Chapter 1

Materials, Methods and Measurements- An Overview

Abstract

This chapter is of introductory nature and is divided into three sections. The first section includes the details of different materials used in the present research work. This consists of the basic features of the clay minerals, dyes and rare earth doped materials such as rare earth titanates and glasses. Second section discusses the various methods used for the preparation and characterization of these materials. The subdivisions of this section contain the fundamentals of self propagated high temperature synthesis, sol gel techniques, and photothermal and fluorescence studies. The last section explains the basic details of the instruments used for characterising the samples. This section gives the particulars of light sources, fluorescence spectrophotometer, spectrophotometer, photoacoustic cell and other measuring instruments. Finally, the scope of the work presented in this thesis is also given.
Materials- Methods- Measurements

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1.5. References
1.1. Section I – Materials:

1.1.1. Part A: Clay minerals:

A1. Introduction:
Clay has become indispensable to modern living. It is the material of many kinds of ceramics, such as porcelain, bricks and tiles as well as an essential constituent of plastics, paints, paper, rubber, and cosmetics. Clay is non-polluting and can be used as a depolluting agent. Of great importance for the near future is the potential of some clays to be dispersed as nanometre-size unit particles in a polymer phase, forming novel nano-composite materials with superior thermo-mechanical properties.\(^1\)

Clay is a widely distributed, abundant mineral resource of major industrial importance for an enormous variety of uses.\(^2\) The term ‘clay’ is ambiguous and has multiple meanings: a group of fine grained minerals—i.e., the clay minerals; and a type of rock—i.e., a sedimentary deposit of fine grained material usually composed largely of clay minerals.\(^3,\,4\) Clay also includes fine grained deposits of non-alumino-silicates such as shale and some argillaceous soils.\(^5\)

Clay minerals are a common constituent of hydrothermal deposits and occur abundantly in all types of sediments and sedimentary rocks, perhaps comprise as much as 40% of the minerals. The fine grained clay minerals are built up of tetrahedrally (T) (Si, Al, Fe\(^{3+}\)) and octahedrally (M) (Al, Fe\(^{3+}\), Fe\(^{2+}\), Mg) coordinated cations organised to form either sheets or chains. Naturally occurring inexpensive clay materials may be found in all countries and have innumerable uses and applications in our daily life which demand their characterization.\(^6\)

A2. Clay mineral properties:
All clay minerals are hydrous.\(^7\) The clay mineral properties are very complex and are dependent on environmental conditions. The complexity arises from the occurrence of different species and properties as well as various modifications of natural clays. Clay minerals are characterised by certain properties,\(^1\) including

1. A layer structure with one dimension in the nanometre range; the thickness of the 1:1 (TM) layer is about 0.7 nm, and that of the 2:1 (TMT) layer is about 1 nm,
2. The anisotropy of the layers or particles,
3. The existence of several types of surfaces: external basal (planar) and edge surfaces as well as internal (interlayer) surfaces.\(^8\)
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4. The ease with which the external, and often also the internal, surface can be modified (by adsorption, ion exchange, or grafting),

5. Plasticity, and

6. Hardening on drying or firing; this applies to most (but not all) of the clay minerals. 
Table 1.1 gives the major differences between the clay and clay minerals.

Table 1.1: Distinction between clay and clay mineral.[1]  

<table>
<thead>
<tr>
<th>Clay</th>
<th>Clay mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>Natural and synthetic</td>
</tr>
<tr>
<td>Fine grained (&lt;2 µm or &lt;4 µm)</td>
<td>No size criterion</td>
</tr>
<tr>
<td>Phyllosilicates as principal constituents</td>
<td>May include non-phyllosilicates</td>
</tr>
<tr>
<td>Plastic [a]</td>
<td>Plastic</td>
</tr>
<tr>
<td>Hardens on drying or firing</td>
<td>Hardens on drying or firing</td>
</tr>
</tbody>
</table>

[a] With some exceptions like flint clays.

Clay minerals belong to the phyllosilicates.[9] The basic structural units in layer silicates are two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of aluminium- or magnesium-oxygen-hydroxyl octahedra. The former unit is called the tetrahedral sheet [7](T) or the silica sheet. [9] The brucite or gibbsite sheets consist of two planes of hydroxyl ions between which lies a plane of magnesium or aluminium ions which is octahedrally coordinated by the hydroxyls. This latter unit is known as the octahedral sheet (M). These sheets are combined so that the oxygens at the tips of the tetrahedra project into a plane of hydroxyls in the octahedral sheet and replace two-thirds of the hydroxyls. This combination of sheets forms a layer. [7] In most clay minerals, such sheets of tetrahedra and of octahedra are superimposed in different fashions.[9]

The structures of phyllosilicates are all based on a T and a M sheet that may condense in either a 1:1 or 2:1 proportion to form an anisotropic TM or TMT layer. The layers or sheets may be negatively charged (as for the majority of clay minerals), positively charged, or essentially uncharged (as in talc). The layer charge density and the nature of the compensating or charge-balancing cation determine many important surface and colloidal properties. An assembly of layers is a ‘particle’, and an assembly of particles is an ‘aggregate’ (Figure 1.1).[1] All phyllosilicates are therefore porous, containing pores of varied size and shape.[1]
A3. Structure and mineralogy of clay minerals:

A3.1. Tetrahedral sheet:

In the tetrahedral sheet or the silica sheet, the silicon atoms are coordinated with four oxygen atoms. The oxygen atoms are located at the four corners of a regular tetrahedron with the silicon atom in the center. In the sheet, three of the four atoms of each tetrahedron are shared by three neighboring tetrahedra. The fourth oxygen atom of each tetrahedron is pointed downward. The $\text{SiO}_4^{2-}$ tetrahedra connected at three
corners in the same plane form a hexagonal network. All the tips of the tetrahedra point in the same direction.

Each tetrahedron consists of a cation, coordinated to four oxygen atoms, and linked to adjacent tetrahedra by sharing three corners (the basal oxygen atoms, \(O_b\)) to form an infinite two-dimensional ‘hexagonal’ mesh pattern along the a, b crystallographic directions (Figure 1.2).\(^{[10]}\)

![Figure 1.2: (a) Tetrahedron [TO₄]; (b) tetrahedral sheet. Oₐ and Oₐ refer to apical and basal oxygen atoms, respectively. a and b refer to unit-cell parameters.](image)

**A3.2. Octahedral sheet:**

In the Al-, Mg-O-OH sheets, the Al or Mg atoms are coordinated with six oxygen atoms or OH groups which are located around the Al or Mg atom with their centers on the six corners of a regular octahedron. The sharing of oxygen atoms by neighbouring octahedrons results in a sheet. The oxygen atoms and hydroxyl groups lie in two parallel planes with Al or Mg atoms between these planes. The oxygen and hydroxyl groups form a hexagonal close packing. This sheet is called the octahedral sheet. This is subdivided into alumina or magnesia sheet, which is also called gibbsite sheet or brucite sheet, respectively.

In the octahedral sheet, connections between each octahedron to neighbouring octahedra are made by sharing edges. The edge-shared octahedra form sheets of hexagonal or pseudo-hexagonal symmetry (Figure 1.3). Common tetrahedral cations
are Si$^{4+}$, Al$^{3+}$, and Fe$^{3+}$. Octahedral cations are usually Al$^{3+}$, Fe$^{3+}$, Mg$^{2+}$ and Fe$^{2+}$, but other cations, such as Li$^+$, Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, V$^{3+}$, Cr$^{3+}$ and Ti$^{4+}$ are also identified. Octahedra show two different topologies related to OH position, i.e., the cis- and the trans-orientation (Figure 1.3).\textsuperscript{[10]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.3.png}
\caption{(a) O$_{oct}$ (OH, F, Cl) orientation in cis-octahedron and trans-octahedron; (b) location of cis- and trans-sites in the octahedral sheet. O$_a$ and O$_b$ refer to apical and basal oxygen atoms, respectively. a and b refer to unit cell parameters.}
\end{figure}

\textbf{A3.3. Subdivision of layer lattice silicates:}

The major subdivision of the layer lattice silicates (Figure 1.4)\textsuperscript{[5]} is based on the type of combinations of the tetrahedral and octahedral sheets. Additional subdivision is based on:\textsuperscript{[7]}

\begin{itemize}
\item whether the octahedral sheet contains two cations per half unit cell (dioctahedral) as in gibbsite or three cations per half unit cell (trioctahedral) as in brucite;
\item the manner of stacking of the tetrahedral-octahedral units upon each other;
\item the amount and type of isomorphous replacement of the cations.
\end{itemize}

The analogous symmetry and the almost identical dimensions in the tetrahedral and the octahedral sheets allow the sharing of oxygen atoms between these sheets. The fourth oxygen atom protruding from the tetrahedral sheet is shared by the octahedral sheet. This sharing of atoms may occur between one silica and one alumina sheet, as in the so-called 1:1 layer minerals. In the 2:1 layer minerals, one alumina or magnesia sheet shares oxygen atoms with two silica sheets, one on each side. This combination of an octahedral sheet and one or two tetrahedral sheets is called a layer.
Most clay minerals consist of such layers, which are stacked parallel to each other. The cohesive force between the layers is primarily electrostatic, augmented by van der Waals attraction.

Figure 1.4: Major subdivisions of layered silicates.

The neutral 2:1 layer structure represents the structure of the mineral pyrophyllite. Since in this material two of the three possible octahedral positions are occupied by trivalent Al, this structure is called dioctahedral. If the three octahedral positions are filled by three divalent Mg atoms, the electro-neutral structure of the mineral talc is represented. This arrangement is called trioctahedral.

Figure 1.5: Model of a 2:1 layer structure. Oₐ, Oₐoct, and Oₜoct refer to tetrahedral basal, tetrahedral apical, and octahedral anionic position, respectively. M and T indicate the octahedral and tetrahedral cation, respectively.
The three-sheet or 2:1 layer lattice silicates (Figure 1.5) consist of an octahedral sheet in between two silica tetrahedral sheets. These three sheets form a layer approximately 10 Å thick. The oxygens, at the tips of the tetrahedral, point towards the center octahedral sheet and substitute for two-thirds of the octahedrally coordinated hydroxyls. The 2:1 clay minerals include the mica and smectite groups which are by far the most abundant of the clay minerals.

Clay minerals are traditionally classified under ‘silicates’ but since their chemical compositions have more oxygen than Si, Al, or Mg, these minerals may arguably be considered as (hydr)oxides of silicon, aluminium, or magnesium. Thus clay minerals and related layer materials may be referred to as porous layered (hydr)oxides. Clay minerals may also be considered as salts of rigid polyanions with infinite radius and their compensating cations or as inorganic polymers where the continuous octahedral sheet is based on a repetition of an octahedron monomer. The other basic monomer is the silica tetrahedron, which is bound on one or both sides to the octahedral sheet.

A4. Montmorillonite:
Montmorillonites belong to the group of layer silicates. The low layer charge (0.3-0.6) dioctahedral minerals which have most of their charge originating in the octahedral sheet are called dioctahedral smectites or montmorillonites. The isomorphous substitution in montmorillonite occurs in the octahedral sheet rather than in the tetrahedral sheet. Most of the montmorillonites were formed by the alteration of volcanic material and basic igneous rocks and have a relatively small amount of Al substituting for Si in the tetrahedral sheet. Montmorillonite species belongs to dioctahedral type smectite group with a layer charge ~0.2-0.6 (Charge per formula unit) and has hydrated exchangeable cations as interlayer material. The idealised formulae (chemical compositions) of montmorillonite is:

$$\text{(Si}_4\text{IV}(\text{Al}_{2-y}\text{Mg}_y)\text{VI})\text{O}_{10}(\text{OH})_{2+y}\text{M}^+\cdot n\text{H}_2\text{O}$$

Many people associate clay minerals with smectites, which have the following properties:

- particles of colloidal size,
- high degree of layer stacking disorder,
- high specific surface area (SSA),
- moderate layer charge,
- large cation exchange capacity (CEC) that is little dependent on ambient pH,
- small pH-dependent anion exchange capacity.
variable interlayer separation, depending on ambient humidity,
propensity for intercalating extraneous substances, including organic compounds and macromolecules, and
ability of some members to show extensive interlayer swelling in water; under optimum conditions, the layers can completely dissociate.

Montmorillonite is an acid leached clay which is used as an adsorbent for decolourization and deodorization of vegetable and animal oils. Leaching of the clay increases its SSA and the pore volume (PV) to improve its adsorption capacity for metallic impurities, phosphatides, oxidation products and pigmentary substance in oils.\(^{12-14}\) The acidity of the montmorillonite clay arises from H\(^+\) in the surface exchange sites.\(^{15}\) Acid leaching increases the relative SiO\(_2\) content and as a result the depletion of cations from the interlayers and octahedral sheets of the montmorillonite.\(^{16}\) Dissolution of the montmorillonite usually starts by leaching of the octahedral layer from the edge of the particles and the hexagonal cavities.\(^{17}\)

Montmorillonites swell in water, and the extent of the swelling is influenced by the hydration of the interlayer cations. The large internal surface area of montmorillonite provides most of the adsorption surface. In addition, the external surface area of montmorillonite is generally greater than that of other clay minerals, due to its small particle size. The most important chemical properties of montmorillonites include high values of CEC, ion selectivity and molecular sorption. The main physical properties of montmorillonites are expansion and collapse, retention of large quantities of water, high cohesion and adhesion, small particle size and an extremely large SSA.\(^{18}\) Montmorillonites, activated in acids, yield products with a highly amorphous SiO\(_2\) content and a new microstructure with pores that have greater adsorption properties.\(^{19}\) Their reactivity is mainly controlled by their large internal SSA, the mean specific charge, and the nature of the interlayer-exchangeable cations.\(^{20-24}\)

Clays are used as catalysts and catalyst-supports in many organic syntheses. Montmorillonite is the most important clay mineral for these uses.\(^{25}\) Montmorillonites are one of the most commonly used clay mineral in industrial applications.\(^{1}\) Montmorillonite remains the most difficult mineral to crystallise in high purity. This may be due, at least in part, to its low magnesium content.\(^{26}\)

* ‘Intercalation’ denotes both interlayer adsorption and interlayer ion exchange reactions.
Montmorillonite are good adsorbents, and may be recommended for the treatment of pesticide poisoning.\cite{27,28}

### A5. Clay-water interactions:

The chemical and physical properties of clay minerals are integrally linked to some aspect of how water interacts with the clay surface. Many of the interesting features of clay–water interactions are observable at the macroscopic level, including such properties as shrink–swell phenomena, water sorption, plasticity and catalysis.\cite{29}

Grandjean and Laszlo\cite{30} deduced from deuterium NMR studies of montmorillonite-water dispersions that the water molecules are strongly polarised and are simultaneously bound to a negative centre by a hydrogen bridge and to an interlayer cation by electrostatic forces. As a consequence, the acidity of interlayer water molecules is increased. An outstanding property of dispersed montmorillonite particles is delamination into individual silicate layers.\cite{31}

Smectites can sorb up to half of their mass with water and that the water sorption behaviour is strongly dependent on the nature of the exchangeable cation.\cite{32} Smectites are nano-materials. The elementary platelets are a few tenths to a few hundreds of nanometres wide and long and 0.96-1.50 nm thick, the exact thickness depending on the number of adsorbed water layers. The elementary platelets carry a negative charge, due to isomorphous substitution. The typical negative charge per $\text{O}_{10}(\text{OH})_2$ unit is $0.25 - 0.60 \ e \ (e = 1.6 \times 10^{-19} \ \text{C})$. The corresponding charge-neutralising and exchangeable cations together with one or two water layers are located in the interlamellar space between the elementary platelets. A group of elementary platelets forms a clay particle. If such a particle is immersed in water, water molecules are attracted into the inter-lamellar spaces and the clay particle swells. Ultimately, the aqueous clay suspension consists of randomly-oriented, more or less freely moving, elementary clay platelets. The degree of swelling depends on the charge density of the clay mineral, size and shape of the elementary platelets and particles, the type and charge of the exchangeable cation and the chemical and thermal history of the clay mineral sample.\cite{33}

Thus, one can transform a clay particle, consisting of a number of more or less well-oriented elementary platelets, into an aqueous suspension with randomly moving, elementary clay platelets. In this state the charge compensating cations are exchangeable with almost any type of cation, be it inorganic, organic or organo-
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This property is the basis for the idea that the elementary platelets of smectites can be converted into nano-particles with preset properties. One needs (1) an exchangeable cation with the desired property such as light absorption, light emission, redox, acid or base; (2) a specific organisation of the exchangeable cation at the surface of the elementary clay platelets; (3) the organisation of the elementary platelets into monolayers and multi-layers. This means that a double organisation is necessary: (i) organisation of the molecules at the surface, and (ii) organisation of the elementary platelets, carrying the desired molecules.\textsuperscript{[33]}

Besides ion exchange, other mechanisms of functionalization of clay mineral particles can be envisaged, such as embedding of the clay mineral particles in a polymer matrix. All these methods can be brought together in the notion of intercalation or intercalation chemistry.\textsuperscript{[33, 36, 37]}

1.1.2. Part B: Dyes:

B1. Introduction:

Dyes are synthetic aromatic water-soluble dispersible organic colorants, having potential application in various industries. The dyestuff usage has increased day by day due to the tremendous growth of industrialisation and man’s urge for colour.\textsuperscript{[38]} Colour removal from dye bearing waste-water is a complex problem because of the difficulty in treating such waste-waters by conventional treatment methods.\textsuperscript{[39, 40]}

In this thesis, some of the thermal and optical properties of certain industrially important dye adsorbed montmorillonites are presented which are evaluated using simple non-destructive techniques. The present investigations are carried out using four industrially important dyes; the basic details of which are given below.

B2. Methylene blue:

Methylene blue (MB) is heterocyclic aromatic chemical compound which is used as a stain in bacteriology and as an oxidation-reduction (redox) indicator. It is an antidote to cyanide and an antiseptic in veterinary. It is also known as tetramethylthionine chloride or Swiss blue and the molecular structure of MB is given\textsuperscript{[41]} in Figure 1.6.

B3. Malachite green:

Malachite green (MG) is a toxic chemical, primarily used as a dye. It is a common basic synthetic dyestuff of triphenylmethane or triarylmethane dye\textsuperscript{[42]} series, which is most widely used for dyeing\textsuperscript{[43]} silk and wool directly and cotton mordanted with
Optical and thermal characterization.....

tannin. MG is inexpensive, effective and readily available for many uses. MG is widely used in aquaculture as a parasiticide and in food, health, textile and other industries for one or the other purposes.\textsuperscript{[42]}

When diluted, it can be used as a topical antiseptic or to treat parasites, fungal infections, and bacterial infections in fish and fish eggs. It is also used as a bacteriological stain. MG is also called aniline green, benzaldehyde green, china green, diamond green B, or victoria green B. The molecular structure of MG is given in Figure 1.7.

\textbf{B4. Rhodamine B:}

Rhodamine B (RB) is a fluorescent tracer dye which is also widely used in many industries. RB is used as a dye laser gain medium. It is a biological stain and a suspected carcinogen. RB is also known as FD and C Red No. 19; Rhodamine O;\textsuperscript{[44]}

Tetraethylrhodamine; Rheonine B; Brilliant Pink B; Basic Rose Red;\textsuperscript{[45]} Geranium lake N; Symulex Pink F; Rhodamine 610;\textsuperscript{[46]} Pigment Violet 1 etc.\textsuperscript{[44-46]} The properties of RB are given\textsuperscript{[47]} in Table 1.2. Figure 1.8 shows the molecular structure of RB.

\textbf{B5. Auramine O:}

Auramine O (AO) is a yellow fluorescent dye used to stain acid-fast bacteria in sputum or in paraffin sections of infected tissue and as an antiseptic agent. It can also be used as a fluorescent version of Schiff reagent.\textsuperscript{[48]} AO fluorescence can be used as a probe for the survey of the physical parameters of chromatophore membranes.\textsuperscript{[49]} AO is also called Pyocataminium aureum; aizen auramine; Pyoktanin Yellow; Canary Yellow;
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Auramine hydrochloride; Benzophenoneidum etc. Molecular structure of AO is given in Figure 1.9.

B6. Concluding remarks:
All the dyes used for the present study are basic dyes. Basic dyes are salts of the coloured organic bases containing amino and imino groups. Basic dyes are cationic which has positive electrical charge and are used for anionic fabrics which are negative-charge-bearing, such as wool, silk, nylon, and acrylics where bright dyeing is the prime consideration. The main characteristics of the dyes used in the present investigation are given in Table 1.2.

Table 1.2: Characteristics of the selected dyes for the adsorption study.

<table>
<thead>
<tr>
<th>Dye</th>
<th>MB</th>
<th>MG</th>
<th>RB</th>
<th>AO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{ab}^\text{max}$ (nm)</td>
<td>662</td>
<td>616</td>
<td>554</td>
<td>431</td>
</tr>
<tr>
<td>C. I. Number</td>
<td>52015</td>
<td>42000</td>
<td>45170</td>
<td>41000</td>
</tr>
<tr>
<td>C. I. Name</td>
<td>Basic blue 9</td>
<td>Basic green 4</td>
<td>Basic violet 10</td>
<td>Basic yellow 2</td>
</tr>
<tr>
<td>Class</td>
<td>Thiazin</td>
<td>triarylmethane</td>
<td>Rhodamine (xanthene)</td>
<td>diarylmethane</td>
</tr>
<tr>
<td>Colour</td>
<td>Blue</td>
<td>Green</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>319.8</td>
<td>364.9</td>
<td>479.0</td>
<td>303.8</td>
</tr>
<tr>
<td>IUPAC* Name</td>
<td>3,7-bis(Dimethyl amino)-phenothiazin-5-ium chloride</td>
<td>4-[(4-dimethylaminophenyl)-phenylmethyl]-N,N-dimethylaniline</td>
<td>[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride</td>
<td>bis[4-(dimethylamino)phenyl]methaninium chloride</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C$<em>{16}$H$</em>{18}$ClN$_3$S</td>
<td>C$<em>{23}$H$</em>{25}$ClN$_2$</td>
<td>C$<em>{26}$H$</em>{31}$ClN$_2$O$_3$</td>
<td>C$<em>{17}$H$</em>{22}$ClN$_3$</td>
</tr>
</tbody>
</table>

* C. I. Colour Index; *IUPAC- International Union of Pure and Applied Chemistry
1.1.3. Part C: Dye intercalated clay minerals:

**C1. Introduction:**
Clay minerals are natural layered silicates composed of sub-microscopic particles.\[35\] One of the most important groups of clay minerals is represented by expandable minerals, smectites. Due to isomorphic substitutions within the structure, smectite layers bear a negative charge. Some interesting physical and chemical properties, such as the tendency to form colloids and their inherent ion-exchange properties, relate to the layered structure and the presence of the net negative charge present in these minerals.\[9\] These properties have a great influence on many chemical and physical parameters of these materials and are important for some processes taking place in nature or utilised by industry.

Research on clay mineral-dye complexes has been stimulated by the possibility of developing

1. photo-functional materials for application in, e.g., photonic devices\[54\] and
2. photoactive materials for the protection of pesticides from breakdown in the soil.\[55, 56\]

**C2. Organisation of molecules at clay mineral surfaces.**\[33\]
Adsorption always involves a kind of organisation of molecules at surfaces. Surfaces usually contain a number of sites, different in strength of interaction. Adsorbing molecules will first fill the sites with the strongest interactions, followed by the weaker ones. In the hypothetical case, that all sites are equal, molecules may occupy surface sites randomly. However, if the molecule-surface interaction is strong, the adsorbing molecules do not distinguish between sites of different strength. They occupy the first site they encounter and fill up the other sites progressively. Thus, depending on the type of sites and the strength of interaction, several models of site filling or organisation of molecules at surfaces are possible. There are also other types of interaction which must be considered besides the molecule-surface interaction. The first one is the molecule-molecule interaction, which is usually described by a Lennard-Jones type of potential: molecules will be organised so as to maximise the intermolecular interaction energy. If adsorption is performed from liquid solution, e.g. aqueous ion exchange, solvent-surface interactions and solvent-molecule interactions come into play. The final organisation of the molecules at the clay mineral surface will be determined by the subtle balance between all possible interactions. Many examples of adsorption and organisation of molecules at clay mineral surfaces can be found in the literature.\[34\]
C3. Dye aggregation in clay dispersions:

The interaction of organic dyes with clay minerals has been studied extensively for decades and reviewed.\[54, 57, 58\] Dye molecular aggregation in clay mineral colloids was reported for the first time by Bergman and O’Konski.\[59\] The aggregation behaviour is sensitive to the kind and amount of metallic ions present in the lattice of the clays, the amount of adsorbed water as well as the structure of the organic guests to be intercalated.\[57\] According to exciton theory\[†\], the band’s position and shape depend on the number and relative arrangement of interacting molecules and their transition moments in the molecular aggregate. Therefore, energies of the observed transitions are variable and may deviate.\[60\]

In the vicinity of clay particles, dye aggregation takes place due to an enhanced polarity of water molecules induced by present inorganic ions in electric double layer. The presence of water as a polar solvent is essential for the aggregation of dye cations.\[61\] Increasing the polarity of the environment increases the degree of aggregation. Enhanced aggregation is observed in aqueous solutions of inorganic salts and is found to be related to the polarising effects of ions.\[62\] A re-arrangement of the dye cations occurs in extant aggregates, which is directed by the charge distribution so that each cation balances one negatively-charged site, thus mapping an intrinsic distribution of the negative charge on the clay surface.\[61, 64\]

The dye/silicate dispersions are dynamic systems, where complex re-organisation and re-distribution of the dye assemblies take place. The layer charge of the silicate substrate controls the formation of the dye’s molecular assemblies, such as dimers and aggregates. The dye species (monomers, aggregates) are characterised by distinctly different optical properties using UV/visible and fluorescence spectroscopies. New bands in the spectra of the dye/clay dispersions are due to the formation of dye cation dimers and/or higher aggregates.\[64\] The aggregation of dye cations on a clay surface may significantly vary depending on the clay specimen.\[65\] The formation of rhodamine aggregates in clay dispersions is interpreted in terms of clay colloid properties. The dye-clay suspension’s spectra depend on parameters like dye loading, clay type, exchangeable cation, clay concentration and age of the suspension.\[66\]

Clay minerals adsorb cationic dyes from aqueous or organic solutions by a cation exchange process. Many investigators have studied the adsorption of organic cations

\[†\] The details are given in chapter 2.
by clay minerals from the point of view of ‘long range’ electrostatic interaction, i.e., the exchange of inorganic metallic cations by organic cations. However, ‘short range’ forces begin to operate when the organic cations penetrate the interlayer space. This includes H bonds between proton donor groups on the organic cations and interlayer water or the O-plane of the silicate layer. In these H bonds, oxygen atoms of interlayer water molecules or of the O-plane act as proton acceptors. An additional type of H bond between water molecules and aromatic cations can be obtained with a geometry in which one of the hydrogen in water molecules is oriented toward the center of the aromatic ring. For this H bond all of the π electrons of the aromatic ring contribute to the bonding interaction. With greater adsorption, the clay flocculates and dimers and higher dye aggregates are formed in the inter-particle space, leading to metachromasy. Metachromasy then increases with the length of the chain.

When smectites are suspended in aqueous solutions, the expansion of the clay mineral structure occurs. The swelling process relates to the expansion of interlayer spaces and is important for adsorption (intercalation) of various organic species. Numerous works have reported on the significant influence of clay minerals on optical properties of organic dyes. Cationic chromophores are frequently adsorbed via an ion exchange reaction in the form of molecular assemblies which are formed by the hydrophobic interactions between dye molecules in water. This process is followed by significant changes of the electronic properties arising due to coupling between transition moments of the chromophores, which is observable using absorption spectroscopy in the visible region. Several works have studied the factors affecting spectral properties of cationic dyes adsorbed on clay mineral surfaces. Molecular aggregation and electronic properties of chromophores are strongly influenced by various parameters, including dye concentration and structure, pH and ionic strength, temperature and presence of organic co-solvents, etc. It is also reported that the dye initially gets adsorbed extremely fast on the surface followed by a re-distribution over the total available surface and the thermodynamic instability of clay mineral suspensions, giving rise to continuous aggregation-deaggregation phenomena of individual clay mineral platelets.

The changes of dye optical properties in clay mineral dispersions depend much on clay specimen used. Even minerals of the same type and structure may induce significantly different aggregation of dye molecules. Although, dye adsorption by smectites results in metachromasy, different types of bonding in clays are observed. Metachromasy is a deviation from Beer’s law, occurring in planar dye molecules
which tend to adhere to each other. Metachromic absorption bands are shifted from the monomer band and reflect different modes of aggregation of the dye molecules.[79] In montmorillonite, metachromasy results from $\pi$ interactions[79] between the adsorbed aromatic dye and the oxygen plane of the alumino-silicate.[77]

Metachromic dyes had been called ‘finger-print probes’ of surface properties of clays.[80] However, for decades, the effect of clay mineral had not been clearly identified. Later, negative charge of clay mineral layers was identified as a chief parameter, which controls molecular aggregation of cationic dyes.[65, 76] The mineral layers consist of alumino-silicate leaflets of 0.95 nm thick. Each leaflet is made up of a layer of alumina sandwiched between two layers of silica. On the face surfaces (the oxygen planes) there is an array of hexagonal pits of oxygen atoms. At the edges, where the leaflet had been broken, one finds mainly oxygen with broken bonds, some of which are protonated, depending on pH. The face surface is negatively charged, because some alumina had been isomorphously substituted by magnesia and Fe$^{2+}$ (octahedral substitution) and some silica was substituted by alumina and Fe$^{3+}$ (tetrahedral substitution). In aqueous suspensions, the exchangeable cations and water form a diffuse double layer around the charged alumino-silicate leaflets. When diluted in water to $< 0.01\%$, monovalent cations (Na or Li) allow the delamination of the clay particles into separate leaflets. Most of the other exchangeable cations would link 3-10 leaflets face to face, producing tactoids. With increasing clay concentration or in the presence of electrolytes, the clay flocculates. Exchangeable cations facilitate the dissociation of interlayer water, producing local acidity. Organic compounds are adsorbed into the interlayer space of montmorillonite either as cations, by electrostatic attraction, or by van der Waals forces.[79]

1.1.4. Part D: Rare earth doped materials:

D1. Rare earth elements:

The rare earth (RE) elements include the lanthanides (Z=58-71) but sometimes taken to contain $^{57}$La, and even $^{21}$Sc and $^{39}$Y.[81] Some authors have classified the REs into two groups of 14 elements each- the lanthanides and actinides. Although these elements share many electronic properties, lanthanides are of greater importance in lasers and amplifiers. Many actinides have no isotopes stable enough to be useful for such devices.[82]
The term REs was coined to these elements because of their extraction from certain (rare) oxide (earth) minerals. In fact; they are more abundant in the earth’s crust than gold, silver, mercury, tungsten, etc. RE elements are never found as the free metals in the earth's crust. Pure minerals of individual REs do not exist in nature; all their minerals contain mixtures of the RE elements.

D2. Optical properties of rare earth ions:
The optical and magnetic applications of RE ions in luminescent devices using single crystals, powders and glasses are important. The following characteristics distinguish the REs from other optically active ions:
1. They emit and absorb over narrow wavelength ranges.
2. The wavelengths of emission and absorption transitions are relatively insensitive to host material.
3. The intensities of these transitions are weak.
4. The lifetimes of metastable states are long.
5. The quantum efficiencies tend to be high, except in aqueous solutions.
All these properties result from the nature of states involved in these processes and lead to excellent performance of RE ions in many optical applications.

Se$^{3+}$, Y$^{3+}$, La$^{3+}$ and Lu$^{3+}$ have no electronic energy levels that can induce excitation and luminescence processes in the visible region or near to it. In contrast, the ions Ce$^{3+}$ to Yb$^{3+}$, which have partially filled 4f orbitals, have energy levels characteristic of each ion and show a variety of luminescence properties around the visible region.

D3. General properties of lanthanides:
The lanthanides (Lns) are all very reactive and electropositive. Their chemistry is dominated by the +3 oxidation state. Despite the high charge, the large size of the Ln(IV) ions results in low charge densities and their compounds are predominately ionic in character. The REs are strongly paramagnetic, in some cases ferromagnetic or anti-ferromagnetic at low temperatures. Their trivalent salts have absorption spectra and in some cases fluorescence spectra with sharp lines in the visible or neighbouring spectral regions.

D3.1. Lanthanide contraction:
The ionic radii of lanthanide decrease smoothly across the series. This decrease in size is the famous lanthanide contraction, which is due to the imperfect screening by the 4f electrons, which leads to an increase in effective nuclear charge as the atomic
number increases in the lanthanide series. As a result, the 4f electrons become increasingly more tightly bound with increasing Z.\[^{[89]}\] This is seen in every period as a shell is filled. It is particularly important for the lanthanides, however, because of the:

- length of a f-series. (There are 2 elements in a s-block, 6 in a p-block, 10 in a d-block but 14 in a f-block)
- directional characteristics of f-orbitals. The f-orbitals are 'angularly diffuse'; the electrons can occupy different volumes of space (lobes) and so avoid each other.
- relativistic contraction consequences for the elements with high Z.

The lanthanide contraction makes the Lns to have a regular variation in chemical properties. The salts become less ionic.\[^{[81]}\]

D3.2. Radiative transitions in rare earth ions:

The REs, particularly the Lns are characterised by a partially filled 4f shell that is shielded from external fields by 5s\(^2\) 5p\(^6\) electrons. Hence, the free-ion energy levels are only weakly perturbed by the surrounding environment and the 4f intra-configurational transitions retain their atomic-like characteristics, e.g. spectral sharpness of the order of 10 cm\(^{-1}\) in good crystalline hosts and long lifetime of the order of 1 ms. Such narrow lines provide sensitive probes of weak perturbations. Technologically, the phosphors emitting spectrally narrow lines are favourable in display devices, where they can provide very pure primary colours. The most intriguing property of trivalent RE ions is that the spectral position of the emission lines is almost independent of the host lattice.\[^{[82]}\]

When incorporated in crystalline or amorphous hosts, the REs exist as 3\(^+\), or occasionally 2\(^+\), ions. The trivalent level of ionisation is the most stable for Ln ions and most optical devices use trivalent ions. All the 3\(^+\) ions exhibit intense narrow-band intra-4f luminescence in a wide variety of hosts, and the shielding provided by the 5s\(^2\) and 5p\(^6\) electrons means that RE radiative transitions in solid hosts resemble those of the free ions and electron-phonon coupling is weak. The trivalent species are the more interesting, though some of the divalent species are luminescent. The positions of RE electronic levels are more influenced by spin orbit interactions than the applied crystal field. The intra- 4f transitions are pairly forbidden and are made partially allowed by crystal field interactions, mixing opposite parity wave functions. Luminescence lifetimes are therefore long, and line widths are narrow. By careful selection of appropriate ion; intense narrow band emission can be obtained across much of the visible region and into the near IR. Radiative transitions between 4f\(^n\)
Optical and thermal characterization…..

electronic states of RE ions in crystals are characterised by very sharp optical transitions- a consequence of
(i) the weak coupling between the 4f electrons and the ionic lattice environment of the RE ion, and
(ii) the fact that the RE ions generally enter identical sites in the crystal.\textsuperscript{[90]}
The RE ions in glass find a range of site types available to them which leads to relatively large inhomogeneous broadening.\textsuperscript{[91]}

The consequences for the static interactions are energy levels that are relatively insensitive to host, have small host-induced splittings, and are only weakly mixed with higher energy states. The dynamic consequences are little or no vibronic structure (phonon-assisted transitions) and weak non-radiative relaxation of excited states, which occurs through phonon emission. The net results are optical transitions between 4f states that manifest themselves as narrow, weak bands or sharp lines, and emission that can be highly efficient. Because the 4f electrons interact only weakly with electrons on other ions, the Hamiltonian for an individual RE ion can be written as\textsuperscript{[82]}

\begin{equation}
H = H_{\text{free ion}} + V_{\text{ion-static lattice}} + V_{\text{ion-dynamic lattice}} + V_{\text{EM}} + V_{\text{ion-ion}}
\end{equation}

Here $H_{\text{free ion}}$ is the Hamiltonian of the ion in complete isolation, $V_{\text{ion-static lattice}}$ and $V_{\text{ion-dynamic lattice}}$ contain the static and dynamic interactions of ion with the host, $V_{\text{EM}}$ treats the interaction of the ion with the electromagnetic field, and $V_{\text{ion-ion}}$ describes the interaction between RE ions.

The static interactions produce the observed electronic structure and dynamic perturbations induce transitions between the electronic states.

Because of the shielding effect, the valence electrons of the trivalent RE ions are weakly affected by the ligand\textsuperscript{[92]} ions in the crystals; a situation that corresponds to the case of a weak crystalline field. Consequently, the spin-orbit interaction of the free ion Hamiltonian is dominant over the crystalline field Hamiltonian term. This causes the $2S+1L_J$ states of the (RE)\textsuperscript{3+} ions to be slightly perturbed when these ions are incorporated in crystals. The effect of the crystal field is to produce a slight shift in the energy of these states and to additional level splitting. However, the amount of this shift and the splitting energy are much smaller than the spin-orbit splitting, and thus, the optical spectra of (RE)\textsuperscript{3+} ions are fairly similar to those expected for free ions. This implies that the main features of a (RE)\textsuperscript{3+} ion spectrum are similar from one crystal to

\footnote{Appendages not including another metal or metalloid atom.}
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another. The interpretation of the absorption and luminescence spectra of lanthanide (RE)\textsuperscript{3+} ions in crystals is based on systematic spectral measurements made in a particular host, lanthanum chloride, given by the Dieke diagram.\textsuperscript{[87, 93]}

Russell- Saunders coupling (LS coupling) is most often used for the states of lanthanides and actinides.\textsuperscript{[82]} Electrons in closed shells impart a constant energy shift to all terms, and thus only the interaction between the 4f electrons need be considered. The LS mixing is more significant for the high-Z REs (Ho, Er, Tm). The host has the least influence on the electronic structure and changes the positions of these levels only slightly. The static effects of the host on the RE dopant customarily are treated by replacing the host with an effective crystal field potential at the ion site.\textsuperscript{[82]}

For luminescent devices, the electromagnetic field interaction term $V_{EM}$ is the most important since it gives rise to the emission and absorption of photons. This involves both the interaction between the electron charge and the electric field, and the interaction between the electron spin and the magnetic field.\textsuperscript{[82]}

For RE ions, the optical transitions from the IR to the UV are between states composed of 4f wave functions. Because the initial and final states have the same parity, electric-dipole processes are forbidden and transitions for free ions can occur only by the much weaker magnetic-dipole and electric-quadrupole processes. Radiative lifetimes for fully allowed electric-dipole transitions are roughly $10^{-8}$ s.\textsuperscript{[82]}

In terms of their spatial extend, the 4f wave-functions for La lie outside the xenon shell, but by Nd they have contracted so much that the maximum lies within the $5s^2\ 5p^6$ closed shells of the Xe structure.\textsuperscript{[89]}

Optical spectroscopy provides information about the interaction between the metallic central ion and its environment through the so-called ‘nephelauxetic effect’ that determines the relative spatial extension of the f-orbitals and subsequently the overlapping with the ligand valence orbitals. But in lanthanide ions, the f-electrons belong to inner orbitals and therefore when engaged in compounds, they are more or less protected from the ligand interactions by closed more external s and p orbitals. The 4f electrons are well localised and they can be considered as quasi-core electrons with a small influence upon the bonding that explains the dominant $+3$ oxidation state across the lanthanide series.\textsuperscript{[82]}
The RE ion-host systems generally fluoresce with radiative lifetimes in the microseconds and milliseconds range. This property makes them ideal for high resolution studies in both the frequency and the time domains.\textsuperscript{[94]} Also, due to their high quantum conversion efficiencies and due to the existence of fast relaxing states above the ground level, these ion-host systems have found application as active laser materials.\textsuperscript{[95]} Spectral holes burnt in the purely electronic transitions observed in the RE doped crystalline or glassy hosts at the cryogenic temperatures may turn out to be the most efficient optical devices for the storage and fast retrieval of information.\textsuperscript{[96]}

The use of RE based phosphor, based on ‘line type’ f-f transitions, can narrow the emissions to the visible range, resulting in high efficiency and a high lumen equivalence.\textsuperscript{[97]} The position of the 4f-5d levels is greatly influenced by the crystal field interaction. This effect is known as the \textit{crystal field depression} of the 5d level, and consequently, the host crystal depresses 4f-5d energy levels for all Lns.\textsuperscript{[97, 98]}

**D3.3. Magnetism of lanthanides:**
The magnetism of lanthanides arises from almost no overlap between f and ligand orbitals and then, magnetic properties are directly related to the degree of localisation. The latter increases with the ability of the ligand to form an ionic bonding. The intra-configuration transitions within the f-configuration are called f-f transitions and are predominantly electric dipole or magnetic-dipole in nature.\textsuperscript{[91]}

**D3.4. Non-radiative transitions in rare earth ions:**
In addition to changing their electronic state through interaction with the electromagnetic field (emission and absorption of photons), RE ions in solids can undergo transitions as a result of their interaction with vibrations of the host material. In crystals, this corresponds to the emission and absorption of phonons. The absence of translational invariance in glasses means that vibrational modes will not have a well-defined wave vector. Reisfeld\textsuperscript{[99]} carried out the first quantitative studies on the non-radiative processes on RE ions in glasses.\textsuperscript{[91]} If the electronic states are spaced closely enough that they can be bridged by one or two photons and the transitions will occur rapidly. The ion makes a non-radiative transition to a lower electronic state through the emission of multiple phonons to conserve energy.\textsuperscript{[100, 101]} If the non-radiative relaxation rate of a level is comparable with its radiative transition rate, the efficiency of luminescent processes originating on that level is degraded. As the transitions occur across gaps many times the energy of the largest phonon, the analysis requires high-order perturbation theory. Although high order electromagnetic
processes (i.e., multi-photon) are extremely weak, multi-phonon processes can be significant because the electron-phonon interaction is stronger and phonons have a density of states that typically are 11 orders of magnitude larger than that of photons.\[100]\] The large variation in vibrational spectra among materials makes the non-radiative relaxation rate extremely host dependent. For a given host, all levels with the same energy gap below them will have roughly the same non-radiative rate. This rate is relatively independent of the nature of the electronic states involved, or even the identity of the RE ion, unless a strong selection rule is involved.\[102]\]

**D4. Applications of rare earth elements:**
The RE elements play a very important role in industrial manufacturing, technology development and biological processes.\[103]\] The RE industry is vital in the economy because of their special photogenic, magnetic, mechanical and nuclear properties. Chemists are increasingly paying attention to studies of the environmental, medical and biological applications of RE elements to develop a RE industry. Therefore, the methods for their rapid, sensitive and accurate determination and separation are of great importance. However, it is extremely difficult to determine them individually without a pre-separation due to the similarity of their chemical properties.\[104]\]

REs and their compounds find applications in metallurgy, petroleum cracking catalysis,\[105]\] ceramic and glass industries, electronics,\[84]\] optoelectronics, superconductivity,\[105]\] computers, permanent magnets, alloys, hydrogen storage and transport, rechargeable hydride batteries, space applications, agriculture and natural science, etc. Ce and Er are used in high performance alloys, Nd, Ho and Dy are employed for laser crystals, Sm for high performance strong permanent magnets, Yb and Tb are applied in magnetic bubble and magneto-optic devices to store computer data and Eu functions as red phosphor in colour television screens.\[83]\] The trichromatic fluorescent lamps made from rare earths such as Eu, Tb as activators and Y, La, Gd as hosts, consume less power than conventional types.\[105]\] Gd is used for detection of tumors, cancer by mammography.\[105]\]

**D5. Rare earth titanates:**
RE titanates (RE$_2$Ti$_2$O$_7$ - RETs) have been used as photocatalysts. The photocatalytic activity strongly depends on the crystal structure. RETs possess a cubic pyrochlore structure with small RE$^{3+}$ ions (Yb$^{3+}$-Sm$^{3+}$), while RET with their larger RE$^{3+}$ (Nd$^{3+}$-La$^{3+}$) exhibit a monoclinic perovskite structure.\[106]\] Synthesis and characterization of RETs were first reported in the 1950s. Generally pyrochlore structures are analogous
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to modified cubic fluorite structure,\textsuperscript{[107-109]} with unit cell containing eight molecules and four crystallographically non-equivalent sites.\textsuperscript{[110, 111]} In RET, the different RE ions on a pyrochlore lattice exhibit specific magnetic properties. The RETs have low dielectric constant values which remain almost constant with temperature changes. This peculiar property makes the RETs and their doped compositions to be attractive candidates for microwave applications as resonators,\textsuperscript{[112-118]} ceramic capacitor formulations,\textsuperscript{[119-125]} etc. The high permittivity of titanates and other ferroelectric materials offer the advantage of obtaining high capacitance values for small volume of material. Also, ceramic titanates generally have low loss factor.

The pyrochlore structure of \( Y_2Ti_2O_7 \) possesses a larger unit cell than the other RET pyrochlore, which accommodates large vacancy concentrations without affecting stability of the compound and offers large ionic conductivity for the material.\textsuperscript{[126, 127]} \( Y_2Ti_2O_7 \) pyrochlore is one of the interesting candidate materials for reinforcement of titanium-based matrices.\textsuperscript{[128]} \( Gd_2Ti_2O_7 \) is an attractive candidate for solid-state ionic devices like fuel cells, chemical sensors,\textsuperscript{[129]} and electrochemical devices.\textsuperscript{[126,127,129-131]} \( La_2Ti_2O_7 \) conducts photocurrent in the UV region due to the charge transfer between oxygen ions and titanium or lanthanum ions.\textsuperscript{[132, 133]} Some applications of pyrochlore are as fluorescence centers, catalysts, host phase in nuclear waste control, as electrolyte and as conducting electrodes in solid oxide fuel cells.\textsuperscript{[109, 134-139]} Optical wave guiding properties were demonstrated for thin films of \( La_2Ti_2O_7 \) that were deposited by laser ablation on substrates like silica-coated silicon and fused silica.\textsuperscript{[133, 135, 140]} \( La_2Ti_2O_7 \) exhibits piezoelectric properties at very high temperature\textsuperscript{[135, 140]} and sustain very high applied fields without dielectric breakdown. \( Nd_2Ti_2O_7 \) addition increases fracture toughness of zirconia.\textsuperscript{[141]} The static optical permittivity values increase with decreasing temperature in \( Dy_2Ti_2O_7 \).\textsuperscript{[142]} Single crystals of \( Dy_2Ti_2O_7 \) exhibit optical properties when the far IR rays fall on it at different temperatures.\textsuperscript{[142]}

**D6. Rare earth doped glasses:**
The absorption and fluorescence spectra of \( Ln^{3+} \) ions embedded in a crystalline or a glassy matrix consist of groups of relatively sharp spectral lines well separated from each other. Each such group corresponds to the Stark (crystal field) structure of a ‘free ion’ level. The mean energies of these groups do not change significantly from host to host and in that sense may represent the energy states of the corresponding free ion.

The covalent bonding between the RE ion and its ligands partially screens the 4f electrons and reduces the effective nuclear charge. This manifests itself as a rescaling
of the entire energy level diagram, which is known as the *nephelauxetic effect*.\[143\] For glasses this translates into host-to-host shifts of up to a few percent in the separations between the energy levels. Covalent silicate glasses emit and absorb at longer wavelengths while ionic fluoride glasses emit and absorb at shorter wavelengths.\[144\]

Lasers and amplifiers are devices that provide gain and so they must have low scattering losses. Hence, one is restricted to use single-crystal or glass hosts. In many applications, crystalline materials are preferred for reasons that include higher peak cross sections and better thermal conductivities, the versatility of glasses and the broader emission and absorption spectra they provide have led to the use of RE doped glasses in many applications.

### 1.2. Section II –Methods:

#### 1.2.1. Part A: Self propagated high temperature synthesis (SHS):

**E1. Introduction:**

The processing techniques such as alkoxide method,\[145, 146\] sol gel techniques,\[147\] self propagated high temperature synthesis (SHS), etc. are some of the low temperature methods to produce functional ceramic powders. Among these, the SHS is a very simple and cost effective technique\[148\] to synthesise phase pure nano-sized ceramic products which are attracting worldwide attention in high-tech ceramics. SHS\[149, 150\] is also described by the terminologies like auto-combustion, combustion synthesis and a lot of other names,\[148, 151\] depending on the nature of the reactants and the exothermicity.\[148\] This technique, an offshoot of pyro-techniques, was evolved by the studies conducted by Merzhanov et al.\[152\] The term ‘Self propagated High temperature Synthesis’ (SHS) was coined by Merzhanov et al. in 1972, for the process of combustion synthesis of refractory inorganic compounds.\[153-161\] To date, the range of SHS products, besides refractory compounds, includes intermetallics, complex oxides, hydrides, chalcogenides, phosphides, etc.\[162\]

**E2. Advanced ceramics:**

Conventional ceramics including refractories are generally made by crushing, grinding, sieving and physical mixing of the raw materials, whereas for producing ‘advanced ceramics’\[163-169\] or ‘high performance ceramics’, chemically homogenous submicron particles of highly reactive ceramic powders are essential to ensure products having minimum porosity, high density, and controlled microstructure. Modern developments in ceramic products are mainly based on non-silicate and much
more sophisticated materials such as binary oxides, carbides, perovskites and also certain completely synthetic materials. Such materials are referred as advanced ceramics or high performance ceramics. There are several advantages for these materials over traditional ceramics. They are further classified on the basis of their chemical composition and specific functional applications. Different methods reported for the production of advanced ceramic powders are mentioned in Table 1.3.

Table 1.3: Different methods for the production of advanced ceramic powders.\cite{85}

<table>
<thead>
<tr>
<th>Solid state technique</th>
<th>Solution technique</th>
<th>Vapour–phase technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Solid decomposition</td>
<td>a) Precipitation-Filtration</td>
<td>a) Vapourization-condensation</td>
</tr>
<tr>
<td>b) Solid state reaction at high temperatures</td>
<td>(i) Co-precipitation</td>
<td>b) Vapour decomposition</td>
</tr>
<tr>
<td>c) SHS method</td>
<td>(ii) Forced hydrolysis</td>
<td>c) Vapour-vapour reaction</td>
</tr>
<tr>
<td>d) Pechini method</td>
<td>(iii) Alkoxide hydrolysis</td>
<td>(i) Conventionally heated</td>
</tr>
<tr>
<td></td>
<td>(iv) Hydrothermal precipitation</td>
<td>(ii) Plasma heated</td>
</tr>
<tr>
<td></td>
<td>b) Solvent vapourization</td>
<td>(iii) Laser heated</td>
</tr>
<tr>
<td></td>
<td>(i) Simple evaporation</td>
<td>d) Vapour-liquid reaction</td>
</tr>
<tr>
<td></td>
<td>(ii) Spray drying</td>
<td>e) Vapour-solid reaction</td>
</tr>
<tr>
<td></td>
<td>(iii) Spray roasting</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iv) Freeze drying</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(v) Emulsion drying</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c) Liquid drying</td>
<td></td>
</tr>
<tr>
<td></td>
<td>d) Sol-gel</td>
<td></td>
</tr>
</tbody>
</table>

SHS has emerged as a facile and economically viable technique for the synthesis and processing of advanced ceramics, nanomaterials etc.\cite{148, 172}. Recent innovations in the combustion and processing parameters have resulted in a better understanding of combustion phenomena and control of microstructure and property of the products.

E3. Basics of reactions:

The SHS reaction is similar to the well known Thermite process developed by Goldschmidt in 1895, for the reduction of metallic compounds,\cite{173, 174} at specified sites. Vladimir Hlavacek suggested that Goldschmidt deserves the credit for the discovery of self propagating reactions of solid-solid non-catalytic systems.\cite{85, 174}
SHS is a science-intensive process. Its comprehension requires erudition in thermodynamics, chemical kinetics, general and structural macrokinetics, materials science, and other allied fields of knowledge.\cite{175}

SHS method uses the energy produced by the exothermic decomposition of a redox mixture of metal salt, usually metal nitrates, with an organic compound like urea glycine, alanine etc. as activator. In the combustion mixture, the nitrates and the activator behave like conventional ‘oxidants’ and ‘fuels’. The reaction is usually carried out by dissolving metal nitrates and fuels in a minimum amount of water in a pyrex beaker and heating the mixture to evaporate off the water. The resulting viscous liquid foams, ignites, and undergoes self-sustained combustion, producing ashes containing the oxide product.\cite{148, 176, 177} During the combustion, exothermic redox reactions associated with nitrate decomposition and fuel oxidation take place. Gases such as \(\text{N}_2\), steam and \(\text{CO}_2\) evolve favouring the formation of fine particle ashes within a few minutes. The properties of the final product, such as particle size, surface area and porosity, depend on the method of combustion. The liberation of gases favours the de-segregation of the products that increases the porosity, and heat dissipation which inhibits the sintering of the products. Exothermicity of combustion is controlled by the nature of the fuel and the oxidiser to fuel ratio.\cite{85} The reaction paths for synthesis have been described in the literature.\cite{148, 173, 178-185}

The combustion reaction occurs spontaneously by utilising the energy released during the exothermic fuel oxidation reaction. Due to the profuse liberation of gases, instant flame is formed which can have temperatures of more than 2000 °C, a stage at which self propagated high temperature is attained.\cite{173, 183-187} During the SHS reaction, the reactants undergo dehydration, the fuel melts, disperses and decomposes with evolution of gases so that the product froths and swells to a foam-like structure and readily starts glowing with instant flame to form the ceramic powders.

The combustion reaction initiates at the sample surface when a heated wire, electric spark, laser beam, etc. induces a heat flux, and the reaction proceeds spontaneously and rapidly.\cite{148, 178-181, 188, 189} The rate of SHS process depends on the exothermic nature of the reaction as well as on the mode of heat supplied/received by the system, state of aggregation of reactants, kinetics of phase/structure transformations\cite{183-187, 190, 191} etc.

The products formed in SHS reactions may be ordinary loose powders, particle agglomerates, foams, cakes, ingots, films, whiskers, fibres and crystals.\cite{179-181} Products...
formed under optimum conditions are of green composition and contain only traces of unreacted reactants or contaminants. The grain size depends on the rate of cooling and kinetics of crystallisation. The products can have porosities in the range of zero for compact materials and 90-95% for foam materials. A range of products like refractory compounds, inorganic composites, organic compounds and polymers by frontal polymerisation have been made by SHS method.

**E4. Advantages:**
Perhaps the most important and interesting aspect of SHS reaction is the conversion of a simple metallic compound into a highly useful ceramic material of desired properties. Common organic compounds are used as activators or fuels through this cost effective method to prepare numerous metal oxide ceramics.

SHS based on exothermic oxidising reduction reactions has many advantages:
- Utilisation of reaction heat generated during the reaction instead of external power, i.e., self generation of energy.
- Low energy capacity of equipment due to the absence of extrinsic heating sources.
- High productivity due to high reaction or burning velocity.
- Simple reagents with fewer operation stages and high combustion temperature.
- The feasibility of remote-handling the processes.
- The lack of considerable amounts of facility-decommission wastes.
- Low boiling point impurities evaporate at the combustion temperature to yield to form high purity and quality products under optimal conditions.
- Stabilisation of metastable phases.
- Formation of virtually any size and shape products.
- A highly cost effective method for the manufacture of ceramics.
- Simple and inexpensive technological equipment is enough.
- Scaling up of the process is not encountered.
- Reactions approach complete conversion with larger quantities, resulting in better yields of products with limited powder agglomeration.
- Process yields hitherto unknown products with unique properties.

In general, SHS is a material and energy saving process and can be used for the production of finished machine parts. SHS technology is free of the so called scale effect typical of other chemical processes – on going from the laboratory scale to industrial-scale production; the quality of SHS products tends to increase.
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E5. Features: [192]
The three main stages of the SHS process are ignition, front propagation, and product cooling.\[162]\SHS processes are characterised by high temperatures, fast heating rates and short reaction times.\[148]\The basic features of the SHS technology are:\[192]\-
- Duration of initiation - 0.05-5.0 s;
- Temperature in a combustion wave is dependent upon the ratio of precursor\[^8\] components and is within 1500-3000 °C.
- The velocity of moving up the combustion wave is 0.5-150 mm/s.

The main feature of SHS is a very short time required for attaining high combustion temperatures due to heat released during exothermic reactions. This feature explains other specific characteristics, such as the high degree of conversion, partial self-purification from impurities, and the feasibility for the direct synthesis of items with a desired structure and even shape, size, and service parameters. The most attractive features of SHS as a method for the preparation of materials and compounds are:\[162]\-
- SHS can be carried out by using relatively simple facilities or even in open air;
- Sometimes (but rarely), a good practical result can be obtained without having any detailed information about the process;
- The process parameters can be roughly estimated by performing thermodynamic calculations;
- The parameters of SHS can be determined by measuring the values of the velocity of the front propagation, the maximum combustion temperature, the extent of conversion, the chemical/phase composition, the amount of impurities, and some structural data as a function of reagents’ particle size, charge density, sample size, initial temperature, ambient gas pressure, etc.;
- The quality control requires a profound knowledge of the structural macrokinetics, which considers the positive and negative nonlinear feedback between the rates of chemical reactions, structural transformations, and heat/mass transfer processes;
- In most cases, controlling the parameters of the end product is a major task objective of these studies.

These features make SHS an attractive method for the manufacture of technologically useful materials at lower costs compared to conventional ceramic processes.\[148]\

---

\[^8\] Starting compounds
E6. Drawback:
The porous nature of the products necessitates a densification step for any practical application.\textsuperscript{[196]}

E7. Applications:
SHS products find their extensive application in mechanical engineering, metallurgy, chemical industry, electrical and electronic engineering, aerospace industry, building industry, etc. SHS products are also used in medicine.\textsuperscript{[175]}

An important task in the synthetic chemistry of SHS is the direct synthesis of materials with a desired structure, thus avoiding preliminary preparation of powders. The greatest advance here was achieved in the synthesis of multi-component ceramics and hard alloys. SHS can be used to prepare crystalline, agglomerate (polycrystalline), and composite powders.\textsuperscript{[197]} The SHS method has the advantages on the control of reaction rate, temperature and the microstructure of resultant product.\textsuperscript{[156, 157, 180-182, 184]} SHS retains a strong position in the manufacturing of ceramic powders. To date, almost any compound can be prepared by SHS upon proper variation of the charge composition and process conditions, such that the expediency of using SHS in solving this or another task is defined only by the economic factors. The world-wide importance of SHS research is evident from various publications.\textsuperscript{[149, 150, 152, 161, 178, 190, 198-200]}

1.2.2. Part B: Sol gel: \textsuperscript{[92, 201-203]}

F1. Introduction:
Sol gel process is a colloidal route used to synthesise ceramics with an intermediate stage including a sol and/ or a gel state.\textsuperscript{[200]} Sol gel processing has been known for a long time; the first silica gels were made in 1845 by M Ebelmen. Sol gel processing methods were first used historically for decorative and constructional materials. Today sol gel methods are reaching their full potential, enabling the preparation of new generations of advanced materials not easily accessible by other methods, yet using mild, low energy conditions.

Sol gel materials encompass a wide range of organic/ inorganic composite materials which share a common preparation strategy. The sol gel processing involving the generation of colloidal suspensions called ‘sols’ which are subsequently converted to viscous gels and thence to solid materials.\textsuperscript{[92]}
**F2. Sol and gel:**
A sol is a dispersion of colloidal particles suspended in Brownian motion within a fluid matrix. Colloids are suspensions of particles of linear dimensions between 1nm and 1µm. The stability of colloidal particles is determined by their resistance to aggregation, and can be remarkably high. When the particles in the sol form long polymeric chains that span the entire sol, a gel is formed.

**F3. The silicon alkoxide sol gel process:**
The silica produced by the sol gel route starting with hydrolysis of silicon alkoxides occur slowly enough to allow detailed study by a variety of methods. For other alkoxides, such as metal alkoxides which are much more reactive, some reactions occur so rapidly that they are not amenable to either study or control, though they follow the same series of steps. The steps are:
1. hydrolysis
2. condensation
3. gelation – formation of a ‘spanning cluster’ across the vessel, giving a network which entraps the remaining solution, with high viscosity.
4. ageing- formation of further cross-links, associated shrinkage of the gel as covalent links replace non-bonded contacts with changes in pore sizes and pore wall strengths.
5. drying- loss of volatile components, first syneresis (expulsion of the liquid as the gel shrinks), then evaporation of the liquid from within the pore structure with associated development of capillary stress which frequently leads to cracking.
6. densification- thermal treatment leading to collapse of the open structure and formation of a dense ceramic.

**F4. Advantages of sol gel synthesis:**
1. The temperature required for all stages apart from densification are low (~ room temperature). Thus thermal degradation of both the material itself and any entrapped species is minimised and high purity and stoichiometry can be achieved.
2. Precursors are volatile and easily purified to very high levels.
3. Since organo-metallic precursors involving different metals are frequently miscible, homogeneous controlled doping is easy to achieve.
4. Mild and convenient chemical processing conditions.
5. Highly porous materials and nano-crystalline materials may be prepared with controlled pore size distribution, both by the chemical composition of the starting material, as well as by the processing conditions.
Optical and thermal characterization…..

6. By appropriate chemical modification of the precursors, control may be achieved over the rates of hydrolysis and condensation, and over colloid particle size and the pore size, porosity and pore wall chemistry of the final material.
7. Using functionalised precursors, covalent attachment of organic and biological species to porous silicate glass structures is possible.
8. By controlling the ageing and drying conditions, further pore size and mechanical strength control may be achieved.
9. Organo-metallic precursors containing polymerisable organic ligands may be used to produce materials containing both inorganic and organic polymer networks.
10. Entrapped organic species may serve as templates for creation of pores with controlled size and shape. Subsequent removal of these species leaves ‘molecular footprints’ with potential as catalytic sites.
11. Since liquid precursors are used ceramic materials, thin films or fibers as well as monoliths of complex shapes can be cast without machining or melting.
12. The optical quality of the materials is often good.
13. The low temperature of sol gel method allows the production of unusual amorphous materials[203] as it is below the crystallisation temperature for oxides.
14. It not only allows for materials to have any oxide composition, but it also permits the production of new hybrid organic-inorganic materials which do not exist naturally.
15. The association of the solid colloidal state with the liquid medium avoids any pollution by the eventual dispersion of dust.
16. The kinetics of the various chemical reactions can be easily controlled by the narrow processing temperatures and by the often dilute conditions.
17. The sol gel method begins by dissolving the materials in a sol. This process allows for a more homogenous distribution of dopant in the final product.

F5. Limitations of sol gel synthesis:
The precursors are often expensive and sensitive to moisture, limiting large scale production plants to specialised applications such as optical coatings. The process is also time-consuming, particularly where careful ageing and drying are required. Finally the problems of dimensional change on densification, and of shrinkage and stress cracking on drying, although not insuperable, do require careful attention. Thus it is necessary to optimise sol gel materials to exploit their advantages to the maximum in applications.[201]
F6. Silica sol gels- Reaction mechanisms and chemical control of reactions:
The properties of the sol gel materials e.g., transparency, porosity, pore size
distribution, surface functionality, strongly depend on the preparation method. By
controlling the conditions during the stages of the process: hydrolysis, condensation,
ageing, drying, one can fine-tune the characteristics of the resulting material.

F6.1. Hydrolysis- Acid and base catalysis:
The first step of the hydrolysis of a silicon alkoxide can occur by acid catalysed or
base-catalysed processes.

a) The role of the precursor molecule:
Hydrolysis of the silicon alkoxide precursor is very sensitive to steric hindrance.
Larger alkoxy groups lead to more steric hindrance and over-crowding of the
transition state, and thus lead to slower reaction. Thus, tetramethoxy silane (TMOS)
hydrolysis is faster than tetraethoxy silane (TEOS). Chain elongation and in particular
chain branching in the alkoxide ligands lead to a dramatic decrease of the reaction
rate. A higher alcohol (e.g., n-propanol) as a co-solvent leads to replacement of
ethoxide ligands during the first hydrolysis step of TEOS. Stable modifying ligands
reduce the hydrolysis and condensation rate so that less-condensed gels are
obtained. Due to hindrance this precursor exhibits a low reactivity towards
hydrolysis and, therefore, the structure of the gels only depends on pH and reaction
temperature, rather than on the amount of water present in the reaction mixture. The
gel structure can be modified through the modification of the reactivity of precursors
in the replacement of the alkoxy groups by other ligands such as acetate.

Because of the hydrophobic nature of the ethoxy groups, TEOS and water are
immiscible and it is necessary to add a co-solvent to achieve miscibility to facilitate
hydrolysis. Many different co-solvents have been used, including different alcohols,
formamide, dimethylformamide, etc. The choice of added co-solvent is important,
since use of a different alcohol from that generated by hydrolysis of the alkoxide can
lead to trans-esterification and affect the whole hydrolysis and condensation reaction
sequence. The co-solvent may also influence the drying process. Such a co-solvent is
referred to as a drying control chemical additive (DCCA).

b) The role of the catalyst:
The hydrolysis of silicon alkoxides is dramatically promoted by the use of a catalyst.
Under acid catalysis the initial step of the hydrolysis i.e, the conversion of the
precursor molecules into the trialkoxy silanol \((\text{RO})_3\text{Si-OH}\), proceeds rapidly. Since one of the electron donating alkoxy groups has been removed, protonation of this silanol species will be less favourable and hence the second hydrolysis step will be slower. Base catalysis proceeds faster when electron donating –OR groups are removed. The consequent generation of completely hydrolysed monomers leads to cross-linking already at early stages in the process where un-hydrolysed monomer is still present. Due to the high condensation rate and the interlinking of the highly cross-linked polymers a porous network is formed and gelation occurs fast.

c) The role of water:
The ratio of water: alkoxide \((\text{R})\) determines the amount of co-solvent required, but this ratio also influences the reaction rate. The stoichiometric ratio of water: alkoxide for complete hydrolysis is 4:1.

\[
\text{Si(OEt)}_4 + 4\text{H}_2\text{O} \leftrightarrow \text{Si(OH)}_4 + 4\text{EtOH} \quad (1.2)
\]

When silicon alkoxides are reacted with low concentrations of water \((\text{H}_2\text{O}/\text{Si}<2)\) initially, partially hydrolysed monomers are formed which condense to form almost completely esterified- either linear or branched- polymeric species. Increasing the water content to 4-10 \(\text{H}_2\text{O}/\text{Si}\) leads to almost completely hydroxylated polymeric strands in acid catalysed systems. In base catalysed gels this leads to the generation of a fully hydrolysed polymer in the presence of still unhydrolysed monomer which induces phase separation. Consequently aqueous regions solvating the hydrophilic polymer and solvent-rich regions with unreacted hydrophobic monomer are formed.\[^{207}\] Increased water concentration \((25-50 \text{H}_2\text{O}/\text{Si})\) leads to separation of the individual polymeric strands and hinders the intermolecular condensation reactions. This leads to the formation of isolated cyclic structures and consequently to the formation of more dense spherical particles.\[^{208}\] The presence of surface silanol groups promotes gelation by increasing the condensation rate.\[^{209}\]

Addition of solvents such as alcohols affects the structure of water by breaking the hydrogen bonds. This increases the solvation of \(\text{H}^+\) and \(\text{OH}^-\) ions and thereby decreases, respectively, the acidity or basicity of the solution and consequently hydrolysis. Increasing the water concentration increases the activity of the catalyst and hydrolysis is promoted.\[^{210}\]

**F6.2. Condensation:**
Condensation reactions can be either water condensation or alcohol condensation.
Materials-Methods-Measurements

F6.3. Gelation:
Gelation is a process according to which a sol, or a solution, transforms to a gel. Gelation occurs when links form between silica sol particles, produced by hydrolysis and condensation, to such an extent that a giant spanning cluster reaches across the containing vessel. This initial gel has a high viscosity but low elasticity. There is no exotherm or endotherm, nor any discrete chemical change, at the gel point; only the sudden increase in viscosity. Following gelation, further cross-linking and chemical inclusion of isolated sol particles into the spanning cluster continues, leading to an increase in the elasticity of the sample.

At neutral pH the polymerisation reaction proceeds through nucleophilic attack of the Si-O$^-$ group. The nucleophilicity of this group can be fine-tuned through the addition of solvents. Polar protic solvents such as formamide and alcohols lower the reactivity through the formation of hydrogen bonds. This decreases the efficiency of the condensation process leading to more highly branched structures and consequently to reduced gel times. The replacement of an alcoholic solvent by dioxane leads to activation of the Si-O$^-$ group. Due to the efficiency of the condensation process, dense gels are obtained. Increasing the amount of formamide leads to a coarsening of the gel structure and to an increase of the pore size.

By acting as a hydrogen bond acceptor formamide and dimethylformamide decrease the acidity of the reaction mixture and thereby the hydrolysis rate in acid catalysed reactions. For the same reasons the nucleophilicity of the silanol groups is enhanced, leading to faster condensation.$^{[211, 212]}$

In an acid catalysed system formamide is hydrolysed to yield formic acid and ammonia according to:
\[
\text{H-(CO)-NH}_2 + \text{H}_3\text{O}^+ \rightarrow \text{H-(CO)-OH} + \text{NH}_4^+ 
\]
(1.3)
This leads to an increase in pH$^{[213]}$ and gives the process initially the character of an acid catalysed process and later of a base catalysed process, leading to high interconnectivity of small oligomers,$^{**}$ and hence to a decrease of the gelation time.$^{[214]}$

F6.4. Ageing:
The ageing rate of the samples depends on pH, temperature and gel composition. As a final result the samples get stiffened and shrunken. Shrinkage occurs because new

$^{**}$ a polymer molecule consisting of a small number of monomers.
bonds are formed where there were formerly only weak interactions between surface hydroxy and alkoxy groups. This shrinkage leads to expulsion of liquid from the pores of the gel, so that gel samples in sealed containers gradually change in appearance from homogeneous gel to transparent shrunken solid monoliths immersed in liquid. This process is known as syneresis.

Coarsening or ripening occurs associated with ageing, in which the material dissolves from the surface of large particles and deposits on the initially narrow ‘necks’ which join particles to each other.

Phase transformations can also occur where gelation has occurred very rapidly or where several precursors of different miscibility with water have been used; there is a possibility that the porous gel contains isolated regions of unreacted precursor. On prolonged soaking in water; this material may react either completely or partially, giving inclusions of material of different structure and composition. If the refractive index of such regions is sufficiently different from that of the host matrix, the whole sample may have a white opaque appearance characteristic of a phase- separated material. This undesirable situation may be avoided by modifying the reaction rate and use of more effective co-solvents in the initial mixture.

During the ageing process the gel hardens by the formation of cross-links. However, the number of new Si-O-Si bonds responsible for this rigidification was found to be remarkably low. The pore structure of sol gel silicates can be modified by ageing them in solvents or solutions other than the mother liquor. The rate of ageing is directly related to solubility: higher temperatures, hydroxide and fluoride ions increase the rate of ageing and thereby the development of the pore size and the pore size distribution. By dissolution and re-precipitation, neck formation occurs between particles, which lead to strengthening of the pore wall preventing collapse of the pores during the drying process.

**F6.4.1. Significance of ageing:**
Ageing effects are often cited as a significant disadvantage in the use of sol gel materials in technological applications, particularly where the sol gel method is proposed as a low-temperature, mild-conditions method for entrapment of organic or biological species.
Materials- Methods- Measurements

i) Ageing usually improves the properties of the material

ii) The ageing process can be controlled by varying the pH, temperature, pressure, ageing liquid medium and initial precursor mixture composition, and may thus be optimised.

iii) Where regular production is envisaged, ageing need not lead to production delay once an initial aged stock has been generated, provided production requirements can be anticipated.

F6.5. Drying:
There are four main stages in the drying of the gelled sample, the details of which are available in literature.[92, 201-203]

F6.5.1. Consequences of drying:

i) As a flat monolith sample dries with its lower face in contact with the container, evaporation is greater from the upper surface. The lower region of the sample therefore has filled pores while an increasingly large region of the upper surface has empty pores. The region of empty pores is able to distribute the residual capillary stress, and thus expands slightly relative to the lower region. Hence these samples tend to develop lower concave surfaces, even on flat- bottomed containers.

ii) Soluble materials from the bulk of the material may be transported along the thin film of liquid on pore walls and deposited as a white efflorescence at or near the surface of the sample. This may be avoided by washing out the material before drying.

iii) As surface layers dry before the bulk of the sample, a slight surface cloudiness may sometimes be observed in partially-dried samples, depending on pore sizes.

F6.5.2. Avoiding cracks:
The cracks formation can be avoided by

1) Supercritical drying.
2) Freeze drying
3) Drying control chemical additives (DCCAs) addition
4) Ageing
5) Gels with large pores

F6.6. Densification:
Heat treatment produces dense glasses and ceramics from gels. By control of the hydrolysis, condensation, ageing and drying stages, materials with a wide range of pore sizes, pore wall characteristics and general microstructure can be prepared. The
detailed effects of the heat treatment therefore depend on the particular characteristics of the material at the end of the low-temperature drying process.

1) At low temperatures (<200 °C) weight loss occurs as pore surface water or alcohol is desorbed, but little further shrinkage takes place, and in some cases a net expansion is observed. In this range, the skeletal structure of the silica gel behaves as a molecular solid rather than as bulk silica.

2) At intermediate temperatures (150-200 °C to 500-700 °C), samples generally show both weight loss and shrinkage. Three processes occur in this range:
   - loss of organics (leading to weight loss but little shrinkage),
   - further condensation (producing both weight loss and shrinkage) and
   - structural relaxation (giving shrinkage with no associated weight loss).

3) At higher temperatures (>700 °C) a sharp increase in shrinkage rate is observed with little or no further weight loss. The transition temperature is close to the glass transition temperature for the material, above which viscous flow occurs leading to rapid densification as thermal energy permits extended structural reorganisation.

F7. Additives for structuring and processing:

F7.1. Drying and control additives:

Fracture and crack formation during the drying of gels is a serious problem which is caused by stress due to changes in pore size during the process and the capillary forces arising from evaporation of the solvent. The methods adopted to overcome these are:

1. Slow rate evaporation method: Here the removal of the solvent is slow and carefully controlled. It requires very long processing times.[]  
2. Supercritical drying: The solvent is removed under controlled pressure. It is the fastest and most reliable process. Since this is a discontinuous process which limits its industrial application.
3. Use of drying control chemical additives (DCCAs): e.g. formamide, dimethylformamide (DMF), and acetonitrile. These agents allow drying at elevated temperatures and ambient pressures without crack formation. The DCCAs change the structure of the sol gel materials. They cause the generation of large pores with narrow size distribution. The capillary forces will be weaker and hence the stress exerted on the gel during drying will be smaller. Since the vapour pressure is higher in larger pores, the increased pore size promotes the evaporation of the solvent. The DCCA binds to the silica surface through hydrogen bonds. This will facilitate the removal of water molecules by preventing their interaction with the silanol groups on the pore walls and the remaining fluid as a lower surface tension.
4. Addition of surfactants: By adhering to the particle surface the surfactant influences the pore formation, but more importantly it modifies the inner pore surface with alkyl chains. These hydrophobic groups decrease the interaction of the water with the pore wall and thereby reduce drying stress.

**F8. Entrapment of functional materials- Efficiency of entrapment:**
The sol gel route is a low temperature method that allows doping of inorganic materials with organic compounds, thereby adding functionality to the resulting glass. The entrapment efficiency depends on\[^{203}\]
- pore size distribution and porosity of the gel,
- the size of the dopant and
- the development and stability of the matrix network.

**F9. The characterization of sol gel materials:**
The analysis of sol gel derived materials is a far from trivial task for two main reasons:
a) The starting materials are very different from the final products both chemically and physically.
b) Due to the enormous versatility of the sol gel method, the resulting materials and their precursors can cover a vast range of both physical and chemical properties.

**F10. Application of sol gel silicates:**
Sol gel technology provides an alternative route to the production of ceramics and glasses. Compared to conventional techniques the sol gel route offers a number of advantages that make the method interesting for the production of materials tailored to specific applications. The special features of the sol gel materials, i.e. they are porous and generally transparent, have opened up the way for many possible applications.

**Optical materials:**

* Undoped glasses: The sol gel method has been extensively explored as a low temperature route to optical components\[^{224, 225}\] in modern communication and information technologies

* Doped glasses: The inclusion of organic compounds in the final glass by sol gel technology allows for a great variety of functions including laser action\[^{226}\] photoluminescence (PL), photochemical hole burning,\[^{227}\] photochromism,\[^{228}\] nonlinear optical behaviour\[^{229}\] and contrast enhancement.

* Contact lenses: Materials for hard contact lenses with good mechanical, biomedical and optical properties can be prepared by sol gel process.
Optical and thermal characterization…..

Chemical sensors:
- Optical chemical sensing: The immobilisation of complexation reagents on optical fibers can be achieved by sol gel process.[230]
- Biosensors: The highly selective and extremely efficient reactions of enzymes make them desirable reagents for sensing purposes. Sol gel materials immobilise the enzymes without losing their function.

Catalysts:
Due to its porous nature silica has been extensively explored as a catalytic material. For this purpose advantage has been taken of two of its principal properties:
- Silica contains a large number of surface hydroxyl groups that can act as acid catalysts, and
- the surface of the silica can be easily loaded with catalytically active sites through impregnation with various metals.
The key parameters which can be controlled through sol gel processing of the catalysts are:
- High SSA.
- Controlled pore size distribution.
- Stable pore structure under preparation and reaction conditions
- Active material distributed on pore surfaces, not in the bulk.
- Active material homogeneously and effectively distributed over surface.
- High purity of active material.
- Easy control of composition for multi-component catalytic species.
- Effective control of crystalline or amorphous structure as desired.
- Mechanical properties adapted to desired operating environment.
- Catalyst resistant to chemical or physical blocking of active sites.

Coatings and membranes:
The sol gel approach offers the possibility to coat large, curved substrates using simple deposition techniques and the ability to obtain homogeneous coatings, as well as coatings with tailored inhomogeneity. Sol gel methods can be conveniently used to produce multilayer coatings and organic-inorganic hybrid materials. Sol gel layers have been used to achieve conductive-, porous-, optical-control-, antireflection-, biocompatible- coatings etc.[231, 232]

However, a number of problems occur, notably the difficulty of obtaining thicker films for micro-machined components, the prevention of substrate structure adversely
affect the nucleation of the desired solid phase from the sol gel film, and the possibility that the reaction and/or inter-diffusion may occur on heat treatment to nucleate the desired phase despite the lower temperatures generally required for alternative processes. The sol gel process is being increasingly used for the preparation of homogeneous and fine ceramic powders suitable for various nuclear,[170] machinable ceramics, and superconductor applications.[233, 234]

1.2.3. Part C: Photothermal phenomena:

G1. Introduction:
Photothermal (PT) science encompasses a wide range of techniques and phenomena based on the conversion of absorbed electromagnetic energy into heat.[235] Optical energy is absorbed and eventually converted into thermal energy by an enormous number of materials. Although the initial absorption processes in many materials are very selective, it is common for excited electronic states in atoms or molecules to lose their excitation energy by a series of non-radiative transitions that result in a general heating of the material.[236] PT phenomena in solid materials are generated by a combination of thermal expansion, thermal diffusion and thermo-elastic bending effects.[237-240] One of these mechanisms may predominate depending on the particular material and/or on the experimental conditions.[241]

![Diagram](image-url)  
*Figure 1.10: Block diagram showing the possible consequences of electromagnetic radiation absorption, leading to ‘prompt’ or ‘delayed’ heat production in competition with other de-excitation channels.*
Optical and thermal characterization…..

PT generation has three types of applications \[235\]

a) PT material probing - no sample modification.

b) PT material processing- the sample changes to another useful form.

c) PT material destruction- applications render the sample useless.

PT material probing is based on the ideas shown in Figure 1.10. The optical excitation of the sample produces several forms of energy: heat, luminescence, chemical energy, or electrical energy. The heat can be produced promptly, or at various time delays due to energy-transfer mechanisms. All these resulting energy forms must add up to equal the absorbed optical energy; in other words, the various de-excitation branches shown in Figure 1.10 are ‘complementary’.\[235\]

\[235\]

Figure 1.11: Basic processes responsible for photothermal (PT) signal generation.

PT material probing or characterization techniques generally rely on the use of high-sensitivity detection methods to monitor the effects caused by PT heating of the sample. Many of these PT effects occur simultaneously (Figure 1.11); e.g., PT heating of a sample in air will produce temperature rise, photoacoustic (PA) waves, and refractive index changes in the sample and in the adjacent air, IR thermal radiation changes, etc., at the same time. Thus, the choice of a suitable PT effect for detection will depend on the nature of the sample and its environment, the light source used, and the purpose of the measurement.\[235\]

The PT method relies on a fraction of the optical energy being absorbed by the sample and being converted rapidly to heat. PT effect: \[236\]

1) is intrinsically non-invasive / non-contact
2) provides the means of producing a precisely defined region of modulated heating.
3) can be used to obtain spectroscopic information about some materials through their selective absorption of parts of the electromagnetic spectrum.
4) as a whole will depend on the optical properties of the material under investigation as well as its thermal properties for all applications.

G2. Photothermal detection and applications:
PT measurements have been proved to be very useful in various fields such as spectroscopy, thermal characterization, and non-destructive evaluation. When a sample is irradiated by a periodic or a pulsed light source, a temperature rise is induced in the sample. It can be measured by probing the variation of some physical parameters either of the sample itself or of the surrounding medium; this latter dependence distinguishes PT from other spectroscopic experiments.\cite{242} The former case is the ‘direct PT detection’ and the latter is the ‘indirect PT detection’. All the PT detection schemes require a modulation in the excitation light or at least a step change in the form of short intense pulses separated by long dark periods (pulsed PT detection) or continuous train of pulses at nearly 50% duty cycle (continuous-modulated PT detection). The former detection scheme is in the ‘time domain’ where the PT signal magnitude and shape are recorded after the pulse excitation, whereas the latter detection scheme is typically in the ‘frequency domain’ where the PT signal magnitude and phase are measured by ‘lock-in detection’ with respect to the excitation.\cite{235} Detection methods for various PT effects are summarised in Table1.4.

PT experiments can lead to quantitative results for various applications such as:\cite{242}
- Spectroscopy (absorption coefficients);
- Thermal measurements (diffusivity, effusivity, etc.);
- Transport properties (carrier diffusivity, spectral dimension, etc.);
- Geometrical parameters (thickness, fractal dimension, etc.).

PT measuring techniques exploit the time dependent heat flow that takes place when a time varying heat source is applied to the sample. This can be appropriately realised either by periodical laser heating or pulsed illumination. Both excitation techniques initiate propagating temperature oscillations, so-called thermal waves. PT measuring techniques are employed to detect subsurface structures inside opaque solids.\cite{243-245}
Optical and thermal characterization…..

Table 1.4: Various photothermal (PT) effects and the corresponding detection techniques.\[235\]

<table>
<thead>
<tr>
<th>Photothermal effects</th>
<th>Detection methods (D/I)*</th>
</tr>
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<tbody>
<tr>
<td>Temperature rise</td>
<td>Laser calorimetry (D/I)</td>
</tr>
<tr>
<td>Pressure change</td>
<td>Photoacoustic (PA) detection (D/I)</td>
</tr>
<tr>
<td>Refractive index change (thermal or acoustic)</td>
<td>Probe- beam refraction (D/I)</td>
</tr>
<tr>
<td></td>
<td>Probe- beam diffraction (D/I)</td>
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<tr>
<td></td>
<td>Thermal lens (D/I)</td>
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<tr>
<td></td>
<td>Photothermal deflection-PTD (D/I)</td>
</tr>
<tr>
<td>Surface deformation (thermal or acoustic)</td>
<td>Optical interferenece (D)</td>
</tr>
<tr>
<td></td>
<td>Probe- beam deflection (D)</td>
</tr>
<tr>
<td>Thermal emission change</td>
<td>Photothermal radiometry (D)</td>
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<tr>
<td>Reflectivity/ absorptivity change</td>
<td>Transient thermal reflectance (D)</td>
</tr>
<tr>
<td></td>
<td>Transient piezo-reflectance (D)</td>
</tr>
<tr>
<td></td>
<td>Optical transmission monitoring (D/I)</td>
</tr>
</tbody>
</table>

*Note: D- direct PT detection, I- indirect PT detection.

H. Photoacoustics:

H1. Introduction:

Pressure variation or modulation resulting from the absorption of modulated light by a sample is usually referred to as PA or ‘optoacoustic’ generation. The name PA is preferred to optoacoustic to reduce confusion with the acousto-optic effect in which light interacts with acoustic or elastic waves in a crystal.\[246\]PA generation mechanisms include electrostriction, thermo-elastic expansion, volume changes due to photochemistry, gas evolution, boiling or ablation, and dielectric breakdown.\[235\]PA technique is a part of a class of PT effects, in which an impinging light beam is absorbed and alters the thermal state of the sample. This ‘thermal state’ can manifest itself as a change in temperature, density, or other measurable property of the sample. One method of detection is to measure the temperature or density of the absorbing material. This is referred to as ‘thermometric detection’.\[247\]

The absorbing sample warms and cools in a cycle if the incoming light is modulated. If the cycle is so fast that the sample does not have time to expand and contract in response to the modulated light, a change in pressure develops. This pressure ‘wave’ can lead to the production of a sound wave. These sound waves can be detected by a sensitive microphone, piezoelectric devices, or optical methods. These techniques are more properly called PA techniques.\[246\]
Since PA measures the internal heating of the sample, it is clearly a form of calorimetry and a form of optical spectroscopy. Although a more appropriate name for the technique is photo-calorimetry, the term PA is used for this methodology whether it employs microphones or piezoelectric detectors. PA is, however, much more than spectroscopy. It is, after all, a photo-calorimetric method that measures how much of the electromagnetic radiation absorbed by the sample is actually converted to heat.\(^{[246]}\)

The magnitude of the acoustic signal depends on such properties of the sample as:\(^{[248]}\)
- the absorption coefficient,
- the duration of the processes of conversion of absorbed radiation to heat,
- the thermo-physical properties, and
- the geometry.

The acoustic oscillations also acquire a certain phase shift relative to the incident modulated radiation, mainly because of a considerable time lag of heat transfer processes in comparison with the propagation of radiation.\(^{[248]}\)

**H2. Photothermal spectroscopy:**
PT spectroscopy is a group of highly sensitive spectroscopic techniques used to measure optical absorption and thermal characteristics of a sample based on the change in thermal state of the sample resulting from the absorption of radiation. This absorption leads to the heating of the sample. The heat raises temperature thereby influencing the sample thermodynamic properties. Measurements of the temperature, pressure, and/or density changes that occur due to optical absorption are ultimately the basis for the PT spectroscopic measurements.

There are several methods and techniques used in PT spectroscopy. Each of these has a name indicating the specific physical effect measured.\(^{[249]}\)

- **Photoacoustic spectroscopy (PAS)** is an indirect method for measuring optical absorption. Indirect methods do not measure light transmission or emission but rather measure an effect of sample absorption. The term ‘indirect’ applies to the optical measurement, not the optical absorbance.
- **PT lens spectroscopy** measures the thermal blooming that occurs when a beam of light heats a transparent sample. It is typically applied for measuring minute quantities of substances in homogeneous gas and liquid solutions.
- **Photothermal deflection (PTD) spectroscopy** or the mirage effect measures the bending of light due to optical absorption. This technique is particularly useful for measuring surface absorption and for profiling thermal properties of layered materials.
Optical and thermal characterization…..

- PT diffraction, a type of four wave mixing, monitors the effect of transient diffraction gratings ‘written’ into the sample with coherent lasers. It is a form of real-time holography.
- PT emission measures an increase in sample IR radiance resulting from absorption. Sample emission follows Stefan's law of thermal emission. These methods are used to measure the thermal properties of solids and layered materials.

The basic principle of PT spectroscopies is the detection of the heat produced in the sample due to non-radiative de-excitation processes resulting from the absorption of intensity-modulated light by the sample. All PT methods exploit the light-induced thermal wave signal which is proportional to the light-to-heat conversion efficiency, and thus they are complementary to other photo-induced energy conversion processes (e.g. photovoltaic and photo-galvanic).

\[ \text{The fraction of incident chopped radiation, when absorbed by the sample, raises the molecules of the sample from the ground electronic state to the excited electronic state and the excited molecules relax to the ground state through non-radiative de-excitation, i.e. periodic heat emission.} \]

**H2.1. Photoacoustic spectroscopy:**

PAS is the oldest form of PT spectroscopy. To get a quantitative spectrum of a sample, the wavelength of excitation is scanned and the corresponding magnitude of the acoustic signal normalised by the excitation pulse energy is measured to provide an ‘excitation spectrum’ called a PA spectrum. The PA spectrum complements the fluorescence excitation spectrum in that it responds to that part of the absorbed energy which is not radiated. The phase of the PA signal with respect to the phase of the input modulation can give information both on the lifetime of the excited state and on the heat energy transfer between the gas and walls of the chamber.

**H2.2. Principle of photoacoustic spectroscopy:**

When light of appropriate energy falls on a sample, absorption of the light can occur leading to excitation of molecules to higher energy states. The excited species have several options to return to the ground state:

a) Emission of light and thus return to the initial state by luminescent decay.

b) Utilisation of the energy for excited state photo-processes such as photochemical events or energy transfer.

c) Dissipation of the extra energy through non-radiative means of relaxation and return to the ground state by the thermal de-excitation mode.
Materials - Methods - Measurements

Of the three processes, the most common mode of de-excitation is the thermal one. The amount of heat released by the sample to its surroundings will be correspondingly less if either or both of the competing processes a) and b) were to occur.\textsuperscript{[253]}

In PAS\textsuperscript{[241, 254-257]} the irradiation of the sample contained in a closed gas cell produces temperature and pressure fluctuations in the gas synchronous with the modulated source signal. A microphone placed in the gas cell picks up these fluctuations. An associated amplifying system produces an electrical signal. The signal’s amplitude and phase monitored over a range of wavelengths contain information about a wide range of optical phenomena.\textsuperscript{[250]} A recording of the pressure variations versus wavelength of illumination reflects the absorption spectra of the material.\textsuperscript{[241]} In PT spectroscopy, one records the variation in thermal emission from the object induced by irradiation.

The physics of PAS involves concepts in\textsuperscript{[250]}

- thermodynamics (internal energy, volume, temperature),
- optics (interference, absorption, Beer’s law),
- heat (diffusion, conduction),
- acoustics (pressure wave propagation), and
- mechanics (viscosity and elasticity).

The experimental parameters obtainable are the magnitude, the phase angle, the in-phase and the quadrature components of the PA signal, while the variable parameters are scanning wavelength, modulation frequency, spectral bandwidth, and phase (of the phase sensitive detector in the PA channel).\textsuperscript{[250]}

The light from the source is intensity modulated, with angular modulation frequency $\omega = 2\pi f$, usually with a rotating blade chopper at frequency $f$, before entering the closed cell containing the sample so that $I = I_0 \sin \omega t$ \hspace{1cm} (1.4)

$\begin{align*}
I_t &= I_0 e^{-\beta c l} \\
I_u &= I(1 - e^{-\beta c l}) \\
&\approx I\beta c l \\
&= I_0 \beta c l \sin \omega t
\end{align*}$ \hspace{1cm} (1.5)

If the sample absorbs some of this light, a part of the absorbed energy will be degraded to random translational motion of the molecules: that is, heat, thus leading to a temperature rise in the cell. This temperature rise in a constant volume enclosure, has associated with it an increase in pressure, through the ideal gas equation $PV = nRT$.
for n moles of gas. Thus, if the gas responds rapidly enough, the pressure in the cell changes in sympathy with the intensity modulations of the incident beam, thus producing a sound wave so as to produce PA signal $Q = Q_0 \sin \omega t$ (1.7) and $Q_0 \propto I_0 \beta cl$. Rigorous theoretical treatment is outlined in ‘I’. A microphone within the cell detects this sound and is usually followed by amplifiers and other processing electronics.$^{[252]}$

H3. Historical perspective:
The PA effect in both non-gaseous and gaseous matter was first reported by Alexander Graham Bell in 1880.$^{[258, 259]}$ He demonstrated that the PA effect in solids was dependent on the absorption of light and that the strength of the acoustic signal was in turn dependent on how strongly the incident light was absorbed by the material in the cell. Bell called his device the ‘photophone’ since he discovered the effect whilst working on ideas for new telephones and experimenting with a voice modulated beam incident on a selenium detector. Later the phenomenon was termed as the PA effect and, when combined with a wavelength dispersed light beam, the ‘photophone’ has become the ‘spectrophone’ or PA detector. The earlier works on PA were done by Tyndall,$^{[260]}$ Röntgen,$^{[261]}$ Rayleigh,$^{[262]}$ Preece,$^{[263]}$ et al. After the initial flurry of interest generated by Bell’s original work, experimentation with PA effect apparently ceased.

The PA effect was completely dormant for nearly 50 years, until the advent of the microphone. Gorelik first proposed that measurement of the phase of the PA signal could be used to investigate the rate of energy transfer between the vibrational and translational degrees of freedom of gas molecules.$^{[264]}$ This was experimentally proved by Slobodskaya and the use of PA effect to study the vibrational lifetimes of gaseous molecules quickly became an established technique.$^{[265]}$ It was not until the early 1970s that the PA effect in nongaseous matter was ‘re-discovered’ by Allen Rosencwaig and his co-workers at Bell Labs and provided a theoretical basis. The Rosencwaig- Gersho (RG) theory of the PA effect for a sample in PA cell (PAC) provided a comprehensive theoretical framework which led to the rapid development and application of the effect. This led to the invention of numerous other detection schemes and to the current widespread interest in PT science.$^{[246, 266]}$

After the official debut of PAS in 1973, the PAS has been developed to study those materials that are unsuitable for the conventional transmission or reflection methodologies.$^{[257, 267-269]}$ PAS is different from the conventional techniques chiefly in
that even though the incident energy is in the form of optical photons, the interaction of these photons with the material under investigation is studied not through subsequent detection and analysis of some of the photons, but rather through the direct measurement of the energy absorbed by the material as a result of its interaction with the photon beam.\textsuperscript{[246]}

**H4. Instrumentation aspects of photoacoustics:**

The basic requirements of the PA detection technique are the following:\textsuperscript{[236, 270]}

- light source + focussing instruments (if needed)
- means of modulating light
- appropriate photoacoustic cell
- microphone and processing electronics

**H4.1. The light source:**

The modulated optical source is a common feature of all PT techniques and phenomena. The heating produced in all cases is non-stationary. There are two major classes of light sources that have been used for PA studies. These sources are arc lamps/ glow sources and lasers.

1) arc lamps/ glow sources have –
   (a) broad wavelength output from UV to far IR
   (b) fast modulation incapability
   (c) made it necessary to use external spectral selection elements like monochromators to get tuneable wavelength
   (d) low intensity

2) lasers have-
   (a) high intensity
   (b) narrow spectral line width
   (c) modulation capability
   (d) no need of focussing

The source beam is focused in many PT systems to provide high spatial resolution and/ or optical density.\textsuperscript{[236]}

**H4.2. Modulation techniques:**

Several methods have been employed to impose a temporal variation on the optical energy applied to a sample. The type of modulation can be:\textsuperscript{[236]}

1. periodic (sinusoidal or square wave);
2. transient (short, long or finite pulse);
3. frequency multiplexed (pseudo-random or frequency modulated);
4. spatially modulated (scanned or periodic).

The first three options impose a temporal variation on the optical beam at a stationary spot on a sample. The last option produces a modulation at the sample surface by moving the heated spot.\(^{[236]}\)

The simplest form of modulating the light is using a rotating slotted wheel placed in the path of the light beam. It offers 100% modulation depths for frequencies from a few Hz to 5-8 kHz. At higher frequencies, the mechanical vibrations and sound associated with the fast rotating blade of the chopper assembly has to be isolated acoustically from the PAC.

Electrical modulation is generally employed in gas discharge tubes. The electro-optic modulation involves the changing of the plane of polarisation of the incoming polarised laser beam in a non-linear crystal with the application of electric field on it. Acousto-optic modulation involves the spatial modulation of the laser by acoustic diffraction of the light in a crystal.

**H4.3. Detection schemes:**
PA signal detection techniques employ either a gas condenser microphone for the detection of the pressure variations in air or a piezoelectric transducer for the detection of thermo-elastic waves in solid media.\(^{[236]}\) The PAC will generally incorporate a suitable microphone with its preamplifier.\(^{[271]}\) The details of the PAC will be given later in **1.3.2**.

**H4.4. Signal processing:**
For periodic modulation, phase-sensitive detection (lock-in-amplifier) can be utilised to process the detected signal. The technique is extremely efficient for extracting very weak signals contaminated along with noise.

**H5. Advantages of photoacoustics:**\(^{[247, 272]}\)
1. It can be performed on all phases of matter.
2. Light that is transmitted, reflected or elastically scattered by the sample is not detected\(^{[250, 251]}\) as the absorption of the electromagnetic radiation is required for the PA signal production. Hence, these signals do not interfere with the inherently absorptive PA measurements. This is of crucial importance when one is working with essentially transparent media, such as pollutant-containing gases, that have few absorbing centers\(^{[246]}\) of the order of parts per trillion.\(^{[273]}\)
The insensitivity to scattered radiation also permits to obtain optical absorption data on highly light scattering materials.\[246\]

It is non-destructive to the sample; the sample does not have to be dissolved in some solvent or embedded in a solid-state matrix. Samples can be used ‘as is’.\[274\]

Depth profiles of analytes can be performed in optically transparent media.

The PA effect results from a radiationless energy conversion process and is therefore a complimentary to radiative and photochemical processes.\[246\]

PAS itself is a sensitive, though indirect method for studying the phenomena of fluorescence and photosensitivity in matter.\[246\]

The basic simplicity of the experimental set up.

Optical absorption spectra of completely opaque materials can be obtained as PA does not depend on the detection of photons.\[246\]

Non-destructive depth-profile analysis\[270\] of absorption as a function of depth into a material can be performed, which is a unique advantage of the PAS.\[246\]

Since the sample itself constitutes the electromagnetic radiation detector, no photoelectric device is necessary.\[246\]

Studies over a wide range of optical and electromagnetic wavelengths are possible without the need to change the detector systems.\[246\]

The feasibility of direct measurement of non-radiative lifetimes.

The ability to gather information from sub-surface layers.

The scope to obtain information on thermal parameters of the sample.\[270\]

PA can be applied to samples which are difficult to examine by conventional spectroscopic methods.\[251\]

Determination of absolute quantum yields by employing calorimetric techniques which are free from the geometrical correction problems of optical methods.\[251\]

Measurement and detection of absorption coefficient of weakly absorbing or opaque and diffuse materials – cases in which straight photoelectric measurement is not possible.\[250\]

PA spectrum complements the fluorescence excitation spectrum.

An increase in S/N ratio with increase in input power.\[236\]

Requires minimal sample preparation.\[236\]

Operation in hostile environmental conditions.\[236\]

Non-contact and the potential for remote sensing.\[236\]

Can be used to determine a very wide range of absorption coefficient magnitudes-\(10^{-3}\) to \(10^{5}\) m\(^{-1}\).\[236\]

Investigation of non-radiative relaxation processes.\[270\]
H6. Limitations of photoacoustics:
1. The source should be sufficiently energetic (at least 10 $\mu$W cm$^{-2}$).\textsuperscript{[246]}
2. The windows of PAC should be reasonably transparent to the radiation.\textsuperscript{[246]}

There are a number of limitations to high sensitivity of PA systems.\textsuperscript{[270]}
1) The background signal arises due to:
   (a) misalignment of the light beam into the cavity and subsequent interaction of the radiation with the walls
   (b) diffraction and scattering at the input elements like diaphragm, edge of the chopper blades etc.
   (c) acoustic noise that can arise from ambient acoustic noise, building vibration and the vibrations of the mechanical chopper.
2) Brownian motion or thermal fluctuation of the gas in the PAC produces noise.
3) The electronic noise is mainly due to the microphone, its related electronics and the pick-up due to the cables.
4) External noises like source and chopper fluctuations can affect the sensitivity of the PAC.

H7. Applications of photoacoustics.\textsuperscript{[275]}

With its various spectroscopic and non-spectroscopic attributes, PA has already found many important applications in the research and characterization of all type of materials, inorganic, organic, biological, and on all three states of matter\textsuperscript{[247]} PAS is particularly useful for samples that are powdered (like catalysts), amorphous, or otherwise not conducive to reflective or transmission forms of optical spectroscopy.

Some of the applications of the PA are listed below.

\begin{itemize}
  \item The measurement of optical absorption spectra.
  \item Quantitative evaluation of the optical quality of different materials.\textsuperscript{[276]}
  \item Band shapes of PA spectra of transparent solids doped with localised absorbing centres.\textsuperscript{[277]}
  \item The characterization of non-radiative relaxation processes in solids.
\end{itemize}

Since the PA signal is sensitive only to the heat deposited in the sample, any absorbed energy which is re-radiated as fluorescence does not contribute to the signal. Therefore PA provides information concerning the balance between radiative and non-radiative relaxation processes in solids.

1. Use of PA to qualitatively infer the existence of levels with strong non-radiative decay channels.\textsuperscript{[276, 278]}
2. The measurement of absolute quantum efficiencies in solids\textsuperscript{[253]} by
   \begin{itemize}
   \item A.) concentration quenching\textsuperscript{[279]} absolute quantum efficiencies of some localised centres in solids\textsuperscript{[279-281]} and
   \item B.) chopping frequency dependence of the PAS\textsuperscript{[282]}
   \end{itemize}
3. The PA response of a multilevel luminescent system, both in frequency\textsuperscript{[283]} and time\textsuperscript{[284]} domains.
   \begin{itemize}
   \item Optical absorption coefficient measurement\textsuperscript{[246, 266, 267]}
   \item Geophysics, solid state electronics, optics and material science\textsuperscript{[250]}
   \item Optical characterization of thin films\textsuperscript{[285]}, thick films, crystalline, and amorphous semiconductors\textsuperscript{[250]}
   \item Determination of thermal diffusivity (TD) of solids\textsuperscript{[250]}
   \item Investigations of phase transitions\textsuperscript{[250]}
   \item Study of metals and ceramic materials\textsuperscript{[250]}
   \item Analysis of particulate matter for their applications to in-stream measurements of powder characteristics\textsuperscript{[286]}
   \item Application to biological materials\textsuperscript{[253, 287-289]}, gases\textsuperscript{[252, 290]}, biology and medicine\textsuperscript{[291]} imaging or PA microscopy\textsuperscript{[292]}
   \item Spectroscopic measurements\textsuperscript{[246]}
     \begin{itemize}
     \item 1) Measurement of absorption or excitation spectrum\textsuperscript{[246]}
     \item 2) Excited state lifetime measurements\textsuperscript{[246]}
     \item 3) The energy yield of radiative processes\textsuperscript{[246]}
     \end{itemize}
   \item Applications arising from the calorimetric or acoustic aspect\textsuperscript{[246]}
     \begin{itemize}
     \item 1) Measurement of thermal and elastic properties of materials\textsuperscript{[246]}
     \item 2) Study of chemical reactions
     \item 3) Thickness measurement of layers and thin films
     \item 4) Performance of a variety of other non-spectroscopic investigations
     \end{itemize}
\end{itemize}

I. Rosencwaig- Gersho (RG) theory\textsuperscript{[266]}

II. Introduction:
The theory of the gas-microphone PA detector was developed in stages. The importance of heat flow from the solid to the gas was identified by Parker\textsuperscript{[293]} Rosencwaig and Gersho\textsuperscript{[266]} proposed a one-dimensional model that attributed signal generation to the action of the heated layer of the gas at the surface of the sample. This ‘thermal piston’ model successfully describes the dependence of the PA signal on acoustic frequency, the optical and thermal properties of the sample, and the thermal
properties of the gas. Effects of thermal expansion of the solid- ‘mechanical piston’ effects- can be important for thick samples of weak absorbers.

In PA effect- essentially an energy-conversion process- the radiant energy absorbed by the sample is converted into kinetic energy of the gas molecules within the solid which is transferred as heat through the solid-gas boundary, eventually resulting in the PA signal. The gas present in the cell behaves as a passive coupling agent between light and the solid and it does not contribute to the final acoustic signal. Nor does the adsorbed gas lying just over the surface of the solid- the solid-gas interfacial layer- seem to give rise to the PA signal.

The PA effect is a non-equilibrium transport process. The PA effect in solids may be modelled by a ‘reservoir 1- system- reservoir 2’ configuration in which the sample is the first reservoir, and the system is the sample-gas interface (really extending up to the microphone), while the microphone could be regarded as the second reservoir. Energy transport takes place via particle transport (which is via gas molecules), the driving forces for the two intimately connected processes being the temperature and the chemical gradients (the former is also time dependent). Thus, all the three important thermal properties: thermal conductivity, thermal diffusivity, and viscosity seem to control the PA effect in a complicated manner.

The RG theory shows that the PA signal depends both on the generation of an acoustic pressure disturbance at the sample- gas interface and the transport of this disturbance through the gas to the microphone. The generation of the surface pressure disturbance depends in turn on the periodic temperature at the sample-gas interface. The RG theory derived exact expressions for this temperature, while it treated the transport of the disturbance in the gas in an approximate heuristic manner, which is, however, valid for most experimental conditions.

I2. The thermal diffusion equations:
Light absorbed by a solid is converted, in part, or in whole into heat by non-radiative de-excitation processes within the solid. Consider that the PAC (Figure 1.12) has a diameter D and length L. The sample is considered to have a diameter D and thickness \( l_s \) and is mounted such that its back surface is against a poor thermal conductor of thickness \( l_b \). The length \( l_g \) of the gas column in the cell is \( l_g = L - l_s - l_b \) (1.8). The following assumptions are made in framing the thermal diffusion equations:
L is small compared to the wavelength of the acoustic signal.

The microphone detects the average pressure produced in the cell.

The gas and the backing materials are not light absorbing.

A sinusoidally chopped monochromatic light with wavelength $\lambda$ is incident on the sample.

The dimensions of the cell are small enough to ignore convective heat flow in the gas at steady-state conditions.

The temperature relative to ambient is zero at the ends of the cell.

The parameters defined in the development of RG theory are:

- $\kappa_j$ - thermal conductivity of the material $j$ (Wm$^{-1}$K$^{-1}$)
- $\rho_j$ - density of the material $j$ (kg m$^{-3}$)
- $\alpha_j = \frac{\kappa_j}{\rho_j c_j}$ - thermal diffusivity (TD) of the material $j$ (m$^2$s$^{-1}$)
- $a_j = \left(\frac{\omega}{2\alpha_j}\right)^{1/2}$ - thermal diffusion coefficient of the material $j$ (m$^{-1}$)
- $\mu_j = 1/a_j$ - thermal diffusion length of the material $j$ (m)

where $j$ can be $s$, $g$ and $b$ for the solid, gas and backing material respectively.

$\omega = 2\pi f$ the angular chopping frequency of the incident light beam (radians per s) and $f$ is the chopping frequency (Hz).

$I_0$ - the incident monochromatic light flux (Wm$^{-2}$).

$\beta$ - optical absorption coefficient of the sample for the wavelength $\lambda$ (m$^{-1}$)

The intensity of the light incident on the sample $I = \frac{1}{2} I_0 (1 + \cos \omega x)$ (1.9)

The heat density produced at any point $x$, due to light absorbed at this point in the solid is $\frac{1}{2} \beta I_0 e^{\beta x} (1 + \cos \omega x)$

Figure 1.12: cross sectional view of a simple cylindrical photoacoustic cell (PAC).
The thermal diffusion equations are

\[
\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha_s} \frac{\partial \theta}{\partial t} \quad -l_s \leq x \leq 0 \quad \text{(sample)} \quad (1.10)
\]

\[
\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha_b} \frac{\partial \theta}{\partial t} \quad -l_b - l_s \leq x \leq l_s \quad \text{(backing)} \quad (1.11)
\]

\[
\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha_g} \frac{\partial \theta}{\partial t} \quad 0 \leq x \leq -l_g \quad \text{(gas)} \quad (1.12)
\]

where, \( \theta \) is the temperature , \( A = \frac{\beta l_s \eta}{2 \kappa_s} \) (1.13)

and \( \eta \) - efficiency at which the absorbed light at wavelength \( \lambda \) is converted to heat by the non-radiative de-excitation processes. For most solids at room temperature \( \eta = 1 \).

The real value of the complex valued solution \( \theta(x,t) \) represents the temperature in the cell relative to the ambient temperature as a function of position and time. The actual temperature field in the cell is \( T(x,t) = \text{Re} \theta(x,t) + T_0 \) (1.14)

where \( T_0 \) - the ambient temperature and \( \text{Re} \) denotes the ‘real part of’.

### I3. Temperature distribution in the cell:

The general solution for \( \theta(x,t) \) in the cell neglecting the transients

\[
\theta(x,t) = \begin{cases} 
\frac{1}{l_b} (x + l_s + l_b) W_0 + W e^{\sigma_b x} e^{iat}, & -l_b - l_s \leq x \leq -l_s \\
0, & -l_s \leq x \leq 0 \\
1 - \frac{x}{l_s} F + \theta_0 e^{-\sigma_s x} e^{iat}, & 0 \leq x \leq -l_g \end{cases} 
\]

where \( W, U, V, E \) and \( \theta_0 \) are complex-valued constants, \( b_1, b_2, b_3, W_0 \) and \( F \) are real-valued constants, and \( \sigma_j = (1 + i)a_j \). \( \theta_0 \) and \( W \) represent the complex amplitudes of the periodic temperatures at the sample-gas boundary \( (x = 0) \) and the sample-backing boundary \( (x = -l_j) \). The quantities \( W_0 \) and \( F \) denote the dc component of the temperature (relative to ambient) at the sample surfaces \( x = -l_g \) and \( x = 0 \), respectively.
The complex amplitude of the periodic temperature at the solid-gas boundary \((x = 0)\) is given by

\[
\theta_0 = \frac{\beta_0}{2\kappa_s(\beta^2 - \sigma_s^2)} \left\{ \frac{(r+1)(b+1)e^{\sigma_s x} - (r+1)(b-1)e^{-\sigma_s x} + 2(b-r)e^{-\beta_s x}}{(g+1)(b+1)e^{\sigma_s x} - (g-1)(b-1)e^{-\sigma_s x}} \right\} \tag{1.16}
\]

where,

\[
b = \frac{\kappa_s a_b}{\kappa_s a_s} \tag{1.17}
\]

\[
g = \frac{\kappa_s a_g}{\kappa_s a_s} \tag{1.18}
\]

\[
r = \frac{(1-i)\beta_s}{2a_s} \tag{1.19}
\]

The actual temperature at \(x = 0\) is given by

\[
T(0,t) = T_0 + F_0 + \theta_1 \cos \omega t - \theta_2 \sin \omega t \tag{1.20}
\]

where \(F_0\) is the increase in temperature owing to the steady-state component of the absorbed heat. \(\theta_1\) and \(\theta_2\) are the real and imaginary parts of the complex number \(\theta_0\) which determine the in-phase and quadrature components of the periodic temperature variation at the surface \(x = 0\) of the sample.

### 14. Production of the acoustic signal:

The periodic diffusion process produces a periodic temperature variation in the gas as given by the sinusoidal (ac) component of the solution \(\theta\)

\[
\theta_{ac}(x,t) = \theta_0 \exp(-\sigma_s x + i\omega t) \tag{1.21}
\]

Taking the real part, the actual physical temperature variation in the gas is

\[
T_{ac}(x,t) = e^{-\sigma_s x} \left\{ \theta_1 \cos(\omega t - a_s x) - \theta_2 \sin(\omega t - a_s x) \right\} \tag{1.22}
\]

The time dependent component of the temperature in the gas attenuates rapidly to zero with increasing distance from the surface of the solid. At a distance of only \(2\pi \mu_s\), the periodic temperature variation in the gas is effectively fully damped out. This thickness of gas is capable of responding thermally to the periodic temperature at the surface of the sample.

The periodic heating of the boundary layer expands and contracts it periodically; making it act as an acoustic piston on the rest of the gas column. This produces an acoustic pressure signal that travels through the entire gas column. If this response is adiabatic, the acoustic pressure in the cell is derived from the adiabatic gas law
where \( P \) is the pressure, \( V \) is the gas volume in the cell and \( \gamma \) is the ratio of the specific heats.

The complex envelope of the sinusoidal pressure variation is given by

\[
Q = \frac{\beta I_0 P_0}{2\sqrt{2k_s^\beta a_g T_0}} \left\{ \frac{(r-1)(b+1)e^{\sigma_s t} - (r+1)(b-1)e^{-\sigma_s t} + 2(b-r)e^{-\beta_s t}}{(g+1)(b+1)e^{\sigma_g t} - (g-1)(b-1)e^{-\sigma_g t}} \right\} (1.24)
\]

where \( P_0 \), \( T_0 \) is the ambient pressure. This equation is evaluated for the magnitude and phase of the acoustic pressure wave produced in the cell by the PA effect.

**I5. Special cases:**

The earliest theory of the PA effect – RG theory\(^{[266]}\) developed an analytical expression for the PA signal in terms of (i) the variations of the gas pressure \( \Delta P(t) \) as a function of time, as the ultimate consequence of the interrupted illumination of the sample which results in the propagation of a temperature wave from the sample surface, and (ii) characteristic parameters of the different media, the solid, the material backing it, and the gas which couples the solid to the detector.

\[
\Delta P(t) = \frac{\mathcal{P}_0 \theta \mu}{\sqrt{2I_s T_0}} \exp \left[ i \left( \omega t - \frac{\pi}{4} \right) \right] (1.25)
\]

One defines optical transparency or opacity from a comparison of the optical absorption length and the sample thickness. Likewise, a sample is defined as thermally thin or thick depending on the relative values of the thermal diffusion length and the sample thickness. The reciprocal of the absorption coefficient and represents the distance into the sample to which the photon penetrates before its intensity is reduced to 1/e of its initial value. The thermal diffusion length of the sample is related to its thermal properties and is a measure of the distance that the released heat diffuses from the point of its generation before it is attenuated to 1/e of its initial value.\(^{[253]}\)

In the one-dimensional heat conduction model of the RG theory the acoustic signal is supposed to arise primarily from the periodic heat flow from the solid to the surrounding gas as the solid is cyclically heated by the chopped light. This heat is generated by light absorbed by the sample and subsequent, predominantly non-radiative, de-excitation processes within the sample. The three important physically measurable ‘lengths’ in the PA effect are sample thickness \( l_s \), optical absorption
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length $l_\beta = 1/\beta$, and thermal diffusion length $\mu_s$ on the relative magnitudes of which arise the various cases of practical interest:

A. Optically transparent solids ($l_\beta > l_s$) in which light is absorbed throughout the sample length and some light is transmitted: (Figure 1.13a)

(i) thermally thin ($\mu_s >> l_s$ and $\mu_s > l_\beta$), the acoustic signal is proportional to $\omega^{-1}$, or

(ii) thermally thin but with $\mu_s > l_s$ and $\mu_s < l_\beta$; even now the signal varies as $\omega^{-1}$. However, when $\mu_s >> l_s$, the thermal properties of the backing material come into play;

(iii) thermally thick ($\mu_s < l_s$ and $\mu_s << l_\beta$); the signal is proportional to $\beta \mu_s$, and, although light absorbed within the first thermal diffusion length $\mu_s$ contributes to the signal; when $\mu_s < l_s$, thermal properties of the backing material are unimportant.

The signal is proportional to $\omega^{-3/2}$.

Figure 1.13: Schematic representation of special cases for the photoacoustic (PA) effect in optically a) transparent solids, b) opaque solids.

B. Optical opaque solids ($l_\beta << l_s$) wherein practically no light is transmitted.

(Figure 1.13b)

(i) thermally thin samples ($\mu_s >> l_s$, $\mu_s >> l_\beta$) with both optical and photoacoustic opaqueness, where the signal is independent of $\beta$. A strong signal depending upon the thermal properties of backing material and varying as $\omega^{-1}$ results.
(ii) thermally thick solids ($\mu_s < l_s, \mu_s > l_\beta$); thermal properties are those of the solid but the signal is still independent of $\alpha$ and varies as $\omega^{-1}$;

(iii) thermally thick solids but with $\mu_s << l_s, \mu_s < l_\beta$; optically very opaque but photoacoustically not opaque (since $\mu_s < l_\beta$); the signal depends on thermal properties of the solid and varies as $\omega^{-3/2}$.

I6. Importance of RG theory: The RG theory predicts that the PAS is always linearly proportional to the power of the incident photon beam, and that this dependence holds for any sample or cell geometry and this is experimentally verified.

When the thermal diffusion length in the sample is greater than the optical absorption path length, the PAS is independent of optical absorption coefficient of the sample. Since the thermal diffusion length $\mu_s$ can be changed by changing the chopping frequency $\omega$, it is possible to obtain the optical absorption spectra on all but most highly opaque solids. This capability of the PAS technique, together with its insensitivity to scattered light, makes its use as a spectroscopic tool for the investigation of solid and semisolid materials. These features give PA a unique potential for non-invasive in vivo studies of tissues, a potential that have important implications in biological and medical research and in medical diagnostics.

If one has a full knowledge of the thermal and geometrical parameters of the sample, one can obtain absolute values for the optical absorption coefficient by measuring the dependence of the PAS on modulation frequency.

J. Photothermal deflection (PTD):

J1. Introduction:
In 1979, Boccara et al. proposed and demonstrated that PT beam deflection (PTD) or mirage effect can be advantageously used for monitoring the temperature gradient field close to a sample surface or within the bulk of a sample. This technique was found to be sensitive and very simple to set up. It is based on the measurement of the time dependent beam deflection, which can be computed for various kinds of probe beams. The mirage effect is sensitive to the gradient of temperature averaged along a line parallel to the probe beam. The calculation of the mirage effect is more complicated for three reasons:
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(1). The method is essentially three dimensional.
(2). The detection destroys the axial symmetry of the pump beam generally used.
(3). The calculation needs the derivatives of the temperature with respect to the spatial coordinates.

J2. Limitations:
The difficulty with PTD localisation is precisely the difficulty of obtaining a probe beam that is small compared with the scale of imaging detail desired. As the probe must pass over the entire sample, it cannot be highly convergent without interference with the sample surface. One is then limited to the probe diameters of the order 50-100µm at the pump position even though one possibly desires to detect defects much smaller in size.\(^{[245]}\) Moreover, the sample surface must be reasonably flat, so that the probe can skim the surface.\(^{[299]}\)

J3. Advantages:
- Vertical cracks may be detected using PTD,\(^{[300, 301]}\) but not with PA.\(^{[245]}\)
- Direct TD measurement can be performed with high degree of accuracy.\(^{[299]}\)
- It requires neither contact with the sample nor thermometry.\(^{[299]}\)
- Only one surface of the sample needs to be accessible.\(^{[299]}\)
- The measurement is inherently local so that measurement of non-uniform or small samples can be made.\(^{[299]}\)
- The diffusivity can be measured in different orientations on anisotropic materials simply by rotating the probe-beam direction.\(^{[299]}\)
- It provides a simple, non-destructive and in situ measurement of TD.\(^{[302]}\)

For materials that have a layered structure, the frequency dependence of the mirage signal can be exploited to provide more detailed information other than TD, such as the thickness of a thin film or the relative thermal effusivity (TE) at the interface.\(^{[302]}\)

K. Thermal property determination by photothermal techniques:

K1. Introduction:
There is an undiminishing demand for reliable measurements of the basic thermal properties of the vast range of materials in use today. The determination of the thermal properties has become an attractive, important and well established application of PT science because the PT techniques combine the non-contact application of well defined amounts of thermal energy with methods for the determination of the resulting temperature changes. The temperature changes employed in a property determination
can be very small because of the very high sensitivity detection techniques that have been developed in the PT sciences. A material’s PT response depends on the two parameters: TD and TE. Consequently, these are the thermal properties that can be obtained by PT methods rather than the primary quantities such as thermal conductivity and specific heat.\(^{[302]}\)

**K2. Thermal diffusivity (TD): (\(\alpha\))**

TD is a physical parameter, the measurement of which provides both direct and indirect information on materials of industrial interest.\(^{[303]}\) This thermo-physical property is defined as

\[
\alpha = \frac{k}{\rho C} \quad (1.26)
\]

TD is the ratio of thermal conductivity \(k\) and volumetric heat capacity (VHC) or thermal capacitance \(\rho C\) where the latter is the product of density \(\rho\) and specific heat capacity \(C\). TD indicates the rate at which heat is distributed in a material. This rate depends not only on the thermal conductivity but also on the rate at which energy can be stored. This thermal transport parameter determines the rate of heat diffusion in the medium. Thus, TD is an indication of the speed with which an unstable temperature distribution has become stable.\(^{[270]}\)

VHC describes the ability of a given volume of a substance to store internal energy while undergoing a given temperature change, but without undergoing a phase change. It is different from specific heat capacity in that the VHC depends on the volume of the material, while the specific heat is based on the mass of the material. If given a specific heat value of a substance, one can convert it to the VHC by multiplying the specific heat by the density of the substance.\(^{[305]}\)

Both frequency and time domain PT techniques can be used for TD evaluation. The measurement is based on the detection of a phase or time delay in PT response with respect to the applied thermal excitation. These non-stationary heat flow techniques have gained acceptance because they are less affected by heat losses, which are difficult to quantify, than a stationary heat flow technique.

The TD is a dynamic thermal property which characterises heat conduction inside a material under non-stationary conditions. This characteristic makes this thermal property essential for the study and modelling of thermal processes.\(^{[306, 307]}\) TD is a parameter that governs heat flow. If a material is subjected to heat input that varies
over time, TD describes how the heat ‘spreads out’ in between the changes in heat input. The rate of the heat flow, and hence how deep the changes in the temperature at the surface penetrate, depends on TD.\textsuperscript{[308]}

The thermal characteristics of a solid have a predominant influence on its PA signal. TD determines the rate of transient (or unsteady) state heat flow through a solid and thus is useful in the calculation of thermal conductivity.\textsuperscript{[250]} This parameter governs the ease of glass formation by rapid quenching of metallic alloys. Microscopically, TD represents the dynamical aspect of the heat conductivity of carriers, and in the kinetic theoretical framework, is proportional to the mean free path of carriers. Thus, from TD and its temperature dependence one can deduce the mechanism of carrier scattering. The higher the TD of a solid, the higher is the rate of temperature propagation.\textsuperscript{[250]}

K3. Thermal effusivity (TE): (e)
Thermal inertia or TE of a material is the square root of the product of the material’s bulk thermal conductivity and VHC. Thermal inertia is a measure of the thermal mass and the velocity of the thermal wave which controls the surface temperature of a material. In heat transfer, a higher value of the VHC means a longer time for the system to reach equilibrium. Thermal inertia is a term commonly used by scientists and engineers modelling heat transfers\textsuperscript{[309]} and is a bulk material property related to thermal conductivity and VHC. SI units of thermal inertia are Jm\textsuperscript{-2}K\textsuperscript{-1}s\textsuperscript{-1/2} and also occasionally referred to as Kieffers,\textsuperscript{[310]} or more rarely, tiu.\textsuperscript{[311]} As the name implies, thermal inertia represents the ability of a material to conduct and store heat.

TE measures the thermal impedance of the material. It is the ability of the sample to exchange heat with the environment and hence it is an important parameter for surface heating and cooling processes. TE is a surface property\textsuperscript{[312]} which is defined as

\[ e = \frac{k}{\sqrt{\alpha}} = \sqrt{k\rho C} \]  \hspace{1cm} (1.27)

Powders would have different effusivity readings depending on their ability to transfer heat through and between their particles. This is also a function of the particle size, shape, density, and moisture of the material. Therefore, one can expect that any change in one of these parameters should result in change of the TE value.\textsuperscript{[313]}

The ability of a material to exchange its thermal energy with surroundings is essentially determined by its TE. Its importance lies not only on the thermal exchange
characteristics, but also on its utility in making complete thermo-physical property of materials. Knowing the value of the TE is useful in calculating the heat accumulation capacity of materials in a transient state. Both the thermal conductivity and the TE of composite materials depend upon various parameters, such as the thermal properties of the constituent phases, and micro-structural parameters including the volumic fraction of each phase, the shape of the particles, the size, the size distribution of the particles and so on.

TE characterises the thermal contact of two samples. TE is a heat transfer property that determines the interfacial temperature when two semi-infinite objects at different temperatures touch. The effusivity of materials varies due to their differing ability to transfer heat. This is due to differences in heat transfer through and between particles. Powders have effusivities that are strongly correlated with their moisture content. In conclusion, TE characterises the transient thermal behaviour that occurs when two materials are brought into contact with each other.

1.2.4. Part D: Fluorescence and absorption:

L1. Introduction:
Optical spectroscopy is a powerful tool to study the non-occupied electronic states of optically active ions containing unpaired electrons when they are embedded in condensed phase media. In the case of RE ions, it provides information about the interaction between the metallic central ion and its environment through ‘nephelauxetic effect’ that determines the relative spatial extension of the f-orbitals and subsequently the overlapping with the ligand valence orbitals.

L2. Absorption spectroscopy:
The electronic excitations between two energy levels cause absorption. In absorption spectroscopy, the attenuation of the transmitted light is monitored to determine the absorption coefficient or the number density of absorbing species. For small absorptions this means the measurement of a small difference of two large quantities, which limits, the signal to noise ratio.

L3. Fluorescence:
Light produced by illuminating a compound with UV radiation is known as ‘photoluminescence’ (PL). Fluorescence is distinguished from other types of PL by the fact that the excited molecule returns to the ground state immediately after excitation,
the time spent in the excited state being typically of the order of $10^{-8}$ s. Fluorescence is the spin allowed transition. The luminescent mineral consists of a host lattice and a luminescent center, called an ‘activator’.[320]

Although the 0, 0 transition gives rise to a band in both the fluorescence excitation and emission spectra, its wavelength may not in fact be identical in both spectra. A small displacement to longer wavelength is usually observed in the emission spectrum due to stoke’s shift arising out of the interaction between the fluorescent solute molecules and molecules of the solvent. In a solution the solvent molecules distribute themselves around the solute molecules in a way which leads to the greatest stability for the system. The greatest stability corresponds to the minimum energy.[320]

**L4. Fluorescence excitation spectroscopy:**
The excitation spectrum directly reflects the absorption spectrum with respect to the line positions.[273] It is still useful to measure the absorption lines with extremely high sensitivity, although their relative intensities may not be recorded accurately. Excitation spectroscopy has its highest sensitivity in the visible, UV and NIR regions at low molecular densities.[273]

**L5. Laser induced fluorescence (LIF):**
LIF is spontaneous emission from atoms or molecules that have been excited by laser radiation. Two radiative transitions are involved in the LIF process. First, absorption takes place, followed by a photon-emission step.

LIF has a large range of applications in spectroscopy.[273]

- LIF is a dominant laser spectroscopic technique in the probing of unimolecular and bimolecular chemical reactions.
- LIF serves as a sensitive monitor for the absorption of laser photons in fluorescence excitation spectroscopy.
- It is well suited to gain information on molecular states if the fluorescence spectrum excited by a laser on a selected absorption transition is dispersed by a monochromator.
- The spectroscopic study of collision processes.
- Application to the determination of the internal state distribution in molecular reaction products of chemical reactions.
The emission and absorption spectra bear a ‘mirror image’ relationship to each other. The emission spectrum is obtained by irradiating the sample at the wavelength of maximum absorption and observing the emitted fluorescence with a scanning monochromator which gives a plot of intensity versus wavelength.

1.3. Section III –Measurements:

1.3.1. Part A: Light sources:

M1. Argon ion laser:
LiCONiX® 5300 series water cooled argon ion laser with TEM$_{00}$ transverse mode and beam diameter 1.3 mm was used as the excitation source in the TD measurement using PT studies. 488 nm output from model 5302A laser has power stability of ±0.5% under light regulation and ±3.0% under current regulation. Forced air cooled 5000PS power supply was used to provide the power to the laser system. The laser system can be operated with an ambient air temperature of 10 to 35 ºC and the optimum air temperature is 22 ±2 ºC. LiCONiX® 60HE heat exchanger is used in the water cooling system.

M2. Pulsed Nd: YAG laser:
355 nm output from model LAB 170, Spectra-Physics Quanta-Ray GCR-170 pulsed Nd: YAG laser is used for the PL studies of RETs. The GCR-170 model has a repetition frequency of 10Hz with maximum output energy of 240 mJ. The harmonic generator of the laser is a KD*P crystal.

M3. Xenon arc lamp:
1000W ozone free Newport model 6271 xenon lamp was used for the PAS studies. The lamp has the ORIEL model 8540 arc lamp power supply and model 66021 ORIEL universal arc lamp housing. The model 8540 is compact, light weight, constant wattage and regulated power supply with a drive circuit for external ignitors and lamp housings with internal ignitors.

M4. Mode-locked Ti: sapphire laser:
Model 3941 mode-locked Tsunami® laser uses Ti: sapphire laser medium. The laser head contains the Ti: sapphire rod and the optics that form the resonator cavity. Broadband femtosecond second performance is obtained from a Tsunami® laser when pumped by a 532 nm Millennia Pro-5sJ laser to give an average power output of 700mW near 790 nm. The pulse width is <100 fs with a peak power >85 kW.
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**M5. Diode pumped solid state (DPSS) laser:**
Micro DPSS laser model BWT-50 (B&W) at 532 nm was also used in PA studies. BWT series are miniature diode-pumped Nd: YVO₄ lasers with integrated internal thermoelectric cooler. They can be operated over a temperature range of -10 to 50 ºC. It has TEM₀₀ mode with a spectral line width <0.1 nm and a beam size of 1 mm.¹³²⁵⁰

**M6. He- Ne laser:**
JDS Uniphase He- Ne gas laser emitting at 633 nm with 4 mW power was used as the probe beam in PTD studies.

**1.3.2. Part B: Photoacoustic cell (PAC)²³⁶**

**N1. Introduction:**
The PAC monitors the temperature changes in the sample, produced by its absorption of optical energy. The cell is a small gas-tight enclosure with a sensitive acoustic microphone built into one wall. Sample temperature changes cause pressure variations in the enclosed gas that are converted to an electrical signal by the microphone. The light incident on the sample is modulated by a mechanical light chopper. The resulting sample heating is periodic and causes a periodic pressure change in the enclosed gas which is converted by the microphone into an ac electrical signal that may be processed using low noise narrow bandwidth techniques. The PAC has proved to be a very sensitive, though indirect, means of detecting the sample temperature changes caused by the PT effect. Many geometric and optical arrangements for the sample chamber, optical source and microphone can be conceived.²²⁹⁰

**N2. Standard photoacoustic cell:**
The standard PAC configuration has a solid sample in a small, gas filled cell, a window above the sample through which a modulated beam is incident, and a microphone in the main gas chamber. Parker²²⁹¹ and Rosencwaig and Gersho²₆₆ showed that periodic heat flow between the sample and gas is the basic mechanism causing a pressure variation in the gas.²⁴⁵

**N3. Designing aspects of photoacoustic cell:**
While designing a PAC the following aspects are to be considered:²²⁷⁰

1) Proper acoustic shielding from the ambient atmosphere. - This can be done with good acoustic sealing, rather thick walls and acoustic isolation of the cells from vibrations in the laboratory.
2) Minimisation of unwanted signals due to interaction of the excitation light with cell walls, windows and microphone. - The material of the cell elements both walls and windows should be able to produce a maximum signal and to suppress background signals. Windows should be chosen with minimum absorption and large enough so that the scattered radiation can be reflected back from the cell. To reduce the background signals from the walls it is necessary to choose highly reflecting or highly transparent materials. Besides, all the inner surfaces must be clean to eliminate the possibility of background signals from surface impurity.

3) Proper configuration and placement of microphone and sample. - To eliminate the influence of scattered radiation on the microphone, it should be located next to the cell chamber and connected by an acoustic channel. To overcome undesirable loss of sensitivity, the volume near the microphone and the volume connecting the acoustic channel should be minimised.

4) Means for maximising the signal from the PAC. - The maximum output signal is obtained when the gas column length in the cell is around the thermal diffusion length of the used gas. The acoustic signal can be enhanced by the use of gases with a lower thermal conductivity, high gas pressures and lower gas temperatures.

5) If needed, heating and cooling facilities for temperature variation of the cell.

6) The cell must be designed and operated to minimise the interaction between detector surfaces and the sample.

The PA signal is an average measurement of the local modulated temperature rise resulting from optical heating. The design of PAC needs to be optimised with regard to signal detection and noise minimisation. The principal noise components arise from environmental noises and secondary PA signal generation due to light absorption by the cell walls and windows. Other factors that may need consideration are: the acoustic response (resonances) of the cell; the type of material to be studied (solid, liquid or gas); the temperature range required and the modulation frequency range. The cell and the detection scheme can be designed to reduce the coherent noise sources. PA noise signals resulting from absorption in cell windows can be reduced by the use of acoustic baffles placed close to the cell windows. PA noise caused by optical absorption at the cell walls can be reduced by highly polishing them.

N4. Photoacoustic cell design:

Design and fabrication of PACs having high signal to noise ratio becomes very important in experiments. Many designs of PACs have been described in literature aiming at signal amplitude enhancement, noise reduction and ease of use.
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For the study of solid samples, a simple and sensitive open PAC (OPC), indigenously designed, was used. In conventional OPC the sample is placed directly on top of the microphone, by leaving a small volume of gas in between the two.\textsuperscript{328-330} Such OPCs can be employed only in the heat transmission configuration. However, the design of the OPC fabricated for the present studies allows one to illuminate the sample from both sides, i.e. it can be used either as an OPC or as a conventional PAC. In order to achieve this goal the microphone is kept in a side chamber and is acoustically coupled to the main chamber through a small cylindrical cavity. The cross-sectional view of the cell is shown in Figure 1.14. When the sample is irradiated through the glass window, it is known as the reflection configuration. In the transmission configuration, irradiation has to be made at the rear surface of the sample.\textsuperscript{331}

The major building block of the cell is an acrylic (perspex) disc of thickness 1 cm and diameter 5.5 cm. The acoustic chamber was made by drilling a bore of diameter 3 mm across the thickness at the centre of the disc. One end of this cylindrical hole was closed with an optical quality glass slide of thickness 1.4 mm and the other end was left open. Another fine bore of diameter 1.5 mm pierced at the middle of the main chamber and perpendicular to it served as the acoustic coupler between the main chamber and the microphone. At a distance of 8 mm from the main chamber the microphone was firmly glued to the orifice of the side tube. Shielded wires were used to take the electrical connections directly from the microphone. Plate-like solid samples having uniform surface quality can be easily stuck at the open end of the sample chamber by using vacuum grease.

![Figure 1.14: Cross sectional view of the open photoacoustic cell (OPC).](image)

1. microphone
2. glass window
3. perspex body
4. sample
5. gas chamber
6. incident laser beam
7. electrical leads
1.3.3. Part C: Measuring instruments:

O1. Spectrophotometer:
JASCO V-570 UV/VIS/NIR Spectrophotometer was used for the absorption and reflectance measurements of the samples.

O1.1. Specifications:
Optical system: single monochromator. UV/ VIS region 1200 lines/ mm plane grating. NIR region: 300 lines/ nm plane grating. Czenry –Turner mount double beam type
Resolution: 0.1 nm (UV/ VIS region) 0.5 nm (NIR region).
Light source: 30 W deuterium discharge tube in 190 to 350 nm region.
20 W tungsten iodine lamp in 330 to 2500 nm region.
Wavelength range 190 to 2500 nm. \[332\]

The beam from the light source is converged and enters the monochromator. It is dispersed by the grating in the monochromator and the light passes out through the exit slit. This light is split into two light paths by a sector mirror, one incident on the sample to be measured and the other on the reference sample such as solvent. The light that has passed through the sample or reference sample is incident on the photomultiplier tube and PbS photoconductive cell which are the detectors. \[332\]

O1.2. Reflectance measurement:
The Model SLM-468 single reflection attachment is designed to measure the relative reflectance of sample using the forward reflected light from the aluminium-deposited plane mirror as reference. It permits the measurement of the reflectance of metal-deposited film, metal plating etc. The wavelength range is 220 to 2200 nm with a beam port diameter of 7 mm and angle of incidence approximately 5°. \[333\]

O2. Fluorescence spectrophotometer:
The fluorescence excitation and emission spectrum of the samples were taken using Cary Eclipse Fluorescence spectrophotometer of VARIAN. It has a single cell holder for liquid sample analysis and a solid sample holder accessory to perform fluorescence measurements on solid samples. The solid sample holder accessory provides both rotational and translational adjustment of the sample. The angle of incidence of the excitation may be varied from 20°- 35°. This is the angle between the exciting light and a line perpendicular to the surface of the sample mounting slide. The source of excitation is xenon lamp. \[334\]
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O3. Monochromator:
ORIEL compact 77250 1/8 meter monochromator with model 77298 grating was used for the wavelength selection for PAS studies. The monochromator has a high throughput or effective aperture f/3.7. The 30 × 30 mm replicated ruled type grating has a blaze wavelength of 500 nm. The grating has a groove spacing of 1200 lines/mm and reciprocal dispersion of 6.4 nm/ mm. The primary wavelength region is 330-750 nm and the usable range is 300-1000 nm.\(^\text{[335]}\)

O4. Monochromator CCD assembly:
Princeton Instruments NTE/CCD air cooled detectors have three distinct sections. The front vacuum enclosure contains the CCD array seated on a cold finger. This finger is in turn seated on a four-stage Peltier thermoelectric cooler. The back enclosure contains the heat exchanger. An internal fan cools the heat exchanger and the heat exits the unit through openings in the housing. The CCD array used is Roper Scientific NTE/CCD-1340/100-EM.

The electronics enclosure contains the preamplifier and array driver board. This keeps all signal leads to the preamplifier as short as possible, and also provides RF shielding.\(^\text{[336]}\) SPEC-10 controller of Princeton Instruments controls the CCD.

SpectraPro-500i is a 500 mm focal length monochromator/spectrograph. It features an astigmatism-corrected optical system, triple indexable gratings and triple grating turret. The SpectraPro-500i includes a direct digital grating scan mechanism with full wavelength scanning capabilities, plus built-in RS232 and IEEE488 computer interfaces. The 1200 grooves/mm grating has an aperture ratio f/6.5. The scan range is 0 to 1400 nm (mechanical range) and an operating range of 185 nm to the far IR and a resolution of 0.05 nm at 435.8 nm.\(^\text{[337]}\)

WinSpec, the spectroscopic software, of Princeton Instruments is used for collecting, storing and processing data from the Roper Scientific system.\(^\text{[338]}\)

O5. Chopper:
The light beam modulation was carried out using mechanical choppers. HMS/ITHACO model 230 light beam chopper with a set of three interchangeable blades of slots 2, 10 or 30 provides three frequency ranges. The frequency ranges from 4 to 200 Hz, 20 to 1 kHz and 60 to 3 kHz for 2, 10 and 30 slotted blades.
respectively.\textsuperscript{[339]} Model SR 540 optical chopper of Stanford Research Systems has options of 6 and 30 slot blades with 4 to 400 Hz and 400 to 3.7 kHz respectively.\textsuperscript{[340]}

\textbf{O6. Lock-in amplifier:}
Model SR830 DSP Lock-In Amplifier of Stanford Research Systems\textsuperscript{[341]} has IEEE-488 and RS 232 interfaces. The lock in amplifier is interfaced to computer using LabVIEW\textsuperscript{TM} 7 Express of National Instruments.\textsuperscript{[342]}

\textbf{O7. Preamplifier:}
Model SR 560 low-noise preamplifier (Stanford Research Systems) provides DC-coupled low noise amplification of single-ended and true differential input signals at gains of 1 to 50,000.\textsuperscript{[343]}

\textbf{O8. Micrometer:}
Mitutoyo digital outside micrometer, series 193 with a resolution ±0.001 mm was used for measuring the thickness of the samples.

\section*{1.4. Scope of the thesis:}
The present thesis deals with the non-destructive characterization of three different types of materials which can be utilised for photonic applications. The simple and cost effective techniques like PA, PTD and absorption and fluorescence spectroscopy are mainly used for the optical and thermal characterization of these materials. Montmorillonites are efficient absorbers of dyes in waste-water. After the dye adsorption, this clay mineral itself is a waste material. Hence, further characterization is necessary for the efficient usage of the dye intercalated clay minerals. RE doped materials have significant roles in the photonics industry due to their atomic line shaped spectra which are almost host independent. Novel advanced ceramic materials can be manufactured by the SHS method. RETs prepared by SHS methods are not much studied using non-destructive photonic techniques. In the present investigations, optical and thermal characterizations of these samples have been carried out. Sol gel process helps one to make low temperature glasses doped with materials of industrial importance in the photonics field. RE doped sol gel silica glasses are also characterised using PA and spectroscopic techniques for further applications in the field of photonics.
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