Chapter-2

Literature Review

2.1 Introduction

Literature review is the stepping stone and the first step on the ladder of any new research. The whole world today is a hub of knowledge with a large amount of information produced daily. Literature review helps the researcher to gather all this information related to his research. One can comprehend and understand all that has been done in one’s field in the past and then can analyze the current trends. One can plan one’s research topic based on previous findings and can try to bridge the gaps which may have been left behind in his field of interest. It helps one to compare and contrast what one is doing in the historical context of research and through this winnowing, one can justify the relevance of one’s research in the larger context of what other researchers have already done, highlighting how one’s research is different and original. [1]

2.2 Literature Review

As a part of Literature survey, at the beginning and throughout the research, many books, websites and research papers were referred in order to fully comprehend the details of the subject. Research on phosphors has been in action since long and has a long history. A young French Chemist named Theodore Sidot was first one to prepare the Zn-S type phosphors for TV tube in year 1886. It was the starting of synthesis of phosphors and scientific research. After that by early 20th century scientist named Leonard and coworkers from Germany performed active and extensive research on the phosphors. They made various kinds of phosphors based on Alkaline Earth Chalcogenides, investigated and proved their luminescence properties. Early lamp phosphors were natural fluorescing minerals like Willemite, Mn-activated Zinc orthosilicate, that were crushed to form a powder and experientially blended together so as to get an approximately white field from fluorescent lamp.

By the late 1920s and 1930s, P.W. Pohl and co-workers investigated Ti^{2+} activated Alkali Halide phosphors in details in Germany. A major inflexion point follows the development in 1940s with synthesis of Sb-Mn co-activated Halophosphate phosphors. In the material, blue emission from the Sb^{3+} activator and the orange emission from Mn^{2+} co-activator could be adjusted such that they could yield a white field parallel to wide range of colour temperature. Homboltz and co-workers also inquired into many phosphor elements for applications used in TV tubes. A book named “Introduction to Luminescence in Solids” was written by Leverenz. The Data in that book regarding the emission spectra remains useful even in today's research and development. After World War II, the advancement in the technology of optical spectroscopy of solids, especially transition metal ions helped to evolve research on phosphor and Solid State luminescence. Rare Earth activated phosphors were developed for use in color TV (Tb^{3+}- green, Eu^{3+}- red and Dy^{3+} - yellow) in 1960s and also they were very efficient. In the year 1970, tricolor lamp was invented. In tricolor lamp, blue emission from Eu^{2+}, red emission from Eu^{3+} and green emission from Ce^{3+} - Tb^{3+} pair was used. At present an addition of Halophosphate and Triphosphate mixture is used in many lamps as conciliation between performance cost and the lamp manufacturing cost. Rare Earth oxysulfide materials doped with different compounds are used nowadays for modern day lighting systems.

In comparison to the field of luminescence, the field of study of thermoelectric properties is much young and is around 50 years old. To date, the main thermoelectric conversion materials from the viewpoint of ZT have been intermetallic compounds such as Bismuth Telluride (Bi_2Te_3), Lead Telluride (PbTe), Zinc Antimonide (ZnSb), SiGe, Iron Silicide ($FeSi_2$), etc.

Among these, in particular, Bi_2Te_3 based compounds have a large ZT in the comparatively low temperature region from room temperature to approximately 450 K and are the most widely used thermoelectric conversion materials at present. In the medium temperature region of 700-900 K, $AgSbTe_2$/GeTe and $CeFe_4CoSb_{12}$ are high ZT thermoelectric conversion materials and up in the high temperature region above 900K, the high ZT materials are $Si_{0.2}Ge_{0.8}$, $Bi_2Sr_2Co_2O_y$ and $Ca_3Co_4O_9$. Thermoelectric studies have also been done on Gadolinium-Selenide, Neodymium-Selenide, Lanthanum-Selenide, Neodymium Sulfide (NdS_2), Gadolinium Sulfide (GdS_2), Dysprosium Sulfide (DyS_2) and Gd_2S_3 - Dy_2S_3 systems. Silicon compound systems like SiGe, β-$FeSi_2$, Ba_8Si_{48}, Mg_2Si, $MnSi_{1.73}$ etc., Metal Oxide systems like $NaCo_2O_4$, $CaC0O_3$, $SrTiO_3$, $SrTiO_3$: Nb etc. and Antimony compound systems like ZnSb, Zn_4Sb_3, $CeFe_3CoSb_{12}$, $LaFe_3CoSb_{12}$ etc are still promising thermoelectric conversion materials. Lately the γ-phase of Ln_2S_3 (where Ln = Rare Earth) are being explored for their potential as thermoelectric conversion materials.

Recent advancements have made it possible to obtain thermoelectric conversion materials in the form of nano thin films, nano wire arrays, superlattice compounds, strongly correlated electron systems and plane structures. All the materials used till date have low power generation efficiency and hence, full scale penetration of thermoelectric power generating systems has not yet progressed even though the history of technical development has reached the half-century mark.

The major research papers which were reviewed are as listed below:

Table 2-1: Literature survey of rare-earth materials reports

Sr. No.	Article Title	Author	Material/ Application	Year
1	The Stabilization of γ - Ce_2S_3 at low temperature by heavy Rare Earths	Florent Marrot, Alain Mosset, Jean-Christian Trombe, Pierre Macaudiere and Patrick Maestro	Ce_2S_3 (Cerium Sulfide)	1997
2	Synthesis and Sintering of Cerium(III) Sulfide Powders	Shinji Hirai,Kazuyoshi Shimakage, and Yasushi Saitou	Ce_2S_3 (Cerium Sulfide)	1998
3	Electronic Transport in Semimetallic Ceriurn Sulfide	M. Cutler, J. F. Leavy and R. L. Fitzpatrick	$Ce_{3-x}S_4$ (Cerium Sulfide)	1964
4	Rare Earth Sulfides as High Temperature Thermodynamic Materials	S. W. Kurnick, M. F. Merriam and R. L. Fitzpatrick	Ce_2S_3, Ce_3S_4 (Cerium Sulfide)	1961
5	Structure and optical properties of α- and γ- Cerium Sesquisulfide	René Windiks and Erich Wimmer	Ce2S3 (Cerium Sulfide)	2018
6	Studies on the Stabilization of Gamma phase Cerium Sulfide	R. L. Fitzpatrick, Z. A. Munir	$Ce_{3-x}S_4$, $Ce_{3\text{-}}xM^n{}_yS_4$ (Cerium Sulfide)	1967

7	Preparation, characterization, and photocatalytic performance of Ce2S3 for Nitrobenzene reduction	Shifu Chen, Huaye Zhang, Xianliang Fu, Yingfei Hu	Ce2S3 (Cerium Sulfide)	2013
8	Preparation of γ-Gd_2S_3 via thermolysis of $Gd[S_2CN(C_4H_8)]_3\cdot$ Phen coordination	Luo Xixian, MA Lubin, XING Mingming, Fu Yao, Sun Min, Tao Pang	Gd_2S_3 (Gadolinium Sulphide)	2012
9	On the Europium activated Gadolinium Sulfide nanoparticles	Manvendra Kumar, Parasmani Rajput, P. K. Singh, A. C. Yadav, S. A. Khan, S. N. Jha, Singh, A. C. Pandey	Gd_2S_3 (Gadolinium Sulphide)	2016
10	Thermal and Electrical Properties of Gadolinium Sulfides at High Temperatures	G. G. Gadzhiev, Sh. M. Ismailov, Kh. Kh. Abdullaev, M. M. Khamidov, and Z. M. Omarov	GdS_2 (Gadolinium Sulphide)	2001
11	Green Hydrothermal Synthesis and Optical Properties of γ-Gd2s3 Nanoparticles	Sonika Khajuria, Jigmet Ladol, Sumit Sanotra, Haq Nawaz Sheikh	Gd_2S_3 (Gadolinium Sulphide)	2015
12	Electronic Structures of Lanthanum, Samarium, and Gadolinium Sulfides	Lu Wang, Chris M. Marin, Wai-Ning Mei, and Chin Li Cheung	LnS_2 and Ln_3S_4 (Ln = La, Sm, Gd)	2015
13	Thermophysical Properties of Sulfides of Lanthanum, Praseodymium, Gadolinium, and Dysprosium	G. G. Gadzhiev, Sh. M. Ismailov, M. M. Khamidov, Kh. Kh. Abdullaev and V. V. Sokolov	LnS_2 and Ln_3S_4 (Ln = La, Pr, Gd and Dy)	2000

14	Thermoelectric properties of Lanthanum Sulfide with Sm, Eu, and Yb additives	J. F. Nakahara, T. Takeshita, M. J. Tschetter, B. J. Beaudry, and K. A. Gschneidner Jr.	$La_{3-x}M_xS_4$ (M = Sm, Eu, Yb)	1988
15	Preparations of R_2S_3 (R: La, Pr, Nd, Sm) Powders by Sullfurization of Oxide Powders using CS_2 gas	Michihiro Ohta, Haibin Yuan, Shinji Hirai, Yoichiro Uemura, Kazuyoshi Shimikage	Ln_3S_3 (Ln = La, Pr, Nd, Sm)	2003
16	Synthesis of Rare Earth Sulfides and their UV-vis absorption spectra	Yuan Haibin, Zhang Jianhui, Yu Ruijin, Su Qiang	Ln_2S_3 (Ln = La to Lu)	2009
17	Structural, phonon, mechanical, optical, and thermodynamic properties of stable β- La_2S_3 from first-principles calculations	Zhang Xian, Gui Wenhua, Wu Qian, Zeng Qingfeng	β- La_2S_3 (Lanthanum Sulphide)	2017
18	Preparation of Lanthanum Sulfide nanoparticles by thermal decomposition of Lanthanum complex	Li Peisen, Li Huanyong, Jie Wanqi	γ-La_2S_3 (Lanthanum Sulphide)	2011
19	Synthesis of La_2S_3 Thin Films by Sulfurization of $LaCl_3$ and $CS(NH_2)_2$	Michihiro Ohta, Shinji Hirai,Hideyasu Asahi, et. al.	La_2S_3 (Lanthanum Sulphide)	2006
20	Investigation of some photoelectric and luminescence properties of γ-La2S3 single crystals	A. N. Georgobiani, M. V. Glushkov, A. A. Kamarzin, et.al.	Photoluminescence of γ-La2S3	1982

21	Characterization of Lanthanum Sulphide	Geoffrey C. Allen, Michael Paul and Michael DunIeavy	LaS_2, La_2S_3 (Lanthanum Sulphide)	1992
22	Deposition and annealing effect on Lanthanum Sulfide thin films by Spray Pyrolysis	G.D. Bagde, S.D. Sartale, C.D. Lokhande	LaS_2, La_2S_3, La_5S_7, (Lanthanum Sulphide)	2003
23	Low Temperature Synthesis of Cubic Lanthanum Sulfide (La2S3) Powders	Prashant N. Kumta, Subhash H. Risbud	γ - La_2S_3 (Lanthanum Sulphide)	1988
24	Low-temperature chemical routes to formation and IR properties of Lanthanum Sesquisulfide (La2S3) ceramics	Prashant N. Kumta, Subhash H. Risbud	β - La_2S_3, and γ - La_2S_3 (Lanthanum Sulphide)	1993
25	Non Aqueous Chemical Synthesis of Tetragonal (β - La_2S_3) Lanthanum Sulfide Powders	Prashant N. Kumta, Subhash H. Risbud	β - La_2S_3, and γ - La_2S_3 (Lanthanum Sulphide)	1993
26	Photoluminescence of the Undoped γ -Ln_2S_3 and Doped γ-[Na] Ln_2S_3 Rare Earth Sulfides (Ln = La, Ce)	R. Mauricot, J. Dexpert-Ghys, M. Evain	γ -Ln_2S_3 and Doped γ-[Na] Ln_2S_3 ((Ln = La, Ce)	1996
27	Preparation and stabilization of γ-La2S3 at low temperature	Luo Xixian, Zhang Ming, Ma Lubin, Peng Yong	γ - La_2S_3 (Lanthanum Sulphide)	2011
28	Stabilization of γ -La_2S_3 by Alkali Metal Ion Doping	Krishnendu Biswas, U.V. Varadaraju	γ - La_2S_3 (Lanthanum Sulphide)	2007
29	Stabilized Lanthanum Sulphur Compounds	George H. Reynolds, Norbert B. Elsner, Clyde H. Shearer	γ - La_2S_3 (Lanthanum Sulphide)	1985

30	Structural characterization of chemically synthesized cubic Lanthanum Sulphide (γ - La_2S_3)	Prashant N. Kumta, Vinayak P. Dravid, Subhash H**.** Risbud	γ - La_2S_3 (Lanthanum Sulphide)	1993
31	Thermoelectric properties of Lanthanum Sesquisulfide with Ti additive	Michihiro Ohta, Shinji Hirai, Hisanaga Kato, Toshiyuki Nishimura and Yoichiro Uemura	La_2S_3 (Lanthanum Sulphide)	2005
32	Thermoelectric properties of Lanthanum Sulfide	C. Wood, A. Lockwood, J. Parker, A. Zoltan, D. Zoltan, L. R. Danielson, and V. Raag	$La_{3-x}S_4$ (Lanthanum Sulphide)	1985
33	The Y_2S_3-La_2S_3-GeS_2 system at 770°K	O.V. Smitiukh, O.V. Marchuk, I.D. Olekseyuk, L.D. Gulay.	Y_2S_3 - La_2S_3 - GeS_2 (Yttrium Sulfide)	2017
34	High Pressure Phase Transformation in Yttrium Sulfide(YS):A First Principle Study	B.D. Sahoo, K.D. Joshi and Satish C. Gupta	YS (Yttrium Sulfide)	2014
35	Electrosynthesis of Yttrium Chalcogenides from a non-aqueous bath	U.K. Mohite and C.D. Lokhande	YS, Y-Se, Y-Te (Yttrium Sulfide)	1996
36	Preparation of Rare-Earth Oxysulfide Luminescent Material	Dilip K. Nath	Patent (Y_2O_2S) (Yttrium Sulfide)	1974

37	Preparation and Characterization of Uniform, Spherical Particles of Y_2O_2S and Y_2O_2S:Eu	Ligia Delgado da Vila, Elizabeth Berwerth Stucchi and Marian Rosaly Davolos	Y_2O_2S (Yttrium Sulfide)	1997
38	Preparation of Nano Y_2O_2S:Eu Phosphor by Ethanol Assisted Combustion Synthesis Method	Luo Xixian, Cao Wanghe, Xing Mingming	Y_2O_2S (Yttrium Sulfide)	2006
39	Y_2O_2S:Eu^{3+} Nanocrystals—Synthesis And Luminescent Properties	J. Dhanaraj, R. Jagannathan and D. C. Trivedi	Y_2O_2S (Yttrium Sulfide)	2003
40	Nanostructured Thermoelectric Materials	T.C. Harman, M.P. Walsh, B.E. Laforge and G.W. Turner	Thermo Electric materials	2005
41	Nanostructured Thermoelectric Materials and High-Efficiency Power-Generation Modules	Timothy P. Hogan, Adam Downey, Jarrod short, Jonathan et. al.	Thermo Electric materials	2007
42	High-Temperature Thermoelectric Energy Conversion--II. Materials Survey	C. WOOD	Thermo Electric materials	1983
43	Comparison between Solid State Reaction and Coprecipitation Method of Titanium Oxide addition on the YBa2Cu3Oδ Ceramics	A. Arlina, Nadiah Ameran and Nik Alnur Aul	Solid State Reaction and Precipiation Method	2020

44	The Progress of Photoluminescent Properties of Rare-Earth-Ions-Doped Phosphate One-Dimensional Nanocrystals	Lixin Yu, Hai Liu	Photoluminescence	2010
45	New methodology for the thermal characterization of thermoelectric liquids	Karim Touati, Michael Depriester, Maju Kuriakose and Abdelhak Hadj Sahraoui	Thermoelectric Properties	2015
46	Turning Down the Heat: Design and Mechanism in Solid-State Synthesis	Andreas Stein, Steven W. Keller, Thomas E. Mallouk	Solid State Method	1993
47	A Review on Synthesis of Nanophosphors – Future Luminescent Materials	Harish Chander	Review Paper on Synthesis Methods	2006
48	Crystal Chemistry of the Rare Earth Sesquisulfides	A. W. Sleight and C. T. Prewitt	Structural Phases	1968
49	Luminescence in Sulfides: A Rich History and a Bright Future	Phillippe F. Smet, Iwan Moreels, Zeger Hens and Dirk Poelman	Review Paper on Different Sulfides	2010
50	R&D Trends in High Efficiency Thermoelectric Conversion Materials for Waste Heat Recovery	Hiroshi Kawamoto	Review Paper on TEC Materials	2009

51	Sintered compact of Lanthanum Sulfide or Cerium Sulfide and method for preparing the same	Uemura Yoichiro, Mitomo Mamoru, Nishimura Toshiyuki, Hirai Shinji, Shimakage Kazuyoshi	Ce_2S_3, La_2S_3	2007
52	Preparation of Sulphide Phosphors	James O. Frey, Harry L. Marshall, Henry B. Minnier	Patent (ZnS + CdS + $BaCl_2$)	1972
53	Preparation of Sulphides and Selenides	Aron Vecht, David William Smith	Patent (ZnS, Cu_2Se)	2002
54	Production of Binary Rare Earth/Sulfur or Transition Metal/Sulfur Compounds	Pierre Colombet, Phillippe Molinie, Michel Spiesser	Patent (Ce_2S_4, La_2S_4, La_2O_2S)	1994

Florent Marrot, et al. reported utilization of few heavy Lanthanide (III) elements like Dysprosium followed by Holmium, Erbium and Terbium for the immobilization of the γ-phase of Ce_2S_3 synthesized in H_2S at low temperatures (600˚C-800˚C). This stabilization needs a minimum atomic ratio Ln/Ce. The Lanthanide elements (Dy, Ho and Er) behave differently from the Alkaline elements or Alkaline-Earths which permit this stabilization whatever be the temperature (600- 1100 ˚C). It is very rare that the γ phase is observed at a lower temperature than the β form. Moreover, this stabilization is only transitory and heating at temperatures more than 800˚C provides the β form [2].

Shinji Hirai et al. synthesized Cerium (III) sulfide (Ce_2S_3) powder synthesized via the sulfurization of Ceria (CeO_2) powder using Carbondisulfide gas. Single-phase α-Ce_2S_3 could be formed via sulfurization at 973 K for 28.8 ks. The preparation of α-Ce_2S_3 became practicable at low temperature, in comparison to sulfurization using Hydrogen Sulfide gas. The formation of α-Ce_2S_3 was accelerated by the addition of Carbon Black to the CeO_2 powder which showed that carbothermic reduction became a dominant reaction, with the increase in the temperature.

The activation energy for the densification of β-Ce_2S_3 powder prepared by vacuum heating α-Ce_2S_3, was obtained by analyzing the data of densification using a kinetic equation that was proposed by other researchers. The sintering behavior could be best explained by a grain-boundary diffusion mechanism that had apparent activation energy of 382 kJ/mol [3].

M. Cutler et al. measured the electrical resistivity (ρ) and Seebeck coefficient (S) between 10 and 1000 ˚K in $Ce_{3-x}S_4$ with values of x ranging from 0 to 0.30. The electrical behavior is semi metallic and can be fitted, in large measure, to the equations of conventional transport theory for S(T) and ρ(T). Above 100˚ K, the electrical resistivity and Seebeck coefficient show a dependence on temperature which seems consistent with a simple model for transport. It suggests that there is a combination of thermal scattering and impurity scattering; the latter is presumably caused by the high concentration of vacancies. In the temperature range below 100 ˚K, anomalies are observed in S(T) and p(T) in samples with small vacancy concentrations. Anomalies in S(T) seem to be caused by phonon drag. The cause of the resistivity anomalies is not yet clear; and there is a possibility that they are caused by local lattice vibrations or by spin scattering by electrons in the 4f shell of the Cerium [4].

S. W. Kurnick et al. have made electrical, optical, thermoelectric and magnetic measurements on crack free cast samples having composition intermediate between Ce_2S_3 and Ce_3S_4 by H_2S reduction of CeO_2 in the presence of Carbon. Melting in Graphite containers was found to be unsatisfactory as the Cerium Sulfide reacted with the Graphite used. Tantalum was also attacked. With Molybdenum, on the other hand, the casting usually separates cleanly from the container after both have been cooled to room temperature. Room temperature Hall effect measurements showed high carrier concentrations, of the order of 10^{21}-10^{22} cm $^{-3}$, and low mobilities, of the order of 0.1-1 cm^2/V-sec. The room-temperature electrical conductivity of samples prepared by melting had varied from a few mho/cm to a few thousand mho/cm**.** Measurements of the thermoelectric parameters had been made at elevated temperatures using small area contact techniques as well as more conventional methods. Values of $ZT = 0.3$ have been measured in Cerium Sulfide without doping [5].

René Windiks and Erich Wimmer studied the structural and electronic properties of the α- and γ-phases of Cerium Sesquisulfide, Ce_2S_3, by first-principles calculations using the GGA+U extension of density functional theory. The strongly correlated f-electrons of Ce are described by a Hubbard-type on-site Coulomb repulsion parameter. A single parameter of $U' = 4$ eV yields excellent results for crystal structures, band gaps, and thermodynamic stability for both Ce_2S_3 allotropes. This approach gives insights in the difference in color of brownish-black α-Ce_2S_3 and dark red γ- Ce_2S_3. The calculations predict that both Ce_2S_3 modifications have optical gaps of 0.8 eV (α-phase) and 1.8 eV (γ-phase). The optical gaps are determined by direct electronic excitations at **k** = G from localized and occupied Ce 4 *f*–orbitals into empty Ce 5*d*-states. The *f* -states are situated between the valence and conduction bands. The difference of 1 eV between the optical gaps of the two Ce_2S_3 modifications is explained by different coordinations of the Cerium cations by Sulfur anions. For both Ce_2S_3 modifications, the calculations yield an effective local magnetic moment of 2.6 μB per Cerium cation, which is in agreement with measurements [6].

R. L. Fitzpatrick and Z. A. Munir prepared $Ce_{3-x}S_4$ and solid solutions of $Ce_{3\text{-}}xM^n{}_yS_4$ with γ structure by first reacting CeO_2 with H_2S gas at 1720 ˚K and then used Graphite radiation shields to obtain the products. They were studied over a wide range of compositions having metal lattice site vacancy x, mole fraction y of metal M with valence n. X-ray diffraction studies of powders subjected to isothermal phase transition conditions over a range of gas pressures in dynamic (~760 torr) and static (~I0-6 torr) experiments have demonstrated that over a wide range of temperature, $Ce_{3-x-y}Ba_yS_4$ (y > 0.2) maintains its y structure, while, $Ce_{2.67}S_4$ transforms to the "complex", or α and β phases. Gamma stabilizations were also observed for Ce_2CaS_4 but was not seen for $Ce_{3-x-y}M^n{}_yS_4$ where M^n = Ce^{+++}, La^{+++}, and Zr^{+++} [7].

Shifu Chen et al. synthesized Ce_2S_3 photocatalysts by a Co-Precipitation method using Cerium Nitrate and Thioacetamide as raw materials. Photocatalytic reduction of Nitrobenzene (NB) under UV or visible light illumination was used to evaluate the photocatalytic activity of the Ce_2S_3 samples. The result indicated that the sample prepared at 300 ◦C for 12 h exhibited the highest activity. For 140 mL 8.13 × 10−4 mol/L of NB in methanol solvent, after illumination for 5 h, about 43.9% and 34.7% of NB were reduced to Aniline over the sample under UV and visible light irradiation, respectively. It was seen that the photocatalytic reduction reaction followed first-order kinetics. The efficiency can be enhanced with the increase of Ce_2S_3 concentration and the optimal amount of Ce_2S_3 used was 4.0 g/L, beyond which retardation was caused due to light scattering and screening effects. The efficiency also increased with an increase in illumination time and the best hole-scavenger was Methanol. Recycle experiments indicated decreased activity with repeat time suggesting that the sample was unstable during the reaction [8].

Luo Xixian et al. have reported that the pure γ-Gd_2S_3 was synthesized by the thermolysis process of a single $Gd[S_2CN(C_4H_8)]_3$ Phen complex forerunner in the stream of Argon carrier gas containing Sulfur vapor. The complex forerunner was decomposed into amorphous Gd_2S_3 and Carbon at about 350°C. Crystalline γ-Gd_2S_3 could be reached at temperature exceeding 600°C, and the obtained γ-Gd_2S_3 showed a very high degree of crystallinity at 800 °C. Carbon intercepted the formation of Gd_2O_2S impurity in the preparation of γ-Gd_2S_3 and blackened the product. At temperature ≥1000 °C, the leftover Carbon impurity could be proficiently removed by introducing Sulfur into the system in the form of CS_2. Thus, the present process provided a favorable large-scale pathway for the synthesis of γ-Ln_2S_3 [9].

Manvendra Kumar et al. synthesized and characterized Eu^{3+} doped Gd_2S_3 nanoparticles which is a potential candidate for T1-weighted MRI contrast elements and molecular marker by Chemical Precipitation route with varying Eu concentrations (Eu^{3+} doped $Gd_{2(1-x)}S_3$:Eu_x with x=0.0, 0.02, 0.04 and 0.06). X-ray Diffraction and Scanning Electron Microscopy were executed to extract the information about structure and surface morphology of prepared nanoparticles, respectively. The oxidation state of the Eu ions was explained by X-ray absorption near edge structure (XANES) spectra, which indicates the presence of only Eu^{3+} ions without any signature of Eu^{2+} ions. 120 MeV Ag^{9+} ions were used for Ionoluminescence (IL) measurements to study its optical properties and application. The IL results elaborate that the luminescence intensity can be increased with increasing of Eu doping and no saturation or degradation of the luminescence were measured for as-prepared nanoparticles. The nanoparticle doped with 2 and 4% Eu clarifies increasing in the IL intensity initially before decreasing to saturation at higher influencies. On the other hand, IL intensity from 6% doped samples decreased exponentially with higher rate and saturated at higher influences [10].

G. G. Gadzhiev et al. studied the temperature dependence of the thermal conductivity, electrical conductivity, thermoelectromotive force, thermal expansion coefficient, and heat capacity in the temperature range from 300 to 1200˚ K for polycrystalline Gadolinium Sulfides GdS_y ($GdS_{1.495}$, $GdS_{1.492}$, $GdS_{1.49}$ and $GdS_{1.487}$) produced both by recrystallization pressing and by crystallization from a melt. The role of the mechanisms of heat and charge transfer was estimated depending on the composition. The reasons for changes in their electrical and thermal properties were analyzed. The thermoelectric efficiency was calculated. It was demonstrated that $Z \geq 0.6 \text{ x } 10^{-3}\ K^{-1}$ at $T \geq 1000$ K [11].

Sonika Khajuria et al. synthesized γ-Gd_2S_3 nanoparticles by green Ionic liquid-assisted Hydrothermal method at low temperature. Ionic liquid [EMIM][$EtSO_4$] was used in the process. Structural and phase analysis was carried out using XRPD studies which suggested a Th_3P_4-type cubic structure and γ-phase for the synthesized nanoparticles. SEM images suggested that the synthesized nanoparticles have cuboidal plate-like morphology which assembles in groups to give flower-like morphology. The calculated particle size by Debye–Scherrer method was 86 nm, whereas observed value by DLS technique was 91 nm. The band gap of as-prepared sample was found 2.95 eV which showed a blue shift when compared to bulk sample which might be due to the pronounced Quantum Mechanical effect on nanoparticles. Photoluminescence spectra for γ-Gd2S3 showed a strong emission peak at 385 nm and a broad shoulder at 475 nm when excited at 260 nm, and thus can serve as a blue color producing material for display applications and light emitting diodes [12].

Lu Wang et al. have elucidated the electronic structures of two lattice structures of Lanthanide Sulfides (LnS and Ln_3S_4) and for three Lanthanides (Ln = La, Sm and Gd) using density functional theory calculations performed with the CASTEP code. Band structures and partial density of states have been calculated for LaS, La_3S_4, SmS, Sm_3S_4, GdS, and Gd_3S_4 using a DFT+U approach (U = 6 eV) which is a first time approach for these systems. LaS, La_3S_4, GdS, and Gd_3S_4 are predicted to be semimetals, while SmS is predicted to be an indirect gap semiconductor, Sm_3S_4 is expected to behave similarly to a heavily degenerate semiconductor [13].

G. G. Gadzhiev et al. obtained experimental data on the temperature dependence of the electrical conductivity (σ), thermoelectromotive force (α) thermal conductivity (λ) and thermal expansion coefficient (β) of Sulfides La_3S_4, ($LaS_{1.33}$), Pr_3S_4, Gd_3S_4, Dy_3S_4, and $LaS_{2.70}S_4$ ($LaS_{1.48}$), $PrS_{1.48}$, $GdS_{1.48}$ and $DyS_{1.48}$ in the temperature range from 300 to 1200° K. They also investigated the temperature dependences of the specific heat capacity (Cp) and the velocity of propagation of longitudinal (V_l) and transverse (Vs) ultrasonic waves in order to estimate the Debye temperature (θ) and the mechanisms of heat and electric transfer. It was shown that the transfer phenomena and thermoelectrical properties of the investigated $Ln_{3-x}V_xS_4$ compositions depend on the concentration of current carriers, cation vacancies, and mobility. It was demonstrated that the compositions of $GdS_{1.48}$ and $DyS_{1.48}$ may be used as high-temperature branches for thermoelectrical converters at $T \geq 900$ K. Gadolinium Sulfide was found to have the highest thermoelectrical efficiency [14].

J. F. Nakahara et al. prepared the compounds La_{3-x} M_xS_4 for M = Sm, Eu, Yb with x = 0.1 to 0.9 by the Pressure Assisted Reaction Sintering (PARS) method in order to determine their potential as high-temperature thermoelectric energy conversion materials and was found to possess the high temperature Th_3P_4 - type structure. These compounds exhibited n-type conduction like the parent La_3S_4 compound. An analysis of the lattice parameters of these alloys suggests that Sm has a valence of 2.2 over the entire composition range. Furthermore, the variation of the Seebeck coefficient and electrical resistivity as a function of electron concentration is different for the Sm-doped alloys than for the Eu and Yb doped alloys, which are all different from that of the pure binary LaS_y alloys. Using measured values of the Seebeck coefficient and electrical resistivity together with estimated thermal conductivity data, the maximum figure-of-merit at 1000 ˚C was obtained for $La_{2.3}$ $M_{0.7}$ S_4 for M = Eu and Yb having a value of 0.6 X 10^{-3} $˚C^{-1}$. The long term stability of the Sm and Eu ternaries is also reported [15].

Michihiro Ohta et al. studied the formation behaviour of of R_2S_3 powders (R: La, Pr, Nd, Sm) synthesized by the Sullfurization of La_2O_3, Pr_6O_{11}, Nd_2O_3 and Sm_2O_3 powders using CS_2 gas in an Argon gas atmosphere. In the synthesis of La_2S_3, La_2O_2S was formed in the initial stage of reaction and single phase β – La_2S_3 was finally formed after long Sulfurization time of 8 hours at temperature above 1023 K. During the synthesis of Pr_2S_3, the intermediate products were $PrS_{1.7}$, Pr_4O_7 and Pr_2O_2S. At Sulfurization temperatures above 1123 K, only Pr_2O_2S was formed in the initial stage and then α – Pr_2S_3 having traces of β - Pr_2S_3 at higher temperatures. In the synthesis of Nd_2S_3, Nd_2O_2S was formed in the initial stage of reaction and at temperature above 1073 K, α – Nd_2S_3 having traces phase β – Nd_2S_3 were formed. In the case of Sm_2S_3, Sm_2O_2S was formed in the initial stage of reaction and single phase α – Sm_2S_3 was formed at temperatures above 1123˚ K. The impurity content of Oxygen and Carbon were dependent on the Sulfurization conditions. In all these cases, with an increase in Sulfurization temperature, it was found that the impurity Oxygen content decreased and the Carbon content in these powders increased [16].

Yuan Hainin et al. reported that Rare Earth Sulfides were systematically synthesized via the Sulfurization of their commercial Oxide powders using CS_2 gas to shorten Sulfurization time. The commercial Rare Earth Oxide powder was placed on a Graphite crucible and inserted into a corundum tube furnace. After being flushed with Ar gas at room temperature, the tube furnace was heated to the setting temperature in Ar atmosphere. And then, CS_2 gas was introduced into the reaction tube by passing Ar carrier gas through a bubbler that contained liquid CS_2. The Sulfurization reaction was carried out for 3 h. Finally, the tube furnace was cooled down to room temperature in an Ar atmosphere. In the preparation of some γ-phase Rare Earth Sulfides, the synthetic Rare Earth Sulfide powders were placed on a Graphite crucible, and inserted into a corundum tube furnace. The sample was annealed at 1500 °C for 1 hour in Nitrogen atmosphere. Diffused absorption spectra were obtained from the reflection spectra of Rare Earth Sulfides and their UV-vis absorption spectra were investigated. For the Rare Earth Sulfides with the same crystal structure, the Sulfurization temperature showed increasing tendency with the decrease of Rare Earth element atomic radii. The UV-vis absorption spectra of Rare Earth Sulfides did not depend on the crystal structure of Rare Earth Sulfides, but on the 4f electronic structure of Rare Earth element. The data showed that the optical band gaps of Rare Earth Sulfides were irregular, and the values ranged from 1.65 to 3.75 eV [17].

Zhang Xian et al. used the plane-wave pseudo potential method to study the thermodynamic properties of β-La_2S_3 like the band structures, density of states, phonon, optical properties etc. calculated from first-principles. Firstly, by using first-principles method, the structures were fully relaxed. Then, the zone-center phonon-mode recurrence was assessed within the framework of density functional jumble theory. Properties related to the structure, phonons, optics, elastic constants, and thermodynamics of β-La_2S_3 were undirected. The dielectric function, refractive index, absorption coefficient, extinction coefficient, infrared (IR) reflectance, energy, heat capacity, and Debye temperature spectra were also given. β-La_2S_3 was a direct-gap semiconductor, and its energy gap was 0.191 eV as per calculation indicated. By using the phonon spectra, it could be considered that the lattice dynamics were strongly stable. A strong IR reflection occurred in a range of 0– 1000 nm, arising from various strong IR-active modes, showing poor transmission properties. Comparatively good transmission properties were measured in the range above 2000 nm, with very low reflectivity and dissipation because of the absence of IR-active or weak modes [18].

Li Peisen et al. suggested that γ-La_2S_3 nanoparticles were successfully fabricated at very low temperature by thermal decomposition of Lanthanum complex $La(Et_2S_2CN)_3 \cdot Phen$. The dissociation mechanism of Lanthanum complex was studied by Thermogravimetric analysis (TGA). γ-La_2S_3 was obtained by dissociation of $La(Et_2S_2CN)_3 \cdot Phen$ via $La_4(Et_2S_2CN)_3$ as an intermediate product. The acquired sample was described by the X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and small element analysis. The results described that the observed samples were cubic phase particles having uniform sizes among 10–30 nm. The band gap of γ -La_2S_3 was 2.97 eV that was bigger than the bulk crystal due to pronounced Quantum Confinement effect [19].

Michihiro Ohta et al. prepared La_2S_3 thin films by submersion of substrates in Methanol solutions of $LaCl_3.7H_2O$ and CS $(NH_2)_2$. For Sulfurization, the samples, were loaded on an Alumina boat and placed into the reaction tube. Before heating, the reaction tube was evacuated using an oil-sealed rotary pump and then purged with Ar gas. The thin films were heat treated at 773–1073 K. When the heat treatment temperature was attained, CS_2 gas was immediately introduced into the reaction tube by bubbling Ar carrier gas through liquid CS_2. The flow rate of Ar gas was fixed at 1.3 mlS^{-1}. After being held for 3.6 ks, the samples were gradually cooled to room temperature under Ar atmosphere. The effects of the substrate and the mole ratio of $LaCl_3.7H_2O$ to CS $(NH_2)_2$ on the phase formation after sulfurization were underscored. When the mole ratio of $LaCl_3.7H_2O$ to $CS(NH_2)_2$ was 2:3, the tetragonal β-La_2S_3 coatings were procured on silica glass and Mo substrates for Sulfurization at 1073 K temperature. On the second side, the cubic γ-La_2S_3 coating was procured on a Soda-lime glass substrate for sulfurization at 973 K temperature. The thin films on Ta and Ti substrates were incorporated of β-La_2S_3 and γ-La_2S_3 phases for sulfurization at 1073 K temperature. The LaS_2 phase was observed as an intermediate product of Sulfurization at about 873 K temperature. When the mole ratio of $LaCl_3.7H_2O$ to $CS(NH_2)_2$ was 1:1, the β-La_2S_3 coating was also observed on silica glass substrate for Sulfurization at 1073° K temperature. The thin films obtained were porous and penetration was observed because the gaseous phases formed during Sulfurization passed through the La_2S_3 layer [20].

A. N. Georgobiani et al. reported an investigation of the photoconductivity, photoluminescence, and thermally stimulated currents in undoped γ –La_2S_3 single crystals. These crystals were prepared from molten Lanthanum Sulfide in an atmosphere containing Sulfur. They had a cubic structure of the Th_3P_4 type with cell parameter 0.87 nm and every ninth cation sub lattice vacant. The band gap was wide (Eg~3.0 eV) and the resistivity was high ($\rho \sim 10^{10}$-10^{11} Ω-cm). The energy positions of centers with deep levels were identified by investigating the luminescence and photoelectric properties of undoped γ –La_2S_3 single crystals. The participation of these centers in the radiative recombination process was considered. It is assumed that the level II participates in the radiative recombination process.

Since it is a slow recombination level, this level ensures a high photosensitivity of the single crystals. This means that it should be possible to establish a fairly high density of free carriers in the conduction band of the semiconductor γ –La_2S_3 which is a necessary condition for the impact excitation of Nd in electrically pumped lasers [21].

Geoffrey C. Allen et al. investigated solution routes to the preparation of Lanthanum Sulphide and Calcium Lanthanum Sulphide ceramics which have been identified as important compounds for application as infrared lense**s.** They examined whether Lanthanum Sulphide [La_2S_3] could be prepared by direct reaction of Hydrogen Sulphide with a suitable Lanthanum compound. Their attempts to prepare Lanthanum Sulphide by treatment of Lanthanum Isopropoxide with H_2S led to material containing metal, Sulphur and hydrocarbon, and, despite all attempts to exclude air and moisture from the reaction, the product always contained Oxygen (up to 20 %). Hence, they decided to prepare the materials by a reaction of H_2S with a compound that did not contain Oxygen in its structure. The compound Lanthanum tris{bis(trimethylsilyl)amide} [abbreviated to $La(tmsa)_3$] was chosen because of its solubility and relatively easy preparation and purification. Binding energy values for these levels were determined from peak center measurements of the single peaks observed. The actual binding energy values of the La3d level are therefore found to be slightly lower than core values, nevertheless the binding energies for the La3d level were similar for all samples, (-837.2 eV), suggesting that Lanthanum is in the same oxidation state in all of the compounds prepared. The binding energy value for the S2p level recorded from La_2S_3 was 160.7 ± 0.2 eV. This value was about 0.6 eV lower than those obtained from the LaS_2 samples, suggesting a more covalent character for the Sulphur species in the latter. In La_2S_3, Sulphur atom exists as $S^{2\theta}$ species, while, in LaS_2, (x ~ 2) it is found in the form of $(S\text{-}S)^{2\theta}$ species [22].

G.D. Bagde et al. prepared Lanthanum Sulfide thin films on glass substrates from aqueous medium using Spray Pyrolysis technique. The thin films were prepared by taking equimolar solutions of Lanthanum Chloride and Thioacetamide in such volume so as to obtain La:S ratio of 2:3. The mixed solution was sprayed form a constant distance of 28 cm at a rate of 4 cc/min with frequency of 0.3 Hz onto preheated glass substrates kept at constant temperature ranging from 150 to 400 ˚C with intervals of 25 ˚C. The Lanthanum Sulfide films were annealed in air at 300˚ C for 2 h. The films were characterized by X-ray diffraction (XRD), optical microscopy, optical absorption, electrical resistivity and thermo-emf measurement techniques. The XRD studies revealed that the as deposited films are amorphous, while annealed films are polycrystalline having mixed phases of La–S as $LaS_{1.94}$, LaS_2, La_2S_3 and La_5S_7 The optical band gap of the as deposited film is decreased from 2.5 to 2.2 eV. The electrical resistivity is of the order of 10^4–10^5 Ω cm and showed semiconducting behaviour. The decrease in optical band gap and electrical resistivity after annealing can be attributed to improvement in crystallinity. Thermo-emf measurement revealed that conductivity of Lanthanum Sulfide is p-type. The effect of preparative parameters such as substrate, temperature and solution concentration on the films was studied. It was seen that the films prepared at less than 0.05 M solution concentration were non-uniform and not adherent, while at higher concentrations, films became spotty and easily detachable from the substrate, which might be due to incomplete thermal decomposition of solution ingredients. It was found that Lanthanum Sulfide films deposited at substrate temperatures less than 275˚ C are non-uniform and not adherent to the substrate. This could be attributed to partial thermal decomposition of the sprayed solution on the substrate. Above 275˚ C, the films formed were powdery and easily detachable, which may be attributed to complete thermal decomposition of the solution before reaching the substrate [23].

Prashant N. Kumta and Subhash H. Risbud reported a wet chemical synthesis route for the preparation of Lanthanum Oxysulfide precursors from metal Alkoxides. The experimental procedure for the present process consisted of preparing a 0.02 M solution of Lanthanum Alkoxide in dry Benzene. Sulfidization of the resultant clear solution was carried out at room temperature by bubbling Hydrogen Sulfide into the Alkoxide solution. The effect of Hydrogen Sulfide is seen immediately when the clear solution became turbid. The reaction was allowed to proceed for about 2 h to ensure complete precipitation. The resultant powders, pale yellow in color, were washed repeatedly using Benzene and Carbondisulfide and then dried in a Nitrogen atmosphere to ensure evaporation of the solvents. The as-prepared powders were loaded into the furnace in a pyrolytic Graphite crucible to prevent flaking of the crucible in the presence of H_2S. Argon gas was flushed through the system and at a temperature of 700 °C, the Argon gas flux was disconnected and the H_2S gas flux turned on. After the desired reaction time at 1000 °C the furnace was shut off. At 700 °C again, the H_2S gas flux was disconnected and Argon gas pumped in to prevent Sulfur from condensing on the sample and on the walls of the reaction tube. Heat treatment of the as-prepared powders was also performed in an N_2 atmosphere to study the stability of the powders and the chemical nature of the Sulfur in the precursor. Using X-ray Diffraction and Scanning Electron Microscopy to characterize the phase development and morphology, it could be shown that the Oxysulfide precursor transformed into the cubic (γ) form of La_2S_3. The present process offers several advantages in comparison with the existing (EDS) process. The amorphous state and the fine size of the precursor particles increase the reactivity of the powders, thereby leading to reduction in the Sulfidization times (8 h) as against 15-20 h needed for the Sulfidization of the Oxides. This would also reduce the subsequent grain growth [24].

Prashant N. Kumta and Subhash H. Risbud reported metal-organic synthesis routes for the preparation of the β- and γ-phases of La_2S_3 by processing modifications and choice of precursor chemistry. Judicious use of the metal-organic and compositional variations of the resulting precursors has been shown to yield the cubic (γ) or the tetragonal (β) forms of La_2S_3 at relatively low temperatures. Cubic Lanthanum Sulfide precursors were prepared using Lanthanum Isopropoxide dissolved in reagent grade Benzene to obtain a clear sol which was Sulfidized yielding ultrafine Alkoxy Sulfide particles using the method described in the above review. Tetragonal Lanthanum Sulfide precursors were prepared using Lanthanum Isopropoxide using a method similar to γ- La_2S_3 synthesis and by Sulfidizing reaction between Lanthanum Nitrate dissolved in Propylene Carbonate and Tert Butyl Sulfide. The reaction was carried out for 2.5 h under reflux conditions, using similar experimental setup conditions as those used in the case of the Alkoxide. The cubic and tetragonal phase Lanthanum Sulfide precursors were both heat-treated using Hydrogen Sulfide and Argon at 1000-1050 °C for a period of 8 h. They were characterized for morphology, microstructure, and thermal stability. Phase evolution studies were also conducted, and the results were discussed in the context of formation of the β- and γ-phases. A Sulfur content of greater than 8 wt. % in the precursor was found to be essential for forming the cubic phase. Results of densification, microstructure, and infrared transmission characteristics are also presented. Hot-pressing experiments showed that the chemically processed Sulfide ceramic with grain sizes of ~6 μm were indeed a good far IR transmitters [25].

Prashant N. Kumta and Subhash H. Risbud developed low temperature non-aqueous chemical synthesis routes using inorganic and metallorganic starting materials to synthesize ultrafine (~ 20 nm) Sulfide precursors. The procedure essentially comprised of preparation of a clear Sol and Sulfidization of the Sol to obtain the Sulfide precursors. The precursors on Sulfidization at 1000 °C for 8 h result in the formation of fine (~ 0.5 - 1.0 μm) β-La_2S_3 particles. The physical, thermal, and microstructural chemistry of these precursors have been assessed using Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD) and Electron

Microscopy (SEM/TEM) with a view to understand the synthesis mechanism and the tetragonal phase formation. The amorphous nature of the precursor is confirmed by the endotherm at ~360 °C followed by a broad crystallization exotherm at ~ 400°C in DSC. The SEM images reveal the particles to be ~ 0.5-1.0μm. The particles are homogeneous and devoid of any secondary phases or precipitates as shown in the bright field TEM image. The presence of Oxygen is crucial in the stabilization of the tetragonal phase of La_2S_3. This is a novel processing method to synthesize the intermediate phase β-La_2S_3 in half the time (8 hr) than is required by the conventional processes (16 hr) involving melt solidification of individual elements and gas-solid reactions using Oxide precursors [26].

R. Mauricot et al. studied the photoluminescence of γ – Ln_2S_3 and Doped γ-[Na] Ln_2S_3 ((Ln = La, Ce) Rare Earth Sulfides under steady state and time resolved excitation and detection conditions. The γ-Ln_2S_3 rare earth (Ln = La and Ce) Sulfides were prepared as powders by passing H_2S over Rare Earth Oxides at high temperatures (1200-1500K) for several hours. The Sodium containing compounds were obtained by a suitable choice of the starting derivatives. The bulk materials were fully characterized by means of X-ray Powder Diffraction and easily identified as γ-Ln_2S_3 phases of the Th_3P_4 type. The higher energy emission observed under time-resolved conditions for γ-La_2S_3 is assigned to a transition from the conduction band to a level located 0.7 eV above the valence band whereas the emission observed under steady state conditions is essentially due to transitions from defect levels under the conduction band. The luminescence observed for the undoped and Sodium-doped Cerium Sulfides is assigned to transitions from the conduction band to the Ce^{3+} 4f levels. Clearly, the luminescence observed under steady state conditions may be separated, employing time resolved conditions into emissions from the intrinsic and perturbed ions. The investigations of the electronic structure of γ-La_2S_3, γ-Ce_2S_3, and γ-[Na]Ce_2S_3 by photoluminescence from powders not only confirmed but also greatly improved the previously reported band models for these semiconductors. It could be concluded that the Ce^{3+} 5d orbitals are delocalized and pertain to the conduction band, and that the 4f orbitals are in the gap, well above the valence band [27].

Luo Xixian synthesized Eu doped γ-La_2S_3 by the Sulfurization of their Oxide powders using CS_2 gas at 700 °C. Lanthanum Oxycarbonate $(LaO)_2CO_3$ was obtained from La_2O_3, Eu_2O_3, diluted Nitric acid and slight excess Oxalic acid solution after pre-sintering in air at 600 °C for 1 h. one gram of $(LaO)_2CO_3$ was placed in Silica boat and Sulfurized in CS_2 atmosphere at 400–1150 °C for 2h at heating rate of 5 °C /min. Ar (25 ml/min) was bubbled through liquid

CS_2 maintained at 30 °C. The γ-La2S3 transformation occurred at significantly lower temperature by the combined contributions of low transformation enthalpy and induced multiple nuclei. During the Sulfurizing reaction process, the cubic Eu_3S_4 crystals of prior formation played a role as γ-La_2S_3 seeds, which provided nuclei sites of the γ-La_2S_3 phase to facilitate the nucleation process. On the other hand, the doped Eu ions could be inserted into the empty tetrahedral S_4 cavities as a solid solution to stabilize the γ-La2S3 phase at temperature excess of 1100 °C [28].

Krishnendu Biswas and U.V. Varadaraju studied the effect of Alkali metal ion doping in the lacunar $La_{3-x}A_xS_4$ structure and synthesized compounds with molecular formula $La_{3-x}A_xS_4$ (A = Li, Na and K) with varying A/La ratios (0.1, 0.15, 0.2, 0.25 and 0.3) by gas–solid reaction method. The required amounts of the starting materials like metal Acetate salts were ground well and heated at 1000 ˚C for 1 h under CS_2 atmosphere. The furnace was heated at a rate of 1 ˚C/min and CS_2 (20 ml/min) was introduced and withdrawn at 700 ˚C while heating and cooling respectively to allow complete decomposition of the Acetate salts into Oxides and also to minimize the Carbon deposition on the samples. Stabilization of the high temperature γ-La2S3 is achieved by doping with Alkali metal cations like Li, Na and K at lower temperatures. The phase is pure till A/La = 0.3. There is a slight increase in the lattice parameters with increasing size of the metal ion indicating the incorporation of the metal ions in the lattice. The band gaps are found to increase with increasing concentration of the dopant, which is attributed to the increase in ionicity of the La–S bond. The optical properties show an increase in yellowness in the doped compositions when compared to the parent compound [29].

George H. Reynolds et al. obtained a patent for maintaining Lanthanum Sulfide in the stable cubic phase form over a temperature range of from 500° C. to 1500˚ C by adding small amounts of Calcium, Barium, or Strontium. This novel compound was an excellent thermoelectric material which could be represented by the formula $(LaM)S_{1.5-x}$ (where x is greater than 0 and less than 0.1, and M = Ca, Ba, Sr). The amount of Calcium, Barium, and Strontium should be effective to maintain the desired cubic phase of Lanthanum Sulfide at temperatures of 500 ˚C or lower. Typically, their amount ranged between about 0.1 and about 5.0 weight percent of the compound, and preferably is in the range from about 0.2 to about 5 weight percent, to stabilize the cubic phase. The thermoelectric material of this invention usable in the temperature range of 500 to 1500 ˚C was made by blending together powders of Lanthanum Sulfide and Barium Sulfide, Calcium Sulfide, and/or Strontium Sulfide in the correct proportions at room temperature. This blend was slowly heated in vacuum to a temperature of approximately 1100-1200° C for a sufficient amount of time for chemical homogenization to occur [30].

Prashant N. Kumta et al. employed low temperature chemical techniques incorporating organometallics to synthesize γ – La_2S_3. Sulfidation of Isopropoxide in a reagent grade Benzene has been shown to generate amorphous Lanthanum Oxysulphides precursors. The powders were heat treated using Hydrogen Sulphide and Argon at l000-1050°C for a period of 8 h to obtain the desired cubic form of Sulphide. Thus, γ – La_2S_3 was synthesized at temperatures as low as 1000°C in only 8 h as opposed to the high temperatures of 1500°C and long Sulfidization periods of 20 h in the conventional melt solidification and gas-solid reaction techniques. The amorphous Oxysulphide precursors were very fine (20 nm) in size and the transformed cubic Sulphide particles ranged from 1-3 µm**.** γ – La_2S_3 powders were hot pressed in an Ar atmosphere with a ram pressure of 27 MPa at a temperature of 1450°C for 15 min. The thermal stability, phase evolution characteristics and microstructure of the fine particles have been investigated using Differential Scanning Calorimetry, X- Ray Diffraction and Electron Microscopy. The sintered hot pressed ceramic exhibited a twofold increase in the grain size. CBED performed on the Sulphide powders and ceramic confirmed the cubic symmetry and identified the space group to be 143d [31].

Michihiro Ohta et al. measured the electrical resistivity, thermopower, and thermal conductivity for the Lanthanum Sesquisulfide (La_2S_3) whose crystal phase is controlled by the Ti additive. X -ray analysis of the samples showed that the β to γ phase transformation is accelerated by the Ti additive. For sample, with 0–2 wt % Ti, the major phase was identified as the β phase while the samples with 8 wt % Ti consisted almost of the γ phase. The samples with 3–7 wt % Ti consist of the mixed β and γ phases. For the samples with 1–3 wt % Ti, the electrical resistivity decreased with increasing temperature like an insulator. On the other hand, for the samples with 5–8 wt % Ti, the electrical resistivity increased linearly with increasing temperature. In all the samples, the thermopower is negative between 300 and 1000 K. The sample with 8 wt % Ti consisting of γ La_2S_3 behaved as a degenerate semiconductor. The thermoelectric figure of merit *ZT* increases with increasing temperature, reaching a value of 0.21 at 1000 K. The Ti additive promoted the formation of the γ phase with the high thermoelectric performance while it stabilized the β phase. Like the γ phase, the β phase is also a candidate material for the high-temperature thermoelectric energy conversion. The transport mechanism could be explained in terms of the Anderson localized model [32].

C.Wood et al. synthesized Lanthanum Sulfide specimens $La_{3-x}S_4$ (LaS_y) in the single phase regime $0<x< 1/3$ (1.33<.y<1.5) by vacuum (10^{-6} to 10^{-5} Torr) hot pressing (~1800 K at ~10 K psi) Lanthanum Sulfide powder (200 mesh) in Graphite dies for a period of approx. 1 h. The Lanthanum Sulfide powders were prepared by Ames Laboratory (Ames, IA), by reacting Lanthanum ribbon with Sulfur in Quartz ampules and melting the product in Tungsten crucibles and then grinding the reactant. X-ray Diffraction measurements showed the hot-pressed pellets to be γ phase. The Seebeck coefficient, electrical resistivity, thermal conductivity, and Hall effect were studied in the composition range $0.04<x<0.3$ ($1.35<y< 1.48$) in order to ascertain its suitability for high-temperature (300 to 1400 K) thermoelectric energy conversion. In this temperature and composition range the material behaves as an extrinsic semiconductor whose degenerate carrier concentration is controlled by the stoichiometric ratio of La to S. Experimental results and theoretical analysis showed that the optimum figure of merit (Z) occurred for the composition range $2.68<x<2.7$ which corresponded to $1.48<y<1.49$ and was obtained at a temperature of 1000 ˚C [33].

O.V. Smitiukh et al. calibrated the isothermal section of the Y_2S_3-La_2S_3-GeS_2 system at 770 K. The entity of a solid solution $Y_{4x}La_{4-4x}Ge_3S_{12}$ (x= 0-0.75) was underlaid for the first time. The crystal structure of the $Y_2La_2Ge_3S_{12}$ compound was observed and studied by X-ray Powder method (space group R3c, Pearson symbol hR38, a = 0.92587(9) nm, c = 0.79121(5) nm, R_1 = 0.0812). Rare-Earth material atoms M (Y, La) form two types of coordination polyhedral, $[M1S2_6S3_3]$ and $[M2S1_2S2_1S3_2S4_2]$ in the special crystal structure of $Y_2La_2Ge_3S_{12}$, and Ge atoms center $[GeS1_1S2_1S3_1S4_1]$ tetrahedral [34].

B.D. Sahoo et al. analyzed the structure and elastic and dynamic stability of YS under hydrostatic compression by using the first principal. The comparison of enthalpies of rock salt type (B1) and CsCl type cubic (B_2) structures observed as a function of compression suggested that the B1→B2 transition should occur at ~ 49 GPa. By using theoretically determined equation of state, various physical quantities such as zero pressure equilibrium volume, bulk modulus, and pressure derivative of bulk modulus were obtained. The single crystal elastic constants derived from the energy strain method agree well with the few experimental values. The activation barrier between B1 and B2 phases calculated at transition point is ~ 17/mRy/formula unit. The lattice dynamic calculations showed that at ambient condition, the

B1 phase is lattice dynamically stable and frequencies of phonon modes in discontigous high symmetry directions of Brillouin zone agree well experimental values and observations. The B2 phase also is dynamical stable at comprehensive condition as well as at ~ 49 GPa supporting our static lattice calculations [35].

U.K. Mohite and C.D. Lokhande reported for the first time, the electrosynthesis of Yttrium Chalcogenide films on a variety of substrates in a non-aqueous bath using Sodium Acetate as a complexing agent. Thin films of Yttrium Sulphide were electrodeposited in a Formaldehyde bath consisting of 0.05M $Y(NO_3)_3$ + 0.1M CH_3CSNH_2 + 0.05M CH_3COONa. The Y-Se films was electrodeposited from the bath consisting 0.05M $Y(NO_3)_3$ + 0.05M SeO_2 + 0.05M CH_3COONa. In order to obtain Y-Te films, initially Yttrium was deposited from the bath consisting of 0.05M $Y(NO_3)_3$ + 0.05M CH_3COONa and then layer of Tellurium was electrodeposited on it from a bath consisting of a saturated solution of TeO_2 + 0.05M CH_3COONa. The layer-by-layer deposited Y-Te films were annealed at 200°C in Nitrogen atmosphere for one hour. The cathode substrates used were stainless steel, Copper, Brass, Titanium and ITO coated glass. It was seen that the deposition potential depended on the nature of the substrate. The electrode position potentials were observed and estimated from the polarization curves. The films were marked out by optical absorption, Scanning Electron Microscope and X-ray Diffraction techniques. The XRD patterns showed polycrystalline nature of Y-S, Y-Se and Y-Te films. From optical absorption studies, the band gap energies Eg of Y-S, Y-Se and Y-Te were found to be 1.85, 1.6 and 1.7 eV respectively [36].

Dilip K. Nath has patented the process of preparing crystalline Rare Earth Oxysulfide luminescent materials which produce improved phosphor crystals that are essentially contaminant-free. Selected Oxysulfides of Yttrium, Gadolinium, Lanthanum, and Lutetium were synthesized by heating a Rare Earth Oxide mixture in H_2S gas to elevated temperatures in the range from about 500°C to 700°C with a Sulfurizing compound selected from the group consisting of KHS and a Potassium compound which reacts to form KHS upon heating with H_2S until the Oxysulfide material is produced in accordance with the formula $Ln_{2-x}Ln'_xO_2S$ wherein Ln is one or more of Y, Gd, La, and Lu and Ln' is one or more of Dy, Er, Eu, Ho, Nd, Pr, Sm, Tb, and Tm, and x is in the range 0.0002 to 0.2. The Oxysulfide material was recrystallized by heating with an Alkali Metal Sulfide in an inert atmosphere to elevated temperatures in the range from about 1050°C to 1450°C [37].

Ligia Delgado da Vila et al. reported the preparation of spherical Y_2O_2S and Y_2O_2S: Eu particles using a solid–gas reaction of monodispersed precursors with elemental Sulfur vapor under an Argon atmosphere. The precursors, undoped and doped Yttrium Basic Carbonates were synthesized by heating a stock solution containing the respective cation Chloride and Urea at 82–84 °C under continuous stirring for 2 hours. Precursors were loaded into a completely sealed principal furnace in an Alumina crucible. Argon gas was flushed through the system during both the reaction and cooling time. Sulfur was heated at 220 °C in an auxiliary furnace. Then the main furnace temperature was gradually increased to 770 °C (heating rate 2 °C min−1) and Sulfur vapor was carried by the Argon stream across the system (flow rate 116 cm^3 min^{-1}). After the desired reaction, auxiliary furnace was shut off and the product was heated at 800 °C for at least 2 h. The products were characterized in terms of their composition, crystallinity and morphology by chemical analysis, X-ray Powder Diffraction (XRD), IR spectroscopy, and Scanning Electron Microscopy (SEM). The Eu-doped Oxysulfide was also characterized by Atomic Absorption Spectrophotometry and Luminescence spectroscopy. The spherical morphology of Oxysulfide products and of basic Carbonate precursors suggests a topotatic inter-relationship between both compounds. The dominant emission arises from the $^5D_0 \rightarrow {}^7F_2$ transition and is observed at 626 nm. This behavior indicates only one emitting Eu3+ symmetry site. No peak arising from $^5D_0 \rightarrow {}^7F_2$ transition at 611 nm is observed suggesting the absence of Oxide impurity [38].

Luo Xixian reported the preparation of Y_2O_2S: Eu nano crystallites by a new Ethanol assisted Combustion synthesis method using Sulfur contained organic fuel in an Ethanol-aqueous solution. Y_2O_2S: Eu nano crystallites with strong photoluminescence and X-ray luminescence were obtained using Thioacetamide as organic fuel. Mixtures of Y_2O_3: Eu and Y_2O_2S: Eu are acquired using Thiourea as fuel, and the content of Y_2O_2S: Eu was increased until it reached to about half of the Y_2O_3: Eu with the increasing amount of Thiourea. $Y_2O_2S0_4$: Eu emerged when S/Y = 6 and increased with increasing Thiourea amount. It was shown that the assistant fuel Ethanol has the effect of decreasing the water needed, simplifying the experiment procedure by dissolving Rare Earth Nitrate and Sulfur-contained organic fuel into an even solution, and prompting the formation of Rare Earth Oxysulfide by igniting firstly during heating that leads to combustion decomposition reaction between Rare Earth Nitrate and organic fuel. The as-prepared nanocrystallines were characterized by X-ray Diffraction, Transmission Electron Microscope, Photoluminescence spectra and X-ray luminescence spectra. XRD results showed that Y_2O_3: Eu existed with cubic crystalline and Bixbyite type structure with space group Ia3 (206). The Excitation spectra revealed that in the doped Oxide samples, the charge transfer (CT) was observed around 250 nm, and a split Eu f-f transition assigned to $^7F_0 \rightarrow ^5L_6$ was around 394 nm. In Eu^{3+} doped Oxysulfide or Oxysulfate samples, there were two CT bands in the excitation spectra around 330 nm and 250 nm and another f-f transition $^7F_0 \rightarrow ^5L_5$ band. In the Emission spectra, for the Eu^{3+} doped Oxide samples the most intense component of $^5D_0 \rightarrow ^7F_2$ transition was observed at 610 nm, which is a typical emission of Eu at the C symmetry site without inversion center. In Oxysulfide samples, the $^5D_0 \rightarrow ^7F_2$ transition presented a maximum at 625 nm and shoulder peak at 615 nm while in Oxysulfate, the main emissions were at 613 and 615 nm [39].

J. Dhanaraj et al. synthesized luminescent Y_2O_2S: Eu^{3+} nano ceramics having an average particle size of 20 nm through a facile Sol gel–polymer thermolysis process employing Urea–Formaldehyde resin. In this synthesis, the Urea–Formaldehyde resin served both as an organic fuel for the pyrolysis reaction and also as the dispersion matrix for the synthesis of the nano ceramic particles. It was prepared conventionally by the addition of Urea and Formaldehyde in the molar ratio 1:2 resulting in a condensation reaction of Urea and Formaldehyde. A mixed $Y/Eu(NO_3)_3$ stock solution was prepared using proper amounts of $Y(NO_3)_3$ and $Eu(NO_3)_3$ solutions obtained from the corresponding Oxides by dissolution in Nitric acid. To 10 ml of this solution, proper amounts of Urea and Formaldehyde solution were added followed by the addition of Sulfur. The mixture was heated at 60 ˚C in order to accelerate the polymerization process and also to evaporate off the excess water. The solidified mass thus obtained was thoroughly ground and thermolysed at 500 ˚C for 1.5 h in Sulfur atmosphere. In this nanocrystalline system, large blue shifts (in relation to the bulk system) of ~ 5000 cm^{-1} and 2000 cm^{-1} in the photoluminescence excitation bands corresponding to the excitonic region and the Eu^{3+} ligand charge transfer region respectively were observed. Considering the structure independent $^5D_0 \rightarrow ^7F_1$ emission as the reference, the observed blue shift in the photoluminescence charge transfer excitation band may be explained by considering possible size dependent changes in optical electronegativity and Quantum Confinement effects in the ligands surrounding the luminescent centre occurring in this large bandgap semiconductor system [40].

T.C. Harman et al. concluded that high values of thermoelectric figures of merit ZT, ranging from ZT = 1.6 at 300 K to ZT = 3 at 550 K, were reported for Bi-doped n-type PbSeTe/PbTe Quantum Dot super lattice (QDSL) samples grown by molecular beam epitaxy

(MBE). These ZT values were determined by directly measuring Seebeck coefficients and electrical conductivities and using the low lattice thermal conductivity value (3.3 mW/cm-K) determined experimentally from measurements of a one-legged thermoelectric cooler. Initial experiments have also shown that high values of ZT (1.1 at 300 K) were achievable for complementary Na-doped p-type PbSeTe/PbTe QDSL samples, in which the conduction and valence bands mirror those in the Bi-doped Pb Chalcogenides [41].

Timothy P. Hogan et al. reported that the best materials for the thermoelectric applications should have high electrical conductivity and thermo power and at the same time low thermal conductivity having low thermo power and conductivity. Such kind of combination of properties was usually found in heavily doped semiconductors. Renewed interest in this topic has many recent theoretical predictions that massive increases in performance were possible for nanostructured materials and this has been experimentally verified and observed. During the studies of Chalcogenide-based bulk thermoelectric materials, it was invented that several compounds spontaneously formed endotaxially embedded nanostructures. These compounds had many of the best known properties for bulk thermoelectric materials in between the range of 500–800 K temperature. In this study, they reported their continued efforts to better understand the role of the nanostructures, while concurrently furthering the development of these new materials and enhancing their applications for future growth of thermoelectric materials. As an example, the use of n-type Lead–Antimony–Silver–Tellurium, and p-type Lead–Antimony–Silver–Tin–Tellurium in thermoelectric power generation devices has also been reported [42].

C. Wood. has reviewed and reported the current status of materials research for high-temperature thermoelectric energy conversion. According to him, two general classes of materials show promise for high temperature figure of merit (Z) values, viz. the Rare-Earth Chalcogenides and the Boron-rich Borides. The electronic transport properties of the Rare-Earth Chalcogenides were explainable on the basis of degenerate or partially degenerate n-type semiconductors. Boron and Boron-rich Borides possesses p-type hopping conductivity, with detailed explanations proposed for the transport differing from compound to compound. Some discussion was presented on the reasons for the low thermal conductivities in these materials. Also it was concluded that ZTs greater than one appears to have been realized at high temperature in many of these compounds [43].

A. Arlina et al. have studied the comparison of TiO_2 additions on the physical properties of $YBa_2Cu_3O_\delta$ superconductor system with nominal starting compositions at x= 0, 1, 2, and 5 wt.% derived via Solid State Reaction (SSR) and Co-Precipitation (COP) method. The Solid State synthesis was carried out using Yttrium Oxide (Y_2O_3), Barium Carbonate ($BaCO_3$) and Copper Oxide (CuO) weighed to give stoichiometry ratio of 1:2:3. The mixture was calcined for 10 hours at a temperature of 960 °C after initial grinding. TiO_2 was added with $YBa_2Cu_3O_\delta$ at difference weight % and finally the calcined powder was pressed into pellet before sintered at 960 °C for 10 hours. Co-Precipitation synthesis was done using Yttrium Acetate ($YC_6H_9O_6.H_2O$), Barium Acetate ($BaO_4C_4H_6.H_2O$), Copper Acetate ($Cu(CH_3COO)_2.H_2O$), Oxalic acid, de-ionized water and 2-Isopropanol. The Acetate was dissolved in Acetic acid, and, Oxalic acid was dissolved in water: Isopropanol. These two solutions were stirred in ice bath to obtain uniform blue suspension which was filtered and dried for 6 hours before calcination at 900 ˚C for 12 hours with intermediate grinding. The samples were characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The result from XRD shown that all the samples were polycrystalline for SSR, while single phase for COP methods. The refined lattice parameters indicated that all the samples have an orthorhombic crystal structure without occurrence of orthorhombic-tetragonal phase transformation. Furthermore, from SEM images for Solid State reaction and Co-Precipitation method, it was seen that the grain size of the samples decreased with TiO2 increase. Small addition of TiO2 derived from Co-Precipitation method enhanced the YBCO microstructures. The Co-Precipitation method was found to have many advantages in comparison to the SSR method regarding the process conditions and the quality of the YBCO powders. The COP process itself was instantaneous and lead to homogeneous stoichiometry of product in comparison to the time consuming SSR, which needed regrinding of the raw materials to achieve the required homogeneity [44].

Lixin Yu and Hai Liu have reported that One-dimensional (1D) nanostructures, such as tubes, wires, rods, and belts, have stimulated remarkable attentions over the past decade due to a great deal of potential applications, such as data storage, advanced catalyst, and photo electronic devices. On the other hand, in comparison with zero-dimensional (0D) nanostructures, the space anisotropy of 1D structures provided a better model system to study the dependence of electronic transport, optical and mechanical properties on size confinement and dimensionality. Rare Earth (RE) compounds have been intensively applied in luminescent and display devices. It was expected that in nano sized RE compounds, the luminescent Quantum Efficiency (QE) and display resolution could be improved. In this paper, they have systematically reported the research progress of luminescent properties of RE-doped 1D Orthophosphate nano crystals including the synthesis of 1D nanostructures doped with RE ions, local symmetry of host, electronic transition processes, energy transfer(ET), and so forth [45].

Karim Touati et al. reported a new and accurate photo thermoelectric (PTE) method for the thermal characterization of thermoelectric liquids. It was demonstrated that thermal parameters (thermal diffusivity, effusivity, and conductivity) of thermoelectric liquids could be simultaneously determined. The main advantage of this approach was to investigate the thermal properties of samples without the need of an external temperature sensor. The formalism of the PTE signal was developed and a procedure for extracting thermal parameters was also proposed. The sample was introduced into a Quartz precision cell covered by a thick CaF_2 window. The knowledge of the exact thickness would allow a better accuracy in the experimental results. The inside surfaces of the Quartz cuvette and the CaF_2 window were coated with gold to absorb the incident light beam and thus to serve as thermal sources as well as electrodes for collecting electrical signals from the sample surfaces. The use of materials with large thermal effusivity contrast between the front and back windows is necessary to obtain both thermal parameters of the sample simultaneously. Electrical leads connected to the electrodes were silver pasted and plugged into a EG&G 7260 lock-in amplifier. An internally modulated LASER was employed to create a temperature gradient of 1 K and a thermal wave across the liquid sample which produced a self-generated voltage due to Seebeck effect. The sample used was Tetradodecylammonium Nitrate salt/1-Octanol mixture. In order to validate the new PTE technique, the results obtained were compared to those obtained by other conventional techniques like BF-PTR and PPE. A good agreement was found between these three techniques demonstrating the relevance and the usefulness of this new methodology. Thus, it provided an accurate and simple way to determine the thermal conductivity of TE liquid materials [46].

Andreas Stein et al. have reported that Solid-State compounds have historically been prepared through high-temperature solid-solid reactions. Traditional Solid State synthetic techniques produce thermodynamically stable products at temperatures in the neighborhood of 1000°C. In these reactions the mechanism is generally not considered and there is little control over the formation of metastable intermediates. Mechanistic Solid-State chemistry and the design of interesting metastable phases can be considered only at temperatures significantly lower than those of "brute force" solid-solid reactions. Today, there is an increasing need for structures "made to order" designed to display a specific set of physical properties and hence the tools of the trade have evolved considerably away from high temperature solid-solid reactions, partly in response to this demand, and partly, because molecular concepts and synthetic strategies have begun to invade the thinking of Solid State chemists. New mechanistic understanding of these reactions suggests possible routes to metastable compositions and structures as well as to thermodynamically stable low-temperature phases that decompose at higher temperatures. Intermediate-temperature synthetic techniques, including flux and Hydrothermal methods as well as low-temperature Intercalation and Coordination reactions, have recently been developed and used to prepare unprecedented materials with interesting electronic, optical, and catalytic properties. Thus, attention to reaction mechanism and the use of molecular building blocks in small-molecule chemistry can result in an ability to prepare new materials of designed structure [47].

Harish Chander reported the chemical methods used for the synthesis of nanophosphors which have been extensively investigated during the last decade due to their application potential for various high-performance and novel displays and devices. A brief review of different synthesis techniques employed all over the world for the development of industrially important nanophosphors have been reported in this study. Many processes such as Chemical Precipitation with and without capping agents, Sol-gel, Sol-gel with heating, Microemulsion, Solid State heating, Chemical Vapour synthesis, Hydrothermal synthesis, Chemical synthesis within matrix, Molecular Beam Epitaxy, Electrochemical route, Autocombustion, Chemical Precipitation from homogeneous solution etc. have been developed for synthesis of nanophosphors. Chemical Precipitation method can be used to control the size by synthesis of nanomaterial in situ to avoid any physical changes and aggregation of tiny crystallites. Sol-gel Strategy has reported lowering of synthesis temperature and controlled growth. Hydrothermal Strategy uses Microemulsion with Hydrothermal treatment and gives small particle size and emission intensity enhancement. Commercial viability of the technique may be low due to costly capping agents and processing difficulties of finished nanophosphors for display devices. The processes of Sol-gel, Sol-gel with heating, Microemulsion, Chemical Vapour synthesis, Molecular Beam Epitaxy and Autocombustion are not likely to be economically and environmentally friendly as these are chemical and energy intensive. Chemical Precipitation with capping using inorganic compounds, Chemical Precipitation from homogeneous solution, Synthesis within a matrix, Electrolysis based process, Hydrothermal synthesis are the techniques that are likely to be technologically acceptable [48].

A. W. Sleight and C. T. Prewitt have synthesized Rare Earth Sesquisulfides of La through Lu as well as Y and characterized them to study their structures. The structures occurring for these compounds are now all known, and the cell dimensions are given many for the first time. All the materials were synthesized by the Solid State method using Rare Earth metal and Sulphur as precursors. Single crystals of most of the Rare Earth Sesquisulfides have been prepared in a Rare Earth Iodide melt using l:l:1 atomic mixture of metal, Sulfur, and Iodine. The nomenclature given is α to A, β to B, γ to C, δ to D, and ε to E. Three structure types were found. The A type exists from La through Dy, the D type from Dy through Tm including Y, and the E type is found for the two smallest rare earths Yb and Lu. It was apparent that Pu_2S_3 may also have the A-type structure, and its cell dimensions were refined by least squares. Although the Th_3P_4 structure (C type) may represent a fourth structure type, it was possible that Sesquisulfides with this structure must be deficient in Sulfur or impure. Electrical measurements on the single crystals generally showed semiconductor behavior as expected [49].

Phillippe F. Smet et al. have reported the long standing history of Sulfide phosphors dating back from atleast the 17th century. Progress in the understanding of the basic principles of luminescence culminated in the several typical applications, uniquely based on Sulfides such as ZnS-based powder electroluminescence and thin film electroluminescence have also been discussed. The potential applications of Rare Earth doped binary Alkaline Earth Sulfides like CaS, SrS, CdS, PbS, Thiogallates, Thioaluminates and Thiosilicates as conversion phosphors has also been reported. It has also given an insight into the 21st century luminescent Sulfide nanoparticles and colour conversion phosphors. Without any doubt, the Sulfides possessed specific properties which made them especially suited as powder electroluminescent phosphor or as thin film electroluminescent materials. However, these lighting techniques have a dim future with the advent of superior techniques like organic LEDs and liquid crystal displays. The research and development in thin film EL has been relatively small but it might still have a future as a full colour display technique in demanding environments due to its intrinsic advantages. The future of Sulfide phosphors could be situated in the field of colour conversion for white LEDs. Doping with Eu^{2+} and Ce^{3+} could tune the emission from deep blue to saturated red by proper selection of host composition. In general, the emission and excitation bands are sufficiently broad allowing both good colour rendering and efficient pumping by the LED. It was necessary to evaluate Quantum Efficiency of photoluminescence and thermal quenching behaviour in terms of intensity reduction and spectral shifts. Use of Sulfides for LED will depend on host-dopant conditions, preparation conditions and long term stability. CdS and PbS Quantum Dots have already shown unique abilities and future potential as luminescent material of a wide range of photonic applications. On the other hand, semiconductor nanoparticles based on Sulfides are yet to show their full potential [50].

Hiroshi Kawamoto has provided an insight into the reasons why high efficiency thermoelectric power generation will be increasingly expected in the future from the viewpoint of various energy systems, the amount of unused waste heat, and production of low Carbon society based on effective utilization of thermoelectric generating systems, and introduces the thermoelectric conversion materials/manufacturing processes and the conditions for penetration of thermoelectric power generating systems. Following this, the current status of R&D on innovative thermoelectric conversion materials by nanostructural control was described. Popularization of thermoelectric power generating system will be indispensable to achieve low Carbon society and reuse of unused waste heat. Thermoelectric power generating modules comprises of a p-type and a n-type semiconductor element. In the heated n-type semiconductor element, the electrons in the high temperature region are activated and are transferred to the low temperature region generating thermal electromotive force and the high temperature side reaches a high electrical potential. The opposite happens in p-type semiconductor. When these two semiconductor elements are combined a current flows between the n-type and p-type semiconductor elements (this phenomenon is termed the Seebeck effect). The power generating performance of thermoelectric conversion materials is expressed by the index Z in the equation $ZT = S^2\sigma T/\kappa$. The present thermoelectric power generating systems have limited field applicability, low power generation efficiency and the materials used, also face problems of unstable supplies and high environmental loads due to use of heavy metals. These problems can be solved by finding thermoelectric conversion materials which offer high efficiency, stability, low cost, secure resources and low environmental loads. Hence, future research and development should shift to metal Oxides and Silicon compounds, nano thin film structures, superlattices, nanowire arrays, strongly correlated electron system compounds etc. [51].

Uemura Yoichiro et al. have obtained a patent for an invention related to Lanthanum Sulfide or a Cerium Sulfide sintered compact having a large thermoelectromotive force (High Seebeck coefficient) particularly useful as thermoelectric conversion materials. They have also described a method of producing such a sintered compact. The sintered compact had a chemical composition of La_2S_3 or Ce_2S_3 and a crystal structure consisting of a mixture of beta and gamma phases having a Seebeck coefficient higher than that of the crystal structure otherwise being in gamma single-phase. The sintered compact was produced by preparing β-phase La_2S_3 material having an Oxygen concentration in the range of 0.7 to 1.0 mass % or α-phase Ce_2S_3 material having an Oxygen concentration in the range of 0.9 to 1.7 mass %, both having high purity with a suppressed carbon impurity concentration of 0.1 mass % or less, and then, charging said raw material into a Carbon die having an inner surface covered with a hexagonal layered Boron Nitride (h-BN) and pressure-sintering the said charged material in a temperature range of 1600 to 2000˚ K under vacuum within the time period in which beta-phase was not vanished [52].

James O. Frey have obtained a patent for developing an improved process for preparing phosphor compositions having a multivalent metal Sulfide host and a source of activator material comprising of at least one metal having a tripositive valence in which at least about 0.5% to about 5% by weight of Barium Chloride flux material is added, and the mixture is heated in an atmosphere of Carbondisulfide and an inert gas carrier like Nitrogen at a volumetric ratio of Carbondisulfide to inert gas of at least about 1:50 to about 1:85. They prepared blue or green emitting CdS + ZnS phosphor using ZnS, CdS, $CuSO_4$, $AlCl_3.6H_2O$ and $BaCl_3$ as starting materials. The mixture was heated at a temperature range of 900 to 1250 ˚C for at least 30 min in an atmosphere of CS_2 and N_2 having a ratio of 45:1 [53].

Aron Vecht and David William Smith have patented a method to synthesize Sulphides and Selenides by dissolving Sulphur or Selenium in an aqueous solution of Hydrazine Hydrate at room temperature and then combining the resulting solution with a solution of an appropriate cation to precipitate the corresponding Sulphide or Selenide. In this process, an excess of Hydrazine Hydrate was used with at least 2:1 mole ratio of Hydrazine Hydrate to the Sulphur or Selenium. ZnS was produced by dissolving Zinc Acetate in 80 ml hot water. 8 g of Sulphur was slowly added to 60 ml of Hydrazine Hydrate and this solution is added to Zinc Acetate solution under stirring. The yellow precipitates are washed with a liter of water and dried at 120 ˚C. In order to obtain CuSe, 20 g of Copper Acetate was dissolved in 200 ml of water. 7.9 g of powdered Selenium was dissolved in minimal amount of Hydrazine Hydrate and this mixture was added to Copper Acetate solution under stirring for three hours. The black precipitates were filtered, washed with water and dried. Solutions of two or more cations might be used to produce ternary compounds of Sulphur and Selenium like Thiogallates. Likewise, both Sulphur and Selenium could be used together to produce SulphoSelenides. An important feature of the method described herein was the dissolution of elemental Sulphur or Selenium which could be of a high purity by chemical reaction with Hydrazine. This may be expressed as $N_2H_4 + 2X = N_2 + 2H_2X$ (where X=S or Se). The method is particularly applicable to the production of doped phosphors by the inclusion of Solutions containing the appropriate dopant [54].

Pierre Colombet et al. have patented an improved process for the synthesis of binary Sulfur compounds, in particular Sulfur compounds of the Rare Earths and Sulfides of the transition metals in which either a Rare Earth compound or an Oxide, Carbonate or Hydroxide of a transition metal reacts with a Sulfur compound of Carbon in the gaseous state like CS_2 within a sealed enclosure. In order to synthesize the material, the Rare Earth Oxide in Solid State was placed into a Pyrex tube. Am ampoule containing liquid CS_2 was introduced into the tube. The tube was sealed at a length of about 10 cm and the assembly was agitated to break the ampoule tip. The reaction tube was placed inside a horizontal furnace and was subjected to slow heating cycle for approximately one hour to 350 to 480 ˚C maintaining this assembly for four hours followed by slow cooling to ambient temperature in 5 to 6 hours. At these temperatures, Carbondisulfide was in the gaseous state because the high amounts 300 to 500 mg created an initial pressure of approximately $25x10^5$ Pa. The tube was then opened to the flame and the residual gases were exhausted by cryopumping. A major advantage of the present invention was improved process for the synthesis of Sulfur compounds of Rare Earths that could be carried out on an industrial scale which conspicuously ameliorated the disadvantages and drawbacks of contemporary methods [55].

2.3 Conclusion

The following conclusions can be drawn from the detailed review of literature available for Rare Earth Sulfides:

(1) Rare Earth Elements are now widely used in auto- and fluid catalysts, metallurgy, medical systems, high technology, clean energy, and military defense systems, and they are especially indispensable in emerging clean technologies, such as wind power turbines, electric vehicles, energy-efficient lighting, and catalytic converters. They are essential ingredients in

energy-efficient lighting systems, plasma displays, medical imaging, automotive catalysts, permanent magnets, and pigments.

Synthesis and characterization of Rare Earth Sesquisulfides (Ln_2S_3, Ln=rare earth) have attracted considerable attention of researchers due to their interesting and excellent physical and chemical properties and wide applications in various technological areas, such as optical electronic and superconducting devices, cold cathode configurations, current controlled devices, switching devices, photoconducting cells, permanent magnets, electrical, catalytic, and biological imaging. γ- Ln_2S_3 has potential applications as heavy metal free nontoxic pigments for plastics and paints, n-type thermoelectric converters, optical materials in IR transmission windows, lasers, masers and magneto-optical devices.

γ- Ce_2S_3 has a semiconductor like behaviour and is used as a safe red pigment for plastics and paints while red coloured Ce_2S_3, black Ce_3S_4 and yellow CeS are used as refractories at high temperatures for casting of Plutonium and Uranium.

Gd_2S_3 is a potential candidate for T1-weighted MRI contrast elements, molecular marking, biological imaging, electrical, catalytic and magneto-optical devices.

γ-La_2S_3 can be used as active elements in electrically pumped lasers, IR lenses and far IR window and dome materials.

Rare Earth Sulfides can be used as thermoelectric materials which are Solid-State energy converters in which the combination of thermal, electrical, and semiconducting properties allows them to be used to convert waste heat into electricity or electrical power directly into cooling and heating. These materials can be competitive with fluid-based systems, such as two-phase air-conditioning compressors or heat pumps, or used in smaller-scale applications such as in automobile seats, night-vision systems, and electrical-enclosure cooling.

Rare Earth Oxysulfide materials are widely used as luminescent host materials of several commercially available phosphors such as red emitting phosphors for colour television picture tube, X-ray phosphors, and long afterglow pigments and storage phosphors for radiographic imaging.

Nanostructured materials containing RE elements either as major components or as dopants, possess sizes ranging from 1 to 100 nm in which most of the bio-molecular interactions take place so the incorporation of RE into nanoparticles allows their use in many different biomedical applications, like bio-imaging, bio-sensing, medical diagnostics, contrast enhancement, hyperthermia, magnetic resonance imaging (MRI), targeting, drug delivery, therapeutics and other tissue repair.

(2) The electronic structure of the Sulfides of the Rare-Earth metals is the result of a complex superposition of the influence of the unfilled 4f electron levels, which in themselves are unable to participate in the chemical bond on the external s-electrons and also on the d-electrons and the influence of the high electronegativity of Sulfur. In individual cases, this leads to the formation of metallic type of bond or ionic type of bond in addition to covalent bonds. The Sulfides for which metallic bonds and structures are characteristic are similar in properties to interstitial phases with their inherent high hardness, melting points and heats of transformation. On the other hand, Sulfide phases high in Sulfur having electronegativity possess semiconductor properties.

Every Lanthanide is most stable as an Ln_2S_3 sesquisulfide compound as Sulfur lacks the Oxidizing power to maintain a +4 oxidation state. These compounds adopt one of five distinct crystal structures dependent primarily on ionic radius and annealing temperature. By convention, these five crystal structures are referred to as the α, β, γ, δ, and ε phases. α-phase is an orthorhombic system, β-phase is a tetragonal system, γ-phase is a rather complex cubic structure, δ-phase is a very low symmetry monoclinic system while the ε-phase is a hexagonal system.

In general, the α-phase Sesquisulfide is the preferred structure for the lighter Lanthanides while δ and ε phases are primarily found in the heaviest Lanthanides. The α-phase exists for La through Dy, the δ-phase for Dy through Tm including Y, and the ε-phase for Yb and Lu.

The UV-vis absorption spectra of Rare Earth Sulfides do not depend on the crystal structure of Rare Earth Sulfides, but on their 4f electronic structures. The data showed that the optical band gaps of Rare Earth Sulfides were irregular, and the values ranged from 1.65 to 3.75 eV.

(3) There exist several methods for the preparation of Rare Earth Sulfides and Oxysulfides: (1) Traditional Sulfide fusion method in which Sulfuration of Rare Earth Oxide is carried out in the flux of $Na_2CO_3/K_2CO_3/K_3PO_4$ at high temperature which is widely employed on an industrial scale because of its high reliability, high luminescent properties and inexpensiveness. (2) Reduction of Rare Earth Sulfate by H_2 or CO (3) Sulfuration of Rare Earth Oxide by H_2S

or CS_2 in an inert atmosphere or in the presence of Carbon (4) Direct reaction between an Oxide or other precursors, such as Oxalate compounds and a Sulfide (5) Sulfuration of Rare Earth Oxide in the atmosphere of N_2 + H_2O + H_2S (6) Sodium Thiosulfate ($Na_2S_20_3$) is employed as a Sulfuring agent to prepare Oxysulfide (7) Solvothermal pressure-relief process employing Rare Earth Nitrates and Thiourea as precursors (8) Pyrolysis of Oxalate or Hydroxide in air at high temperature (9) Thermolysis of an organic complex in a stream of Argon gas containing Sulfur vapour (10) Induction melting in a current of Helium (11) Spray Pyrolysis technique using Rare Earth Chloride and Thioacetamide for thin film preparation.

It is observed that CS_2 is a more effective and strong Sulfurizing agent than H_2S and Rare Earth Sulfides could be prepared at relatively lower temperature by using CS_2. The Rare Earth Oxysulfide is an intermediate phase and can be converted into Rare Earth Sulfides by applying higher temperatures.

The traditional solid state synthetic techniques produce thermodynamically stable products usually by solid-solid reactions at temperatures in the neighborhood of 1000°C. In these reactions, the mechanism is generally not considered and there is little control over the formation of metastable intermediates. The Co-Precipitation method has been proved to have many advantages in comparison to the SSR method regarding the process conditions and the quality of the product. The COP process itself is instantaneous and leads to homogeneous stoichiometry in powders in comparison to the time consuming SSR, which needs regrinding of the raw materials to achieve the required homogeneity.

(4) Thermoelectric Properties of Rare Earth Sulfide have been studied and show many variations. LaS, La_3S_4, GdS, and Gd_3S_4 are predicted to be semimetals. SmS is predicted to be an indirect gap semiconductor while Sm3S4 is expected to behave similar to a heavily degenerate semiconductor.

In case of Cerium Sulfide, the semiconductor is an electrical insulator at the Ce_2S_3 end of the composition but its conductivity increases with increasing Cerium content, the Ce_aS_4 composition being semi-metallic.

The tetragonal (β) and cubic (γ) phases of La_2S_3 exhibit good thermoelectric properties. When doped with Ti, it was observed that for the β-La_2S_3 phase, resistance decreases with increase in temperature while for the γ-La_2S_3, it increases with temperature increase. It is seen that even mild variations in composition or synthesis techniques can grossly alter thermoelectric parameters.

2.4 Choice of Materials

The study and review of available literature in the field of Rare Earth Sulfides and its optical and thermoelectric properties shows that most of the research in this field has been done on Lanthanum Sulfide. However, most of the work has been carried out in order to understand its synthesis and stabilization of its γ-La_2S_3 phase which has major applications in thermoelectric conversion materials and as a potential candidate for IR windows and lenses. The photoluminescent properties of Lanthanum Sulfide have been studied using reflectance spectra obtained using calorimeter or using monochromator in which values were recorded at sub-zero temperatures while the thermoelectric properties are studied mostly for the γ-phase and somewhat for the β-phase.

Cerium Sulfide is the next widely studied Rare Earth Sulfide. Most of the studies carried out on Cerium Sulfide pertain to their synthesis, stabilization of phases, electron transport systems and thermoelectric properties. Photoluminescence studies using Cerium Sulfide as host material have not been done.

Studies on Gadolinium Sulfide are recent and most of them have been done on its synthesis by different methods and on their thermal and electrical properties in order to use them as potential thermoelectric conversion materials.

The studies on Yttrium sulfide provide information about the synthesis of its Oxysulfide and monosulfide phases which are very important phosphor materials since ancient times. Studies for the improvement of their luminescent properties and preparation of their nanoparticles have also been undertaken. The optical and thermoelectric properties of Y_2S_3 have not been conducted till date though, its synthesis has been studied.

Keeping in view all the above facts, it was decided to choose Lanthanum sulfide, Cerium sulfide, Gadolinium sulfide and Yttrium sulfide in this study and explore their optical and thermoelectric properties.

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