Evaluation of kinetic parameters of UV and gamma irradiated natural calcite

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Abstract: ***The present paper reports the thermo luminescence (TL) and chemical characterization of natural calcite collected from nandini mines of C.G. Basin. The sample was irradiated with Co-60 gamma source given a dose of 0.5kGy. The heating rate used for TL measurements are 6.7^{o}C/sec for the present study. The sample displayed a good TL peak around 294^{o}C and the corresponding kinetic parameters are calculated. Effect of annealing temperature is also described for natural calcite at 400^{0}C annealing temperature. Also TL glow curve recorded for UV irradiation using 254nm UV source. The induction coupled plasma activated emission spectra (ICP-AES) analysis was done to find out percentage of elements in the calcite mineral.***

Keywords: Thermo luminescence; annealing effect; ICP-AES, Kinetic Parameter.

INTRODUCTION:

Natural calcite and aragonite minerals are studied everywhere as used in construction industry, basic material for manufacture of cement and white washing powder and also used for wall painting and industrial pollution control. Naturally occurring minerals commonly exhibit the thermo stimulated luminescence (TSL) emission. Among these, quartz, calcite and fluorite are well-studied minerals because of their excellent TSL sensitivity. Calcite crystals are commonly found as a major constituent of limestone, speleothem, coral, etc. Calcites normally incorporate various impurities (Pb, Mn, Cu, Co, Mg, Fe, etc.) during crystallization. In earlier work on natural calcites, on both pure and natural minerals, TSL glow curves and TSL emission characteristics were studied by many authors [1–13].

MATERIALS AND METHODS:

The natural Calcite samples were collected from Nandini mines of C.G. Basin. 20 Micron size sample was prepared by grinding in a mortar and pestle. Sample studied for TL are annealed for 1 h at 400^{o}C, and immediately cooled to room temperature to remove any trapped water molecules in the mineral particles. The TL glow curve was recorded using TLD Reader Model No. I1009 supplied by Nucleonix Sys. PVT. LTD., Hyderabad. Detail of TLD reader is reported elsewhere [18 -20]. The sample was irradiated with Co-60 gamma source used to give a dose of 0.5kGy and the heating rate used for all the TL measurements are 6.7^{o}C/sec. The excitation source is a xenon lamp. The ICP-AES chemical analysis was done by ELAN DRC II at NGRI - Hyderabad.The sample (calcite) was characterized at Inter University Consortium (IUC) Indore for X-ray diffraction. XRD data were collected over the range 20-70 degrees at room temperature. The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of x-ray was 0.154 nm (Cu K-alpha). The X-rays were detected using the fast counting detector based on Silicon strip technology (BrukerLynxEye detector).

RESULTS AND DISCUSSION:

Fig.1 is the XRD patterns of the mineral under study. It can be concluded from the XRD the mineral is in single phase. The size of the particle computed from the width of first peak using Debye Scherrer formula.

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Where λ is the wavelength of X-ray, θ is the diffraction pattern angle and β is the corrected full width half maximum (FWHM) of the XRD peaks (corresponding to 2θ).

D = 0.9*1.54/0.17Cos (29.66) = 154nm.

The calculated crystallite size is 154nm. Which itself is interesting nature of the natural mineral under study. Corresponding d values calculated.

Table 1: Calculation for "d" spacing and FWHM (Full width half maximum)

S. No.	Position 2 θ	Net height (counts)	FWHM [Å]	d-spacing [Å]
1.	29.66	9192	0.17	3.00
2.	36.33	647	0.20	2.47
3.	39.83	862	0.27	2.36
4.	43.56	1580	0.16	2.07
5.	47.89	1536	0.24	1.89
6.	57.79	538	0.33	1.59
7.	61.23	421	0.48	1.51

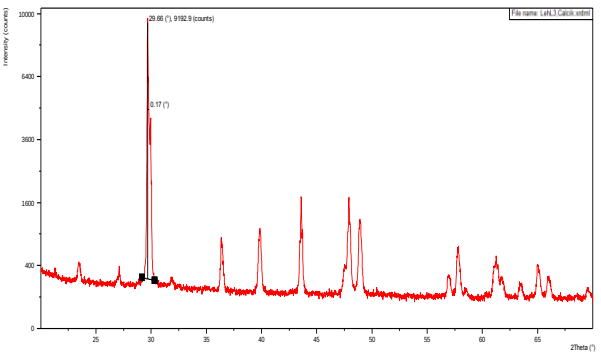

Figure 1 XRD pattern of natural calcite

Fig.2 show the TL glow curve of Calcite collected from Nandini mines of C.G. Basin. The mineral was irradiated with UV 365nm source and given a dose of 20 min UV. The heating rate used for TL measurements are 6.7°C/sec. The sample displays a well resolved TL peak at 388°C with other shoulder peaks 188°C, 305°C and the corresponding activation energy (E) values are calculated using the formulas modified by Chen and others [14-17]. The shape factors (μ), Activation Energy E and Order of Kinetics b and the trap depth for the prominent glow peaks of the studied Calcite, evaluated from second order kinetics are presented in Table 2.

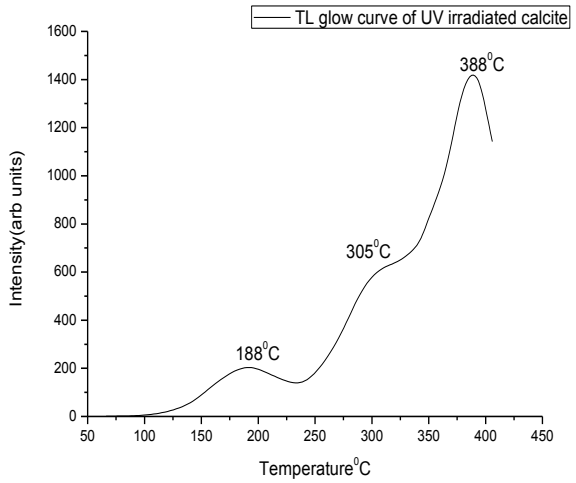

Figure 2 TL glow curve of UV irradiated calcite for 20 min UV exposure

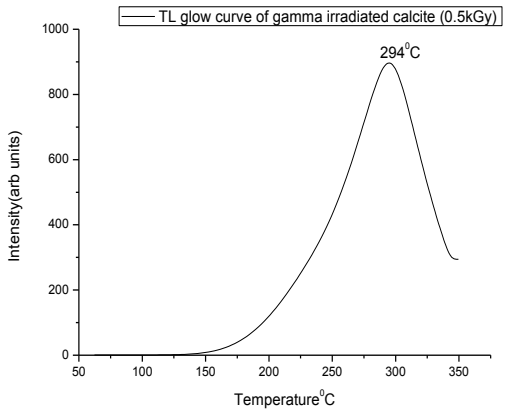

Figure 3 TL glow curve of gamma irradiated calcite for 0.5kGy gamma dose

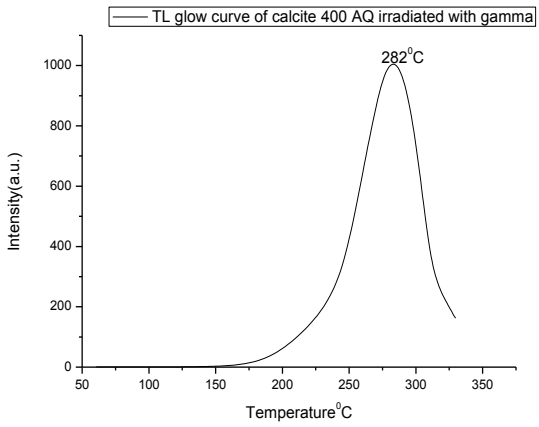

Figure 4 TL glow curve of gamma irradiated calcite for 0.5kGy gamma dose annealed at 400°C

TABLE.2: shape factors (μ), Activation Energy (E) and Frequency factor (s) of UV & gamma irradiated natural Calcite collected from Nandini mines of C.G. Basin

UV /gamma	T_1	T_m	T_2	τ	δ	ω	μ = δ / ω	Activation energy	Frequency factor
UV 20 min	348	388	406	40	18	58	0.31	1.37	3×10^{11}
Gamma 0.5kGy	253	294	329	41	35	76	0.46	1.00	9×10^{9}
400 AQ gamma 0.5kGy	251	282	306	31	24	55	0.43	1.27	5×10^{12}

The peak shape factor of 388^{o}C (figure 2) TL peak in calcite sample was found to be ~0. 31 which follows first order of kinetics. The values of E and s derived from different Chen's peak shape methods tabulated in Table 2. The TL kinetics, the activation energy, attempt to escape frequency of electrons in the trap associated with 388^{o}C were found to be first order 1.37eV, $3x10^{11}$ sec^{-1}.

For the peak at 294^{0}C (figure3) TL glow curve of gamma irradiated natural calcite the corresponding activation energy and frequency factor are calculate (Table1).

Fig.4 shows the TL glow curves of the mineral under study with annealed and quenching by 0.5 kGy gamma dose. It is found that as the annealing temperature increases the TL peak temperature shifts to lower temperature side.This is due to structural collapse of the mineral when heated at 400^{o}C. The remains are mainly CaO+ all the elements present in oxide form.

Table.3 is the results of induction coupled plasma activated emission spectra (ICP-AES) analysis

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Table.3. Elemental Analysis of Calcite using ICP-AES

Sample name	Ca (as CaO)%	Mg (as MgO)%	L.O.I. (in %)	SiO2 (Silica) %	Fe (as Fe_2O_3) %	Al (as Al_2O_3)%	Mn (as)MnO%	Other Trace Elements	Total (in %)
Calcite	58.38	0.98	37.09	1.78	0.20	0.24	0.26	1.07	100

CONCLUSION:

It is concluded that from the above study that the thermoluminescence studies of natural calcite for different exposure such as gamma and UV shows very good TL glow peaks at different temperature the activation energy is high for annealed natural calcite sample and low for gamma irradiated natural sample which indicates the formation of traps in natural calcite.

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