Thermo luminescence (TL) glow curve and kinetic of $CaZrO_3:Eu^{3+}$ phosphor

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Abstract: -Behaviour displayed by thermo luminescence(TL) glow curve analysis of Eu^{3+} doped $CaZrO_3$ phosphor prepared by combustion synthesis technique. The sample was synthesized by combustion method because it is less time taking method as well as low temperature synthesis method. The structural and morphology of prepared phosphor were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) technique. The XRD analysis indicated that the prepared phosphor shows cubic structure and particle size was determined by Scherer's formula. The particle size found ~36nm. The SEM analyses also confirm the formation of nano particles as well as connectivity with grain. For the thermo luminescence study the prepared sample irradiated by UV lamp the wavelength is 254nm. Every time 2 mg of sample use for TL record at fixed hating rate $5^0C\ s^{-1}$, sample shows well resolved higher temperature peak at 273^0C. The high temperature peak shows more stability and less fading in prepared phosphor which is suitable for TL dosimetry. Also the variation with UV dose (5 to 30min) shows sublinear response with dose. Both trapping and detrapping phenomenon occurs in the sample. The information about trap level formation is calculated by trapping parameters such as activation energy or trap depth, order of kinetics and frequency factor. All the trap parameters calculated by peak shape method. The trap depth calculation was done by different method for compare the activation energy.

Keywords: Thermo luminescence, kinetic parameters, trap depth, UV dose.

I. INTRODUCTION:

Alkaline earth zirconates belong to family of oxides with general formula $A^{2+}B^{4+}O_3$(where A=Ca, Pb, Sr, Ba, Zn, Ni, Fe; B=Ti, Zr, Si, Hf) having perovskite type structure[1–4]. ABO_3perovskites doped with acceptor-ions shows proton conductivity at high temperature, this makes its use in electrochemical devices[5]. Alkaline earth zirconate hosts are known for their outstanding properties like high thermal and chemical stability, single phase crystalline structure, high refractive index and wide band gap to have potential in electronic ceramic industry, gas sensors, optical coatings, filters and so on[6]. The zirconates being high temperature materials are used as a special class in crucibles for superconductor synthesis, refractory materials and deposition substrates [7]. The physical and chemical properties of this material can be greatly enhanced by doping of luminescent center induced by interaction of host and the dopant ion [8].

The dopant europium ion exhibits very interesting photoluminescence properties in different oxidation states. Eu^{2+} ion shows 5d-4f transition which can vary from ultraviolet to yellow emission. Xia et al. have reported blue and yellow emission in multiplex compounds of halides and borates e.g. bright yellow emission originated from $Ca_2BO_3Cl:Eu^{2+}$synthesized by solution combustion method and blue emission in novel $Ca_2B_5O_9Br:Eu^{2+}$ phosphor prepared by microwave method, which have proved to be promising phosphors for white light emitting diodes[9,10].

The present paper reports the thermo luminescence glow curve and calculation of kinetic parameters of Eu^{3+} doped $CaZrO_3$ phosphor. Sample was synthesized by combustion synthesis technique and the characterization done by XRD and SEM study. The TL glow curve of prepared sample with the variation of UV dose (5 to 30min) shows sublinear response with dose.

II. EXPERIMENTAL:

The starting reagents are high purity $Ca(NO_3)_2$, ZrN_2O_7, $Eu(NO_3)_3{\cdot}6H_2O$ and urea. Mixtures was mixed in stoichiometric amount of metal nitrates were dissolved in minimum quantity of deionized water in 200 mL capacity pyrex beaker. Then urea was added in this solution with molar ratio of urea to nitrates based on total oxidizing and reducing valencies of oxidizer and fuel (urea) according to concept used in propellant chemistry [8]. Finally the beaker containing solution was placed into a preheated furnace maintained at 550 °C. The material underwent rapid dehydration and foaming followed by decomposition, generating combustible gases. These volatile combustible gases ignite and burn with a flame yielding voluminous solid. Urea was oxidized by nitrate ions and served as a fuel for propellant reaction. The powders obtained were then further calcined from 700°C for 3 h to increase the luminescence efficiency [11].

The sample was characterized using XRD and SEM techniques. 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 a fast counting detector based on Silicon strip technology (BrukerLynxEye detector).Observation of particle morphology was investigated by SEM (scanning electron microscope) (JEOL JSM-6360).Thermally stimulated luminescence glow curves were recorded at room temperature by using TLD reader I1009 supplied by Nucleonix Sys.Pvt.Ltd. Hyderabad [12-14]. The obtained phosphor under the TL examination is given UV radiation using 254nm UV source. Heating rate used for TL measurement is 6.7^0Cs^{-1}.

III. RESULTS AND DISCUSSION:

The XRD pattern of the sample is shown in figure 1. The width of the peak increases as the size of the particle decreases. The size of the particle has been computed from the full width half maximum (FWHM) of the intense peak using Debye Scherer formula. Particle size of sample in the range 36nm is found. Formula used for calculation is

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

Here D is particle size

β is FWHM (full width half maximum)

λis the wavelength of X ray source

θis angle of diffraction

D = 0.9*1.54/0.252*Cos (30.36) =36nm

The structural information and particle size calculation is present in table 1.

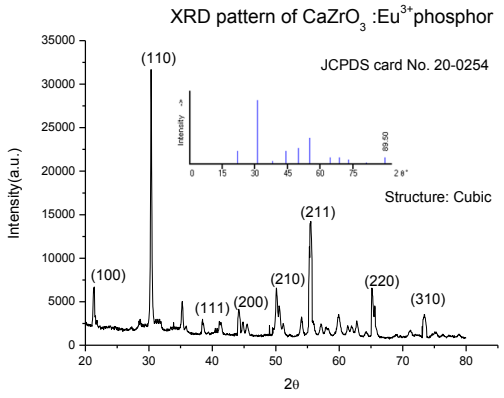

Figure 1 XRD pattern of $CaZrO_3$:Eu^{3+} (1 mol%)

Table 1 Structural analysis with particle size by XRD technique

S. No.	2θ	FWHM	D (nm)	h k l
1.	21.33	0.31	23nm	100
2.	30.36	0.20	36nm	110
3.	38.50	0.23	32nm	111
4.	44.20	0.25	30nm	200
5.	50.25	0.62	9nm	210
6.	55.47	0.36	15nm	211
7.	65.31	0.41	12nm	220
8.	73.42	0.32	22nm	310

From XRD technique it is found that the sample shows most of the pure phase there is no any effect of impurity ion on phasing of the sample. But some impure phase found which is negligible for that and the formation of impure phase is responsible for thermoluminescece glow curve of prepared sample. The nano crystalline pure cubic sample does not show any TL glow curve but in our sample the some impurity phase and defect formation due to combustion synthesis technique is responsible for good TL glow curve.

SEM result:

For surface morphology and particle size analysis was cleared by SEM analysis (figure 2). Here the prepared sample shows good morphology and connectivity with grain with some defects and agglomerates formation when sample was prepared by combustion synthesis technique. Here the particles are nano crystalline as well as some particles goes to micro crystalline range.

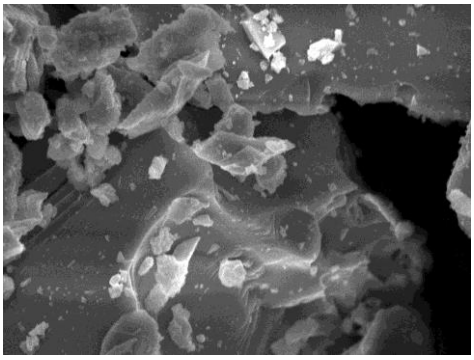

Figure 2 SEM image of $CaZrO_3$:Eu^{3+}

(2mol%)

Thermo luminescence glow curve:

The TL glow curve with the variation of UV exposure time at fixed concentration of Eu^{3+} (1 mol%) of $CaZrO_3$ phosphor shows good TL glow peak at 273^0C (figure 3). The behaviour displayed by TL glow curve with the variation of UV exposure shows sub linear response with dose firstly the TL intensity increase with increasing UV exposure time for 10minute after that it will be decreases with dose than after further increases up to 25 minutes UV exposure which results indicates that the high temperature peak shows high stability and less fading in TL glow curve. The prepared sample may be useful for TL dosimetry. However, thermo luminescence is a technical tool gives the information about trapping parameters. So the trapping parameters of prepared phosphor calculated by peak shape method with the variation of UV exposures. The knowledge about trapping parameters for calculating trap information in traps centre such as required energy for

escaping one electron from trap centre known as activation energy or trap depth "E" so the trap depth calculated by different methods proposed by several authors[15-18] (table 2). Also the order of kinetic and frequency factors are calculated (table 1). From different formula of trap depth calculation it is found that the most suitable formula given by Chen et al. [18]. The trap depth is found in the range of 0.72 to 0.91 eV and nearer match with different method for 25 minutes UV exposure time.

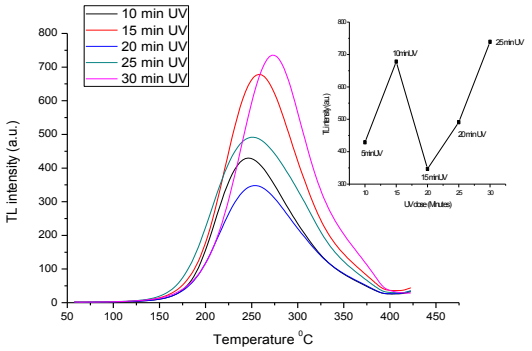

Figure 3 TL glow curve of $CaZrO_3:Eu^{3+}$(1mol%) with the variation of UV exposure time

Table 2 Calculation of kinetic parameters shape factors (μ), Activation Energy "E" and frequency factor "s"

UV Min	T_1	T_m	T_2	τ	δ	ω	μ = δ / ω	Activation energy	Frequency factor
5min	206	245	300	39	55	94	0.58	0.91	9×10^9
10 min	214	257	310	43	53	96	0.55	0.85	1×10^9
15 min	207	253	314	46	61	107	0.57	0.79	4×10^8
20 min	200	250	312	50	62	112	0.55	0.72	3×10^9
25 min	229	273	320	44	47	91	0.51	0.88	4×10^9

Table 2 The trap depth for the prominent glow peaks of the studied $CaZrO_3:Eu^{3+}$(1mol%) evaluated from second order kinetics

Methods	5 min UV	10 min UV	15 min UV	20 min UV	25 min UV
$E\ (eV) = T_m(K)/500$	0.49	0.51	0.50	0.5	0.54
$E(eV) = 23KT_m$	0.48	0.50	0.50	0.49	0.54
$E(eV) = 38KT_m$	0.80	0.84	0.82	0.81	0.89
$E\ (eV) = \frac{2KT_m^2}{\delta}$	0.18	0.21	0.18	0.17	0.27
$E_\omega = C_\omega \frac{KT_m^2}{\omega} - b_\omega(2KT_m)$	0.14	0.14	0.12	0.10	0.15
$E_\tau = C_\tau \frac{KT_m^2}{\tau} - b_\tau(2KT_m)$	0.12	0.11	0.095	0.074	0.12
$E_\delta = C_\delta \frac{KT_m^2}{\delta} - b_\delta(2KT_m)$	0.16	0.16	0.14	0.12	0.18

IV. CONCLUSION:

It is concluded that from above study the prepared sample synthesized by combustion synthesis techniques shows nano crystalline behaviour most of the peak from XRD are single phasing but some impurity formation occurs which is responsible for good TL glow curve. The particle size varies from 9 to 36nm range. Surface morphology was determined by SEM and it shows good connectivity with grains including some agglomerates and defect in the prepared phosphor. The optimized concentration of Eu^{3+} (1mol%) in host lattice $CaZrO_3$ shows resolved peak at 273^0C shows sublinear response with dose firstly intensity increases than decrease with UV dose both phenomenon trapping and detrapping occurs. The high temperature peaks shows the more stability and less fading in the prepared sample. The knowledge of kinetic parameters evaluated by different methods most of the peaks shows second order of kinetic the value of shape factor (μ)~0.52. Also the trap depth values variaes in between 0.73 to 0.91eV.

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