by the present authors such as sample weight selection, irradiation source and fading\(^7-12\). The aim of the present work is to study the experimentally observed quenching in TL of natural salt. Quenching parameters were evaluated for this sample. Simulations are used where necessary.

MATERIALS AND METHODS

The Natural salt Dap Chi (local name) was extracted by the process of evaporation of salty water, available in the state of Mizoram. The natural salt was crushed to fine powder, and given thermal treatment at 110 C for 90 minutes in oven before irradiation. Samples of 20 mg \(\pm\) 2 mg were used for each measurement\(^9\). Samples were irradiated from a \(^{60}\)Co gamma source at a low dose of 0.5 Gy from a Cobalt Th780C machine. The dose rate of the \(^{60}\)Co source at the time of irradiation was 0.0253 Gy/sec. TL measurements of the irradiated samples were carried out immediately after irradiation in a commercial PC based TL reader, model TL1009I photomultiplier tube Hamamatsu/ET make Type No. 6095 (Nucleonix System Pvt. Ltd, Hyderabad, India) operating at 750 volts. A second TL measurement gives background radiation with black body radiation. The TL glow curves presented are after background subtraction. The heating rate used was 5 C/sec with the final temperature set to 300 C. The samples were protected from direct light during the whole process by properly packing with black polythene. The TL glow curves were recorded and TL peaks shifted to higher temperature as the heating rate increases. The XRD analysis of the sample is shown below:
THEORY

The explanation of thermal quenching effect can be described by Mott-Seitz model\textsuperscript{4} and the thermal quenching luminescence efficiency is given by in equation 1.

\[ \eta(T) = \frac{1}{1 + C \exp(-W/kT)} \]  

(1)

where the quenching parameters; \( C \) is a dimensionless constant and \( W \) is the quenching activation energy. \( T \) is the temperature of the sample, and \( k \) is the Boltzmann constant.

**From the first order kinetic** A first order glow peak under the linear heating rate (\( \beta \)) given by \( T(t) = T_0 + \beta t \), is described by Randal Wilkins expression,

\[ I(T) = n_0(s/\beta) \exp(-E/kT) \exp\left(-(skT_0^2/\beta E)\exp(-E/kT)(1 - 2kT/E)\right) \]  

(2)

where \( E \) (eV) is the trap depth, \( k \) is Boltzmann’s constant, \( s(\text{s}^{-1}) \) is the frequency factor, \( n_0 \) is the trapped electron concentration at \( T_0 \).
The experimentally observed TL glow curve corresponds to a quench TL glow peak $I_{QU}(T)$. This quench TL intensity is found by multiplying the quenching efficiency $\eta(T)$ by the unquenched TL intensity $I_{UNQ}(T)$ in equation 2 as follows:

$$I_{QU}(T) = I_{UNQ}(T)\eta(T)$$  \hspace{1cm} (3)

The peak integral is given by

$$\text{PeakIntegral} = \frac{1}{\beta} \sum_i I_{QU}(T) \Delta T_i$$ \hspace{1cm} (4)

**Evaluation of W and C**

The thermal quenching parameters can be evaluated from a set of quenched experimental data. The equation for which is

$$I_{QUE} = A\eta(T)$$ \hspace{1cm} (5)

where $A$ is the peak integral of the unquenched glow peak. By approximating the quenching function, equation 1, at the peak maximum ($T_M$),

$$I_{QUE} = \frac{A}{1 + C \exp(-W/kT_M)}$$ \hspace{1cm} (6)

And by rearranging

$$\ln \left( \frac{A}{I_{QUE}} - 1 \right) = -\frac{W}{kT_M} + \ln C$$ \hspace{1cm} (7)

The plot of $\ln \left( \frac{A}{I_{QUE}} - 1 \right)$ against $\frac{1}{kT_M}$ in equation (7) is a straight line with slope $-W$ and intercepts $\ln C$, from which $W$ and $C$ can be evaluated$^2$.

**Kinetic Model**

Under the assumption [8] that each recombination produces a photon and that all produced photons are detected (no-quenching), the rate equation may be written as

$$I(t) = -\frac{dm}{dt} = n_e m A_m$$ \hspace{1cm} (8)
where \( m \), \( n_c \) and \( A_m \) are concentration of holes, concentration of free electrons in the conduction band and the probability of recombination respectively. Under of quasi-equilibrium condition, charge neutrality and negligible re-trapping, equation (8) reduces to Randal Wilkins first order equation (2).

The kinetic model in figure 2 is basically derived from the Mott-Seitz model; therefore we go directly in to the kinetic model.

\[
\frac{dn_2}{dt} = A_{CB} n_c (N_2 - n_2) - A_R n_2 - n_2 A_{NR} \exp(-W/kT) \tag{9}
\]

\[
I(t) = A_R n_2 \tag{10}
\]

where \( n_2 \) and \( N_2 \) are concentrations of electron filled traps and electron traps at the excited state of the recombination centre, \( n_c \) is concentrations of electrons in the conduction band, and \( A_R \) and \( A_{NR} \) are the probability for radiative and non-radiative transitions respectively.
If $A_{NR}$ is zero, then $n_2$ electrons available in the excited state of recombination centre by $A_{CB}$ will emit radiation by $A_R$. Therefore equation 9 will reduce to equation (8). However, as heating rate increases it is usually observed that $A_{NR}$ dominates over $A_R$.

It is believed that at a particular heating rate for a given quenching parameters, $A_{NR}$ and $A_R$ are equal in magnitude.

RESULTS AND DISCUSSIONS

Un-quench and quench TL glow curves

Since the VHR method is independent of the order of kinetic, and evaluation of trapping parameters by VHR is less influenced by thermal quenching, we analyzed with the first order kinetic equation. Thus, the un-quench TL glow curves in Figure 3, are obtained from first order equation (equation 2) with input parameters $E=1.11 \text{ eV}$, $s = 2.41 \times 10^{10}$, for all heating rates. These input parameters were calculated from the slope and intercept, obtained from VHR curves as introduced by Hoogenstraaten for first order kinetics.

Again, using equation 3, the quench glow curves are obtained. The number of trapped electrons $n_0$ at $T_0$, which appeared on the left hand side and right hand side of equation 3 cancelled each other. The quenching parameters $C$ and $W$ required for in equation 3 are obtained from the calculated values (see values of $W$ and $C$). The un-quench and quench glow curves are presented in Figure 3.

![Figure 3: TL glow curves of un-quench and quench. Kinetic parameters for this TL curves were obtained from experimental data.](image-url)


The relation between peak temperature and heating rate is quadratic, i.e., the shift of peak temperature to higher temperature side is much slower in quench than the unquenched glow curve. The FWHM decreases in quench glow curve, whereas the FWHM of the unquenched glow curves are increasing.

In Figure 5, the behaviour of peak integral (or counts) from equation (4) is shown. The value of $\Delta T$'s are 1.31 K, 1.29 K, 1.26 K, 1.25 K for $\beta = 275$ K/s, 276 K/s, 277 K/s and 278 K/s respectively. The un-quench integral is constant (i.e. peak area is conserved). The quench integral rapidly decreases with increasing heating rates, may be due to the increase of non-radiative recombination. These observations/results may support the theoretical simulation.
results of TL intensity versus temperature for constant doses between quench and unquenched TL glow curves, reported by Munish Kumar et al\textsuperscript{14}.

**Evaluation quenching parameters W and C**

Figure 6: The plot of ln(A/IQUE-1) versus 1/kTM from equation (7).

Figure 6 is obtained from equation (7). From the slope and intercept of this curve gives $W = 2.76$ and $C = 8.36 \times 10^{26}$. This value is very large when compared with $W = 1.08$ eV and $C = 2.9 \times 10^{12}$ for Al$_2$O$_3$:C and $W = 0.64$ eV and $C = 2.8 \times 10^{7}$ for quartz\textsuperscript{3,4}. From the kinetic model of thermal quenching (Figure 2), if a recombination centre is just above the valance band and far below the $E_f$, there is a large energy gap (i.e. $W$). This may be the reason for high value of quenching activation energy.

**Comparison of $\eta(T)$ for simulation parameters and calculated parameters**

The value $W$ and $C$ obtained from the experimental data are very high as compared to the value 1.11 eV and $2.41 \times 10^{10}$ used for simulation of the un-quenched glow curve. The method applied here is only approximation, i.e. it involves a single value $\eta(T_W)$ as representative of the thermal quenching factor $\eta(T)$ across the whole glow peak. However the differences between the calculated and the original quenching parameters are not as significant as they seem except for the heating rate 278 K/s in this experiment (Figure 7). The solid line in figure 7 corresponds to $\eta(T)$ using $W = 1.11$ eV and $C = 2.41 \times 10^{10}$, whereas the open circles are calculated using the calculated value $W = 2.76$ eV and $C = 8.36 \times 10^{26}$. 

$$y = -2.7681x + 65.061$$

$$R^2 = 0.9978$$
3.4. $A_R$ by $A_{NR}$ ratio

Form Figure 5, the behaviour of the normalized area of quench TL glow curves as a function of the heating rates has the following linear relation:

$$y = -0.248x + 70.957$$

From this relation the heating rate which produces the quench area equal to half of the unquenched area is 280.0685 K/s (this heating rate produces 1.5, which is half of the unquenched area i.e. 3). Since glow curve area is proportional to TL emission, therefore, the ratio of $A_R$ by $A_{NR}$ at 280.0685 K/s can be written as

$$\frac{A_R}{A_{NR}} = 0.5$$

By substituting this value to equation (9), we get

$$dn_z / dt = A_{cr} n_z (N_z - n_z) - A_{r} n_z \{1 - 2\exp(-W / kT)\}$$

Again, the peak maximum temperature and heating rate of the quench glow curve has a quadratic relation (Figure 4). Extrapolating this relation to 280.0685 K/s, gives peak...
temperature 500.234 K. Substituting this maximum value and \( W \) value, to above equation gives the exponential term of the order of \( 10^{-28} \). This exponential term and \( C = 8.36 \times 10^{26} \); when substituted to (equation 1), the thermal quenching efficiency is found to be 0.544662309. This value is very much in agreement with the value reported by G.I. Dallas\(^{15}\) et al in their theoretical simulation that for every \( W \) and \( C \) pair, the thermal quenching efficiency at its maximum temperature is \( 0.54 \pm 0.007 \).

**CONCLUSION**

This study confirms that the TL glow curves of natural salt exhibits thermal quenching. The important conclusion is that even without considering the constituent elements and their concentration of the sample, the Mott-Seitz model can be successfully applied to explain the observed phenomena of quenching in natural salt and may confirm the reliability of the above models. This study also supports the work of G.I. Dallas et al, and may be applied to other similar quenching studies.

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**REFERENCES**


