Thermally assisted tunneling of charge carriers between trapping sites in calcite ($CaCO_3$) mineral

J.M. Kalita* and G. Wary

Department of Physics, Cotton College, Guwahati-781001, India

*E-mail: jitukalita09@gmail.com

Abstract. Thermally Stimulated Luminescence (TSL) mechanism of natural orange calcite mineral has been studied. The glow curve of X-ray irradiate sample has been studied in un-annealed and 673 K annealed samples by a Computerized Glow Curve De-convolution (CGCD) technique. It has been observed that after exposure to X-ray, both the un-annealed and 673 K annealed samples show three distinct peaks at around 323, 360 and 409 K in the glow curves. Study on the effect of post-annealing treatment on the excited sample reveals that the 323 K peak can be thermally bleached by annealing at ~340 K, however it is very significant that the 360 K TSL peak can't be bleached by increasing the post-annealing temperature up to 380 K. CGCD analysis reveals that the activation energies corresponding to the 323, 360 and 409 K peaks are found to be around 0.70, 0.60 and 1.30 eV respectively. The low activation energy peak observed at relatively high temperature and existence of the 360 K peak after post-annealing the sample beyond its peak maximum temperature are due to thermally assisted tunneling of trapped charge from 1.30 to 0.70 eV trapping sites in calcite. This analysis leads to an important conclusion that though theoretically the glow peak observed at relatively high temperature should have high activation energy, but due to charge tunneling phenomenon between the trapping sites, glow peak observed at high temperature may have relatively low activation energy.

1. Introduction

Thermally Stimulated Luminescence (TSL) analysis is an efficient tool to study the presence of trapping sites as well as movement of the charge carriers among the trapping sites. For TSL analysis, at first the sample is exposed under high energy radiation. Due to high energy irradiation the valence electrons excite to the conduction band. If some localized energy state available in between the valence band and conduction band then these charge carriers (electron/hole) may get trapped at the localized energy state. At the stimulation stage the sample is heated at a constant rate. At this stage the trapped electron eject out from the trapping site and recombine with the holes via the conduction band. The recombination is sometime radiative and non-radiative. The radiative recombination caused the emission of light. The plot of the amount of emitted light as a function of temperature of the sample is often called TSL glow curve. The shape and position of a glow peak is characterized by various physical parameters such as activation energy (trap depth), frequency factor, order of kinetics etc. A glow curve may compose of more than one glow peak. Each glow peak in a glow curve corresponds for a unique set of some physical parameters. Therefore proper analysis of the glow curve can give the accurate estimation about the trapping site available in the energy gap which plays a vital role in the whole luminescence phenomenon.

Calcite ($CaCO_3$) is a naturally occurring high sensitive luminescent mineral. Because of its high sensitivity, it becomes an attractive nominee for many applications including geological dating [1], medical dosimetry [2] as well as generic defect studies [3–5]. Townsend et al. [6] studied thermoluminescence (TL) spectra of X-ray irradiated natural calcite and its pure habit, Iceland spar, and observed line structures in the emission spectra. Analysis of the TL spectra showed that Mn impurity was the most recognized recombination site in calcite [3–8]. However, in geological calcite sample some differences in the behavior of the spectra have been observed [9]. Though luminescence properties of calcite mineral had been studied by several researchers, but there are still some extraordinary results that need to be addressed. According to the theory of TSL, the glow peak observed at high temperature should have high activation energy relative to the peak observed at low temperature, but in calcite a glow peak was observed at high temperature that has relatively low activation energy [5]. The luminescence mechanism of calcite is very complicated and it cannot be explained with the help of ordinary luminescence model commonly available in the literature. In the present case luminescence mechanism in calcite has been discussed in detail with the help of TSL analysis.

2. Experimental works

Rarely orange color natural calcite mineral was procured from Geological Survey of Assam, Govt. of Assam (India) which was originated from Umrangso, Karbi Anglong, (India) (latitude: 25°30' N, longitude: 92°44' E). It was crushed by roll crusher and then ground in a ceramic mill to powder form. To study the TSL characteristics, at first the sample was divided into two parts; one part was kept un-annealed and the other part was annealed at 673 K for 30 minutes. For TSL analysis taking 10 mg sample in each aliquot the samples were exposed under X-ray (dose rate: 0.05mGy/s). TSL glow curve of the irradiated sample was recorded by NUCLEONIX-TL 1009I TL reader at 2 K/s heating rate.

3. Results and discussion

Figure1 shows the TSL glow curve of calcite mineral after 60 mGy X-ray irradiation. Three glow peaks P_1, P_2 and P_3 have been observed at around 323, 360 and 408 K in the glow curve. A natural TL (NTL) glow peak (P_0) has been observed at around 472 K in the fresh un-irradiated sample. However after X-ray irradiation no TSL peak has been observed at that temperature. Comparing the glow curves it can be observed that due to the pre-annealing at 673 K, no any dislocation of the peaks is observed. This signifies the thermal stability of the trapping sites that are present in the crystal. The glow curves of both the samples have been analyzed by Computerized Glow Curve De-convolution (CGCD) technique on the basis of Kitis general order equation (equation (1)) [10] and various TL parameters such as activation energy (E), order of kinetics (b) and frequency factor (s) have been estimated.

$$I(T) = I_{\mathrm{m}} b^{b/(b-1)} \exp\left(\frac{E}{kT}\frac{T-T_{\mathrm{m}}}{T_{\mathrm{m}}}\right) \times \left[(b-1)(1-\Delta)\frac{T^2}{T_{\mathrm{m}}^2}\exp\left(\frac{E}{kT}\frac{T-T_{\mathrm{m}}}{T_{\mathrm{m}}}\right) + Z_{\mathrm{m}}\right]^{-b/(b-1)} \quad (1)$$

Here I is TL intensity, T is absolute temperature, I_{m} is peak maximum intensity, T_{m} is peak maximum temperature, k is Boltzmann's constant, $\Delta = 2kT/E$, $\Delta_{\mathrm{m}} = 2kT_{\mathrm{m}}/E$ and $Z_{\mathrm{m}} = 1+(b–1)\Delta_{\mathrm{m}}$. In this method, the activation energy, the peak maximum temperature and the order of kinetics are independent variables that are determined by iteration to a best fit. For each glow curve the goodness of fit is testedby the Figure of Merit (FOM) [11]. All de-convoluted glow curves are accepted when their FOM values are lower than 2%. A de-convoluted glow curve of 673 K annealed sample has been shown in Figure 2. The results are reported in Table 1. This analysis reveals that the activation energies corresponding to the 323, 360 and 409 K peaks are found to be around 0.70, 0.60 and 1.30 eV respectively. The activation energy corresponding to the NTL peak is about 1.49 eV. But after X-ray irradiation all the naturally trapped charge carriers move to the other trap sites. As a result no TL peak has been observed.

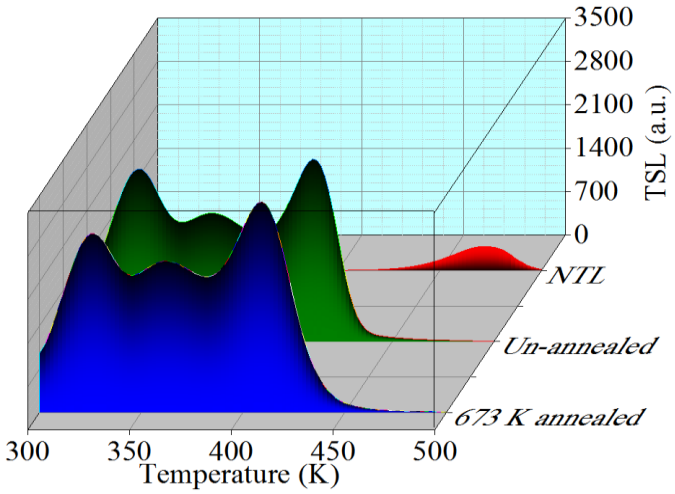

Figure 1. TSL glow curves of natural calcite mineral.

In order to study the trap spectroscopy of calcite in a more detail manner, the un-annealed and 673 K pre-annealed samples are heated at 2 K/s up to 340 K and 380 K temperatures after exposure to 60 mGy X-ray dose. The reason for selecting these two specific temperatures is to thermally bleach the peaks P_1 and P_2 respectively. Figure 3(a,b) shows the glow curves of both the samples after post-annealing at 340 and 380 K temperature for 6 minutes. As expected the 323 K glow peak (P_1) has completely bleached out in both the post-annealed samples; however it is very significant that the P_2 peak observed at ~360 K doesn't disappear after post-annealing at 380 K. In both the cases, a significant shift of the peak P_2 towards high temperature side has been observed but there is no dislocation of the peak P_3 due to the post-annealing treatments. The shift of peak P_2 towards high temperature side is due to the peak overlapping effect as discussed by McKeever [12]. Comparing both the glow curves it can be concluded that the glow curves of 380 K post-annealed samples are exactly identical with the 340 K post-annealed samples. The glow curves have been analyzed by CGCD technique and the results are reported in Table 2. The activation energies of the peaks P_2 and P_3 are found to be 0.61 eV and 1.30 eV respectively. These values are well consistent with the results obtained for pre-annealed samples.

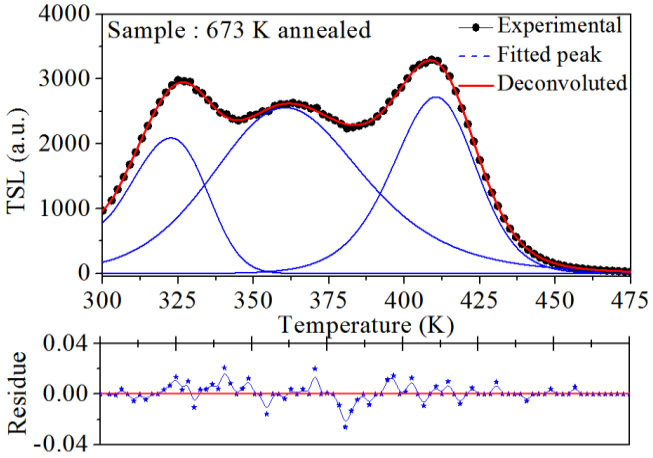

Figure 2. De-convoluted glow curve of 673 K annealed sample along with the residual of the fit.

Table 1. TL parameters evaluated by CGCD analysis.

Sample	Peak	T_m (K)	b	E (eV)	s (s^{-1})	FOM (%)
Un-annealed	P_0	472.0	1.15	1.49	2.54×10^{12}	0.14
	P_1	322.5	1.13	0.70	1.35×10^{11}	0.98
	P_2	360.0	1.90	0.60	2.47×10^{7}	
	P_3	412.4	1.10	1.30	1.36×10^{15}	
Annealed at 673 K	P_1	323.3	1.18	0.71	1.35×10^{11}	1.56
	P_2	360.2	1.93	0.61	1.56×10^{7}	
	P_3	410.4	1.20	1.29	5.26×10^{14}	

This analysis shows that during the excitation the electrons are excited and get trapped at the trapping sites. After excitation when the temperature of the sample increases, at temperature around 323 K, electrons release from the 0.70 eV trapping site and recombine with the holes resulting the P_1 TSL peak. Further, increase in temperature caused tunneling of a few electrons from 1.30 eV trapping site to 0.70 eV trapping site and from 0.70 eV trapping site direct recombination takes place at the recombination center. Due to this center-to-center recombination process, the peak P_2 has been

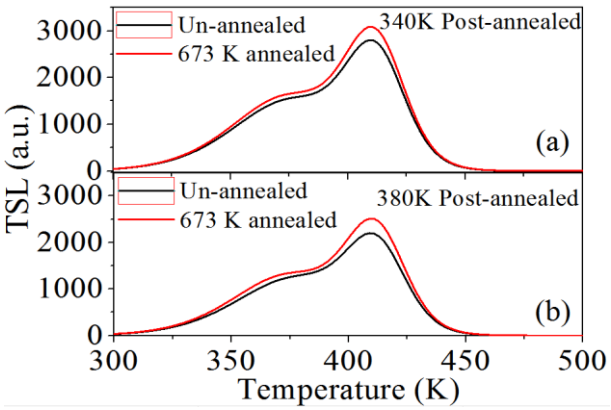

Figure 3. Glow curves of un-annealed and 673 K annealed samples after post-annealing at (a) 340 K and (b) 380 K for 6 minutes.

Table. 2: TL parameters of 340 and 380 K post-annealed samples evaluated by CGCD technique.

Sample	Post-annealing temperature (K)	Peak	T_m (K)	b	E (eV)	s (s^{-1})	FOM (%)
Un-annealed	340	P_2	370.3	1.10	0.60	1.50×10^{7}	1.25
		P_3	411.8	1.15	1.31	9.56×10^{14}	
673 K annealed		P_2	369.4	1.13	0.61	2.15×10^{7}	0.95
		P_3	411.8	1.22	1.31	8.18×10^{14}	
Un-annealed	380	P_2	369.5	1.11	0.61	1.43×10^{7}	1.32
		P_3	412.1	1.12	1.30	9.16×10^{14}	
673 K annealed		P_2	370.1	1.18	0.60	1.95×10^{7}	1.13
		P_3	412.2	1.23	1.30	7.47×10^{14}	

observed at relatively high temperature. However it is significant that, even after this temperature assisted tunneling process, sufficient numbers of electrons left on the 1.30 eV trapping site, and at temperature around 408 K, the residual trapped electrons release from that 1.30 eV trapping site and recombine with the holes that result the P_3 TSL peak. Due to this thermally assisted tunneling process the peak P_2 has not disappear in 380 K post-annealed sample. A plot of peak integrals versus the 340 K and 380 K post-annealed samples has been shown in Figure 4. It has been observed that the peak

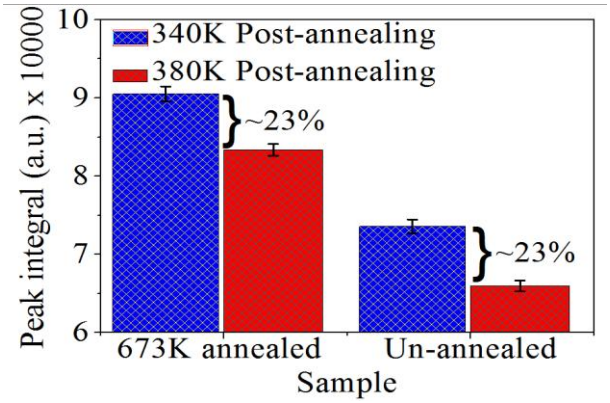

Figure 4. Plot of peak integrals versus the two different types of samples after post annealing at 340 K and 380 K.

integrals of 380 K post-annealed samples reduced to 23% from that of the 340 K post-annealed samples. This report quantitatively signifies that because of annealing up to 380 K for 6 minutes, approximately 23% of trapped electrons transferred from 1.30 eV trapping site to the 0.70 eV trapping site by the tunneling mechanism. This analysis quantitatively give support to the previous conclusion about the thermally assisted tunneling mechanism reported independently in Visocekas et al [13] and Kalita et al [14].

4. Conclusion

Thermally Stimulated Luminescence (TSL) mechanism of natural calcite mineral has been studied in detail. After X-ray irradiation a complex glow curve have been observed. De-convolution analysis reveals that the glow curve composed of three overlapping glow peaks having activation energy around 0.70, 0.60 and 1.30 eV respectively. The post-annealing treatments on the excited sample reveals that the there is thermally assisted tunneling of charge carriers from 1.30 eV to 0.70 eV trapping sites in calcite. Due to this tunneling mechanism a TSL peak having low activation energy has been observed at relatively high temperature. This analysis leads to an important conclusion that though theoretically the glow peak observed at relatively high temperature should have high activation energy, but due to charge tunneling phenomenon between the trapping sites, the glow peak that observed at high temperature may have relatively low activation energy.

Acknowledgment

Authors thank to UGC (University Grand Commission), New Delhi for providing the UGC major research project (Project No.: 42-910/2013 (SR)).

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