

# Europium doped silicate phosphors: Synthetic and characterization techniques

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## Abstract

In this review article, different synthetic procedures and characterization techniques used for the development of materials are discussed briefly. The stability and high luminous intensity of silicate materials makes them practically important in the field of white light emitting diodes (WLEDs). During the experimental designing of our research, we have understood carefully the theoretical and methodological strategy regarding the synthesis of phosphors and then, a large number of silicate based luminescent materials have been prepared using sol-gel technology. Among them, a series of silicate materials having composition  $M_{(2-x)}Eu_xSi_2O_7$  ( $M = Y, Gd, La$  and  $x = 0.03$  moles) have been described in this review prepared with sol-gel process. Intense peak in europium (III) doped  $M_2Si_2O_7$  silicates originate from  ${}^5D_0 \rightarrow {}^7F_2$  transition of  $Eu^{3+}$  ion available in crystal lattices. X-ray diffraction pattern have triclinic structure for  $Y_2Si_2O_7$  and  $Gd_2Si_2O_7$  silicate phosphors. However, hexagonal and monoclinic structures are obtained for  $La_2Si_2O_7$  material at different temperatures employed for further annealing. Transmission electron microscopic analysis is used to study the morphology and particle size of prepared phosphors. Excellent luminescence response of these silicate phosphors make them suitable for photonic applications and also open up new avenues for solid state lighting, cathode ray tubes, fluorescent lamps and scintillators etc. Copyright © 2017 VBRI Press.

**Keywords:** Silicate,  $M_2Si_2O_7$ , europium, luminescence, sol-gel, crystal lattice, solid state lighting.

## Introduction

Special interest has been shown by material scientists for the exploration and characterization of silicate based luminescent materials because of their low cost, high stability and moisture resistant properties [1]. Rare earth doped silicate materials possesses high luminescence efficiency and also reflects some remarkable optical, electrical and magnetic properties [2]. When rare earth ions are doped into the silicate host, then optomagnetic properties of the materials get changed due to the occupation of metal ion sites by doped ion in host lattice. Therefore, spectroscopic properties of doped ions should be kept in mind during the design and development of advanced silicate phosphor materials having specific practical approach in white light emitting diodes. For the research and development of white LEDs, highly efficient and stable red silicate materials having low color related temperature and high color rendering index are required [3-7].

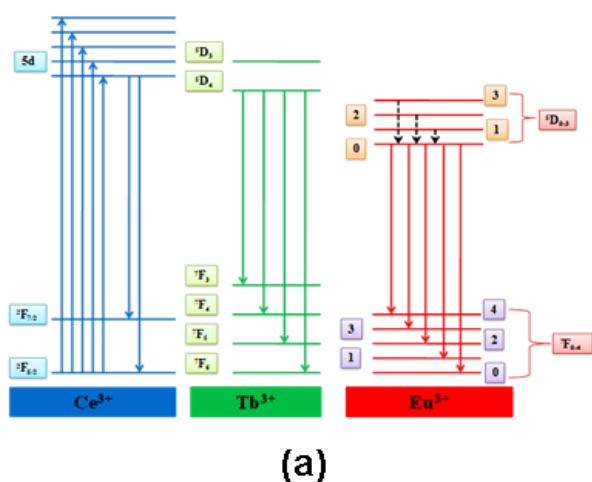
Disilicates of rare earths have been widely studied and then special attention is focused to the host lattices of  $Y_2Si_2O_7$ ,  $Gd_2Si_2O_7$  and  $La_2Si_2O_7$  materials because of their potential applications in the field of nuclear medical diagnostics, high energy physics, positron emission tomography (PET), plasma display panels, flat panel display, for ionizing radiation detection, solid state lighting and for gamma ray and thermal neutron

monitoring etc [8-11]. When these materials are doped with lanthanide ions, then they show excellent luminescence response that can be used in lasers and several display devices for example  $Y_2Si_2O_7$  material when doped with Cerium (III) ion finds its practical applicability in cathode ray tubes [12].

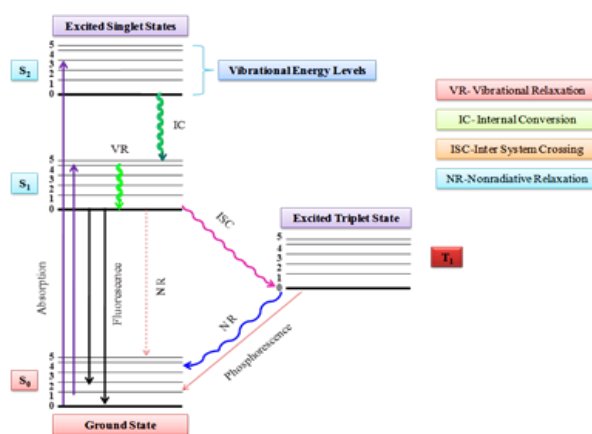
A large number of disilicates having chemical formula  $RE_2Si_2O_7$  ( $RE = Sc, Y, Ln, Sm, Eu, Ho, Er$ ) are known for their polymorphic structures [13]. Disilicates of Samarium, Europium, Holmium and Erbium (III) all exhibit a high degree of polymorphism reflecting unstable ( $4f^5$ ,  $4f^6$ ,  $4f^{10}$  and  $4f^{11}$ ) electronic configuration of these ions in this state. Crystal chemistry of these rare earth disilicates is found to be quite complicated because the phase of these materials changes with temperature. From the past time, many efforts have been made for developing new silicate materials having excellent luminescence properties. Europium (III) doped  $M_2Si_2O_7$  ( $M = Y, Gd$  and  $La$ ) are also very efficient phosphor materials and exhibits the phenomenon of polymorphism. Over the past decades, different synthetic procedures were used for preparing  $M_2Si_2O_7$  type of luminescent materials like solid state reaction [14-17], spray pyrolysis [2], solution combustion method [18] and hydrothermal method [19-21] etc. But, sol-gel technique is an attractive and potential alternative for the synthesis of silicate phosphors because it is much simple, has high chemical homogeneity, low processing temperature, controls the

size and morphology of the particles and has good optics transparency [22]. Currently, there is growing interest in preparing disilicates by sol-gel process at low temperature [23-25].

The aim of present review is to briefly explain the different synthetic procedures and characterization techniques used to develop silicate based phosphor materials with their future prospectives. A series of Europium (III) doped  $M_2Si_2O_7$  ( $M = Y, Gd$  and  $La$ ) silicate phosphors has been synthesized using sol-gel technique at 950 °C. X-ray diffraction analysis is carried out to know the structural aspects of these prepared materials. Knowledge of crystal structure and phase transitions is important to improve the luminescence properties of phosphor materials. Prepared silicate phosphors have also been characterized using more techniques like Photoluminescence analysis (PL), Fourier transform infrared spectroscopic analysis (FTIR) and Transmission electron microscopic analysis (TEM) etc.



(a)



(b)

**Fig. 1.** (a) Energy level diagram showing different transitions of rare earth (III) ions like europium, terbium and cerium and (b) Jablonski diagram illustrating the mechanism of luminescence in phosphors.

### Synthetic strategies

Different man-made methods have been used by researchers for preparing silicate based phosphor materials. Phosphors are the highly pure inorganic materials consisting of a small amount of activator ion and an inert host matrix. Different host lattices may be

used like oxides, sulfides, silicates, aluminates, borates, alumino-silicates, halides, nitrides, oxy-nitrides, selenides, stannates, phosphates, titanates etc. for exploring phosphor materials [26-31]. The function of host lattice is to absorb the incident radiation and transfer it to the activator ion. Rare earth ions are widely studied for selecting a suitable activator ion in combination to a host lattice. Synthetic methods used for material exploration also depend upon the spectroscopic properties of these activator ions. Most commonly used activator ions are europium, terbium and cerium. Red phosphor materials are prepared by doping europium (III) ions that emits strong orange-red light. Green emitting phosphor materials are prepared by doping terbium (III) ion as an activator. Europium (II) and cerium (III) ions are the blue emitting ones used for synthesizing blue phosphors. Europium (II) also emits green light but that depends upon the type of host lattice used for material synthesis. The energy level diagram of these activator ions are shown in (Fig. 1a) illustrating the different transitions. In silicate phosphors,  $Eu^{3+}$  ion shows spectral peaks due to  $^5D_{0-3} \rightarrow ^7F_{0-4}$  transitions. After studying an immense volume of literature, it is logical to say that different synthetic routes have been proposed by researchers for materials exploration and these are discussed briefly.

### Solid state reaction

Basically, Solid state materials chemistry concerns with the physical and chemical properties of materials in solid state. This method is used to prepare a wide range of materials like aluminates, silicates, alumino-silicates, nitrides, sulfides and a number of metal oxides. A large number of reactions were experimented out for silicate synthesis using this method.  $La_2Si_2O_7$  silicate materials were synthesized using solid state method [32]. The composition  $La_{9.33-x}Sb_x(SiO_4)_6O_2$  where ( $0 \leq x \leq 2.0$ ) of ceramics were successfully explored for solid oxide fuel cells using this synthetic route [33]. Traditionally,  $Y_2Si_2O_7$  silicate material was prepared by solid state reaction between yttrium oxide and silicon oxide at high temperature (1200-1600 °C) using more durations of time (100 h) [34].  $Eu^{2+}$  doped strontium silicates were also produced using solid state reaction method [35].

The starting materials used for silicates synthesis must be highly pure, have fixed composition and in powder form. Stoichiometric amount of initial precursors like oxides of metals, dopant and silicon are weighted, ground and mixed in agate mortar [14]. For silicates formation, precursor solution may also be prepared by dissolving stoichiometric amount of metal carbonates and silica powder in distilled water and then undergoes stirring at low temperature [36]. Different fluxes like  $Li_2CO_3$ ,  $NH_4F$ ,  $NH_4Cl$ ,  $BaF_2$ ,  $YF_3$ ,  $AlF_3$ ,  $H_3BO_3$  [37] etc. are also added to the initial precursors in order to improve the crystalline nature of materials, speeds up the reaction rate and lowering the reaction temperature. Flux increases the luminous efficiency of powders and also affects the morphological characteristics of silicate materials [38, 39]. Reaction conditions and structural properties of the reactants affect the feasibility and rate of reaction. Reaction occurs very slowly at low temperature, but,

increase in temperature enhances the diffusion rate between reactants, provides the necessary energy and hence increases the rate of reaction. Thus, solid state synthesis is carried out at high temperature (1200-1600 °C) so that reaction occurs at an appreciable rate. Finally, inorganic luminescent materials are prepared in the powder form or as single crystal. Easy availability of starting materials and simplicity of this method is useful for preparing a large number of phosphor materials. This method is environmental friendly and no toxic waste is produced after the completion of reaction. The final product is structurally pure and in powder form having desired properties. This method gives rise to thermodynamically stable products. But, one of the main short coming of this method is that reaction time is very long and high temperature processing conditions are required for material synthesis which enhances the particle size of materials. This technique is considered to be poorly efficient due to the ease of mixing with impurities [40]. Repeated milling and washing with chemicals tends to degrade the luminescence property of materials and gives deformed shaped crystals.

#### *Co-precipitation method*

Co-precipitation is also one of the simple, convenient, easy to set up and cost effective method to produce magnetite, maghemite and silicate based nanoparticles [41]. Several silicate based luminescent materials have been prepared by co-precipitation process.  $\text{Sr}_2\text{MgSi}_2\text{O}_7$ :  $\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  materials were prepared by this synthetic procedure. Preparation was done using APTES (aminopropyl) triethoxy silane) to carry out the precipitation of metal nitrates [42]. Co-precipitation process gave rise to  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  and (Y, Gd)  $\text{SiO}_5$ :  $\text{Tb}^{3+}$  green emitting materials [43, 44].  $\text{La}_{9.33+x}\text{Si}_6\text{O}_{26+1.5x}$ , where, ( $x = 0-0.67$ ) composition was also investigated by this method using  $\text{NH}_3$  as a precipitant [45].

Silicates materials are prepared by keeping in mind the composition of final products. T. T. H. Tam *et al.* synthesized  $\text{Eu}^{2+}$  doped  $\text{Ba}_2\text{MgSi}_2\text{O}_7$  silicate materials using the procedure given here [46]. Dissolved the stoichiometric amount of metal nitrates in distilled water and correspondingly dissolved tetraethyl ortho silicate along with activator oxide in ethanol and nitric acid solution. Aqueous form of all these initial precursors was allowed to stir for one hour till the formation of homogenous solution. After that, they were allowed to mix and stirred again continuously for three hours. Consecutively, a stoichiometric amount of ammonium hydroxide solution was also added to carry out the precipitation process. The resulting solution was then continuously stirred at 100 °C, till there was the formation of white gel. Then, allowed the gel to dry at 200 °C. Further the sample was calcined at high temperature for more duration of time. Grinding of the powder was done with the help of agate mortar. If the doping of  $\text{Eu}^{2+}$  ion occurred, then as prepared powder undergo ion reduction using  $\text{H}_2/\text{N}_2$  (10 %) mixture of the gas at high temperature for long time. In co-precipitation process, pH is the most important factor that must be carefully controlled for single phase product formation. Several other factors also

influences the co-precipitation process like concentration of starting reactants, precipitant concentration, separation of solid precipitant from filtrate and drying and calcinations of powder form of materials.

According to modified co-precipitation method [47], some changes have been reported during the process of silicates formation. In this modified technique,  $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$  powder was dissolved in  $\text{C}_2\text{H}_5\text{OH}$  with some drops of nitric acid and then stirred the solution for about half an hour. Further, stoichiometric amount of activator and metal nitrates dissolved in DMF (N, N-dimethyl formamide) solvent was slightly heated for complete dissolution of precursors. After the appearance of transparent solution, this mixture was allowed to cool at room temperature and then added silica solution to this mixture gently with continuous stirring. Subsequently, sodium hydroxide solution was added into the mixture to carry out the precipitation process. Again solution was stirred for some more time. Filtered the precipitate obtained and washed with  $\text{C}_2\text{H}_5\text{OH}$ . The precipitate was allowed to dry at 80 °C for some more duration of time. Finally, the sample was calcined to high temperature. If  $\text{Eu}^{2+}$  ion was used as a dopant, then use reductive atmosphere of  $\text{H}_2$  and  $\text{N}_2$  and then allowed to cool the sample.

In the Modified co-precipitation process, DMF was used as a solvent because initial precursors like metal nitrates and chlorides can be suitably dissolved in this solvent. It was used to avoid the agglomeration of silicate particles by reducing the rate of precipitation reactions. Co-precipitation method requires very low reaction temperature, gives rise to uniformly distributed nanosized materials and suitable for large scale production of phosphor materials. However, there is wide agglomeration, poor grain size distribution and morphological study of nanoparticles prepared using this method.

Now these days, Modified Co-precipitation technique is used to overcome these limitations. In this method some stabilizing agents are used to achieve better particle properties of luminescent materials. To carry out reaction in modern co-precipitation technique, inert atmospheric conditions are employed to carry out reduction process.

#### *Spray pyrolysis method*

Spray Pyrolysis is one of the most common, inexpensive, simple and quite versatile method used for synthesizing the sub-micron and spherical shaped luminescent materials [48, 49], multi component oxides, chloro silicates, metals, catalysts and nano powders [50-53]. Spray pyrolysis is a continuous and single step process that gives rise to the materials having finite size and uniform shape of particles in non-aggregated form. Spray pyrolysis may be applied in the form of aerosol spray pyrolysis or flame spray pyrolysis for producing phosphor materials. FSP (Flame Spray Pyrolysis) is the modified form of ultrasonic spray pyrolysis.

Different silicate based reactions were experimented out by spray pyrolysis process.  $\text{Y}_2\text{Si}_2\text{O}_7$ :  $\text{Eu}/\text{SiO}_2$  core shell luminescent materials were synthesized using flame spray pyrolysis technique. In these silicate materials, a

phosphor core present at the centre was surrounded by a silica coating. This coating helped in stabilizing the surface of particles and resulted into luminescence enhancement of core materials [54]. Mn doped  $Zn_2SiO_4$  materials were synthesized by this technique using filter expansion aerosol generator [55].  $Ca_8Mg(SiO_4)_4Cl_2$  luminescent materials doped with europium was successfully synthesized using pyrolysis technique from the colloidal solution having  $NH_4Cl$ . Europium doped barium strontium silicate materials were also explored using pyrolysis process in the presence or absence of ammonium chloride as a flux [56]. This technique gave rise to  $Y_2SiO_5$ ;  $Tb^{3+}$  green emitting materials having  $NH_4F$  as flux [57].  $Eu^{2+}$  doped strontium silicate phosphors were also prepared using this technique and characteristics of the powder were studied with or without the addition of flux like  $NH_4Cl$  [58].  $Eu^{3+}$  doped  $La_2Si_2O_7$  materials were explored using spray pyrolysis process and their photoluminescence characteristics were also studied. Mechanical activation effects on yttrium disilicates formation was studied in 2001 by G. Tzvetkov and N. Minkova.

Process of spray pyrolysis used for material synthesis completed in 4 steps. Drop formation occurred from the precursor in first step which on evaporation resulted in shrinkage of drop size. Now, precursors got transformed into oxides that resulted in the formation of solid products at the last step [48]. The experimental set up involved an ultrasonic generator to produce droplets, filter precipitator and burner. The precursor solution was prepared by dissolving metal nitrates, corresponding activator ion and silica content in deionized water. For aerosol formation of precursor, the initial solution was allowed to set on an ultrasonic vibrator. Now,  $O_2$  and fuel gas ( $CH_4$  diluted with  $N_2$ ) was provided via outer and inner circular coaxial tube for oxidation of precursor aerosols. Vacuum pump was also used to withdraw the aerosol. Finally, silicon fibre filter was used for collecting the particles [54]. Later on, some changes were made during the processing of silicate formation, where, prior to filtration, the precursor aerosols were preheated in the furnace at low temperature for solvent evaporation and then, introduced in furnace at high temperature for decomposing the precursors. There is a good control on the chemical composition and morphology of products [59] which are highly pure and homogenous. However, materials synthesized using large scale spray pyrolysis technique has hollow and porous nature which is a major drawback. This hollowness or porosity has strong effects on the thermal stability and morphological characteristics of the phosphor materials. To overcome the limitation of hollowness or porosity, modified spray pyrolysis technique is proposed where artificial colloidal solution has been employed for material synthesis [60].

#### Hydrothermal method

Hydrothermal is a single step, low temperature, high yield, cost effective, more controllable [61-63] and scale up method used for synthesizing submicron to nanosized advanced materials. According to K. Byrappa and M. Yoshimura “the term hydrothermal refers to any heterogeneous chemical reaction in the presence of a

solvent (whether aqueous or nonaqueous) above room temperature and at pressure greater than 1 atm. in a closed system” [64]. Hydrothermal processing is used to synthesize powders, single crystals, fibers and ceramic materials [65]. It is a self purifying technique which requires low processing temperature and used to explore nanomaterials at high vapour pressures and temperature.

Nekrasov and Kashirtseva reported the synthesis of  $Y_2Si_2O_7$  materials using hydrothermal method. But, there was the requirement of long processing time (nearly 100 days) for the single phase  $Y_2Si_2O_7$  product formation at  $300^\circ C$  [12]. Yttrium disilicates materials were also prepared by Ana. I. Becerro and others using hydrothermal technique at  $365^\circ C$  [66]. Z. Sun *et al.* also synthesized  $Y$ - $Y_2Si_2O_7$  materials at  $1400^\circ C$  by pressure less solid liquid reaction method. They reported the effect of different concentrations of additive ( $LiYO_2$ ) on the single phase evolution of this material. When there was no additive, diffraction profile represented a mixture of all  $Y_2SiO_5$ ,  $Y$ - $Y_2Si_2O_7$  and  $Y_{4.67}(SiO_4)_3$  phases in the sample. But, when the powder was calcined at  $1500^\circ C$  for 8 hour then 3 mole percent concentration of this additive was found to be suitable for single phase evolution of  $Y$ - $Y_2Si_2O_7$  material [67]. Crystals which are unstable near the melting point can also be synthesized using hydrothermal technique. There is no need of further reheating in powders obtained by this method that prevents the particles from agglomerations. The resulting products are highly pure and homogenous having a good control on morphology of materials. The product formation occurs at low temperature reaction conditions. But, the main limitation of this method is that there is the requirement of expensive autoclaves and long processing time for carrying out the reactions.

Now a day, hydrothermal method has been coupled with various other processes including ultrasound-assisted, electrochemical-assisted, surfactant-assisted and microwave-assisted hydrothermal processing to control the reaction medium and improve the material characteristics [64]. Today, Modified microwave assisted hydrothermal synthesis is in trend for preparing these phosphor materials which reduces the processing time and energy required for carrying out the reaction. This method also has a potential to improve the material characteristics like morphology and crystallite size of particles.

#### Combustion method or self propagating high temperature (SHS) synthesis

Combustion is a simple, rapid, versatile, low cost and effective method for producing a wide range of technologically useful oxides, ceramic, catalysts and nano sized phosphor materials [68-70]. This is one of the most suitable and scale up method for producing highly pure and homogenous products having desired properties of phosphor materials. Combustion is a promising powder preparation technique because it provides high temperature environment favorable for material synthesis. Different oxides like  $Y_2O_3$ ;  $Eu^{2+}$ ,  $Y_2SiO_5$ ;  $Ce^{3+}$ ,  $Y_3Al_5O_{12}$ ;  $Tb^{3+}$  and  $BaMgAl_{10}O_{17}$ ;  $Eu^{2+}$  etc. has been successfully prepared by this technique [71].

Phosphor materials were synthesized by combustion of aqueous solutions having stoichiometric composition of

starting reactants like metal nitrates and fuels. This process involved highly exothermic reaction between metal nitrates (oxidizers) and fuels like urea, glycine, (CH) carbonyl dihydrazide, (ODH) oxalyl dihydrazide, citric acid, (MDH) malonic acid dihydrazide and (TFTA) tetra formal tris azine which played the role of reducers. Semisolid paste of this redox mixture when introduced in a muffle furnace at high temperature resulted in a voluminous and fluffy powder in large amounts. Chemical reaction between reactants started at (500 °C), mixture ignited vigorously producing flame and process was completed within few minutes [71, 72]. A number of gases were evolved during combustion like CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, NO<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub> etc. Different fuels were used for producing oxide materials but, easy availability and high exothermicity of the urea made it a first choice for producing a large variety of alumina based materials [73]. By variation of fuel and oxidizer flow rates, flame temperature and particle residence time can be easily controlled. Factors affecting combustion synthesis are stoichiometric ratio, particle shape, size and processing of reactant particles, ignition technique and adiabatic temperature etc. This method is comparatively simple and of low cost. Due to very short reaction time, the process goes to completion within 10 minutes and results into the formation of highly pure final products. But, combustion process has some complications during the synthesis of nanophosphors materials because there is the requirement of additional heating in this process for exploring the pure phase nanosized materials. This method is not environment friendly because some harmful gases like CO<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub>O etc. are also evolved during the processing of these materials. Combustion procedure is difficult to control due to very short reaction time. Post processing steps like grinding or milling are also required which may introduce some impurities in the final products.

#### *Microwave method*

Microwave heating is one of the fast synthesis technique used for preparing nanoparticles, polymers, metals, oxides, halides, sulfides, phosphates etc [74-76]. This method is used to produce nanoparticles of different metals like gold, silver, copper, palladium, platinum etc. [77] and effectively used for synthesizing layered silicates. Microwave heating can be used for synthesis purpose in field of nanomaterials science, metal nanoparticles, solid state and organic chemistry.

Some work was also reported on material synthesis using microwave method. C<sub>3</sub>S or (Ca<sub>3</sub>SiO<sub>5</sub>) material was prepared using microwave technique [78]. Europium (III) doped Sr<sub>2</sub>SiO<sub>4</sub> materials were also explored by microwave sintering technique [79]. Microwave heating is a rapid synthetic method that controls reaction parameters, nucleation process and have excellent morphological control on nano-porous materials [80]. This method also reduces the processing time of chemical reaction and suppresses the formation of side products. But, the equipment used (dedicated microwave reactor) in this technique is not economically beneficial.

#### *Sol-gel method*

Silica gel and powders can be easily prepared from rice husk ash either by applying thermal treatment (500-1400 °C) or by leaching due to acidic or basic solution followed by neutralization with an acid [81]. Sol gel is an effective, versatile and low cost synthesis technique used for the preparation of nano-scale materials of excellent brightness and chromaticity [82, 83]. This synthetic route is very simple and used for large scale production of silicate based phosphor materials having high luminous efficiency. Several other luminescent materials based on different host lattices like oxides, halides, borates, phosphates, tungstates, molybdates, sulfides, oxysulfides etc. have also been synthesized using sol gel technology [49]. Rare earth doped lutetium pyrosilicates (Lu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) nanosized materials were also synthesized by this technique [77]. Eu<sup>3+</sup> doped Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> phosphors were prepared using this synthetic procedure [84]. Tb<sup>3+</sup> doped M<sub>2</sub>SiO<sub>4</sub> type of silicate based nanomaterials were also successfully synthesized using sol-gel process [1]. Now, the method used for preparing a series of Europium (III) doped M<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (M = Y, Gd and La) is explained briefly here. Comparative study of different conventional techniques applied for the various material syntheses is also compiled in **Table 1**.

#### *Synthesis of M<sub>2-x</sub>Eu<sub>x</sub>Si<sub>2</sub>O<sub>7</sub> materials*

Nano-crystalline Eu<sup>3+</sup> doped M<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> type of luminescent materials were prepared by sol-gel technique at 950 °C. Chemicals used were mainly Eu(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O and M(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O (M = Y, Gd and La) of analytical grade and purchased from Chemical Drug House in 99.9 % purity. A stoichiometric amount of europium nitrate and metal nitrates of Y, Gd and La were mixed homogeneously in a silica crucible using de-ionized water. On the other hand, two moles of silica powder were dissolved in concentrated HNO<sub>3</sub> solution in a round bottom flask (RBF). Then the contents of RBF were allowed to stir on a magnetic stirrer for 10 minutes. After that a gel was obtained. Now, added the mixture of crucible into the gel and again stirred it for nearly 30 minutes on a magnetic stirrer. Stirring was done to achieve uniform mixing of the precursors. Again, the precursors were transferred from RBF into the crucible. Heated the mixture of crucible on heating plate at 100 °C and it was now in the form of a semi-solid paste. The paste was then heat treated at 950 °C in a furnace for 1 hour to produce white colored silicate powders. Powders obtained were annealed at a temperature of 1050 °C and 1150 °C to study the effect of reheating on crystal structure and optical properties of these materials. These silicate powders were then observed in the presence or absence of ultraviolet light.

#### *Instrumentation*

X-ray diffraction study was carried out for phase purity and crystal phase identification using Rigaku Mini Flex 600 Diffractometer having a scanning speed of 4°/min. with 0.02° step interval. Diffraction pattern was recorded from 10-70° using CuK $\alpha$  radiation having a wavelength of 1.5416Å. The phase variations of the samples were checked at different temperatures through XRD. Optical properties of the samples were measured at room

temperature using Horiba Jobin YVON Fluorolog Model FL-3-11 Spectrophotometer equipped with Xe lamp as the excitation source. To determine the shape and size of phosphor powders, Transmission electron micrographs were taken with the help of Hitachi F-7500. Fourier Transform Infrared Spectroscopic study of these materials was carried out using Bruker Alpha ATR instrument.

### Characterization techniques

These days' nanotechnology has rapidly emerged as a new field of development in material research where nanosized materials are prepared and their properties are studied in detail. Today materials science requires nondestructive, easy processing and widely used characterization techniques for determining the

characteristics properties of phosphor materials. It is all possible due to the suitable microscopic tool available for characterization of these materials. These tools mainly include PL, XRD, FTIR, SEM and TEM which determines the optical, structural and surface properties of phosphor materials. Photoluminescence spectroscopy is used to study the luminescence properties of materials. X-ray diffraction helps in the identification of phase and lattice properties of powdered materials. Fourier Transform Infrared Spectroscopy gives information about the structure and chemical bonding in materials. Electron microscopic tools like SEM and TEM uses high energetic electron beam to view the images of a sample under investigation and helps in investigating the morphological characteristics of light emitting materials.

**Table 1.** Comparative analysis of the techniques used for phosphor materials synthesis.

Synthetic methods	Type of material synthesis	Reaction conditions	Examples	Advantages	Disadvantages
Solid State method	Aluminates, silicates, alumino-silicates, nitrides, sulfides and a number of metal oxides.	Reaction is carried out at high temperature (1200-1600 °C) with different fluxes (Li <sub>2</sub> CO <sub>3</sub> , NH <sub>4</sub> F, NH <sub>4</sub> Cl, BaF <sub>2</sub> , YF <sub>3</sub> , AlF <sub>3</sub> , H <sub>3</sub> BO <sub>3</sub> ) increasing the luminous efficiency of powders.	Y <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> , La <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> , and the composition La <sub>0.33-x</sub> Sb <sub>x</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub> where (0 ≤ x ≤ 2.0).	i) Environment friendly method. ii) Easy availability of starting materials. iii) Simplicity of the method. iv) Thermodynamically stable product formation. Uniformly distributed nanosized materials obtained.	i) Long reaction time. ii) High temperature processing conditions are required which enhances the particle size of materials. iii) Repeated milling and washing with chemicals tends to degrade the luminescence property of materials. Wide agglomeration, poor grain size distribution and morphological study of nanoparticles.
Co-precipitation	Magnetite and maghemite nanoparticles.	Co-precipitation method requires very low reaction temperature.	Sr <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub> , Ba <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub> , La <sub>10</sub> Si <sub>6</sub> O <sub>27</sub> (Y,Gd)SiO <sub>5</sub> .	There is a good control on the chemical composition and morphology of the products formed.	Materials synthesized using large scale spray pyrolysis has hollow and porous nature that affects the thermal stability and morphological characteristics.
Spray Pyrolysis	Multicomponent oxides, chlorosilicates, metals, catalysts, nanopowders, submicron and spherical shaped materials.	Process involves drop formation from the precursors and its shrinkage due to evaporation. Finally, precursor transformation to solid products.	Y <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> :Eu/SiO <sub>2</sub> , Zn <sub>2</sub> SiO <sub>4</sub> , Ca <sub>8</sub> Mg(SiO <sub>4</sub> ) <sub>4</sub> Cl <sub>2</sub> , Y <sub>2</sub> SiO <sub>5</sub> and La <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> .	i) Reheating is not required that prevents the particles from agglomeration. ii) Highly pure and homogenous product formation.	Requirement of expensive autoclaves and long processing time.
Hydrothermal method	Submicron to nanosized materials, single crystals, fibres and ceramic materials.	Product formation occurs at low temperature reaction conditions.	Specially, Y <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> materials and crystals which are unstable near the melting point.	Scale up method for producing highly pure and homogenous products having desired properties.	It requires additional heating for exploring pure phase nanosized materials. ii) Not ecofriendly.
Combustion method	Oxides, ceramics, catalysts and nanosized phosphor materials.	Exothermic reaction occurs between metal nitrates and organic fuels at a temperature of ~500 °C in ~5-10 minutes.	Y <sub>2</sub> O <sub>3</sub> , Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> , BaMgAl <sub>10</sub> O <sub>17</sub> materials.	i) Rapid synthetic method. ii) Controls the reaction parameters, and reduces the processing time.	Equipment used (dedicated microwave reactor) is not economically beneficial.
Microwave method	Polymers, oxides, halides, sulfides, metal nanoparticles, phosphates and layered silicates.	Reaction is happened at low temperature under microwaves.	Ca <sub>3</sub> SiO <sub>5</sub> and Sr <sub>2</sub> SiO <sub>4</sub> silicates.	i) Simple and low cost method. ii) High chemical homogeneity. iii) Controls the size and morphology of the particles. iv) Has good optics transparency.	Present method.
Sol-Gel method	Specially, used for large scale production of silicate materials because silicate sol formed by this method is very stable. Also used to produce glass and ceramic materials at mild conditions.	Highly pure and uniform nanomaterials achievable at low processing temperature.	Lu <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> , Y <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> , M <sub>3</sub> Y <sub>2</sub> Si <sub>3</sub> O <sub>12</sub> and M <sub>2</sub> SiO <sub>4</sub> type of luminescent materials. Important wet chemical technique also applied to synthesize organic-inorganic hybrids materials.		

### Photoluminescence characterization technique

Advances in nano science have made photoluminescence technique as a method of choice in different fields of materials chemistry. Photoluminescence is the spontaneous generation of light from a substance due to absorption of photons under external energy excitation.

Photoluminescence is a contactless and nondestructive technique used to study the luminescence properties of materials [85]. This characterization technique is very simple and straight forward. The instrumental units include laser, sample holder, optics, monochromator and a detector. Lasers are used as an excitation source because they can be readily focused, intense and monochromatic in nature. A Xenon lamp may also be used for excitation but, in that case there is a need of one more monochromator for tuning the excitation wavelength. Monochromator scatters polychromous light into different wavelength of lights with the help of prism. Diffraction gratings (planar or concave) are also used to disperse the white light. This technique gives information about the photoluminescence intensity, life time measurements, peak emission wavelength, quantum efficiency and band gap determination of phosphors. It also helps us in understanding recombination mechanism, impurity levels and defect detection in crystals [86]. Photoluminescence investigation also helps us to study the electronic transitions and lattice properties of silicate materials. The different transitions in a molecule can be easily explained on the basis of Jablonski diagram.

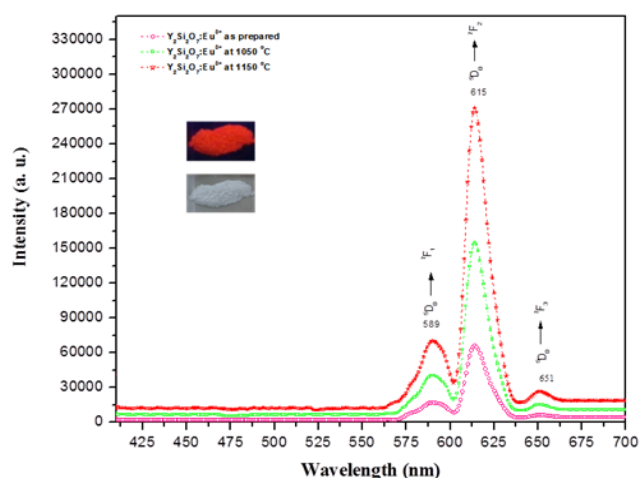
Jablonski diagram is an energy level diagram used to explain the phenomenon of fluorescence and phosphorescence. This diagram also clarifies the different electronic states of a molecule and transitions associated with it. When a molecule absorbs a photon of suitable energy, then electrons present in the ground state ( $S_0$ ) gets promoted to higher excited singlet states ( $S_1$  and  $S_2$ ). This transition is very fast (nearly  $10^{-15}$  sec.) and the process of absorption of radiation by a molecule is termed as Absorbance. When this electron returns to its ground state then it dissipates energy by several means including vibrational relaxation, internal conversion, intersystem crossing, fluorescence, phosphorescence etc. as shown in the (Fig. 1 b) Immediately, after the absorption process, a nonradiative transition referred as vibrational relaxation is followed where relaxation occurs between different vibrational energy levels within the same excited state ( $S_1$ ) of a molecule. Vibrational relaxation is also a very fast ( $10^{-14}$ - $10^{-11}$ sec.) transition. Internal conversion is also another kind of nonradiative transition where transition of an excited electron occurs from one vibration energy level of a higher excited singlet state ( $S_2$ ) to the vibrational energy level of lower excited singlet state ( $S_1$ ). Internal conversion is the result of strong overlapping between vibrational and electronic energy states. Dissipation of energy from higher excited singlet states ( $S_2$ ) to the lower one ( $S_1$ ) occurs most probably by internal conversion. Excited electron may also lose its energy by undergoing transition from excited singlet state ( $S_1$ ) to excited triple state ( $T_1$ ) by a process known as Inter system crossing. Inter system crossing (ISC) is also a type of nonradiative transition takes place in time duration of  $10^{-8}$ - $10^{-3}$  sec.

These are the spin forbidden transitions. Further this excited electron comes to ground state by loss of energy in the form of light via two optical processes termed as fluorescence and phosphorescence. If electronic transition occurs between the states of same multiplicity ( $S_1$ - $S_0$ ), then this process is called fluorescence. Time duration during the fluorescent transition lasts for nearly  $10^{-9}$ - $10^{-7}$  sec. where electronic transition occurs from higher excited singlet state ( $S_1$ ) to the singlet ground state ( $S_0$ ). If electron undergoes spin inversion during the transition or transition occurs between the states of different multiplicity ( $T_1$ - $S_0$ ), then the process is referred as Phosphorescence. Time needed for phosphorescent transition is  $10^{-3}$  or higher. Electron from excited singlet ( $S_1$ ) and triplet state ( $T_1$ ) also comes to the ground state non radiatively.

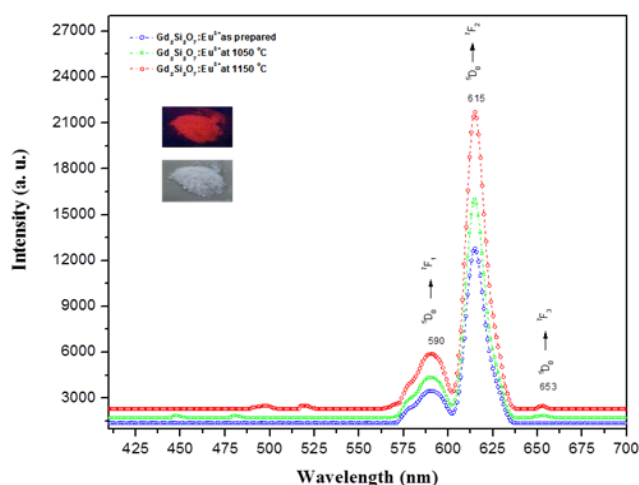
Photoluminescence analysis has comparable advantages over the other spectroscopic techniques as only a small amount (nearly 20 mg) of the sample is required and there is no need of sample to be in solution form for powdered phosphor materials. This technique is highly sensitive and very small time is required for the analysis of materials [87]. It describes the spectral profile of the material

### Optical characterization of $M_2Si_2O_7$ materials

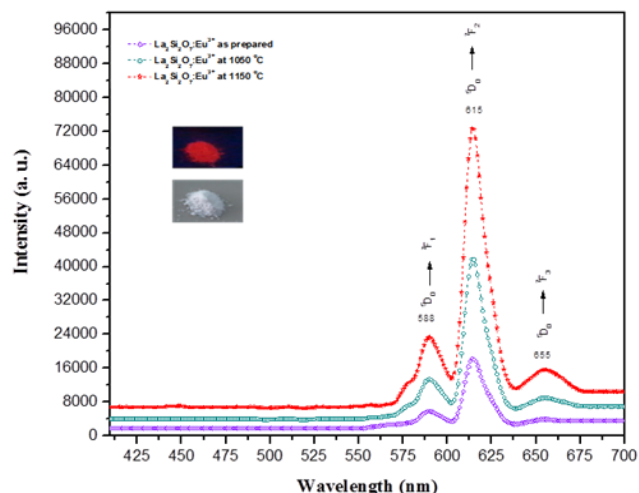
Optical properties of  $M_{(2-x)}Eu_xSi_2O_7$  ( $M = Y, Gd, La$  and  $x = 0.03$  moles) type of phosphor powders were studied by recording their emission spectra as shown in (Fig. 2). Photoluminescence (PL) emission spectra of these silicates exhibited various spectral lines corresponding to the well known  ${}^5D_0 \rightarrow {}^7F_J$  ( $J = 0, 1, 2, 3, 4$ ) transitions of Europium (III) ion available in lattice. Emission spectra of these materials were recorded under 395 nm excitation.  $Y_2Si_2O_7$ ,  $Gd_2Si_2O_7$  and  $La_2Si_2O_7$  materials give rise to sharp spectral peaks from 400-700 nm due to the different transitions of  $Eu^{3+}$  ion. The most intense transition in all disilicates is found to be at 615 nm due to the  ${}^5D_0 \rightarrow {}^7F_2$  transition of Europium (III) ion. The photoluminescence emission at 615 nm is due to the ( ${}^5D_0 \rightarrow {}^7F_2$ ) electric dipole transition where  $Eu^{3+}$  ion occupies non inversion-symmetric site. However, emission around 588 nm is due to the magnetic dipole transition ( ${}^5D_0 \rightarrow {}^7F_1$ ) where, europium (III) ion occupies a site with inversion symmetry in these silicate materials [2, 22]. Electric dipole is the dominant transition that improves the color purity in these materials. Luminescence intensity of these silicate enhance with the reheating temperature of materials. Sample preparation at high temperature resulted in an enhancement of particle size and crystallinity of materials. From these disilicates, the highest photoluminescence emission is observed for  $Y_2Si_2O_7$  phosphor at the synthesis temperature. However, least emission intensity is seen for  $Gd_2Si_2O_7$  from the photoluminescence spectra given in (Fig. 3). Color coordinates of these phosphor materials were calculated using chromaticity calculator and reported in Table 2. CIE coordinates of  $Y_2Si_2O_7$  at 1150 °C were found to be in the range of  $x = 0.58$  and  $y = 0.35$  which show strong red emission under UV excitation and this value is in close agreement with previous report [16].



(a)

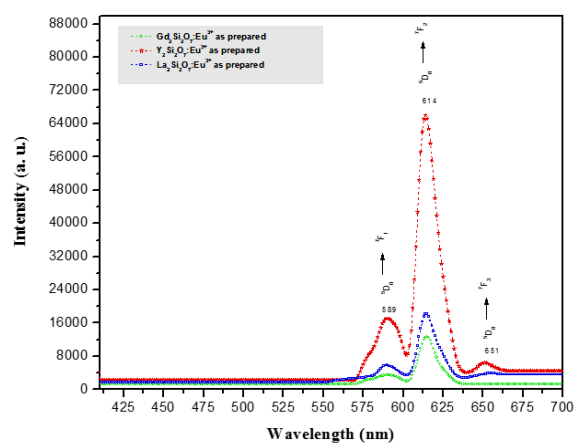


(b)



(c)

**Fig. 2.** Photoluminescence emission of  $\text{Eu}^{3+}$  doped materials a)  $\text{Y}_2\text{Si}_2\text{O}_7$ , b)  $\text{Gd}_2\text{Si}_2\text{O}_7$  and c)  $\text{La}_2\text{Si}_2\text{O}_7$  at different temperatures with their visibility in the presence and absence of ultraviolet light.



**Fig. 3.** Relative emission spectrum of  $\text{Eu}^{3+}$  doped silicate phosphors at the synthesis temperature.

### Decay study of silicate materials

Decay profiles of these silicate materials were registered at 615 nm under the excitation at 395 nm. Decay curve of most intense transition of  $\text{Eu}^{3+}$  ion was analyzed to check the decay time of these materials. As, described by Blasse and Grabmaier, [88] decay behavior of these materials can be checked using **Equation 1**.

$$I(t) = I_0 \exp(-t/\tau_1) \quad (1)$$

where,  $I(t)$  = luminescence intensity and  $\tau_1$  is the decay time noticed after excitation time  $t$ . Decay graphs were normalized to compare the differences between the life times of these materials. Decay times of these silicates were calculated using single exponential dependence and shown in **Table 2** with some other parameters. Decay curves may also be fitted by using a bi exponential temporal dependence **Equation 2**.

$$I(t) = I_{01} \exp(-t/\tau_1) + I_{02} \exp(-t/\tau_2) \quad (2)$$

Here  $I(t)$  = luminescence intensity,  $t$  corresponds to time after excitation and  $\tau_i$  ( $i = 1, 2$ ) is the decay time of the  $i$ th component. The average decay time may be calculated using the **Equation 3**.

$$\langle \tau \rangle = \tau_1^2 I_{01} + \tau_2^2 I_{02} / \tau_1 I_{01} + \tau_2 I_{02} \quad (3)$$

Photoluminescence intensity of a particular transition is correlated with its decay time [89] and this correlation is also observed in case of these silicate materials. Intense transition of  $\text{Eu}^{3+}$  show maximum decay time for nano crystalline  $\text{Y}_2\text{Si}_2\text{O}_7$  material and minimum for  $\text{Gd}_2\text{Si}_2\text{O}_7$  material as in **Table 2** and similar results are also obtained from relative emission spectra of these materials as mentioned above.



Table 2. Showing parameters of Eu<sup>3+</sup> doped silicate materials.

Type of Lattice	Color coordinates		<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub>	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>2</sub>	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>3</sub>	Size	Size	A <sub>1</sub>	Decay Time τ <sub>1</sub> (ms)
	x	y				(XRD)	(TEM)		
Y <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> :Eu <sup>3+</sup>	0.58	0.35	589	615	651	46.26	50.00	1.59189	3.05920
Gd <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> :Eu <sup>3+</sup>	0.48	0.30	590	615	653	48.36	37.01	0.96800	0.70554
La <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> :Eu <sup>3+</sup>	0.52	0.34	588	615	655	44.06	48.55	1.48025	2.48739

### X-Ray diffraction analysis

X-ray diffraction analysis is a rapid, indispensable, quality control, analytical and nondestructive technique used for material characterization. Diffraction analysis is used to determine the crystal structure, particle size and helps in phase identification of materials [90]. Diffraction is X-ray based method that gives information about chemical composition, microstructure analysis, crystallinity and stress analysis, percent phase composition, inter-planar spacing and lattice parameters of an unit cell. X-ray diffraction is also called polycrystalline diffraction that provides structural information about phosphor materials. A wide range of materials like soil, ceramics, cement, pharmaceuticals, glass, clays, rocks, chemicals, polymers, semiconductors and powders have been characterized using X ray diffraction study.

Instrumentation of diffraction pattern includes X-ray source, sample holder and detector. Usually, X-ray tube is used as the source of X-rays. Then rays generated from the source are allowed to incident on material under investigation and then beam of X-rays is diffracted in several directions which correspond to constructive interference that satisfies Bragg's equation and results a diffraction peak in the spectrum. If there is destructive interference then, no diffraction peak is observed in the pattern. According to Bragg's equation:

$$n\lambda = 2d\sin\theta \quad (4)$$

Where,  $\lambda$  is the wavelength of radiation used,  $d$  is interplanar spacing and  $\theta$  is Bragg's angle of incidence that X-ray makes with plane. Diffraction profile helps in the identification of different polymorphic forms of a material. It also predicts the crystalline and amorphous form of a material [91]. Crystallinity of a material may be recognized by the presence of sharp diffraction peaks in the XRD spectrum. However, the disappearance of sharp peaks or occurrence of some broad peaks reveals the amorphous phase of any material. Using X-ray pattern, it is easy to index the diffraction peak because of the presence of a large number of known crystal structures in computer aided library. PDF (Powder Diffraction File) is a database that contains thousands of diffraction patterns. Modern computer programs like JCPDS Win software help us in predicting the phase of our material by comparing it with all the patterns available in databases. X-ray diffraction helps in calculating crystallite size of materials [92]. Position and intensity of the peaks

revealed by XRD helps in predicting the crystal structure of any material. Crystal structure of any material is dependent upon the average ionic radius of rare earth element and its synthesis temperature used [93]. X ray diffraction pattern is unique for every material and it gives useful information about peak shape, position, width and intensity. The final product is not necessary structurally pure, but may have some peaks of impurities which can also be estimated by diffraction analysis.

### X-Ray diffraction study of M<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> materials

Diffraction pattern of as synthesized as well as annealed powders were recorded for phase identification of materials. The diffraction pattern of the sol-gel derived M<sub>(2-x)</sub>Eu<sub>(x)</sub>Si<sub>2</sub>O<sub>7</sub> (M = Y, Gd, La and x = 0.03 moles) nano-phosphors are shown in (Fig. 4). The nitrate precursors used for material synthesis were reported to be removed earlier at some low (500 °C) temperature [94]. Main characteristic peak for Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> phosphor is obtained at  $2\theta = 29.32^\circ$  which is in close agreement with previous reports [22, 90].

Synthesized Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> material is found to be in triclinic form with some low intense silica peaks. When, this sample is further heated to a temperature of about 1150 °C, then diffraction peaks of this material are indexes to the  $\alpha$ -form by comparing its X-ray pattern with JCPDS card no. 38-0223 [23, 95]. Although a slight difference is also found in the position and intensity of some peaks of this material when referring to the pure standard pattern available in literature [9]. Annealed powder of this material has triclinic structure with space group P<sub>1</sub> and resembles with JCPDS chart no. 21-1457 [22]. Now, JCPDS chart no. 21-1457 has been revised by JCPDS No. 38 - 0223 [96]. Due to the polymorphous nature of these silicates, it is very difficult to identify the phase of materials because phase variations are observed along with temperature. Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> material is expected to be iso structural with  $\alpha$ -H<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> consisting of isolated chain-like Si<sub>3</sub>O<sub>10</sub> groups and SiO<sub>4</sub> tetrahedron [22, 96]. Powder pattern of Gd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> phosphor is also found to be nearly similar to those observed for Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> material when compared with JCPDS No. 21-1457 [97].

Although, a slight difference in the position and intensity of peaks is also observed for Gd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> material which indicates low crystallinity of Gd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> as compared to Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> material. Amorphous phase in La<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> material is reported to be observed around 600 °C [98]. La<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> phosphor crystallizes in the form of lanthanum oxy apatite having hexagonal crystal structure at the

synthesis temperature which is closely matched with JCPDS No. 49-0443 having space group  $P6_3/m$  and  $Z = 1$ . Lanthanum oxyapatite ( $La_{9.33}(SiO_4)_6O_2$ ) structure is formed during the sol-gel synthesis of lanthanum disilicates well above 800 °C [99, 100]. Existence of this oxy apatite as the main phase has also been supported by Alberto J. Fernandez-Carrion et. al during the synthesis of A- $La_2Si_2O_7$  material by two processes namely sol gel and solid state at 1100 °C. Some low intense reflections of A- $La_2Si_2O_7$  along with  $La_2SiO_5$  and  $La_2O_3$  were also noticed by them at this temperature. They found the existence of this apatite phase as the main phase even at the high temperature conditions (1150 and 1200 °C) and observed the simultaneous formation of (tetragonal) A- $La_2Si_2O_7$  and (monoclinic) G - $La_2Si_2O_7$  phases of material [2]. In our case, the  $La_2Si_2O_7$  silicate obtained using sol gel process when further calcined to a temperature of about 1150 °C, crystallized as a single phase material. The diffraction pattern of this sample when compared with ICSD Card No.-71807 then, it was found that this sample crystallized in monoclinic form having a space group of  $P1\ 21/c\ 1$  [98]. Evolution of  $\alpha$  as the strong phase in our yttrium disilicates material for a temperature range of 950-1150°C was also supported by an earlier report [101]. The crystallite size of these phosphor materials is shown in Table 2 and calculated using Debye Scherrer's Equation 5:

$$D = k\lambda/\beta\cos\theta \quad (5)$$

where, D is the crystallite size,  $k = 0.9$ ,  $\lambda$  is the wavelength of x ray used,  $\beta$  is FWHM (Full Width At Half Maximum) and  $\theta$  is the Bragg's angle of incidence that X-ray makes with plane.

#### Fourier transform infrared spectroscopic analysis

FTIR (Fourier Transform Infrared Spectroscopy) is a nondestructive, simple and molecular spectroscopic technique used for recording the infrared absorption spectrum of materials. This absorption spectrum determines the vibrational frequencies of a molecule which in turn gives information about the structure and chemical bonding. Fourier Transform Infrared Spectroscopy is an additional characterization technique used to determine the presence or absence of different species in any material by recording its spectrum. FTIR is a rapid and inexpensive technique applied on organic and inorganic samples.

Fourier Transform Infrared Spectrometers are the third generation spectrometers used to acquire broadband near infrared (12800~4000  $cm^{-1}$ ) to far infrared (50~1000  $cm^{-1}$ ) spectra. Interferometer is an optical device which gives rise to a unique signal encoding all infrared frequencies. Interferometers make the use of a beam splitter for splitting the incident infrared beam into two parts. Beam splitters are specific for a particular range in infrared region. For far and near infrared region, mylar and silicon is suitable. However, for mid infra-red region, Ge-coated KBr or calcium fluoride is used. Beam from the two mirrors (one mirror is stationary while other is continuously moving) interfere with one another resulting

into a signal from interferometer called interferogram (raw data). This unique signal can't be interpreted directly. Now, there is the need of a special mean for decoding the individual frequencies or for converting raw data into the actual spectrum which is accompanied by a mathematical process (Fourier Transformation) digitized by computer.

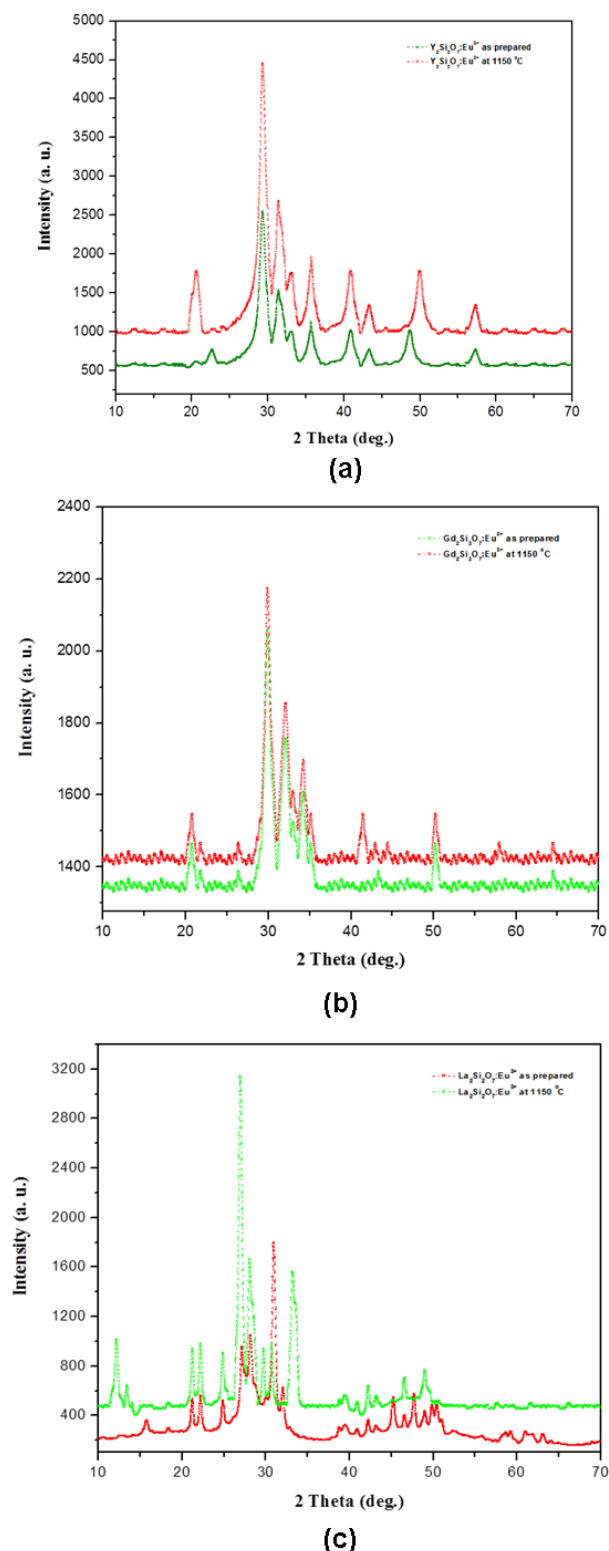


Fig. 4. Diffraction pattern of  $Eu^{3+}$  doped materials (a)  $Y_2Si_2O_7$ , (b)  $Gd_2Si_2O_7$  and (c)  $La_2Si_2O_7$  materials at different temperatures.

FTIR shows some comparable advantages over dispersive techniques and one of them is Fellgett advantage in which Fourier transform infra-red spectrometer selection guide collects all wavelengths simultaneously that results into a higher signal/noise ratio. This is also referred to as the multiplex advantage. FTIR spectroscopy gives information in a very short scan time. In FTIR instruments, there is no need of calibration by user because these are self-calibrating having Helium-Neon laser as an internal wavelength calibration standard. These instruments are mechanically simple indicating very little chances of breakdown. FTIR studies of  $Gd_2O_3$  prepared by doping  $Yb^{3+}$  gives information about the presence of different molecular species in it [102]. Fourier transform infrared spectra of strontium cerium oxide ( $Sr_2CeO_4$ ) a blue phosphor also revealed the presence of different functional groups [103].

#### *Fourier transform infra-red analysis of $M_2Si_2O_7$ materials*

FTIR spectral information of sol-gel derived  $M_2Si_2O_7$  ( $M = Y, Gd$  and  $La$ ) materials are represented in (Fig. 5). FTIR spectra of these silicate based materials exhibited different peaks from 4000-600  $cm^{-1}$  region. IR near normal reflectance spectrum of  $Y_2Si_2O_7$  material exhibited a number of IR active modes for its different polymorphs. For  $\gamma, \alpha, \beta$  and  $Y$  phase of yttrium disilicate material 36, 129, 15 and 33 infra-red active modes were reported. Band at 1077-1100  $cm^{-1}$  was assigned due to the stretching vibrations of Si-O-Si bonds [19] and the spectrum of yttrium silicate reveals nearly similar peaks at 1063  $cm^{-1}$ . Actually, Y-O absorption band was reported to be in the region of 560 and 460  $cm^{-1}$  [104]. Emergence of Y-O peak predicted the dissociation of yttrium nitrate used as a precursor during the synthesis of this material [105]. This structural information related to Y-O bond is obtained from the infra-red spectrum of yttrium oxide materials. Band present in a region 617  $cm^{-1}$  corresponds to the Y-O-H deformation mode having a close match with previous studies [106]. Peak corresponds to the Gd-O vibration is reported to be around 542  $cm^{-1}$  in  $Gd_2Si_2O_7$  material and this information is obtained from its oxide phosphor [107-109]. Absence of peaks from 3400-3500  $cm^{-1}$  indicates the absence of  $H_2O$  molecules in the material. There are some more peaks in the spectrum of these materials. Incorporation of lanthanum nitrate occurs in silica gel during the synthesis of lanthanum silicate material. Sharp nitrate peaks have been reported to be around 1455, 1425, 1325, 1300, 1050, 1040, 870, 810, 780, 740, 715  $cm^{-1}$  [110]. At high temperature, these nitrate peaks gets reduced confirming the dissociation of lanthanum nitrate species. The absence of nitrate peaks in the spectrum clearly confirms that there is no coordination of nitrate group with the lanthanum ion. It means lanthanum nitrate undergoes dissociation resulting in the formation of lanthanum silicate.

The peak at 1063  $cm^{-1}$  is attributed to the stretching vibration of Si-O-Si bond. Peak corresponding to La-O stretching is located at 617  $cm^{-1}$  in the spectrum of lanthanum disilicate material which was reported to be around 620  $cm^{-1}$  region [111]. From the FTIR spectra of these silicate materials, we have found that at high

temperature, absorption peaks due to  $-OH, H_2O$  and  $NO_3^-$  disappears completely and there will be the emergence of some new peaks in the spectrum corresponding to M-O, Si-O or Si-O-Si vibrations resulting in the formation of products.

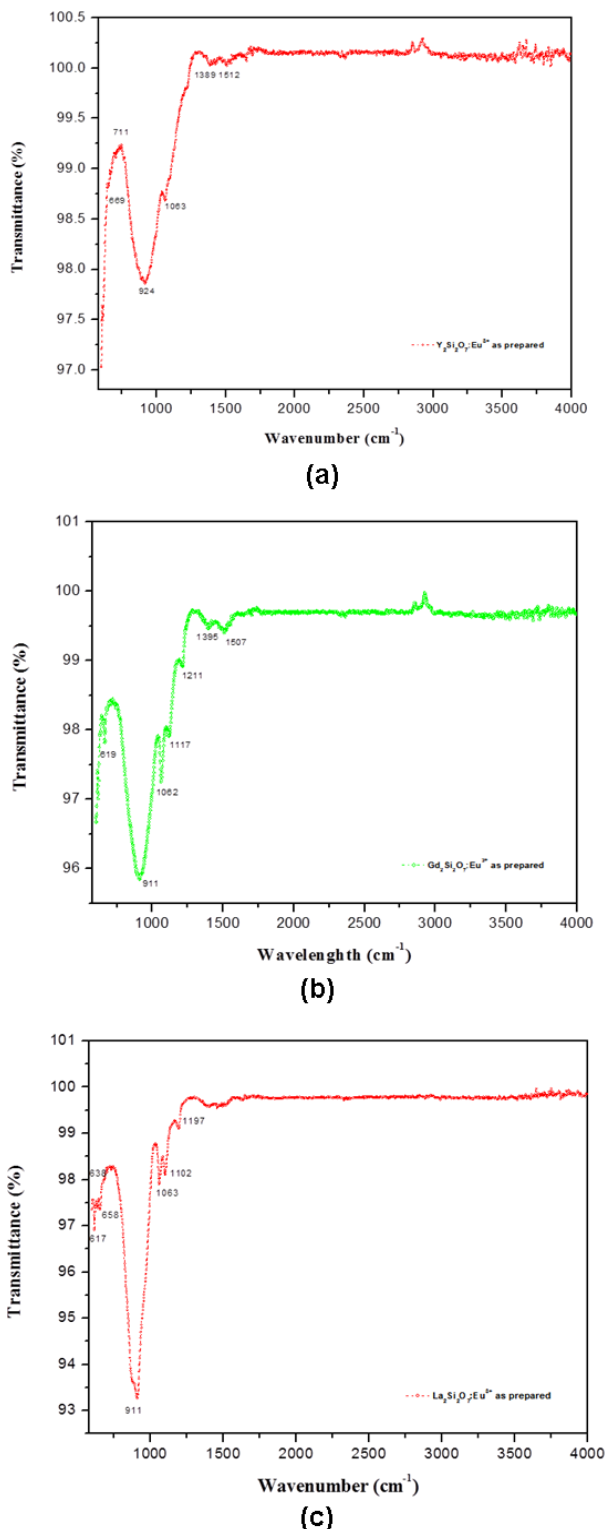
#### *Scanning electron microscopy*

Scanning electron microscopy is a nondestructive analysis that generates a number of signals at the sample surface and produces a number of images by scanning it with high energy electronic beam. SEM is a simple and versatile technique that provides information about the surface morphology, topology and chemical composition. This microscopy can also be used to image the surfaces of polymer nano composites, nano coatings, nano fibres, nanoparticles and fractured surfaces [112]. Scanning Electron Microscopy (an imaging technique) has wide applicability in the field of cement and concrete petrography. SEM is the most useful and popular tool whose spatial resolution is upto nanometer level and used for the characterization of a wide range of materials like particles, coating, films and surfaces. A number of silicate based luminescent materials were characterized using scanning electron microscopy. Carbon nanomaterials were characterized using scanning electron microscopic technique [113]. SEM determined the morphological features in  $Tb^{3+}$  doped  $Y_2SiO_5$  materials prepared using modified spray pyrolysis technique [60]. Scanning electron microscopic images in Y-  $Y_2Si_2O_7$  explained the morphology of fractured surfaces and interfaces in material [114]. These electronic images also clearly depicted the grain growth at different temperatures by having a close insight on to its fractured surfaces.

#### *SEM structure*

This instrument consists of two main parts electronic console and column. Electronic console contains knobs and switches for adjusting the instrumental properties. Electronic column includes electron gun which is responsible for producing electronic beam under vacuum. This beam is allowed to pass through a small region using electromagnetic deflection coils. Condenser lens help to converge the beam while apertures, scanning system and specimen chamber scans the surface of sample in raster pattern and results in generating images of a material. A vacuum system is also available to maintain vacuum inside the electronic column. Electron sample interaction [115] gives rise to several emissions like secondary electrons, backscattered electrons, X-rays, diffracted backscattered electrons, light and heat etc. Electron scattering may be elastic or inelastic depending upon sample beam interaction. Backscattered electrons illustrate compositional contrast in samples and produced due to elastic scattering of electrons. Inelastic scattering results in production of secondary electrons which determines the surface properties of materials. Scintillators and solid state detectors are used for the detection of signals like secondary electrons and backscattered electrons. On contrary to light, Scanning Electron Microscope uses electrons for imaging the surfaces and has higher magnification and deep field of

focus [116]. SEM is easy to use and requires only a very small amount of sample for characterizing solid materials. Data acquisition is fast and in digital form. Precautions must be taken that sample should be in solid form, conductive and stable in vacuum. Instead of TEM, SEM has limited applicability for characterizing nanoparticles because these materials have a potential to undergo agglomeration.

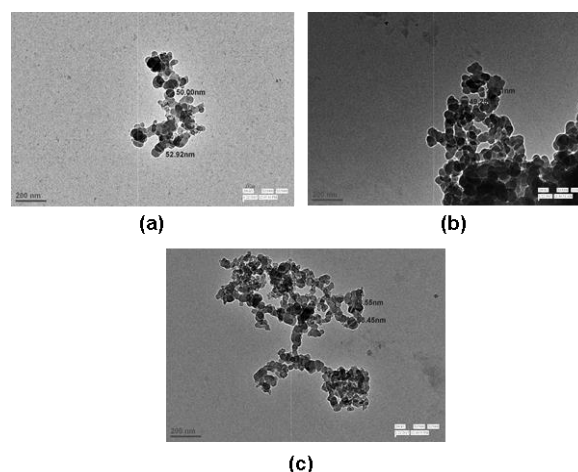


**Fig. 5.** FTIR spectra of silicate materials (a)  $Y_2Si_2O_7$ , (b)  $Gd_2Si_2O_7$  and (c)  $La_2Si_2O_7$  at 950 °C.

### Transmission electron microscopy

Transmission electron microscope produces images of the material under investigation by transmitting high energy electronic beam through it. It is one of the most powerful and versatile technique used in material science to study the morphological and crystallographic information about phosphors. TEM instrumentation includes illumination system having electron source and condenser lens as well as apertures, image forming system like objective lens and aperture, projective system include lens of projector and system like ZnS screen.

This is the most expensive and widely used characterization technique applied in the field of materials research, nanocomposites, semiconductors and nanotechnology [117, 118] where results are displayed on a fluorescent screen. TEM data helps to make the products efficient by visualizing its images. TEM reveals the rough estimation of particle size and crystallinity of luminescent materials [39]. Micro structural developments were also studied in nanocomposites with the help of HRTEM [119]. TEM has the capability to produce high quality images. TEM has high resolving power than other conventional microscopes and hence has significant approach in the field of quantum mechanics.



**Fig. 6.** TEM micrographs of  $Eu^{3+}$  doped materials (a)  $Y_2Si_2O_7$ , (b)  $Gd_2Si_2O_7$  and (c)  $La_2Si_2O_7$  at 950 °C.

### Transmission electron microscopic analysis of $M_2Si_2O_7$ materials

High resolution transmission electron micrographs were taken for the morphological investigation of silicate materials. Tem micrographs clearly reveal that particles are nearly spherical and aggregated as seen in (Fig. 6). TEM also estimated the crystallite size of  $M_{(2-x)}Eu_xSi_2O_7$  silicate materials which were prepared using sol gel technique. Crystallite size of prepared materials is reported in Table 2. Particle size of the as prepared luminescent materials is found to be in 50 nm range which explained the importance of selection of these phosphors for photonic applications.

### Applications of silicate materials

Silicate phosphor materials are used in a number of applications like solid state lighting, display devices

including plasma and field emission displays, cathode ray tubes, lasers, fluorescent lamps, scintillators, nuclear medical diagnostics, gamma ray and thermal neutron monitoring etc. Some examples of silicate based light emitting materials used in these applications are discussed briefly here.

#### *Solid state lighting*

Solid-state lighting (SSL) is emerging as an alternative to the pre-existing lighting technologies and is highly desirable. This type of lighting involves (LEDs) semiconductors light emitting diodes, OLEDs (organic light emitting diodes) and PLEDs (polymer organic light emitting diodes) as the source of illumination. As a new solid state light source, LEDs are considered as the next generation lighting device because of their long life time, energy saving, reliability, safety and environment friendliness characteristics. To fulfill the need of light emitting diodes applications, silicate phosphors have been designed and developed from the past years. Recently,  $\text{Eu}^{3+}$  doped  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  is the new orange-red emitting phosphor used for white LEDs applications [120].  $\text{Eu}^{2+}$  activated an orange-yellow  $\text{Li}_2\text{SrSiO}_4$  phosphor was also designed for light emitting devices [121]. Blue-emitting phosphors such as  $\text{Ba}_9\text{Y}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$ ,  $\text{CaSrSiO}_4:\text{Eu}^{2+}$ ,  $\text{BaBeSiO}_4:\text{Eu}^{2+}$  have great potential for use in ultra-violet chip excited white light emitting diodes [122]. The single phase white light emitting  $\delta\text{-Gd}_2\text{Si}_2\text{O}_7$  is the promising silicate phosphor used in solid state lighting [10]. Some other silicate materials such as  $\text{Ba}_3\text{MgSi}_2\text{O}_8$ : Eu, Mn,  $\text{BaMg}_2\text{Si}_2\text{O}_7$ : Eu, Mn,  $\text{MgCa}_2\text{Si}_2\text{O}_7$ : Eu, Mn,  $\text{M}_2\text{SiO}_4:\text{Eu}^{2+}$  (M =  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ),  $\text{NaY}_9\text{Si}_6\text{O}_{26}:\text{Ce}^{3+}$ ,  $\text{Na}_3\text{YSi}_2\text{O}_7:\text{Ce}^{3+}$ ,  $\text{Ba}_2\text{CaZn}_2\text{Si}_6\text{O}_{17}:\text{Eu}^{3+}$ ,  $\text{Y}_2\text{Si}_2\text{O}_7:\text{Tb}^{3+}$ ,  $(\text{Ba}, \text{Sr})_2\text{SiO}_4$ : Eu,  $\text{K}_2\text{Ba}_5\text{Si}_{12}\text{O}_{30}:\text{Eu}^{2+}$  (KBSO: $\text{Eu}^{2+}$ ) have potential applicability in LED based solid state lighting devices [123, 124].

#### *Display devices*

Display device is an output device used for presenting the information in visual form.  $\text{RE}^{3+}$  doped (Ln = Eu, Ce, Dy and Sm)  $\text{BaCa}_2\text{Si}_3\text{O}_9$  and  $\text{K}_2\text{CaSi}_3\text{O}_9$  silicate materials have been used in the field of lighting and display devices [125]. Europium (III) doped  $\text{Y}_2\text{SiO}_5$  material is found to suitable for lamp and display industries because it exhibits high luminescence efficiency and good stability under the conditions of high irradiance with an electronic beam [126].  $\text{Ba}_2\text{Gd}_2\text{Si}_4\text{O}_{13}:\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$  and rare earth doped  $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$  materials could be used in display device applications.

#### *Plasma display panels (PDPs)*

Green emitting material including  $\text{Mn}^{2+}$  doped  $\text{Zn}_2\text{SiO}_4$  is the most common and widely studied silicate phosphor used for plasma display panels (PDPs) and cathode ray tubes [127]. Rare earth ( $\text{Mn}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Eu}^{2+}$ ) doped zinc silicate material in powder form or in the form of thin film have potential application in plasma display panels, field emission displays and thin film electroluminescence devices.  $\text{Eu}^{2+}$  doped  $\text{CaMgSi}_2\text{O}_6$  material is used in plasma displays as blue phosphors

[128].  $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ ,  $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$  and  $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$  are the efficient phosphors for plasma display panels.  $\text{Ca}(\text{La}, \text{Gd})_4\text{Si}_3\text{O}_{13}:\text{Tb}^{3+}$ ,  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ ,  $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$  and  $\text{Ba}_2\text{CaZn}_2\text{Si}_6\text{O}_{17}$  phosphors find use in plasma display applications [129].

#### *Field emission display (FEDs)*

A field emission display (FED) is a type of flat panel display technology where, electrons from emission sources strike the colored phosphor to generate a color image. Flat panel display (FPD) involves both emissive and non-emissive type of technologies. Of the emissive display technologies, Field emission displays offers several advantages over competing electroluminescence and plasma technologies because they promise thin panel thickness, low power consumption, self-emission, distortion-free image and quick response. Blue oxide phosphor such as  $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$  showing high chemical stability and suitable material for FEDs. A novel blue-emitting zirconium silicate phosphor  $\text{K}_2\text{ZrSi}_2\text{O}_7:\text{Eu}^{2+}$  also have potential application in LEDs and FEDs [130].

#### *Cathode ray tubes (CRT)*

Cathode ray tube is a vacuum tube involving a phosphorescent screen that is used to view the images. A large number of silicate materials have been synthesized for use in cathode ray tubes especially cerium (III) doped  $\text{Y}_2\text{Si}_2\text{O}_7$  material finds its practical applicability in cathode ray tubes [12]. Cerium doped lutetium oxy orthosilicate phosphor materials were studied as a powder for cathode ray tubes.

#### *Solid state lasers*

A laser is a device that emits light coherently through optical amplification based on the stimulated emission of electromagnetic radiation.  $\text{RE}_2\text{Si}_2\text{O}_7$  matrix when doped with active lanthanide ions show excellent luminescent response in solid state lasers, display panels and high energy phosphors.

#### *Fluorescent lamps*

Fluorescent lamps use fluorescence process to generate visible light.  $\text{CaSiO}_3:\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$  material has application in low-pressure fluorescent lamps [131].

#### *Scintillators*

Rare earth activated  $\text{Lu}_2\text{Si}_2\text{O}_7$  and  $\text{Gd}_2\text{Si}_2\text{O}_7$  materials are widely used in scintillators.  $\text{Gd}_2\text{SiO}_5$  and  $\text{Gd}_2\text{Si}_2\text{O}_7$  doped with rare earth ions like (Ce, Pr, Eu, Dy etc.) exhibited excellent optical properties required for applications in laser production and scintillator detectors.

#### *Gamma ray detection and nuclear medical diagnostics*

$\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$  can be used for gamma ray detection in nuclear medical diagnostic instruments  $\text{Gd}_2\text{SiO}_5:\text{Ce}^{3+}$ ,  $\text{Lu}_{2(1-x)}\text{Y}_{2x}\text{SiO}_5:\text{Ce}^{3+}$ ,  $\text{Gd}_2\text{Si}_2\text{O}_7:\text{Ce}^{3+}$  silicate materials are widely studied for gamma ray detection and nuclear medical diagnostics applications.

## Conclusion

The rising development of optoelectronic display applications has fuelled an increasing requirement for the novel techniques for the preparation of materials having excellent optical as well as electronic characteristics. The performance in certain aspects of designed materials has even exceeded than that of other existing materials. We anticipate that the new developments, which may shape the potential of optoelectronic knowledge, will be on the rise with the help of silicate materials. To accomplish that purpose, a series of red phosphors  $M_{(2-x)}Eu_{(x)}Si_2O_7$  ( $M = Y, Gd$  and  $La$  and  $x = 0.03$  moles) has designed and successfully synthesized using present sol-gel technology. It has been observed that these powders possess high luminescence intensity and exhibited strong red light due to  $Eu^{3+}$  ion available in crystal lattices. These characteristics have indicated that the optimal  $M_{(2-x)}Eu_{(x)}Si_2O_7$  composition which may have a high potential in the powder form to develop new materials of different types. XRD pattern indicated that crystal lattice has a triclinic form in  $Y_2Si_2O_7$  and  $Gd_2Si_2O_7$  materials.  $La_2Si_2O_7$  material has hexagonal and monoclinic structure that depended on its synthesis and annealation temperature used for its preparation. Effect of temperature on photoluminescence properties of these silicates has been studied and discussed successfully. TEM results indicated that particles are nearly spherical and has a size of ~50 nm. Hence, silicate phosphors demonstrate the practical approach in different field including lighting, lasers, display panels, scintillators and in nuclear medical diagnostic systems etc. The host lattices of these nano-phosphor materials would be a better choice for research significance and would help in exploring new luminescent materials for further photonic applications. Additional direction of photonic applications are in the development of silicate materials having better particle properties and chromaticity coordinates that can be integrated with ultraviolet LED chips to generate light.

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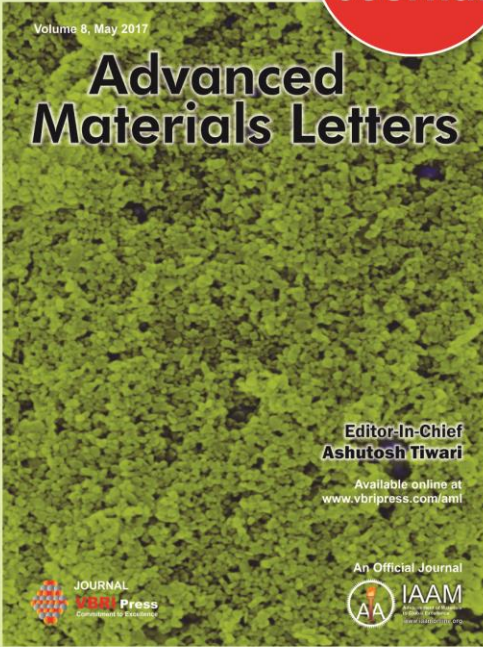
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