

Luminescence and impedance analysis of $\text{CaSiO}_3:\text{Tb}^{3+}$ nanophosphors material prepared by combustion method for OLED

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Abstract— Calcium Silicate acquires a higher luminous efficiency when it is doped with rare earth activated ions. The luminescence behaviour of unoped CaSiO_3 was investigated by a very few research groups. Effect of Tb^{3+} ion composition on the structural and phosphorescence properties from $\text{CaSiO}_3:\text{Tb}^{3+}$ nanocrystals has been evaluated using powders grown by the solution combustion technique. The surface morphology were analyzed by SEM and the chemical composition of phosphor characterized by EDX analysis. The XRD study indicates that as the terbium concentration increases the phase changes from CaSiO_3 to $\text{Ca}_3\text{Si}_2\text{O}_7$. Broad band emissions peaking between 280 - 360 nm derived from excited states of Tb^{3+} ions were observed for all powders grown from various Tb compositions. The green emission transition at 550nm due to an electronic transition of $^5\text{D}_4-^7\text{F}_5$ was found to be more prominent and intense. Intensity of afterglow phosphorescence was greatly influenced by the composition of the activator ions. It is found that the composition shows optimum PL properties at 7% of terbium Tb^{3+} ions concentration. The impedance spectroscopic study shows that the present phosphor shows electrical behavior like dielectric material in AC field. The activation energy of phosphor analysed by Chem's imperials formula in thermoluminescence analysis found to be 0.86eV. It is found that the prepared luminesce material is a new alternative for making cheap green organic light emitting diodes(OLED's).

Keywords—Impedance spectroscopic, Thermoluminescence, Photoluminescence, Energy Dissipative spectroscopic.

I. INTRODUCTION

Phosphors are widely used in photo emissive displays i.e. LED's, OLED's (Organic light emitting diodes) and FOLED (flexible organic light-emitting display) etc. The properties of thin films phosphor were highly influenced by structure, properties of the films and nature of the impurity added. To meet the current need of the optoelectronic applications such as flat panel displays, photovoltaic cells, smart windows, light emitting diodes and optical wave guides, solar cell, touch panel controls, electromagnetic shielding of CRT used for video display terminals, the phosphors should have high electrical conductivity and maximum optical transmittance in the visible region [1,2].

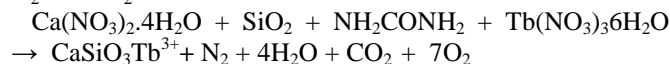
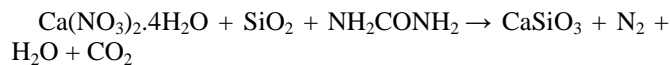
However, all currently used phosphors still need considerable improvement such as in lower current saturation, high efficiency, and better chromaticity [3]. Oxide phosphor (including silicate phosphor and Indium oxide In_2O_3 etc) is more chemically stable than other phosphors under high Coulomb loading. Metal silicates have been widely reported as promising host materials for rare earth

and transition metal ions with excellent luminescence properties in the blue, green and red spectral regions [4]. Calcium silicate phosphor would be ideal from the manufacturing point of view because both calcium and silica are abundant and are relatively inexpensive. The lanthanide ions doped alkaline earth silicates are an important class of phosphorescence materials because of their high quantum efficiency in visible region, long persistence of phosphorescence, good stability, colour purity and good chemical, thermal and radiation resistance [5]. The Tb^{3+} ion shows good luminescence performance in different bulk host materials and through the sol-combustion high quality powders with good crystallinity and homogeneous composition can be obtained at a relatively low temperature. In present paper it is used as an activator in calcium silicate hosts and its luminescence properties which mainly attribute to the $5\text{D}_3-7\text{F}_6$ (blue) and $5\text{D}_4-7\text{F}_0$ (green) is analysed. It is observed that with the increasing concentration of Tb^{3+} , the cross relaxation between the 5D_3 and 5D_4 energy level takes place which results in the enhanced green emission of $5\text{D}_4-7\text{F}_0$ transition [6,7]. Various experimental methods, such as sol-gel-microwave process, precipitation [8,9], combustion

reaction or microwave combustion methods[6], have been investigated to synthesis phosphors, among these methods, we here we introduce combustion reaction method because of low synthesis temperature and short reaction time. In the present paper we report the synthesis of $\text{CaSiO}_3:\text{Tb}^{3+}$ luminescent powders via the combustion process, and investigate their microstructure, luminescence and electrical properties as a function of the Ca:Si molar ratios and the Tb^{3+} doping concentration.

II. METHODOLOGY

Tb^{3+} -activated calcium silicate ($\text{CaSiO}_3:\text{Tb}^{3+}$) nanophosphors have been synthesized by means of simple combustion synthesis method. The starting material include calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; Merck), silica fumes (SiO_2 , 99.9% surface area $200 \text{ m}^2/\text{g}$), terbium nitrate $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and urea (NH_2CONH_2). Stoichiometric composition of the metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valences of the components. Mixture of these compound was placed over a muffle furnace and it heated upto a temperature of $700\text{--}800^\circ\text{C}$. At this temperature as the mixture undergoes dehydration and ignition, it release various gaseous products such as oxides of carbon and nitrogen etc. Once the materials ignited, the combustion propagates on its own without the need of any external heat. After combustion the silicate in foamy form was obtained. The chemical reaction in this process during combustion of the redox mixture for the synthesis of CaSiO_3 could be written as:



To determine the optimum amount of silica a series of phosphors was made in which the mole ratio of cation to silica was varied. The amount of activator that could be added to these phosphors was also varied from 0 to about 10%. XRD patterns of synthesized samples were recorded on an X-ray diffractometer with $\text{Cu K}\alpha = 1.5406 \text{ \AA}$, which was operated at 40 kV voltage and 40 mA anode current and the diffraction pattern were collected in 2θ values from 10° to 80° . Photoluminescence (PL) data were collected at room temperature using by RF- 5301PC SHIMADZU spectrofluorophotometer (RF- 5301PC) with a built-in 150 W xenon lamp as the excitation source and a grating to select a suitable wavelength for excitation. The kinetic parameters were determine by thermoluminescence (TL) analysis using Chem's imperial method. Surface morphology and EDX analysis performed with the help of SEM (JEOL-JSI microscope) fitted with EDX. The impedance spectroscopic method employ to determine electrical behaviour of

phosphor material at room temperature and above, in the frequency range 50 Hz to 5 MHz. A computer controlled multifrequency LCR Bridge (Model HIOKI 3520 - 01, Japan) was used during these measurements.

III. RESULTS AND DISCUSSION

3.1: X-rays diffraction Analysis

An XRD pattern of CaSiO_3 nanophosphors in which the concentration of Tb was changed from 1 to 10 mole % is shown in Fig. 1.

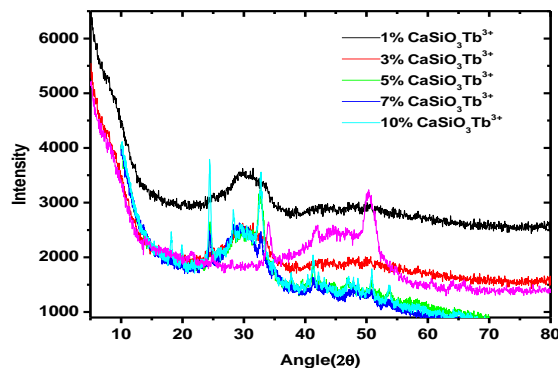


Fig. 1: The XRD pattern for $\text{CaSiO}_3:\text{xTb}^{3+}$ at different mole% of Tb

It reveals that the whole spectrum that can be indexed in peak position corresponds to crystalline hexagonal CaSiO_3 phase. The new peaks obtained on introducing terbium ion indicates that as the terbium concentration increase there is phase changes from CaSiO_3 to $\text{Ca}_3\text{Si}_2\text{O}_7$. The later phase may be favoured as a result of some Si sites is substituted by the Tb ions. The crystal field symmetry and hence the effect of field on the shifting of emission lines is strongly dependent on the relative contents of these two phases. The average crystallite size was calculated from the XRD pattern using Debye Scherrer relation $D = \frac{k\lambda}{\beta \cos\theta}$ where D is the crystallite size for the (hkl) plane, λ is the wavelength of the incident X-ray radiation [$\text{CuK}\alpha$ (0.154 nm)], β is the full width at half maximum (FWHM) in radiations, and θ is the corresponding angle of Bragg diffraction. It is seen that the X-ray diffraction pattern shows diffraction peaks at diffraction angle $2\theta = 25.1^\circ$ (1 1 1), 28.0° (2 1 1), 30.16° (20 1), 35.24° (2 1 0), 37.83° (3 1 1) etc. The crystalline size calculated corresponding to these angel based on the Debye-Scherer's formula, are $\sim 80\text{nm}$, 76nm , 71 nm , 69 nm , 68 nm , respectively and the average crystallite size is $\sim 68.50 \text{ nm}$.

3.2: Photoluminescence

The excitation spectra of the samples monitored at 545 nm is shown in Fig. 2(a). There are two bands at about 240 nm and 280–360 nm. The peak at 244nm corresponds to strong

absorption peak at obtained from spin-allowed transition of $7F \rightarrow 5D$ of Tb^{3+} . This is presumably resulted from the randomness of intense combustion process, and the strong influence of $f \rightarrow d$ transition of Tb^{3+} . It is subjected to two kind of host lattice and incompletely transformation from Tb^{4+} to Tb^{3+} owing to lack of reductive atmosphere. The group of weak peaks covering 280–360 nm belongs to $f \rightarrow f$ transition of Tb^{3+} in the two host matrix of $CaSiO_3$ and $Ca_3Si_2O_7$.

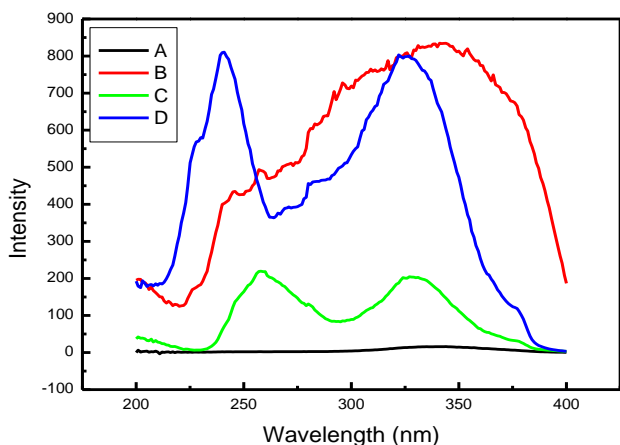


Fig. 2(a) Excitation spectra of $CaSiO_3:Tb^{3+}$ 1A Tb=1%, 1B Tb=3%, 1C Tb=5%, 1D Tb= 10%

The phosphorescence emission spectra of the $CaSiO_3:Tb^{3+}$ phosphors grown from various Tb^{3+} ions doping are showed in Fig. 2(b) that were obtained by exciting the samples at the wavelength 257 nm, and represent emission corresponding to transitions ($^5D_4 \rightarrow ^7F_{3,4,5,6}$). Particularly, the green emission transition at 545nm has been found to be more prominent and intense which is due to an electronic transition of $^5D_4 \rightarrow ^7F_5$ [10-12]. Such green strong emission displaying powder phosphors will find applications in the development of coated screens in certain electronic systems.

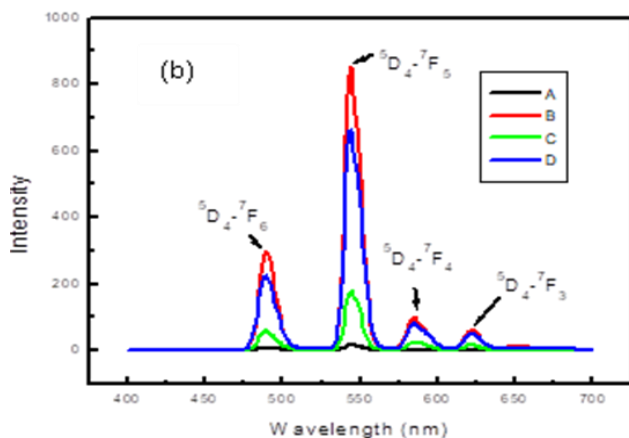


Fig. 2(b) Emission spectra of $CaSiO_3:Tb^{3+}$ 1A Tb=1%, 1B Tb=3%, 1C Tb=5%, 1D Tb= 10%.

The graph of maximum PL intensity of $CaSiO_3: x\% Tb^{3+}$ where x is the different percentages of Tb^{3+} ($0 \leq x \leq 10$) as a function of the Tb^{3+} concentrations is shown in Fig. 2(c) and the effects of Tb^{3+} ions is represented in Fig. (2d) where the position of the emission peak in the phosphorescence shows almost no change, regardless of the diversity of the Tb^{3+} ions doping.

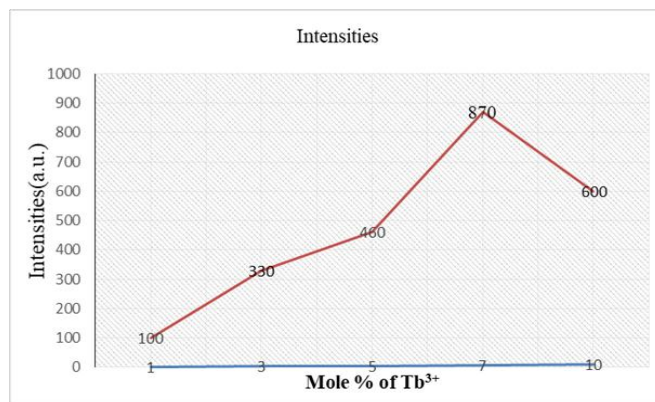


Fig. 2(c) Graph of Tb^{3+} ions concentration versus maximum peak intensity

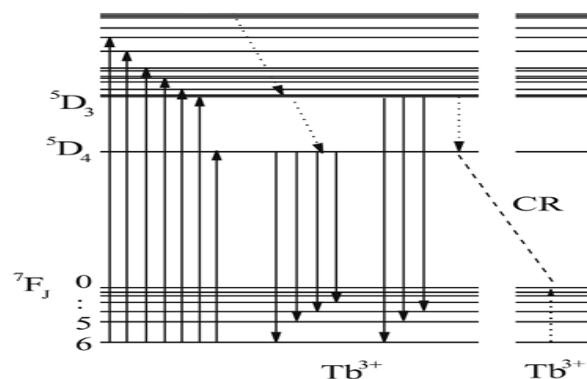


Fig. 2(d) Energy level scheme of Tb^{3+} ions in a crystal showing cross relaxation process [10]

It implying that no obvious change occurs in the crystal field effect on 5d electronic states of Tb^{3+} ions, even though the molar ratio of Tb^{3+} ions doping varies. It also represent that the PL spectrum of $CaSiO_3:Tb^{3+}$ (7%Tb) is the highest intensity than the other Terbium concentrations and has a band around 540nm in a green region. An increase in Tb^{3+} concentrations up to 7% Tb^{3+} ions increases the luminescence intensity possibly due to an increase in activator centres. Further increase in Tb^{3+} ions above 7% result in luminescence quenching caused by cross relaxation processes. The emission peaks intensity increased when the amount of Tb^{3+} increased, and a maximum value was found in the $x=7\%$ sample, thereafter the emission intensity

quenches gradually. Persistent luminescence curves of the phosphor powders were shown in Fig. 3.

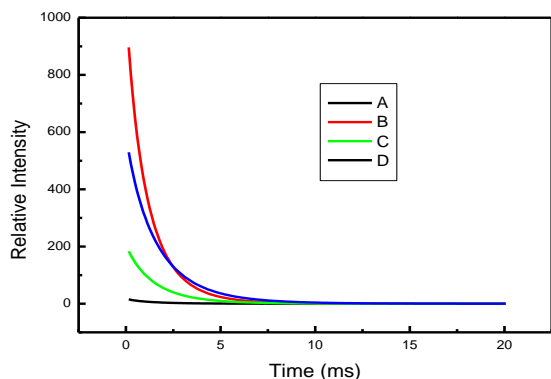


Fig. 3 Afterglow characteristics of $\text{CaSiO}_3:\text{Tb}^{3+}$ 1A Tb = 1%, 1B Tb = 5%, 1C Tb = 7%, 1D Tb = 10%

It can be seen from the curves that the materials showed differences in initial intensity and medium persistence when they were efficiently activated by fluorescent lamp. The results indicate that the initial luminescence intensity and the decay time of phosphors are enhanced with increase in Tb^{3+} concentrations. The sample with Tb =7% significantly enhanced the initial luminescence property of the green luminescence.

The decay behaviour can be analysed by curve fitting [11, 12], relying on the following triple exponential equation:

$$I = I_1 \exp\left(-\frac{t}{\tau_1}\right) + I_2 \exp\left(-\frac{t}{\tau_2}\right) + I_3 \exp\left(-\frac{t}{\tau_3}\right)$$

where I represents the phosphorescent intensity; I_1, I_2 and I_3 are constants; t is the time; τ_1, τ_2 and τ_3 are the decay constants, deciding the decay rate for the rapid, medium and slow exponentially decay components, respectively. The fitting results of parameters of τ_1, τ_2 and τ_3 are listed in Table 1.

Table 1 Results for fitted decay curves of the phosphor powders with different Tb^{3+} moles.

Tb moles %	1	5	7	10
Component	Decay constants (ms)			
Fast (τ_1)	0.89	0.31	0.27	0.99
Medium (τ_2)	2.21	1.03	1.30	0.99
Slow (τ_3)	1.38	1.93	2.36	2.18

Three components namely slow, medium, and fast component are responsible for the persistent luminescence

from the synthesized phosphor. A trend can be observed that the decay constants of the phosphors decrease gradually with the increasing of Tb^{3+} ions doping to $\text{CaSiO}_3:\text{Tb}^{3+}$ phosphors.

3.3: Impedance Spectroscopic analysis of phosphor

The electrical properties were measured by impedance spectroscopy method in the frequency range 50 Hz to 5 MHz at room temperature using LCR meter. The impedance plots (Z' vs Z'') of prepared phosphor electrolytes at room temperature are shown in Fig.4.

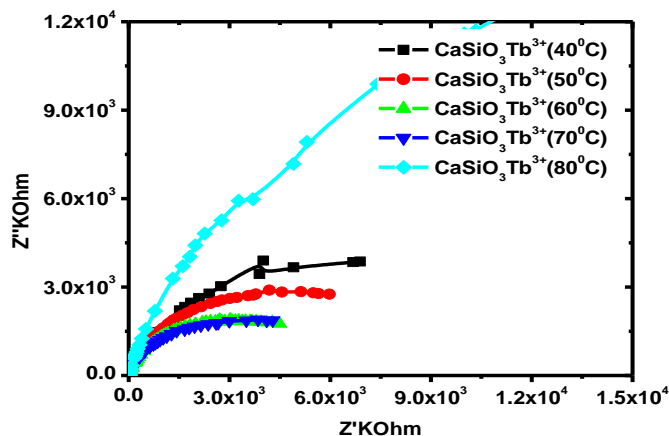


Fig. 4: Cole cole plot of Tb^{3+} in CaSiO_3 at different temperature

It showed a normal impedance behaviour such as a depressed semi-circular portion [15]. It shows the bulk relaxation at high frequency, in addition to the dc conductivity tail at low frequency. The high frequency semicircle corresponds to the bulk response of the films. These results suggest that the migration of ions may occur through the volume of calcium silicate. At lower temperatures < 50°C, the shape of the plots tends to straight line with a large slope indicating the low conducting behaviour of the sample. The temperatures at and above 50°C the slope of the curve decreases, bowing up to the real axis. The Z' vs. Z'' curve is composed of two semicircles, a small semi-circle at high frequencies indicates the effect of grain and large semicircle at low frequencies indicates the grain boundary effect

3.4: DIELECTRIC PROPERTIES

The frequency dependence of impedance and dielectric loss are shown for the calcium silicate nanocomposite film is investigated, at 313K to 353C, as shown in Fig: 5. This figure shows a plateau in the high frequency window physically means that the polarization within the sample can't go up with rate of polarity change of the applied field. This means that there is no significant effect of frequency at any temperature. Further decrease of the frequency increases the Z' values accompanied by spreading out according to the

measuring temperatures. These high values of impedance and the dispersion within the lower frequency window indicate Interfacial polarization i.e. Maxwell-Wagner-Sillars, MWS, which means blocking of rare earth ion at the internal grain boundary layers.

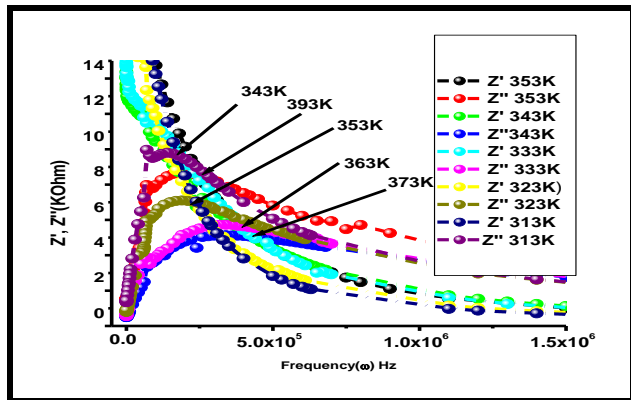


Fig.5: Permittivity and dielectric loss spectra for calcium silicate Tb^{3+} at different temperature.

The high values seen in both dielectric properties at low frequencies may be originated from separation of ions at the interface and/or dc conductivity [16,17]. More inspection of the figure shows that there is more effect of measuring temperature in spreading out the permittivity values in case of room temperature. This may be explained according to the hypotheses of the presence of some moisture in case of samples that raising reasonably the effect of measuring temperature and/or the slowly aging at room temperature allowed better arrangement for the molecular and atomic structure of the sample by increasing time for more homogeneity for the silica distribution within the sample than that aged at 353K which didn't have that time for the proper homogeneity to occur.

Frequency dependence of the dielectric shows the loss (Z''), may indicate two relaxation processes in case of 353K. Both become faster and of higher intensity in increasing measuring temperature. The lower frequency peak supposed to be due to the well-known MWS-polarization whereas the higher frequency one describes a relaxation dynamic on the molecular scale. On the other hand the separation between the two peaks is vanished in case of room temperature instead became a very broad shoulder. Further, Z'' at room temperature film shows an increase with increasing measuring temperature indicating positive temperature coefficient (PTC) whereas it shows some deviations for that at higher temperature. The calcium silicate Tb^{3+} film as shown in Fig.5. has the same attitude except intermediate temperature. For both sample at room temperature both peaks are merged showing one broad, shoulder like, peak.

III.CONCLUSION AND FUTURE SCOPE

The $Ca_xSi_yO_z:Tb^{3+}$ phosphor was synthesized by solution combined process showing crystalline structure. The initial luminescence intensity and the decay time of phosphors are enhanced with increase in Tb^{3+} concentrating, with $Tb = 7\%$ it shows optimum luminescence property of the green luminescence.

The luminescent properties of the phosphors can be greatly modified by the doping of Tb^{3+} ions. The phosphorescence emission spectra with an appropriate amount of Tb^{3+} result in a very intense and bright initial phosphorescent emission. The samples at the wavelength 257 nm, represent emission corresponding to transitions ($^5D_4 \rightarrow ^7F_{3,4,5,6}$) the green emission transition at 545nm has been found to be more prominent and intense which is due to an electronic transition of $^5D_4 \rightarrow ^7F_5$. Phosphorescence decay time is found to be influenced greatly by the terbium composition of the phosphor. The impedance spectroscopy analysis showed a decrease with increasing frequency while they showed increase with increasing measuring temperature. Generally, both ϵ' and ϵ'' values became closer to each other at frequencies $> 10^3$ Hz. The improvement in structural performance of the prepared films make them candidates for various applications. Present study is helpful for future researcher to work in the field of luminescence and search new alternative cheapest and highly luminesce material for device application i.e. LED,s, or OLED,s.

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Dr. Nirbhay Kumar Singh Assistant Professor having their research interest in the field of material science, Luminescence and computational chemistry. Having their contribution in various national and international research journal.



Mr Ohm Prakash Verma working in the field of Organic Light emitting diodes. He is mainly working on computational chemistry. Many research based on SIESTA software for the analysis of various properties of material is introduced by him.

