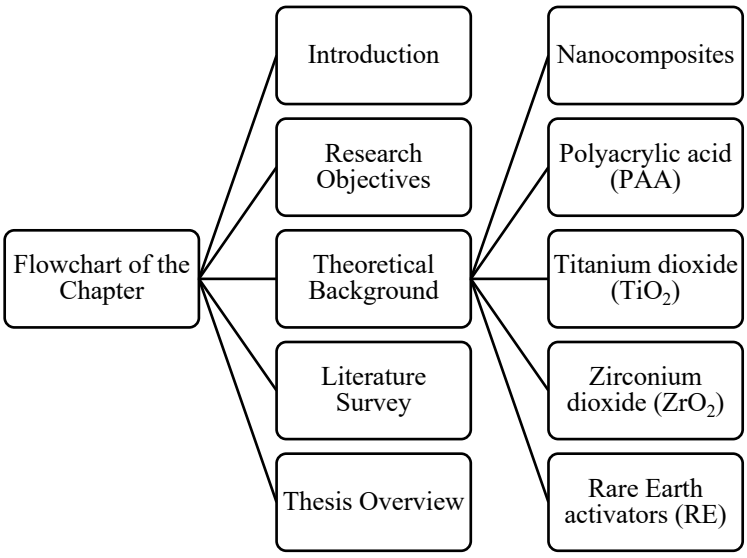
Chapter 1

Introduction

The proposed thesis is initiated with understanding the subject entitled "S*tudy of Optical Properties of Transition/RE Oxide- Polymer Nanocomposites*". In this title, the term "nanocomposites" becomes the focal point of the presented subject. Therefore, the description is initiated with understanding the term. In general, nanocomposite is a mixture of different component materials, in which at least one being of nanometre scale. It may possible that such materials may display combined features of all components or quite new properties resulting from mutual interactions between components.

Organic-inorganic polymer composites have recently found wide technological applications. During past few years, a special interest is focused on nanocomposites based on polymer networks involving nanoparticles being characterized by different electric, magnetic or optical features. Different kinds of materials, among which are sulphides, organic compounds and oxides nanocrystals, have been proposed as nano-fillers in these composites.

In particular, nanoparticles embedded in a transparent matrix have attracted attention as advanced technological materials because of their high transparency, high refractive index and attractive optoelectronic properties. Many applications are using high refractive index polymers ranging from anti-reflection coatings for solar cells to high RI lenses. We synthesis novel and less investigated rare earth (RE) doped transition metal oxide-polyacrylicacid (PAA) nanocomposites. This chapter includes objective of the work, theoretical background, literature survey and the outline of the thesis. The flowchart of the chapter is given below.



Flowchart of Chapter

1.1 Introduction:

Polymer nanocomposites are materials in which nanoscopic inorganic particles are dispersed in an organic polymer matrix in order to improve the performance properties of the polymer. Polymer nanocomposites represent a new alternative to conventionally filled polymers. Because of their nanometer scale, filler dispersion nanocomposites exhibit noticeably improved properties when compared to the pure polymers or their traditional composites. There is increasing research interest in polymeric nanocomposites owing to improvements in electrical, thermal, optical, and mechanical properties and their great potential for highly functional materials [1]. Synthesis and optical properties of polyacrylicacid capped lanthanide-doped BaFCl nanocrystals were studied [2].

1.2 Research Objectives:

The research objectives of the study are:

- To synthesize novel and relatively less investigated rare earth doped transition metal oxide- polyacrylicacid nanocomposites.
- To authenticate the preparation of material using standard characterization techniques.
- To study the optical properties such as fluorescence emission, absorption, optical bandgap, variation of absorption co-efficient, variation of extinction co-efficient, refractive index and variation of refractive index of the composites.
- To explore the material from application point of view.

1.3 Theoretical Background:

The general properties of materials used for the study like nanocomposites, Poly Acrylic Acid (PAA), Titanium dioxide (TiO_2), Zirconium dioxide (ZrO_2), Rare Earth activators (RE) have been discussed with their uses in this theoretical background.

1.3.1 Nanocomposites

In a broad sense the word “composite” means “made of two or more different parts” Or “A composite is a combination of two or more different materials that are mixed in an effort to blend the best properties of both [3].” A composite material consists of an

assemblage of two materials of different natures completing and allowing us to obtain a material of which the set of performance characteristics is greater than that of the components taken separately. Composite materials take advantage of the different strengths and abilities of different materials. They offer unusual combinations of properties of component materials such as weight, strength, stiffness, permeability, biodegradability, electrical, and optical properties that is difficult to attain separately by individual components. A composite material can be custom tailored to have specific properties that will meet special requirements.

A nanocomposite is a composite material, in which one of the components has at least one dimension that is nanoscopic in size that is around 10^{-9} m. An important microstructural feature of nanocomposites is their large ratio of interphase surface area to volume [4].

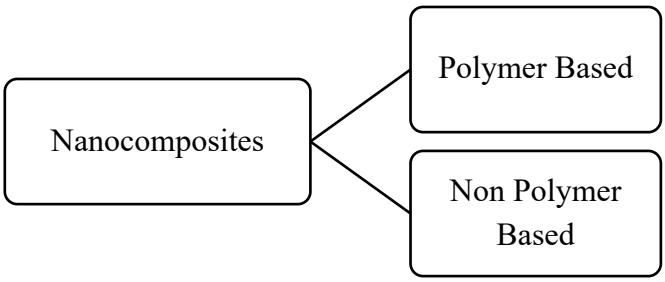
On the bases of their engineering and applied science applications, nanocomposites can be classified:

(1) Functional i.e. based on electrical, magnetic, and/or optical behaviour
(2) Structural i.e. based on their mechanical properties.

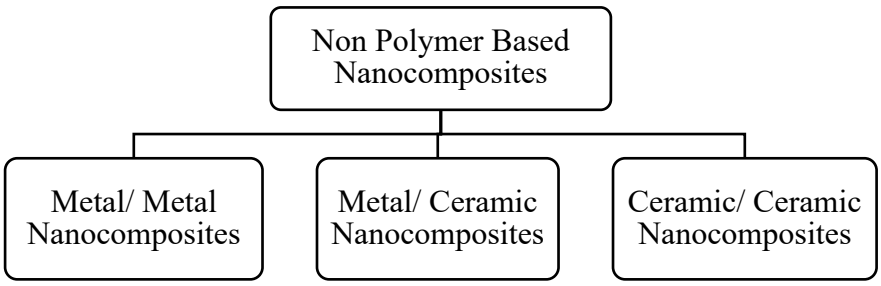
Depending on the type of filler, i.e., the nanoscale material of the nanocomposites, for sensing applications they are divided into:

(1) Metal oxide-based nanocomposites
(2) Polymer-based nanocomposites
(3) Carbon-based nanocomposites
(4) Noble-metal-based nanocomposites

Nanocomposites can further be classified as:



Non-Polymer Based Nanocomposites:



I. Metal/ Metal Nanocomposites:

Bimetallic nanoparticles are as combination or canter shell structures or being examined in some perceptiveness due to their improved catalytic properties and changes in the electronic/optical properties identified with individual, separate metals. They are assumed, the mix of two sorts of metals and their fine structures resulted into their fascinating Physico-chemical attributes.

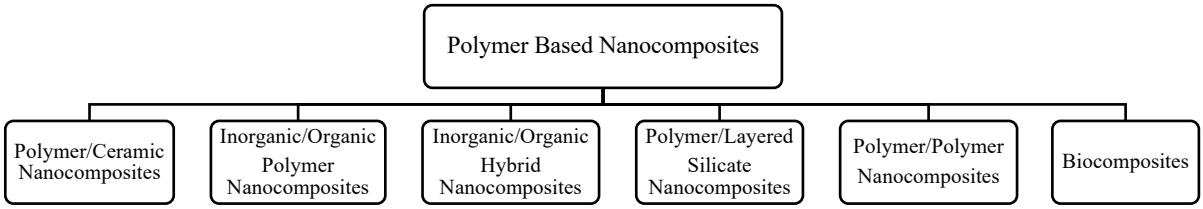
II. Metal/ Ceramic Nanocomposites:

In these kinds of composites, the electric, magnetic, synthetic, optical and mechanical properties of the two stages are consolidated. Size decrease of the parts to the nanoscale causes improvement of the previously mentioned properties and prompts new application. The polymer precursor methods offer an attractive rough to such composites demonstrating a synthetically inactive and hard ceramic matrix.

III. Ceramic/ Ceramic Nanocomposites:

Ceramic Nano composites could solve the issue of fracture failures in artificial joint implants; these would expand patient's portability and take out the significant expense of surgery. The utilization of Zirconia-toughened alumina nanocomposite to shape Ceramic/ceramic inserts with potential life spends of over 30 years.

Polymer Based Nanocomposites:



Polymer nanocomposites are composites with a polymer matrix and filler with at least one dimension less than 100 nm.

I. Polymer/ Ceramic Nanocomposites:

Nanocomposites comprise of single ceramic layers (1nm thick) homogeneously scattered in a persistent matrix. Natural Bone is a nanocomposite-bone comprising of around 30% framework (collagen) material and 70% nanosized minerals (hydroxyapatite).

II. Inorganic/ Organic Polymer Nanocomposites:

Metal polymer nanocomposites stand out due to remarkable properties of metal clusters, which are scattered in polymer matrix. The normal size of such metal cluster is roughly 1-10 nm. The properties of clusters and nanoparticles are totally different from those of mass materials and individual particles or atoms.

The size and grains depend upon versatility of the metal molecules on the polymer surface. For instance, because of Poly (methyl methacrylate) (PMMA) polymer the cluster size relies upon the measure of the cross connecting of the polymer, which clearly changes the portability of the metal molecules.

III. Inorganic/ Organic Hybrid Nanocomposites:

Hybrid inorganic/organic materials are not just physical combinations; they can be broadly characterized as nanocomposites with natural and inorganic parts closely mixed. Indeed, crossovers are either homogenous framework resulting from monomers and miscible organic/inorganic components, or heterogynous frameworks (nanocomposites) where at least one of the segments has the scale of nanometre.

IV. Polymer/ Layered Silicate Nanocomposites:

Polymer/Layered silicate (PLS) nanocomposites materials are drawing in remarkable interest in polymer science research. As of late the PLS nanocomposites have pulled in extraordinary interest both in industry and academics, since they frequently show remarkable improvements in materials when contrast and virgin polymer and conventional macro and macro composites. Hectorite and montmorillonite are among the most generally utilized smectite-type-layered silicates for the readiness of the nanocomposites.

V. Polymer/ Polymer Nanocomposites:

Polymers are like never before constrained to be chip and offered property profiles. The gap between block co-polymer self-assembly and offer nanostructured plastic blessed with still unexplored combinations of properties is getting smaller. Combinations of various polymers frequently stage isolated, in any event, when their monomer blended homogenously.

VI. Bio composites:

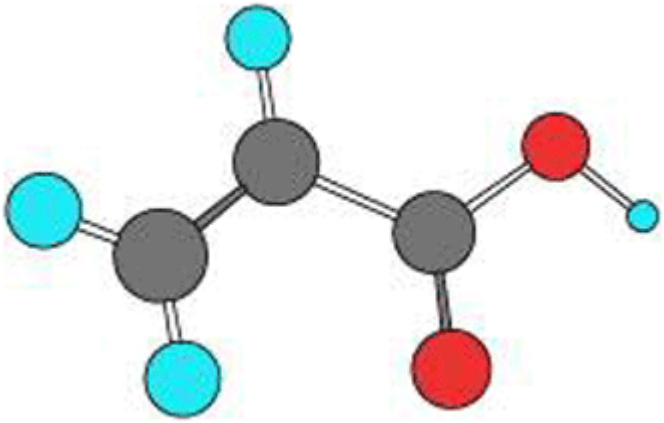
Metals and metal alloys are being used in medical fields like orthopaedics, dentistry and other load bearing applications. Ceramics are being used with emphasis on either their chemically inert nature or high bioactivity; all polymers are being used for soft tissue replacements and also used for many other non-structural applications.

Naturally occurring composites are within us all. Collagen is highly rich and varies with more than 14 types discovered. All variations are formed from tropo-collagen molecules, which are inelastic [5].

Applications of Polymer Nanocomposites (PNCs):

Owing to their unusual combination of properties, Polymer nanocomposites have wide range of applications in various fields. The key areas of application include electronic devices, absorbers, electromagnetic shielding, drug delivery systems, lubricants, UV protection gels, fire retardant materials, anti-corrosion barrier coatings and paints.

1.3.2 Polyacrylic acid (PAA)



Structure of Polyacrylic acid (Grey – C, Blue – H, Red – O) [6]

Polyacrylic acid (PAA; trade name Carbomer) is a synthetic high-atomic weight polymer of acrylic acid. The IUPAC name is poly(1-carboxyethylene). They may be homopolymers of acrylic corrosive, or crosslinked with an allyl ether of pentaerythritol, allyl ether of sucrose or allyl ether of propylene. PAA is an anionic polymer in a water solution at neutral pH, i.e. the large number of the side chains of PAA will lose their protons and contains a negative charge. This makes PAAs polyelectrolytes, with the ability to retain and absorb water and swell to usually their original volume.

Polyacrylic acid is a weak anionic polyelectrolyte, whose degree of ionisation is dependent on solution pH. In its non-ionised form at low pHs, PAA may associate with various non-ionic polymers (such as polyethylene oxide, poly-N-vinyl pyrrolidone, polyacrylamide, and some cellulose ethers) and form hydrogen- bonded interpolymer complexes. PAA can also form polycomplexes with oppositely charged polymers (for example, chitosan), surfactants, and drug molecules (for example, streptomycin) in aqueous solutions.

Applications of PAA:

Acrylic acid faces the classic reactions of a carboxylic acid. It creates the corresponding ester when reacted with an alcohol. The esters and salts of acrylic acid are collaboratively called acrylates (or propenoates). Methyl, butyl, ethyl and 2-ethylhexyl acrylate are the most common alkyl esters of acrylic acid. Acrylic acid and its esters promptly consolidate with themselves (to form polyacrylic acid) or other monomers (e.g. acrylamides, acrylonitrile, vinyl compounds, styrene, and butadiene) by reacting at their double bond,

forming homopolymers or copolymers, which are utilized in the production of different plastics, coatings, glues, layers, bundling materials, elastomers, just as floor shines, metal clean, glass substitution and paints [7]. Acrylic acid is a compound, which is utilized in numerous ventures like the diaper business, the water treatment industry or the materials business.

1.3.3 Titanium dioxide (TiO_2)

Titanium dioxide (TiO_2) also known as **Titania** is a wide band gap semiconducting material. TiO_2 is chemically inert, cheap and easy to synthesize. It is a naturally occurring mineral. TiO_2 exists in three diverse crystal structures specifically Anatase, Rutile and Brookite. Among these, the Anatase and Rutile phase has major applications as they can be synthesized easily [8]. As of late, it has been accounted for that Brookite likewise shows better photograph catalytic properties [9].

Anatase TiO_2 has bandgap of 3.2 eV, Rutile 3.0 eV, whereas Brookite TiO_2 has bandgap between 3.0 eV and 3.2 eV [10] mentioned in **Table 1.1**. The Rutile stage is thermodynamically steady while Anatase and Brookite are metastable stages and can be effectively changed into Rutile on heating [11]. Anatase transforms to equilibrium phase at temperatures between 550° and 1000 °C. The transformation temperature depends on the impurities or dopants as well as on the morphology of the material. Rutile TiO_2 is widely used in white pigments because of its high refractive index. Rutile TiO_2 is optically positive whereas Anatase TiO_2 is optically negative. The different physical parameters are listed in **Table 1.1**.

Table 1.1: Physical properties of the TiO_2 phase

Phase	Refractive Index	Bandgap (eV)	Density(gm/cm3)
Anatase	2.48	3.20	3.78
Rutile	2.60	3.00	4.23
Brookite	2.58	3.00 to 3.20	4.08

Crystal structure of TiO_2:

Among the three phases of TiO_2, Rutile and Anatase have tetragonal crystal structure. These crystals are created by chains of distorted TiO_6 octahedra. The unit cell of most stable Rutile phase contains two TiO_2 units. The coordination number for the titanium cations is 6. They are surrounded by an octahedron of 6 oxygen atoms via two apical and four equatorial bonds of length 1.976 A° and 1.946 A° respectively [12]. The oxygen anions have a co-ordination number of 3 resulting in three coplanar titanium cations via one apical and two equatorial bonds. The unit cell of metastable Anatase phase contains four TiO_2 units whereas unit cell of Brookite contains eight TiO_2 units. The Ti – Ti distance in Rutile is shorter than in Anatase. These primary structural changes lead to the change in mass density. Anatase phase is 9% lesser dense than Rutile. Two surfaces (101) and (001) of Anatase crystal are exposed. The (101) surface is most stable and constitutes 94% of the crystal surface.

Three different surfaces (110), (101) and (001) of Rutile crystal are exposed. The most stable (110) surface forms 56% of the total crystal surface [12]. The unit cells of different structure of TiO_2 are shown in **Figure 1.1**.

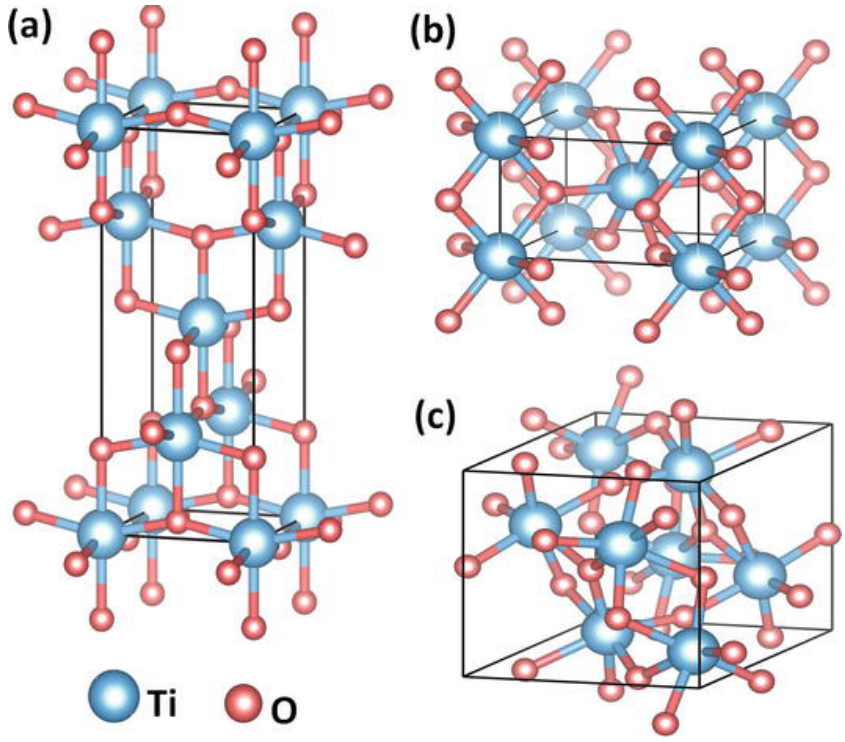


Figure 1.1: Unit cell of different TiO_2 structures (a) Anatase, (b) Rutile and (c) Brookite [13]

Applications of TiO_2:

Titanium dioxide (TiO_2) is a widely utilized material for optical and defensive applications due to its high straightforwardness in the noticeable area, incredible mechanical durability and chemical stability in the aqueous solution [14, 15]. TiO_2 films are important for such applications as catalysis, optical coatings, gas sensors, and other electronic gadgets.

The physical and chemical properties of TiO_2 are with the end goal that it gets appropriate for a wide range of utilizations. It comprises two most important optical properties i.e. the extinction coefficient and the refractive index are generally called optical constants. The measure of light that transmits through thin film material count on the amount of the reflection and the absorption that take place along the light path. It has been used mostly as a pigment in paints, sunscreens, ointments, toothpaste etc. For instance, TiO_2 has high corrosion resistance and chemical stability and an excellent optical transparency in the visible and near infrared regions which makes it applicable in metal polish, replacement of glass and packaging. It also has high refractive index that makes it suitable for antireflection coatings in optical devices like solar cells and others [16-28].

1.3.4 Zirconium dioxide (ZrO_2)

Zirconium dioxide (ZrO_2) is also known as **Zirconia**. ZrO_2 has a great potential for technological applications because of its electrical and mechanical properties [29]. ZrO_2 is one of the most studied ceramic materials. It has excellent properties such as high melting point, high refractive index, good thermal and chemical stability, high fracture toughness, high density, high hardness and good resistance against oxidation [30].

ZrO_2 exists in three different polymorphs namely Monoclinic, Tetragonal and Cubic. At room temperature it remains in Monoclinic phase. As temperature increases, it transforms into Tetragonal and then Cubic phase. The Tetragonal phase is stable at 1170°C and Cubic phase at 2370°C. The volume of crystal expands as cubic phase transforms to tetragonal and afterward to monoclinic phase. The cubic phase of ZrO_2 can be stabilized at room temperature by doping with different oxides like MgO, CaO, and Y_2O_3 [31-33]. ZrO_2 is an insulating material with a bandgap of 3.6 to 6 eV. However, it behaves as a semiconductor when prepared by sol gel method or doped with transition metal [34].

It has been reported that ZrO_2 exhibits low phonon energy, increasing the number and probability of radiative transitions in the Rare Earth (RE)-doped samples. This fact has

increased the interest in developing rare earth doped of zirconium oxide, which is suitable for making optical waveguides. Doping rare earth elements into zirconia results in structural modification, which influences the electronic structure of the lattice, thereby emerging a change in the optical properties. Hence, it is of interest to follow the spectroscopic consequences accompanying the structural modifications.

Crystal Structure of ZrO_2:

ZrO_2 has three different crystal structures Monoclinic, Tetragonal and Cubic. Monoclinic and Cubic are stable phases whereas Tetragonal is a metastable phase ZrO_2. **Figure 1.2** shows different phases of ZrO_2.

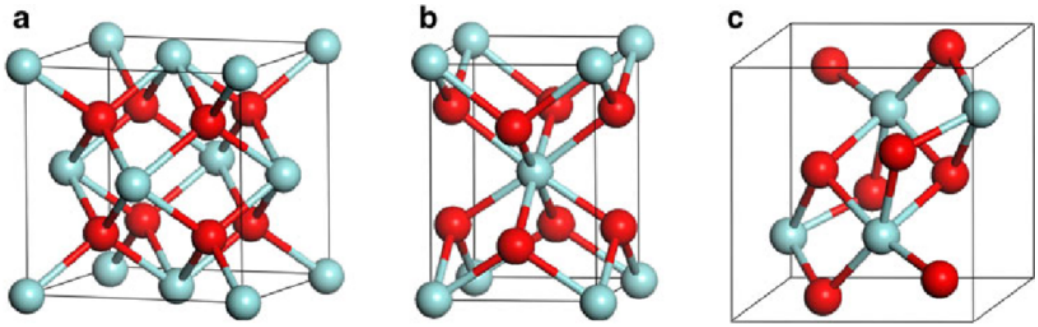


Figure 1.2: (a) Cubic ZrO_2, (b) Tetragonal ZrO_2, (c) Monoclinic ZrO_2 [35]

Monoclinic phase is a natural form of Zirconia. It is also known as baddelyite. Zr^{+4} ions of monoclinic ZrO_2 have coordination number of seven for the oxygen. The average distance between the Zirconium ion and three of the seven Oxygen ions is 2.07 A° while between Zirconium ion and other four Oxygen ions is 2.21 A°. In Tetragonal phase, Zr^{+4} ions have coordination number of eight. The distance between the Zirconium ion and four Oxygen ions is 2.065 A° and that between Zirconium and other four oxygen ions is 2.455 A°. The Cubic structure of ZrO_2 is also known as fluorite. It can be represented by a cubic lattice with eight oxygen ions which are surrounded by a cubic arrangement of cations [36]. The single crystal of Cubic ZrO_2 has low fracture toughness and strength but very high thermal shock resistance. The atomic density of Monoclinic phase is 96% of that of Cubic phase and 97% that of Tetragonal phase. The transformation from Monoclinic to Tetragonal and then to Cubic phase is results into toughening of the material [37]. Tetragonal to Monoclinic transformation can also be triggered by applying stress. Hence strain will be produced in structure. The reverse transformation also leads to toughening

and depends on volume expansion as well as shear strain when tetragonal phase transforms to monoclinic phase.

Applications of ZrO_2:

Zirconia has exceptional thermal, electrical, optical and mechanical characteristics. Because of these characteristics, it is used in refractory materials, insulations, catalyst, anti-corrosion coating, oxygen sensors, fuel cells, membranes, high temperature induction furnace susceptors and for clinical purpose [38,39].

Nano-size Zirconia has attracted much attention due to its specific optical and electrical properties as well as other potential applications in transparent optical devices, electro-chemical capacitor electrodes, catalysts and advanced ceramics. Applied in various fields like light emitting displays, ceramic, glass replacement, paint, optical fibers, clothing, packaging, etc.

ZrO2 is an innovatively significant material because of its superior hardness, high refractive index, chemical stability, optical transparency, photothermal stability, low thermal conductivity, high thermomechanical resistance, high thermal expansion coefficient and high corrosion resistance [40-42]. These unique properties of ZrO2 have led to their widespread applications in the fields of optical [43], structural materials, solid-state electrolytes, gas-sensing, thermal barriers coatings [44], corrosion-resistant, catalytic [45].

1.3.5 Rare Earth (RE)

The Rare Earth activators (RE) are the 15 lanthanide elements (Z = 57–71) including scandium (Z = 21) and yttrium (Z = 39). Also known as Rare Earth Elements (REEs). The lanthanides are divided into two parts. Light REs, from lanthanum to europium (Z = 57–63), and Heavy REs (HREs), from gadolinium to lutetium (Z = 64–71). The HREs, such as dysprosium, terbium, and europium, have the highest demand of all the Rare Earths in the world market.

Since 2000, global demand for REs has in- creased at an annual rate of 8–12%. By 2015, global demand for REs is predicted to reach 210,000 metric tons, which is 60% higher than 2008 levels. As demand increases, concerns about access to supplies of REs will grow. As of 2012, China has control of nearly all of the world's REs. Thus, manufacturers around the world are considering alternative means of ensuring access to REs, including

identifying potential RE substitutes, improving recycling methods, and increasing the efficiency of use of REs [46].

Rare-earth materials are used in lighting and optical applications such as light-emitting diodes (LEDs), lasers, and electronic video displays to enable color and light adjustment, miniaturization of microelectronics parts, and compliance with environmental and energy-efficiency standards. The advantageous characteristics of REs include their unique electron configuration, optical properties of fluorescence and high refractive index, high conductivity, ability to store and release oxygen catalytically, high magnetic anisotropy, large magnetic moment and efficient hydrogen storage. Some other applications of rare earth mentioned in **Table 1.2**.

Table 1.2: Rare Earth materials and Their Uses [47]

Cerium (Ce)	Catalysts, polishing, metal alloys, lens polishes (for glass, television faceplates, mirrors, optical glass, silicon microprocessors, and disk drives), yellow color in glass and ceramics.
Dysprosium (Dy)	High-power magnets, lasers, hard disk drives. Used by DOE in guidance and control systems and electric motors.
Erbium (Er)	Infrared Lasers, glass colorant, vanadium steel, fiber-optic technology.
Europium (Eu)	Liquid crystal displays (LCDs), fluorescent lighting, glass additives. Red and blue phosphors, lasers, mercury-vapor lamps, fluorescent lamps, NMR relaxation agent. Used by DOE in targeting and weapon systems and communication devices.
Praseodymium (Pr)	Improved magnet, corrosion resistance, pigment, searchlights, airport signal lenses, photographic filters, core material for carbon arc lighting, colorant in glasses and enamels.
Terbium (Tb)	Phosphors for lighting and display, lasers, fluorescent lamps, magnetostrictive alloys such as terfenol-D, naval sonar systems, stabilizer of fuel cells.
Thulium (Tm)	High-power magnets, Portable X-ray machines, metal-halide lamps, lasers.

1.4 Literature Survey:

Table 1.3: Literature survey of materials

Sr. No.	Article Title	Author	Material	Year
1	Synthesisand photoluminescence properties of titanium oxide (TiO_2) nanoparticles: Effect of calcination temperature	N.C. Hortia,b, M.D. Kamatagi, N.R. Patil, S.K. Nataraj, M.S. Sannaikar, S.R. Inamdar	TiO_2	2019
2	Investigations on Amphoteric Chitosan/TiO_2 Bionano-composites for Application in Visible Light Induced Photocatalytic Degradation	M. Bahal, N. Kaur, Nidhi Sharotri, and Dhiraj Sud	Chitosan/ TiO_2 Bionano-composites	2019
3	Synthesis and optical properties of pure monoclinic zirconia nanosheets by a new precursor	Fatemeh Davar, Mohammad Reza Loghman-Estarki	zirconia	2014
4	Effect of calcination temperature on structural, vibrational, optical, and rheological properties of zirconia nanoparticles	Elaheh K. Goharshadi, Mahboobeh Hadadian	zirconia	2012
5	Infrared spectroscopy and luminescence spectra of Yb^{3+} doped ZrO_2 nanophosphor	Raunak Kumar Tamrakar, Neha Tiwari, Vikas Dubey, Kanchan Upadhyay	Yb^{3+} doped ZrO_2	2015

6	Preparation and characterization of $ZrO_2:Eu^{3+}$ phosphors	Limiao Chen, Younian Liu, Yadong Li	$ZrO_2:Eu^{3+}$	2004
7	Nanosized-hybrid colloids of poly(acrylicacid)/titania prepared via in situ sol–gel reaction	Hung-Jen Chen, Pei-Chi Jian, Jui-Hung Chen, Leeyih Wang, Wen-Yen Chiu	polyacrylic acid/ titania	2007
8	Synthesis of TiO_2/PAA nanocomposite by RAFT polymerization	Behnaz Hojjati, Ruohong Sui, Paul A. Charpentier	TiO_2/PAA	2007
9	Preparation of Polyacrylic Acid/TiO_2 Nanocomposites and Its Application in Photodegradation of Methyl Orange	Xiangfu Meng, Zhiwei Zhang, Ying Zhang, Zhichang Xiao and Qingli Wei	Polyacrylic Acid/TiO_2	2011
10	Synthesis and characterization of anticorrosion zirconia/ acrylic nanocomposite resin coatings for steel	Ubong Eduok, Jerzy Szpunar, Eno Ebenso	zirconia/ acrylicacid	2019
11	Synthesis, characterization and luminescence properties of Tb^{3+} and Eu^{3+}-doped poly(acrylic acid)	A. Rosendo, M. Flores, G. Cordoba, R. Rodrıguez, R. Arroyo	Tb^{3+} and Eu^{3+}-doped polyacrylic acid	2003

Literature 1: "Synthesis and photoluminescence properties of titanium oxide (TiO_2) nanoparticles: Effect of calcination temperature" by N.C. Hortia,b, M.D. Kamatagi, N.R. Patil, S.K. Nataraj, M.S. Sannaikar, S.R. Inamdar.

This paper demonstrates the synthesis of titanium oxide (TiO_2) nanoparticles with co-precipitation method by titanium oxysulphate and sodium hydroxide as precursors. The calcination of nanoparticles was performed at three different temperatures (i.e. 300 °C, 400 °C, 500 °C and 600 °C) and its effect on morphological, structural and optical

properties were investigated. At room temperature, pure anatase phase of TiO_2 was obtained, while elevated calcination temperature produced anatase–rutile phase. UV-vis spectroscopy characterizations revealed the robust quantization up to 10 nm, and the absorption peak position, as well as optical band gap, found to be dependent on the calcination temperature[48].

Literature 2: "Investigations on Amphoteric Chitosan/TiO_2 Bionanocomposites for Application in Visible Light Induced Photocatalytic Degradation" by M. Bahal, N. Kaur, Nidhi Sharotri, and Dhiraj Sud.

The green synthesis done by ultrasonic radiations was exploited to acknowledge novel acrylic acid joined amphoteric chitosan/TiO2 (CAT) bio nanocomposites. The acrylic acid was joined onto chitosan within the sight of potassium persulfate by methods for the free radical polymerization reaction. The degradation of industrial dye-malachite green was researched by the photocatalytic action of CAT prompted by white light. The rate constant of the degradation reaction was discovered to be 7.13 X 10^{-3} min^{-1} from the kinetics of the degradation of the malachite green [49].

Literature 3: "Synthesis and optical properties of pure monoclinic zirconia nanosheets by a new precursor" by Fatemeh Davar, Mohammad Reza Loghman-Estarki.

In this paper, the polymeric complex cycle has been utilized to synthesis pure monoclinic zirconia nanosheets. Zirconium acetylacetonate, citrus extract and ethylene glycol were the antecedents for Zr4+, chelating and polymerization agents respectively. The proportion of ethylene glycol (EG): citrus extract (CA): transition metal (TM) has been influenced the morphology, structure and size of zirconia nanoparticles. The SEM results proposed that an expansion in a mole proportion of EG:CA:TM from 5:5:1 to 90:5:1, the glasslike stage and morphology of zirconia nanoparticles were changed from semispherical nanoparticles (cubic stage) to nanosheets (monoclinic stage). The EG:CA:TM mole proportion of 5:5:1 brought about the enormous imperfections in the zirconia nanoparticles, while that of 90:5:1 came about into more noteworthy crystallinity without any deformities [50].

Literature 4: "Effect of calcination temperature on structural, vibrational, optical, and rheological properties of zirconia nanoparticles" by Elaheh K. Goharshadi, Mahboobeh Hadadian.

In the microwave-assisted synthesis of zirconia nanoparticles were reported by Elaheh et al. Subsequently, the nanoparticles were calcinated in the temperature range from 100 °C to 600 °C. When calcinated exceeds 400 °C, the monoclinic phase was obtained for the zirconia nanoparticles. Despite having the Newtonian fluid behaviour of ethylene glycol (EG), the nanofluid of zirconia–EG shows non-Newtonian fluid behaviour. Additionally, the viscosity of the zirconia–EG nanofluid was influenced by the particle volume fraction and temperature [51].

Literature 5: "Infrared spectroscopy and luminescence spectra of Yb^{3+} doped ZrO_2 nanophosphor" by Raunak Kumar Tamrakar, Neha Tiwari, Vikas Dubey, Kanchan Upadhyay.

Synthesis of Yb^{3+} doped ZrO_2 was carried out by the combustion synthesis method (CSM), and upconversion luminescence was studied for the samples. The emission spectra were found to be in the near-infrared (NIR) region, which was attributed to the transition between $^2F_{7/2}$–$^2F_{5/2}$ states for Yb^{3+} ion. The change in the intensity profile of the emission profile was studied by varying concentration of Yb^{3+} ion. With an increase in the concentrations of Yb^{3+} ion, the emission was also increased [52].

Literature 6: "Preparation and characterization of ZrO_2:Eu^{3+} phosphors" by Limiao Chen, Younian Liu, Yadong Li.

The nanocrystalline ZrO_2:Eu^{3+} powders with various phases were synthesized in basic media through the surfactant-assisted hydrothermal process. The luminescence was found to be affected by both the annealing temperature and the crystalline phase. The luminescence intensity was strongly dependent on the phase and shape of nanoparticles, and the chromaticity was obtained for $Zr_{0.98}Eu_{0.02}O_2$ [53].

Literature 7: "Nanosized-hybrid colloids of poly(acrylic acid)/titania prepared via in situ sol–gel reaction" by Hung-Jen Chen, Pei-Chi Jian, Jui-Hung Chen, Leeyih Wang, Wen-Yen Chiu.

Nanosized-hybrid colloids of poly(acrylic acid)/titania (PAA/TiO_2) was synthesised via in situ sol-gel technique, and titanium isopropoxide (TIP) was used as a precursor in the butanol solution of PAA. Two synthesis routes were employed, by adding titanium precursor before and after the dissolution of PAA, leading to differentiated phase

separation and gelation phenomenon; however, the stable colloidal solution was yielded from both the routes. The chelation was found to be increased with an increase in the ration of PAA to TIP. The SEM observations revealed that the degree of aggregation and the growth of titania was strongly dependent on the conditions of hydrolysis, condensation, chelation of the precursor and the volume of water in the solution [54].

Literature 8: "Synthesis of TiO_2/PAA nanocomposite by RAFT polymerization" by Behnaz Hojjati, Ruohong Sui, Paul A. Charpentier.

In order to surmount the challenges associated with nanoparticles/polymer composite such as agglomeration and to achieve homogeneous dispersion, in this study, the particle-polymer interaction was improved by exploiting living polymerization set at the surface of titania nanoparticles. The living polymerization was achieved by using bifunctional RAFT agent, 2-{[(butylsulfanyl)carbonothioyl]sulfanyl}propanoic acid). The FTIR results suggested successful functionalization of titania nanoparticles by RAFT agent. It was also observed that even after the coordination of RAFT agent with TiO_2 nanoparticles, the polymerization was still living. The "graft-from" polymers were observed around the titania nanoparticles via electron microscopy images. The study suggests an optimized route to achieve monodispersed nanoparticles in a polymer matrix[55].

Literature 9: "Preparation of Polyacrylic Acid/TiO_2 Nanocomposites and Its Application in Photodegradation of Methyl Orange" by Xiangfu Meng, Zhiwei Zhang, Ying Zhang, Zhichang Xiao and Qingli Wei.

In this paper, synthesis of TiO_2 nanoparticles (anatase stage) in the framework of polyacrylic corrosive (PAA) was acknowledged by direct aqueous course. The underlying, optical and morphological examinations uncovered that the titania nanoparticles were in-situ framed inside the matrix of PAA and the PAA/TiO_2 nanocomposite gave upgraded photocatalytic action. The three-dimensional (3D) organization of PAA gave ideal conditions to the organic compound to be in the region of nanoscale photoactive sites [56].

Literature 10: "Synthesis and characterization of anticorrosion zirconia/acrylic nanocomposite resin coatings for steel" by Ubong Eduok, Jerzy Szpunar, Eno Ebenso.

In this paper, the synthesis of zirconia nanoparticles (ZrO_2NPs) by sol-gel method is reported by using the zirconium ethoxide as a precursor. Consequently, zirconia-

modified acrylic nanocomposite resins were realized by integrating the ZrO_2NPs with the acrylic base resin. The prepared inorganic/organic hybrid resin composite was coated on Q235 steel to study the improvement in its corrosion prevention activity in the 3.5% NaCl solution. The corrosion was found to be reduced with the applied coating of the composite. In addition to the protection against corrosion, the particles strengthened the overall mechanical properties of the coatings [57].

Literature 11: "Synthesis, characterization and luminescence properties of Tb^{3+} and Eu^{3+} doped poly(acrylic acid)" by A. Rosendo, M. Flores, G. Cordoba, R. Rodrıguez, R. Arroyo.

The reported strategy promises the facile method in order to realize polymers with enhanced and exciting optical properties. The synthesis of Tb^{3+} and Eu^{3+} doped polyacrylic acid (PAA) was carried out by initiating polymerization in the aqueous solution. During the polymerization, the potassium persulfate was used as an initiator, and the monomer was moderately neutralized with various amounts of Tb_2O_3 and Eu_2O_3. The spectroscopic results suggested that the formation of a robust Ln–O chemical bonds lead to the homogeneous distribution of the dopant ions in the polymeric material. It was observed that Tb^{3+} dopant induced enhanced luminescence for Eu^{3+} by energy transfer from $^5D_4$ level of Tb^{3+} to $^5D_0$ level of Eu^{3+} [58].

1.5 Thesis Overview:

The first chapter of the thesis deals with the introduction of rare earth doped transition metal oxide- polyacrylicacid nanocomposites. The chapter also gives details regarding the applications of synthesized nanocomposite materials and deals with the general properties of materials used for the study like polyacrylicacid (PAA), Titania (TiO_2), Zirconia (ZrO_2), rare earth elements. The thesis background and objectives associated with the subject is explained in **Chapter 1.**

Chapter 2 is on instrumentation. The chapter gives details of the various instrumentation techniques like X-ray Diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDS), Particle Size Analyzer by Dynamic Light Scattering (DLS) technique and Fourier-Transform Infrared Spectroscopy (FTIR). The instruments used

for investigating the optical properties of synthesized nanocomposites like UV-Vis Spectroscopy (UV-Vis) and Photoluminescence Spectroscopy (PL) has been also discussed in the chapter.

Chapter 3 focusses synthesis as well as characterization of TiO_2:RE polyacrylicacid nanocomposites. This chapter gives the process of synthesizing rare earth RE (Ce, Dy, Er, Eu, Pr, Tb, Tm) doped Titania (TiO_2) by hydrothermal technique with 0.1mol% & 0.2mol% doping concentration of rare earth elements. Fourteen such samples were synthesized and incorporated with polyacrylicacid (PAA) with 1mol% & 2mol% respectively to develop thin films of polyacrylicacid- TiO_2:RE nanocomposites and further characterized by various techniques as described in chapter 2.

In **Chapter 4**, synthesis and characterization of Zirconia based nanocomposites were described. It gives the process of synthesizing rare earth RE (Ce, Dy, Er, Eu, Pr, Tb, Tm) doped Zirconia (ZrO_2) by hydrothermal technique with 0.1mol% & 0.2mol% doping concentration of rare earth elements. Fourteen such samples were synthesized and incorporated with polyacrylicacid (PAA) with 1mol% & 2mol% respectively to develop thin films of polyacrylicacid- ZrO_2:RE nanocomposites and characterized by various characterization techniques as mentioned in chapter 2.

Chapter 5 is devoted to investigating the potential applications of the synthesized nanocomposites and discuss the material from application point of view. As mentioned earlier, because of their high transparency, high refractive index, and attractive optical properties, polyacrycacid-rare earth doped transition metal oxide nanocomposites applied in various field like packaging, glass replacement and anti-reflection coatings in solar cells, UV shielding films etc. The results of the optical studies are correlated to the applications.

The work undertaken in the thesis and future perspectives on different hybridization combinations concluded in **Chapter 6**. It also mentions some of the lacunae of the researcher's study, its scope for future prospects.

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