CHAPTER 1

INTRODUCTION

1.1 Introduction to silicate materials

This chapter gives a brief introduction to silicates describing the importance of luminescence which is relevant to this thesis.

1.1.1 Scope of the work

Recently, laboratory synthesized nanomaterials attracted the research community a lot not only because of their basic science aspects but also by their novel properties which lead to new technological applications [1-4]. Nanostructured materials are the intermediate class between the molecular scale and micro-sized entities. They are attracting considerable attention because as the size is reduced a remarkable alteration takes place in the bulk properties such as structural, magnetic, optical, dielectrical, thermal etc due to quantum confinement effects [5-7]. This quantum confinement made the nanomaterials to find an important application in field of luminescence as nanophosphor. It is found that the properties of luminescence strongly depend on particle size and the type of host [8]. So we have selected silicates as host material.

The invention of a new family of silica materials has dramatically expanded the range of crystallographically defined pore sizes from the micropore to the nano regime [9]. Silicates are the most complicated class of minerals which attracted most of the
researchers. On earth, a wide variety of silicate materials occur in an even wider range of combinations as a result of the processes that form and re-work the crust. Thus, 90% of the earth crusts are made of silicates and about 30% of all minerals are silicates [10]. Exploration of new type of nano structured silicates with unexpected properties makes it technologically and economically important [11]. It is the low cost and richest resource available in nature.

Lot of nano silicates have been reported [12-14], but our study was concentrated on alkaline earth silicate. In spite of wide range of application, owing to less attention given in the past and considering its practical importance we extended our studies on the synthesis, characterization, luminescence studies of undoped, doped, co-doped new phosphor and design of phosphor formed the subject matter of this work.

1.1.2 Nanomaterials

Particles of nanometer sizes began to attract the attention of scientists in different fields of science in the last 15–20 years. More active development in this direction dates back to the 1990’s, when the first international conferences on nanomaterials were held and the first relevant scientific journals appeared. In fact, nanoscience comprises closely interrelated concepts of chemistry, physics, and biology, which are aimed at the development of new fundamental knowledge. In nanoparticles, a considerable number of atoms pertain to the surface, and their ratio increases with a decrease in the particle size. Correspondingly, the contribution of surface atoms to the system’s energy increases [15-16].
For nanoparticles, two types of size effects are distinguished. One of these is their intrinsic or internal effect, which is associated with specific changes in superficial, bulk, and chemical properties of a particle. The other being the external effect, represents a size-dependent response to external factors unrelated to the internal effect.

Due to the reduction in the spatial dimension, or confinement of particles or quasi particles in a particular crystallographic direction within a structure generally leads to changes in physical properties of the system in that direction. Hence classification of nanostructured materials and systems essentially depends on the number of dimensions which lie within the nanometer range as indicated below.

a) Systems confined in 3 dimensions [Zero dimension structures]

b) Systems confined in 2 dimensions [One dimension structures]

c) Systems confined in 1 dimension [two dimension structures]

Properties which may be affected by reduced dimensionality include:

**Physical properties:**

- Size, shape, **specific surface area**, aspect ratio
- Agglomeration/aggregation state
- Size distribution
- Surface morphology/topography
- Structure, including crystallinity and defect structure
- Solubility
Chemical properties:

- Structural formula/molecular structure
- Composition of nanomaterial (including degree of purity, known impurities or additives)
- Phase identity
- Surface chemistry (composition, charge, tension, reactive sites, physical structure, photocatalytic properties, zeta potential)

Magnetic properties:

- The large surface area to volume ratio results in a substantial proportion of atoms having different magnetic coupling with neighboring atoms leading to differing magnetic properties.
- Magnetic nanoparticles are used in a range of applications like imaging, bioprocessing, refrigeration as well as high storage density magnetic memory media.

Electronic properties:

- The changes which occur in electronic properties as the system length scale is reduced are related mainly to the increasing influence of the wave-like property of the electrons (quantum mechanical effects) and the scarcity of scattering centers.
- As the size of the system becomes comparable with the de Broglie wavelength of the electrons, the discrete nature of the energy states becomes apparent once again, although a fully discrete energy spectrum is only observed in systems that are confined in all three dimensions.
• In certain cases, conducting materials become insulators below a critical length scale, as the energy bands cease to overlap. Owing to their intrinsic wave-like nature, electrons can tunnel quantum mechanically between two closely adjacent nanostructures, and if a voltage is applied between two nanostructures which aligns the discrete energy levels in the DOS, resonant tunnelling occurs, which abruptly increases the tunnelling current.

**Optical properties**

• In small nano clusters, reduced dimensionality on electronic structure has the most profound effect on the energies of highest occupied molecular orbital (HOMO) which is valence band and the lowest unoccupied molecular orbital (LUMO), essentially the conduction band.

• The optical emission and adsorption occurs when the transition of the electrons occur between these two states.

• Semiconductors and many metals show large changes in optical properties such as color, as a function of particle size.

However, nowadays, the progress in fundamental scientific research virtually removes the boundaries and shortens the time between discovery of a new phenomenon and its practical application. Fundamental studies should be aimed at solving the definite problems of practice.
1.1.3 Silicates

Silicate is a compound containing an anion in which one or more central silicon atoms are surrounded by electronegative ligands. Silicate species most often consist of silicon with oxygen as ligand. Silicon anions with a negative net electrical charge must have that charge balanced by other cations to make an electrically neutral compound. In the vast majority of silicates, including silicate minerals, the Si atom shows tetrahedral coordination by 4 oxygens. In different minerals the tetrahedra show different degrees of polymerization. They occur singly, joined together in pairs, in large finite clusters including rings, in chains, double chains, sheets, and three dimensional frame works. These silicates are found in both amorphous and crystalline form. Silicate materials are divided according to structure of their silicate anion. Our study compound belongs to Nesosilicate which is has a lone tetrahedron shape [17].

![Structure of Silicate](image.png)

**Figure 1.1** Structure of Silicates

Silicate materials find many applications in the technical field. Among the various host materials silicates have been extensively investigated because of their stability, visible light transparency and relatively easy preparation. These alkaline earth silicates have attracted much attention and become an interesting topic in the field of luminescent
materials because of their higher chemical stability and water resistant property when compared with sulfide phosphorescent phosphors and strontium aluminate phosphors [11, 18-20].

Phosphor materials have a great potential for application in electrical and optical fields. These silicate phosphors are low dimensional structures so, it is easy to implant other ions into the host lattice and to create traps located at suitable depth where the excitation energy is stored and emission of light takes place later at room temperature [21].

1.1.4 Luminescence

Light is a form of energy. To create light, another form of energy must be supplied. There are two methods of producing light i.e by incandescence and luminescence. In luminescence light is not generated by high temperatures but it occurs at low temperatures. Luminescence is cold light that can be emitted at normal and lower temperature.

The mechanism involved in luminescence is that some energy source kicks an electron from an atom out of its lowest energy "ground" state into a higher energy "excited" state. Since excited states are unstable the material undergoes another transition back to its unexcited ground state, the absorbed energy is liberated in the form of either light or heat or both [22]. The excitation involves only the outermost electrons orbiting around the nuclei of the atoms.

Luminescence is emission of light by a substance not resulting from heat it is thus a form of cold body radiation. It can be caused by chemical reactions, electrical energy,
subatomic motions, or stress on a crystal. A luminescent system is constantly expending energy to drive the emission process.

The term 'luminescence' was introduced in 1888 by Eilhard Wiedemann [23]. To illustrate the diversity of luminescence emissions, the following represent some of the more commonly observed types of luminescence:

1.1.5 Types of Luminescence

1. **Electroluminescence** is produced by the passage of an electric current through an ionized gas [24]. *Example* -- A gas discharge lamp.


3. **Triboluminescence** is derived from the Greek word tribo meaning to rub. It is emitted when certain crystals are stressed, crushed, or broken [25].

*Example* -- Certain types of sugar crystals.

4. **Sonoluminescence** is delivered in fluids presented to exceptional sound (pressure) waves

5. **Chemiluminescence** derives its energy from chemical reactions. It is the breaking of chemical bonds that supplies the energy [26].

6. **Bioluminescence** can be considered a subdivision of chemiluminescence. It occurs when chemiluminescent reactions take place in living systems and usually involves an ATP reaction [27]. *Example* - Light emitted by fireflies and glow-worms.
7. **Cathodoluminescence** is light that is generated from the exposure of substances to cathode rays [28].

8. **Photoluminescence** derives its energy from the absorption of light energy (most commonly in the wavelength ranges of infrared, ultraviolet, or visible light) [29].

9. **Thermoluminescence** is phosphorescence triggered by temperatures above a certain threshold [30].

1.1.6 **Historical aspects of Luminescence**

The phenomenon of Luminescence has been known from ancient times in different civilizations in the Indian Vedas, Chinese book of odes, in antique Greece and in Rome, the glow that may be attributed to bio and chemiluminescence was mentioned. The concept of glow of non-thermal origin was introduced by Aristotle. Herodotus, is the one who claimed for the first time regarding the mineral luminescence from Aristotle’s work in 1280 A. Magnus mentioned that the mineral luminescence should be considered to TL glow of heated diamond. After these studies in 17, 18 and 19th centuries, countless observations related to natural and artificial phosphors are reported.

The history of luminescence in general may be considered only in its earliest stages. By the end of the 19th C and beginning of the 20th century, it breaks the history of individual branches and begins the history of luminescence of solids, organic compounds, fluorescent analysis, chemiluminescence, electroluminescence, crystal phosphors, luminescence of rare earths etc. From ancient times the nature of luminescence was investigated in the minerals. They have become the convenient objects for identifying the luminescence and hence till today the physicists have paid much attention on them.
1.1.7 Thermoluminescence

The wonder of TL goes back to 1663 when Robert Boyle reported his perception of the glow from a precious stone diamond when warmed in a dark to the Royal society. After this, nonstop work on TL was accounted for by such a large number of researchers like Henry Becquerel, Marie Curie etc. In 1930’s, theoretical and experimental work on TL has been reported by Urbach. In 1945, to do quantitative calculations, TL model was developed by Randall and Wilkins. Finally, the application of TL to dosimetry dates back to 1940’s [31].

Thermoluminescence is a common technique used for dosimetry of ionizing radiations. The energy absorbed by a phosphor on being exposed to some ionizing radiations is released as light on subsequent heating of the material. Heat is not the primary source of the energy here, only the trigger for the release of energy that originally came from another source. Thermoluminescence (TL) means not temperature radiation but enhancement of the light emission of materials already excited electronically by the application of heat. The quantum of intensity of light emitted by the phosphor on heating reflects the amount of irradiation dose given to it [32].

The understanding of TL starts with the band structure in solids. In insulators and semiconductors there will be valence and conduction band separated by a forbidden gap. At absolute 0Kvalence band will be completely filled and uppermost conduction band will be empty. At T> 0 K, some of the electrons are excited across the energy gap from completely filled valence band to empty conduction band. This transition leaves behind the hole in valence band. This band scheme applies to perfect crystals [33].
In crystals, various types of defects are present which include vacant lattice sites, interstitial atoms and impurity atoms. These defects change the periodicity of the lattice as well as the band structure which results in the creation of energy levels in the forbidden gap which serves as defect sites. Well known defect centers produced due to irradiation are F-center and V-center. F-center is an anion vacancy in the crystal lattice arising after trapping of an electron. F-Center is derived from the Greek word Farbe means color. When there are sufficient F-centers, the crystal absorbs sufficient light in the limited frequency range and as a result the crystal is coloured. Another radiation induced defect center is V- center which forms a group of defects absorbing light in the violet region [34].

After irradiation, the electrons gains sufficient energy and rise to the conduction band and in between them, they are trapped in defects centers. When the solid is heated, the trapped electrons gain necessary energy to escape from the traps back to the conduction band. After that, they make direct transition to valence band or they can recombine with holes or they may become retrapped. If the electron trapped energy levels are close to the conduction band this thermal untrapping may occur at room temperature but if the traps are deeper which requires some heating for the electrons to be released which is known as thermoluminescence [35].
Figure 1.2 Schematic representation of thermoluminescence process

Figure 1.3 Schematic representations of band structure and defect levels
A necessary condition for a solid to be a suitable luminescent material for TL dating is that the traps should be deep which cannot be emptied easily. Thus the energy levels of the trapped electrons and holes should be situated sufficiently far from the bottom of the conduction and top of the valence band respectively.

In the above simple model, shown in figure 1.3 the recombination centre R is a luminescent centre where the recombination of the electron and hole leaves the centre in one of the higher excited states. Return to the ground state is coupled with the emission of light quanta, i.e. TL. The intensity of TL I (t) in photons per second at any time ‘t’ during heating is proportional to the rate of recombination of these holes and electrons at R. If ‘m’ (m$^3$) is the concentration of holes trapped at R the TL intensity can be written as

$$TL\ intensity, \ I(t) = -\frac{dm}{dt}$$  \hspace{1cm} (1.1)

The rate of recombination will be proportional to the concentration of free electrons in the conduction band $n_c$ and the concentration of holes ‘m’ i.e.

$$I(t) = -\frac{dm}{dt} = n_c mA$$  \hspace{1cm} (1.2)

Where A $\rightarrow$ recombination probability.

The rate of change of the concentration of trapped electrons $n$ is equal to the rate of thermal release minus the rate of retrapping.

$$-\frac{dn}{dt} = np - n_c (N - n)A_c$$  \hspace{1cm} (1.3)
Where ‘N’, is the concentration of electron traps and ‘A’, the probability of retrapping.

The rate of concentration of electrons is equal to the rate of thermal release minus the rate of retrapping and the rate of recombination as given below.

\[
\frac{dn_c}{dt} = np - n_c(N - n)A - n_c mA
\]  

(1.4)

To develop an analytical expression some simplifying assumptions must be made. An important assumption is that at any time ‘t’

\[
\frac{dn_c}{dt} \ll \frac{dn}{dt}, \frac{dn_c}{dt} \ll \frac{dm}{dt}
\]

(1.5)

This assumption is called Chen and McKeever [36], the quasiequilibrium assumption since it requires that the free electron concentration in the conduction band is quasistationary. The trapped electrons and holes are produced in pairs during the irradiation. Charge neutrality dictates therefore that,

\[ n_c + n = m \]  

(1.6)

Which for \( n_c = 0 \) means that \( n = m \) and

\[ I(t) = -\frac{dm}{dt} \approx -\frac{dn}{dt} \]  

(1.7)

Since \( dn_c/dt = 0 \) one gets from (3a) and (3b)

\[ I(t) = \frac{mA n_s \exp \left\{ -\frac{E}{kT} \right\}}{(N - n)A + mA} \]  

(1.8)
First order Kinetics

Equation (6) cannot be solved analytically without additional simplifying assumptions. Randall and Wilkins [37-38] assumed negligible retrapping during the heating stage, i.e. mA >> (N-n) Ar. Under this assumption, equation (1.7) can be re-written as

\[ I(t) = -\frac{dn}{dt} = sn \exp\left\{ -\frac{E}{kT} \right\} \]  \hspace{1cm} (1.9)

This differential equation describes the charge transport in the lattice as a first order process and the glow peaks analysed from this equation are called first order glow peaks. By solving the above equation (1.7) we get

\[ I(t) = -\frac{dn}{dt} = n_0 s \exp\left\{ -\frac{E}{kT} \right\} \exp\left\{ -\int_0^t \frac{E}{kT(t')} \, dt' \right\} \]  \hspace{1cm} (1.10)

Where \( n_0 \) is the total number of trapped electrons at time \( t=0 \). Usually, the temperature is raised as a linear function of time according to equation

\[ T(t) = T_0 + \beta t \]  \hspace{1cm} (1.11)

where \( \beta \) is the constant heating rate and \( T_0 \) the temperature at \( t = 0 \). This gives for the intensity as function of temperature

\[ I(T) = -\frac{1}{\beta} \frac{dn}{dt} = n_0 s \frac{1}{\beta} \exp\left\{ -\frac{E}{kT} \right\} \exp\left\{ -\frac{s}{\beta} \int_{T_0}^T \exp\left\{ -\frac{E}{kT'} \right\} \, dT' \right\} \]  \hspace{1cm} (1.12)

This is the well-known Randall-Wilkins first-order expression of a single glow peak, the peak as a characteristic asymmetric shape being wider on the low temperature side than on the high temperature side. On the low temperature side i.e., in the initial rise of the glow peak, the intensity is dominated by the first exponential (\( \exp (-E/KT) \)). Thus, if I is
plotted as function of 1/T, a straight line is expected in the initial rise temperature range, with the slope of \(-E/K\), from which the activation energy \(E\) is readily found.

It may be noted that the temperature at the peak maximum, \(T_m\), stays fixed. This is a characteristic of all first order TL curves. The condition for the maximum can be found by setting \(dI/dt = 0\), then we get

\[
\beta E/kT_m^2 = s \exp \left\{-\frac{E}{kT_m} \right\}
\]  

(1.13)

In this equation \(n_0\) does not appear, which shows that \(T_m\) does not depend on \(n_0\). In the application in dosimetry \(n_0\) is the parameter of paramount importance since this parameter is proportional to the absorbed dose. It is simple to see that the area under the glow peak is equal to \(n_0\) since,

\[
\int_0^\infty I(t) \, dt = -\int_{n_0}^{n_\infty} \frac{dn}{dt} \, dt = -\int_{n_0}^{n_\infty} dn = n_0 - n_\infty
\]  

(1.14)

And, \(n_\infty = 0\) for \(t \to \infty\)

\[
I(T) = I_m \exp \left[1 + \frac{E}{kT} - \frac{T_m}{kT_m} \frac{T^2}{T_m^2} \exp \left\{\frac{E}{kT} - \frac{T_m}{kT_m} \right\} \right] \left(1 - \Delta - \Delta_m \right)
\]  

(1.15)

Second order kinetics:

Garlick and Gibson [39] considered the possibility that retrapping dominates i.e. \(mA << (N-n) A_r\). Further, they assumed that the trap is far from saturation, i.e. \(N >> n\) and \(n = m\).

With these assumptions, eqn. (6) becomes

\[
I(t) = -\frac{dn}{dt} = s \frac{A}{N A_r} n^2 \exp \left\{-\frac{E}{kT} \right\}
\]  

(1.16)
Now, it may be seen that $dn/dt$ is proportional to $n^2$ which means a second order reaction.

With the additional assumption of equal probabilities of recombination and retrapping, $A=A_r$, integration of equation (1.14) gives

$$I(T) = \frac{n_0^2 S}{N \beta} \exp\left(-\frac{E}{kT}\right) x \left[ 1 + \frac{n_0}{N \beta^2} \exp\left(-\frac{E}{kT'}\right) \right]^2$$

(1.17)

This is known as Garlick–Gibson TL equation for second order kinetics. The main feature of this curve is that it is nearly symmetric, with the high temperature half of the curve slightly broader than the low temperature half. It is seen that $T_m$ decreases as $n_0$ increases. It can be derived [40] that the temperature shift can be approximated by

$$T_1 - T_2 \approx T_1 T_2 \frac{k}{E} \ln f$$

(1.18)

Where, $T_1$ is the temperature of maximum intensity at a certain dose and $T_2$ the temperature of maximum intensity at $f$ times higher dose. From equation (1.16), it follows further that for a given increase of the dose, the shallower the trap i.e., the smaller $E$, larger the peak shift.

Also, for second order kinetics the glow peaks, equation 1.15, can be approximately written in terms maximum peak intensity $I_m$ and maximum peak temperature $T_m$

$$I(T) = 4I_m \exp\left(\frac{E}{kT} - \frac{T_m}{kT}\right) X \left[ \frac{T^2}{T_m^2} (1 - \Delta) \exp\left(\frac{E}{kT} - \frac{T_m}{kT}\right) + 1 + \Delta_m \right]^2$$

(1.19)

**General – order kinetics:**

But, in some cases, the TL peak will fit neither first-nor the second-order kinetics. May and Partridge [41] used an empirical expression for general order TL kinetics, namely,
\[ I(t) = -\frac{dn}{dt} = n^b s^I \exp\left( -\frac{E}{kT} \right) \]  

(1.20)

Where \( b \) is defined as the general order parameter

\[ I(T) = \frac{s^n}{\beta n_0} \exp\left( -\frac{E}{kT} \right) X \left[ 1 + (b-1) \frac{s^n s^\beta}{\beta T_0} \exp\left( -\frac{E}{kT} \right) dT^b \right]^{-\frac{b-1}{b}} \]

(1.21)

Where now \( s^{11} = S_1 n_0 b^{-1} \) with unit \( S^{-1} \). Eqn 1.19 includes the second order case \((b=2)\) and reduces to eqn 1.10. When \( b \rightarrow 1 \). It should be noted that according to eqn 1.18 the dimension of should be \( m^{3(b-1)} S^{-1} \) which means that the dimension changes with the order \( b \) which makes it difficult to interpret physically. Still, the general order case is useful since intermediate cases can be dealt with and it smoothly goes to I and II order when \( b \rightarrow 1 \), and \( b \rightarrow 2 \) respectively.

Since there is no existing TL material which can be explained by simple model advanced models comes into existence. In general, a real TL material will be having more than a one single electron trap. All the traps will not be active in the temperature range in which the specimen is heated. A thermally disconnected trap can be filled with the electrons during irradiation but this has a trap depth which is much greater than the active trap. Thus, when the solid is heated only the electrons which are trapped in the deeper levels are unaffected.

**Advanced models**

The one trap-one centre model shows all the characteristics of the TL phenomenon and explains the behavior of the TL glow shape under variation of the dose and heating rate. However, a real TL material will show more than one single electron trap. Not all the
traps will be active in the temperature range in which the specimen is heated. Electrons trapped in the deeper levels are unaffected and thus the deep electron trap is said to be thermally disconnected. But, its existence has bearing on the trapping filling and eventually on the shape of the glow peak [42]. Piters and Bose [43] have incorporated defect reactions into the rate equations and glow curves are simulated. After the discovery of TL, research was carried out to discover suitable material for solid state radiation dosimeter. M.C. Keever works suggest some properties which are required for selecting a suitable material for dosimetric use [44].

- High TL sensitivity [37]
- Peak temperature should be around 200-280 °C [45]
- Response directly proportional to the irradiation dose [36].

1.1.8 Factors affecting the thermoluminescence

Some of the general characteristics of thermoluminescence dosimetry (TLD) described by A.J.J. Boss [46] are as follows.

**Sensitivity:**

The sensitivity of the TL relies on the thermally stimulated material, TSL read out instrument condition and measurement parameters. Further TL given out from the material depends on whether it is mono or poly crystalline powders, mass or thin, sintered or not. Continuously the sign measured from the instrument may not be precise on the grounds that it relies on upon somany elements like condition kept up at the season of
estimation, limit/capacity of the measuring instrument, warming rate, potential looked after and so on [35].

**Dose Response:**

The TSL signal is a function (F) of the absorbed dose (D). Ideally, the F(D) shows a linear dose response over a wide dose range at least over the range of interest of the application. However, most materials used in practical dosimetry show a variety of non-linear effects. The some of the dosimetric requirements in some major application areas requires linear response.

A pattern that is found frequently as the dose increased is first a linear response then a supra linear and finally during the approach to saturation a sub linear response. The normalized dose response function (also called supra linearity index) F (D) is defined as

$$F(D) = \frac{F(D) / D}{F(D_1) / D_1}$$

Where, F (D) is the dose response at dose D and D_1 is low dose at which the dose response is linear. The ideal TLD material has F (D) =1 in a wide dose range. If F (D) >1 the response is called supralinear, if F(D) < 1 the response is called sub linear [47].

**Annealing behavior:**

One of the benefits of this technique is reusability of the material. After TL read out we can reuse the same material for other reason same as the first one. For this anneling procedure is required. This anneling processs includes cooling the material to room temperature after holding it in high temperature. The procedure includes 3 noteworthy steps first it conveys back the TL sign to zero by clearing every one of the traps which
have not purged amid the read out. Next it brings back the warm harmony which was built up in the material before illumination. At last it resets thermally separated and profound traps in the material

**Fading:**

Fading is only misfortune in the quality of the TSL signal when it's presented to light. Common daylight is adequate for fading to occur. At the point when material is presented to sunlight charge transporters may escape out of the traps and move back to the ground state may happen before TSL read out. Along these lines while managing delicate materials test must be done in dim room. So fading can be maintained a strategic distance from [34].

**Physical forms:**

Physical type of the material likewise had its impact on TSL signal. Since power of the TSL signal relies on upon the introduction region if the region is all the more then force is likewise more. In this way it relies on upon whether the sample is in powder structure are strong, single precious stone or polycrystal. Typically powder structure will indicate better result.

**1.1.9 Applications of thermostimulated luminescence**

Thermostimulated luminescence is perhaps one of those rare physical phenomenons, which is more successfully applied than understood. Its application potential was first shown in 1953 and since then with the development of better instrumentation and basic understanding, its applications have engulfed a whole spectrum of disciplines such as
Archeology, Biology and Biochemistry, Forensic Sciences, Geology, Radiation Dosimetry, Radiation Physics, Space Science, Spectroscopic analysis, TSL photography and so on [48]. The important aspects of these applications are briefly summarized in the following sections.

**Archeology**

Thermistimulated glow procedure has been observed to be effective in this field. Its utilized as a part of

- Dating old ceramics and different minerals
- Detecting workmanship imitations.
- The age touched base from the TSL gathered subsequent to the season of terminating of the sample is genuinely illustrative of the archeological age

Fundamental clax network is going to incorporate TSL delicate materials in this way TSL is transmitted from the samples. This is going to get radiation both inside and remotely. From radio dynamic components it will get interior radiations and outside is from radioactive substance of the encompassing. In any case, the aggregate illumination rate ought to be of the order of 1 out of which major contribution is from the internal component.

**Biology and biochemistry**

Utilizations of animated procedure in the investigation of bio and biochemical frameworks are finished by the estimation in the LNT-RT range.An attempts are made to concentrate on
• Presence of bio substance mixes like hydroxyl and amino benzoic acids, urea, nucleic acids, proteins.

• Presence of organic samples plant leaves, green growth and microscopic organisms.

• Poorer stability of the distinctive types of chemicals.

• The inter and intra molecular transfer of radiation damage in nucleic acids, proteins and their constituents could be corrected with their TSL behavior.

• The photosynthetic electron transport courses in the Z graphs, extra courses outlined and the collaboration in the middle of salts and proteins could be comprehended from the TSL designs.

**Forensic science**

TSL can give us an alluring system on materials included in criminal cases viz: glass, soil, safe protection materials, and so forth i.e. when the TSL characteristics do not match, it can be said with certainly that a particular sample has not come from a known sources.

The significant perceptions in criminological sciences are

• To develop and manage strategies to contrast evidentiary materials and same materials of known origin.

• Materials to be dissected non-damagingly for confirmation perspective.
• To reduce the probability of any coincidental matching and improve the confidence on the TSL measurements whose signal to noise ratio may be bad, examinations may be made of the TSL glow curves from the virgin samples as well as after a heavy artificial gamma or X-ray irradiations and also of the TSL emission spectra.

**Geology**

TSL dating method has been successfully employed in estimating the age of radioactive mineralization of a deposit in India by measuring the TSL of smoky quartz crystals collected from a non-radioactive intrusive layer in between two radioactive veins in the deposit. Here, TSL technique is made use for identification of minerals, classification of mineral deposits, age determination, thermal histories of mineral deposits, radioactive trace estimation in rocks, stratigraphy etc.

In large limestone quarries, geological technique is employed to asses the ages of sedimentary rocks, TSL characteristics of various samples collected from the same stratum over a half-mile face were identical but differed greatly even for a few feet displacement on either side of the stratum. Thus, this could provide a means of determining whether two samples of sedimentary rocks were laid down at the same time in the same environment, although they are widely separated geographically.

TSL technique has been suggested in paleothermometry to determine magma temperatures and measurements on granite samples have been used to obtain radial profiles from the center of a nuclear explosion in Algeria.
Quality control in industry

Even as early as 1938, the application of TSL in the control of feldspars in ceramic products has been described. The amount of TSL given out by a ceramic after artificial irradiation is directly indicative of its feldspar content at trace levels where a particular process is repeated many number of times to produce batches of the same material and any uncontrollable variations in the feldspar contents can be checked quickly and efficiently. The lattice defects, which permit the adsorption reactions, might also play a role in the TSL emitted by these substances and the nature and intensity of TSL glow curve in such cases could be used as a criterion in controlling the preparative parameter of the desired catalyst.

In principle, TSL method could be employed in the quality control of many glass, ceramic and semiconductor products. Recently, it has been shown in the case of textile fibers that low temperature TSL glow curve changes can be correlated with structural differences and/or chemical tracer impurities. However, these have not yet received the attention of the industries.

Radiation dosimetry

Important developments in the understanding and applications of the TSL owe their origin singularly to the efforts made in the use of this phenomenon in the field of radiation dosimetry and in the research for more sensitive dosimetric phosphors. The main basis in thermostimulated luminescence dosimetry (TSLD) is that TSL output is directly proportional to the radiation dose received by the phosphor and hence provides a means of estimating unknown irradiations. Thus, it finds immense use in the monitoring
of doses received by radiation workers on a routine basis on weekly/monthly/yearly basis depending upon whatever a situation may warrant. Hence, the relevant dose which is medically significant to radiation workers from protection point of view is not readily obtained. Some of the phosphors like LiF, BeO, CaSO$_4$, CaF$_2$ and Mg$_2$SiO$_4$ which are more sensitive towards radiation.

**Miscellaneous applications of TSL**

TSL methods have been attempted on lunar materials to understand the thermal histories and recent surface activities. The annual average lunar surface temperature could also be estimated from the TSL measurements. The variation in the TSL output of various regions of the meteorite sample could be extrapolated to get an idea of pre-entry shape of meteorites. In radiation physics, TSL detectors offer excellent possibilities to obtain data pertaining to reactor shielding studies. These have been suggested to use TLS for measurements of microwave and laser outputs. There have been interesting applications of TLD in diagnostic or therapeutic medical procedures by making in vivo dose measurements. The TSL measured from the roof tiles nearly twenty years after the atomic bombing of Hiroshima and Nagasaki cities, have given valuable information on radiation dose distributions.

Mineralogists make use of this TSL photography for direct recording of distribution pattern of TSL sensitive material. The technique has been advocated as a tool for the environmental analysis of sedimentary core samples in identifying slit and clay layers, CaCO$_3$ and FeO nodules and some digenetic and sedimentary features. In a similar approach, the image screens containing TSL phosphors have been used for the storage of
X-ray or thermal neutron radiographs. Radioluminescence, is extensively used in the spectro chemical analysis of elements like lanthanides, Mn, Ag etc in certain matrices at even ppm levels. If the glow pattern is known, the temperature or radioluminescence measurements can be judiciously chosen to improve detection limits even further.

1.1.10 Photoluminescence.

Fluorescence and Photoluminescence are luminescence where the energy is supplied by electromagnetic radiation. Photoluminescence is generally taken to mean "luminescence from any electromagnetic radiation" [49], while fluorescence is often used only for luminescence caused by ultraviolet, although it may also be used for other photoluminescences. Fluorescence is seen in fluorescent lights, amusement park and movie special effects, the redness of rubies in sunlight, "day-glow" or "neon" colors, and in emission nebulae as seen with telescopes in the night sky. Bleaches enhance their whitening power with a white fluorescent material. In fluorescence, the emission stops in about $10^{-8}$ sec or less, whereas in phosphorescence emission stops in about seconds or even minutes [50].

Photoluminescence is defined as the spontaneous emission of light from the material under optical excitation [51]. It is a very efficient contact less non destructive widely used technique for the analysis of the electronic properties. When light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created. Eventually these excitations relax and electrons return to the ground state. If radiative relaxation occurs, the emitted light is called PL [52]. The PL intensity gives a
measure of the relative rates of radiative and non radiative recombination; it also provides information on the quality of surfaces and interfaces.

**Figure 1.4** schematic representations for Photoluminescence

Photoluminescence should not be confused with reflection, refraction, or scattering of light, which cause most of the colors seen in daylight or in bright artificial lighting. Photoluminescence is distinguished in that the light is absorbed for a significant time, and generally produces light of a frequency that is lower than, but otherwise independent of, the frequency of the absorbed light.

The energy of the emitted light relates to the difference in energy levels between the two electron states involved in the transition between excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process. The recombination helps in identifying surface interface and impurity level.
Defects and impurity levels are detected using the PL studies. The intensity of the incident light controls a critical property of PL experiment, the density of photoexcited electrons and holes.

In PL studies, defects and impurities break the periodicity of the lattice and perturb the band structure locally. The perturbation usually can be characterized by a discrete energy level that lies within the band gap. Depending on the defect or impurity, the state acts as a donor or acceptor of excess electrons in the crystal. Optical transitions provide direct access to the energy level structure of a system. Photons of a particular energy that are absorbed or emitted by the sample provide evidence of electronic states differing by that energy within the material. The intensity of the incident light controls a critical property of PL experiment, the density of photoexcited electrons and holes. When the carrier density is low, the measurement is dominated by discrete defect and impurity sites in the interfaces and within the bulk of the material. Features of the emission spectrum can be used to identify surface, interface and impurity levels and to gauge interface roughness and alloy disorder. When the surface structure is poor, the PL spectrum changes with increasing excitation energy, the strength of the defect related lines increasing relative to bulk features. Correlation of these changes with penetration depth indicates the location of near surface defects.

1.1.11 Factors affecting photoluminescence.

To design a phosphor the basic requirements are choice of the host component, choice of the activator, and killers of luminescence.
1. **Choice of the host components.**

In outlining a phosphor the inorganic host comprises of one of a few distinct cations joined with one of a few unique anions. Anion might be basic or it might comprise of a gathering of particles like borates, silicates or phosphates. Besides, the anion might be optically inactive or optically dynamic. The host cations are those particles which have the uncommon gas electron configuration or closed electron shells as a consequence of which are optically dynamic. It ought to be obvious that both the cation and anion determination must be optically straightforward since the ingestion excitation process needs to happen in an activator site. We need to choose a cation in a manner that they should be balanced out in the host gem in the required valence. The phosphors in view of the salt metal cation would display the high energy efficiencies of luminescence.

2. **Choice of the activator**

In picking an activator one must have the capacity to frame and balance out the activator in legitimate valence state inside the host crystal the electronic design $d^{10} s^2$ ($^{1}S_0$). All the ions of this electronic arrangement can't be exhibited as an activator in light of the apparent trouble of adjustment of the required valence state, paying little heed to the host crystal. Further the activator cation and the host cation should be coordinated in size in order to get maximal productivity in the created phosphor. Confound makes strain in the cross section and restrains the genuine dissolvability of the activator in the host grid. The activator cation should be of the same valence state
as that of the host cation. Something else, the activator will substitute into the cross section with the arrangement of cation opportunities.

3 Killers of luminescence

Cations having unpaired electrons turn as quenchers of luminescence. For the most part, cations are acceptors since they can't experience an excitation move due to ground state coupling to the neighborhood phonon modes. They work on the other hand to radiance process. To acquire a phosphor having a high level of luminescence productivity it is critical to bar all move metals from the host gem in light of the fact that the nearness of little measure of polluting influence goes about as enemies of luminescent proficiency. High level of virtue is compulsory to acquire a phosphor with a high vitality effectiveness and high quantum proficiency.

1.1.12 Applications of photoluminescence.

PL is a very efficient, contactless, non destructive widely used technique for the analysis of opto electronic properties of semiconductors and insulators. PL helps in better understanding of recombination mechanism and identification of surface, interface and impurity levels [53]. PL finds application in band gap determination. Common radiative transition in semiconductor occurs between states in the conduction and valence bands with the energy difference known as band gap energy. Assessment of the material quality can be done by the PL studies. Material quality can be measured by qualifying the amount of radiative recombination keeping in mind that non-radiative recombination is
associated to localize defect levels that are determined to material quality and subsequently to device performance.

1.2 LITERATURE REVIEW

V.B. Bhatkar et al have synthesized various silicates by solution combustion method and showed that combustion method is suitable for the preparation of silicates. Among these silicates ZnSiO$_4$: Mn and BaSi$_2$O$_5$: Pb can be reproduced by this method of synthesis. Ce$^{3+}$, Eu$^{2+}$, Pb$^{2+}$ are good activators [12]. The effect of flux and firing temperature on structure and luminescence properties of Sr$_2$SiO$_4$:Eu$^{2+}$ was studied by Jee Hee Lee et al [54]. Eu (I) increases with increase in flux but decreases with increase in firing temperature. Further with increase in Eu$^{2+}$ concentration, red shift was observed and β phase transfers to α phase.

Pr$^{3+}$ doped Sr$_2$SiO$_4$ was synthesized by Li Zhang et al using solid state method [55]. Synthesis condition was optimized along with varying calcinations temperature to get white light emission in Sr$_2$SiO$_4$:Pr$^{3+}$. J.S. Kim et al synthesized M$_2$SiO$_4$:Eu$^{2+}$ (M= Ba, Sr, Ca). By varying M$^{2+}$ cation they studied the emission color variation [56]. The variation of emission peak intensity and emission peak of phosphor by varying pre treating temperature was studied by Wei- hsiang et al. It was showed that the product pre treated at 1200°C has the maximum emission intensity [57].

SUN Xiaoyuan et al have synthesized green yellow emitting Sr$_2$SiO$_4$:Eu$^{2+}$ phosphor by solid state reaction and studied the phase variation and PL variation with variation in the concentration of Eu$^{2+}$ and showed that β-Sr$_2$SiO$_4$:Eu$^{2+}$ phosphor could be good candidate for generally white light [58]. Temperature dependent PL studies of M$_2$SiO$_4$:Eu$^{2+}$ (M= Sr,
Ba, Ca) was studied by Jong su Kim et.al and showed that normal red shift ws observed in Sr$_2$SiO$_4$:Eu$^{2+}$ [59].

Sr$_2$SiO$_4$:Eu$^{2+}$ was co doped with different dopants to study the luminescence properties. N. Lakshminarasimhan et.al [60] have noticed that Sr$_2$SiO$_4$:Eu$^{2+}$ co doped with Dy$^{3+}$ was a suitable codopant. E.D.Bacce et.al reported the luminescence behvaour of Eu$^{3+}$-O$^{2-}$ associated with Sr$_2$SiO$_4$ doped with Eu$^{3+}$ or codoped with Zn$^{2+}$ ions. Here, Zn$^{2+}$ acts as charge compensating agent [61]. QIAO Yanmin et.al have synthesized Sr$_2$SiO$_4$ using Eu$^{2+}$ and Eu$^{3+}$ as dopants. Structural and optical properties were studied and from these studies they confirmed that Sr$_2$SiO$_4$:Eu$^{2+}$ is suitable for white LED’s [8].

Alkaline earth orthosilicate were synthesized by Tony Joseph et.al to study the dielectric properties. It was found that the di electric property of Sr$_2$SiO$_4$ lies between Ba$_2$SiO$_4$ and Ca$_2$SiO$_4$ [19]. Yong Sun Won et.al showed the presence of two sites in Sr$_2$SiO$_4$:Eu$^{2+}$ [62]. The two peak emissions of Eu$^{2+}$ in Sr$_2$SiO$_4$ were cross checked from density functional theory. Sr$_2$SiO$_4$:Eu$^{2+}$ nanorods are synthesized by sol gel method by Chongfeng Guo et.al [63]. Further they studied the luminescent properties. It was observed that it emits light in blue green region.

Chia Hao Hsu et.al aim was to enhance the PL intensity of Sr$_2$SiO$_4$:Eu$^{2+}$ by tuning different size of silica particles. It was observed that there was a larger shift in emission wavelength and emission intensity was high for silica size of 10nm and it was suitable for light tenability [64]. Sang Ho Lee et.al have synthesized the different phases of Sr$_2$SiO$_4$:Eu$^{2+}$ by spray pyrolysis method using NH$_4$Cl flux [65]. The structural and
optical properties of both the phases are studied. It is found that β phase had higher photoluminescent intensity than α phase.

The effect of flux on the PL intensity was studied by Hoang-Duy et.al using different fluxes. The relative intensity of two emission bands strongly depends on the flux. It was concluded that in Sr$_2$SiO$_4$ lattice there are two Sr$^{2+}$ sites [66]. Jee Hee Lee et.al showed the correlation between phase transition and luminescent properties of Sr$_2$SiO$_4$:Eu$^{2+}$ using different fluxes and varying the concentration of Eu$^{2+}$ [67]. Hai Guo et.al have synthesized yellow emitting phosphor Sr$_2$SiO$_4$:Eu$^{2+}$ by solid state method using different fluxes. Out of all those fluxes, NH$_4$F is superior to other fluxes [68].

Ashley P. Black et.al [69] Synthesized Sr$_2$SiO$_4$ phosphor and tuned its emission wavelengths by La/N contents. As a result, emission changed from yellow to orange. Karol Szczodrowski et.al incorporated Ti into the Sr$_2$SiO$_4$ host and studied the PL and TL properties which shows that incorporation of Ti increases the persistence luminescence time [70]. Modification of the Co ordination and environment of Eu$^{2+}$ in Sr$_2$SiO$_4$:Eu$^{3+}$ was done to achieve full color emission by Li-Cheng Ju et.al [71]. Santosh K. Gupta et.al have synthesized Sr$_2$SiO$_4$:Eu$^{2+}$ by reverse micellar route and studied the white light emission and TL studies [72].
1.3 OBJECTIVES

The objectives of the present work are listed below.

- To explore the possibilities to extend the novel combustion process for the preparation of undoped, rare earth single doped and co-doped silicates.
- To choose suitable fuels for the synthesis of silicates.
- To characterize the combustion derived products and study their particulate nature, formation of compound, morphology, and sintering behavior.
- To study the effect of dopant and co-dopant over crystalline phase formation, defect creation.
- To study the photoluminescence and thermoluminescence properties of undoped, doped, co-doped and flux added nanopowders which are derived by combustion method.
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