S Y N O P S I S

Of

The Ph.D. Thesis Entitled

OPTICAL PROPERTIES OF RARE EARTH DOPED PERVOSKITE MATERIALS

Submitted For The Degree

Of

DOCTOR OF PHILOSOPHY

By

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INTRODUCTION

Rare earth doped inorganic luminescent materials are well known for the emission of energy at discrete wavelengths in the electromagnetic spectrum. These luminescent materials are known as a phosphor. These phosphors have many uses in lighting devices such as cathode ray tubes (CRT), tri-phosphor fluorescent lamps, x-ray intensifying screens, etc. That type of phosphors have some other utilization in the display such as plasma display panels and field emission displays. The primary application of phosphors for LEDs (light emitting diodes) technology changes the history of the solid state lighting. LEDs are significantly energy-efficient lighting device with a long lifetime **[1]**.

Luminescent phosphors are solid, which transforms numerous types of energy into electromagnetic radiation over and above thermal radiation. The electromagnetic radiation emitted by a luminescent phosphor is usually ranging in between the UV to IR wavelength range. The luminescence from the phosphors can obtain by exciting the phosphor by various methods such as UV/ visible radiation (photoluminescence), by a beam of energetic electrons (cathodoluminescence), by x-rays (x-ray excited luminescence), etc. Thermoluminescence is one of the distinct manners to get luminescence, which is stimulation by the heating of phosphor, preliminary excited in a different way.

Luminescence measures the energy levels of the luminescence centers appeared inside the phosphors. The energy level of a luminescence center is defined as its characteristic state, which is associated with the physical nature of the center and to the energetic and dynamic processes that the luminescence center undergoes. A center keeps several different reserves of energy levels including electronic, vibrational, rotational, transitional, etc. In luminescence phosphors, the energy levels of attention are those, which are associated with electronic and vibrational transitions [2].

Perovskites are the compounds presenting the general formula ABO_3. Generally, in this structure, the A site is occupied by the larger cation, while the B site is occupied by the smaller cation. Perovskites are one of the most prominent families of materials displaying features suitable for distinct technological applications. Perovskite compounds such as $PbZrO_3$, $BaTiO_3$, $PbTiO_3$ are most commonly used as piezoelectric compounds. Thin films like $BiFeO_3$ show multiferroic behavior, while compounds like $SrTiO_3$ have shown excellent photocatalytic properties [3]. The origin of such characteristics lies in the structure of perovskites. The perovskite structure has corner connected BO_6 octahedra and 12 oxygen coordinated A cations located in between the eight BO_6 octahedra. The entire structure of the

octahedral connection results in a cubic lattice. The dependence on the ionic radii and electronegativity of the A and B site cations, tilting of the octahedra takes place, due to this tilting lower symmetry structures are observed in perovskite. As seen from the perovskite structure, B site cations are strongly bonded with the oxygen (or any other anion), while A site cations have comparatively weaker interactions with oxygen. Depending on the type of the cations occupying the lattice sites, these interactions could be modified to yield the different perovskite geometries.

Distinct degrees of tilting of the octahedra give rise to various crystal fields, which result in separate electronic and optical properties. The degrees of tilting may affect the band structure, electron-hole transport properties, photoluminescence, and dielectric behaviour **[4]**. From the point of view of photoluminescence, perovskite structures may offer significant advantages over the similar binary oxides for several reasons. Some advantages are perovskites could offer favorable band edge potentials, which allow various photo-induced reactions. The second advantage is A and B site cations in the lattice give a broader scope to design and alter the band structure as well as other photophysical properties. Perovskite phosphors have been studied to a vast area because of their promise for being visible light active **[5]–[7]**. Perovskites are broadly divided into simple (ABO_3 type) perovskites and complex perovskites (double, layered, etc.).

MOTIVATIONS

Rare earth activated perovskite phosphor materials have produced tremendous interest and considerable attention because of their easy synthesis processes, low cost and low environmental impact as well as favorable properties like luminescent, dielectric, semiconductor, catalytic, magnetic and fluorescent **[7]–[11]**. Rare earth elements are widely used in luminescence phosphors as activators which play a significant role in the host phosphor because of their emission color based on 4f–4f and 5d–4f transitions. Different perovskite phosphor has been developed to enhance the optical property by the varying different parameters such as synthesis method, different temperature, different doping ions, and varying doping concentrations.

OBJECTIVES AND SCOPE OF THE WORK

The major importance of the research work is to synthesis a luminescence phosphor that can give the efficient luminescence and having multiple applications in solid state

lighting devices. Inorganic double perovskite phosphor was selected as a host material for the obtaining the purpose and trivalent rare earth ions were taken for doping.

To achieve the aim of the research work, the following research objectives were carrying out.

- To synthesis undoped and rare earth doped perovskite phosphor, hydrothermal method and high temperature combustion method was taken as synthesis process. The phosphors were synthesized for different concentrations of different doping rare earth ions at temperature 900°C in combustion method.
- The structural study and phase formation of the synthesize phosphors were accomplished by x-ray diffraction (XRD). The bond formations of the phosphors were characterized by Fourier Transform Infrared spectroscopy (FTIR) and surface morphology was carried out by Scanning Electron Microscopy (SEM).
- The analysis of optical properties of the phosphor was carried out by photoluminescence (PL).

EXPERIMENTAL METHOD

Sr_2GdTaO_6, Sr_2GdNbO_6 and Sr_2CeNbO_6 were synthesized by combustion method, solid-state reaction method and hydrothermal method, respectively. The Sr_2GdTaO_6, Sr_2GdNbO_6 and Sr_2CeNbO_6 was doped by double rare earth ions, single rare earth ion and undoped, respectively. The samples were characterized by X-ray diffraction, FTIR and Photoluminescence.

RESULTS AND DISCUSSION

X-ray diffraction

Fig.1 shows XRD of the (a) Sr_2CeNbO_6, (b) Sr_2GdNbO_6: Eu (III) and (c) Sr_2GdTaO_6: Eu(III), Er(III). All the reflection peaks of the X-ray profile are indexed and lattice parameters are determined with the help of a standard computer program Powder-X. Tolerance factor of Sr_2CeNbO_6, Sr_2GdNbO_6 and Sr_2GdTaO_6 are 0.88, 0.81 and 0.83 respectively which was calculated using general formula of tolerance factor below: **[12]**

$$T_f = \frac{R_A + R_O}{\sqrt{2}\left(\frac{R_B + R_{B'}}{2} + R_O\right)}$$

Where, R_A, R_B, $R_{B'}$ and R_O are the ionic radii of A, B, B' and O respectively

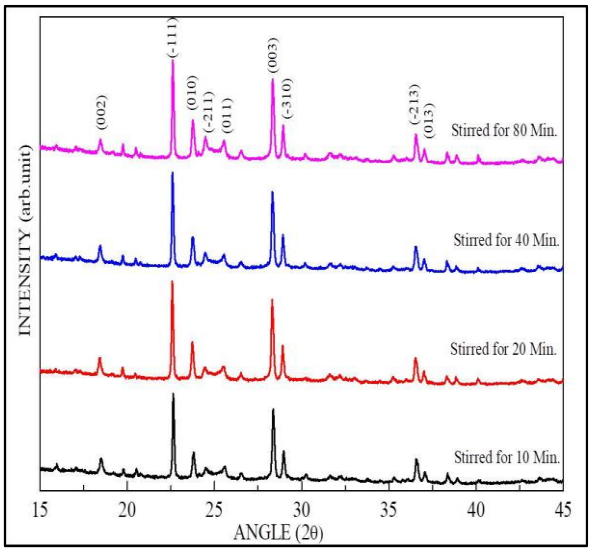

Fig. 1 (a)

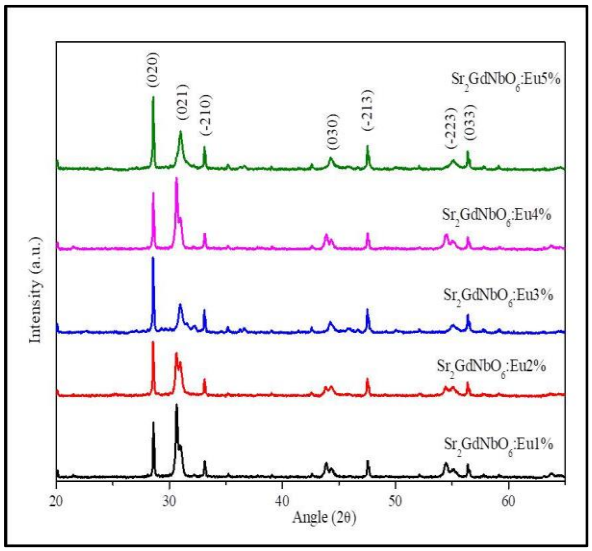

Fig. 1 (b)

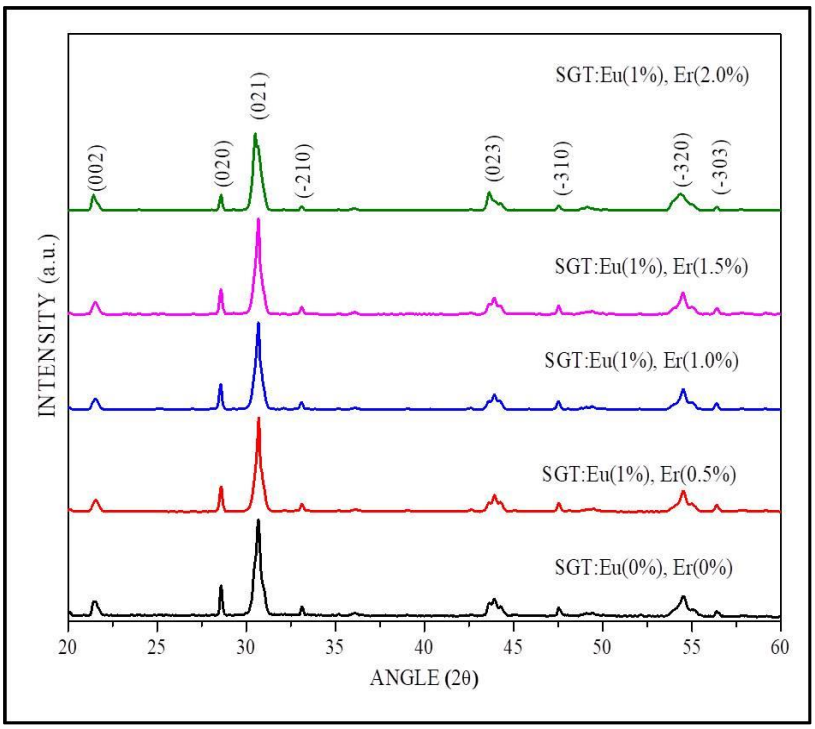

Fig. 1 (c)

Fig. 1 XRD of (a) Sr_2CeNbO_6 (b) Sr_2GdNbO_6: X%Eu^{3+} and (c) Sr_2GdTaO_6: 1.0 %Eu^{3+}, X% Er^{3+}.

FTIR

Fig. 2 shows FTIR spectra of Eu(III), Er(III) doped Sr_2GdTaO_6 and Sr_2CeNbO_6. In the FTIR spectra of Eu(III), Er(III) doped Sr_2GdTaO_6, the energy band at 380 cm^{-1} involves the asymmetric bending mode of the TaO_6 octahedra while the other strong broadband at 566 cm^{-1}can be assigned to the asymmetric stretching mode of the TaO_6 octahedra. A very small peak at 1627 cm^{-1} is of the carrier KBr.(H_2O)n. The absorption peaks at 992 and 860 cm^{-1} due to legend formation were assigned to stretching characteristics of $SrCO_3$ **[13]–[15]**.

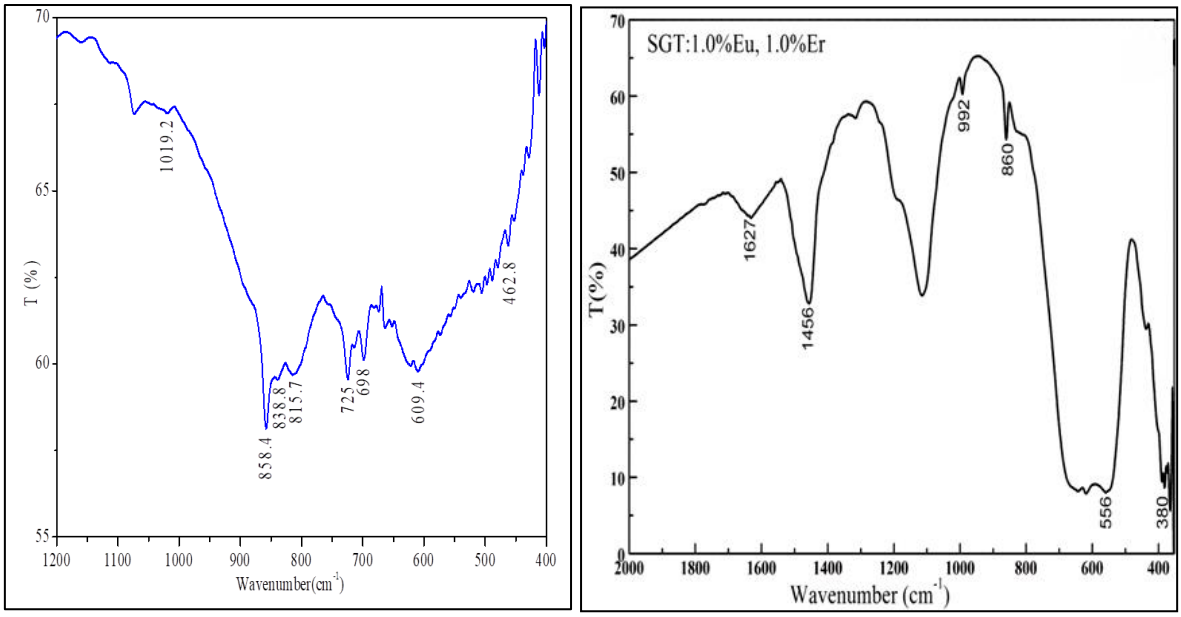

Fig. 2 (a) **Fig. 2 (b)**

Fig. 2 FTIR spectra of (a) Sr_2CeNbO_6 and (b) Sr_2GdTaO_6: 1.0 %Eu^{3+}, X% Er^{3+}.

For Sr_2CeNbO_6, the observed shoulder peak at 702 cm^{-1} also suggests the overlapping of Sr_2O_6 and NbO_6 stretching bands with the displacement toward higher frequencies of the NbO_6 bands. The symmetric stretching vibrations from 838.8 cm^{-1}, strongly support that the possible existence of edge connected Nb-O octahedral **[16], [17]**.

Photoluminescence

Fig. 3 shows photoluminescence of (a) Sr_2CeNbO_6 and (b) Sr_2GdTaO_6. Figure 3 (a) shows the excitation and emission spectra, recorded at room temperature of Strontium Ceria Niobate (SCN). These samples were excited at wavelength of 316nm. The broadening of the peak at 396nm indicates the nanocrystallinity of the SCN and these emission peaks attributes to the violet band. The emission spectra show two shoulder peaks at 451nm and at 469nm

[18]. Transition lines of europium and erbium are shown in fig. 3(b). A strong emission peak at approximately 610–630 nm can ascribe to the electric dipole transition of the $^5D_0$ - $^7F_2$ transition. The emission peak at approximately 580–600 nm is due to the magnetic dipole transition of $^5D_0$ - $^7F_1$. The substitution of Eu^{3+} at Sr^{2+} site in Sr_2GdTaO_6 is accompanied by Sr^{2+} ion vacancy (due to charge imbalance) and lattice strain (due to different ionic radius). The Eu^{3+} doped Sr_2GdNbO_6 samples exhibits visible emission bands around 582, 596 and 613 nm. These are assigned to the magnetic dipole (MD) and electric dipole (ED) transitions of europium $^5D_0$ - $^7F_1$, $^5D_0$ - $^7F_2$. The emission peak at approximately 580–600 nm is due to the magnetic dipole transition of $^5D_0$ - $^7F_1$, which is lower than that of intensity of $^5D_0$ - $^7F_2$ transition, confirms that the Eu^{3+} ions are located at the non-inversion symmetric sites **[19]–[21]**.

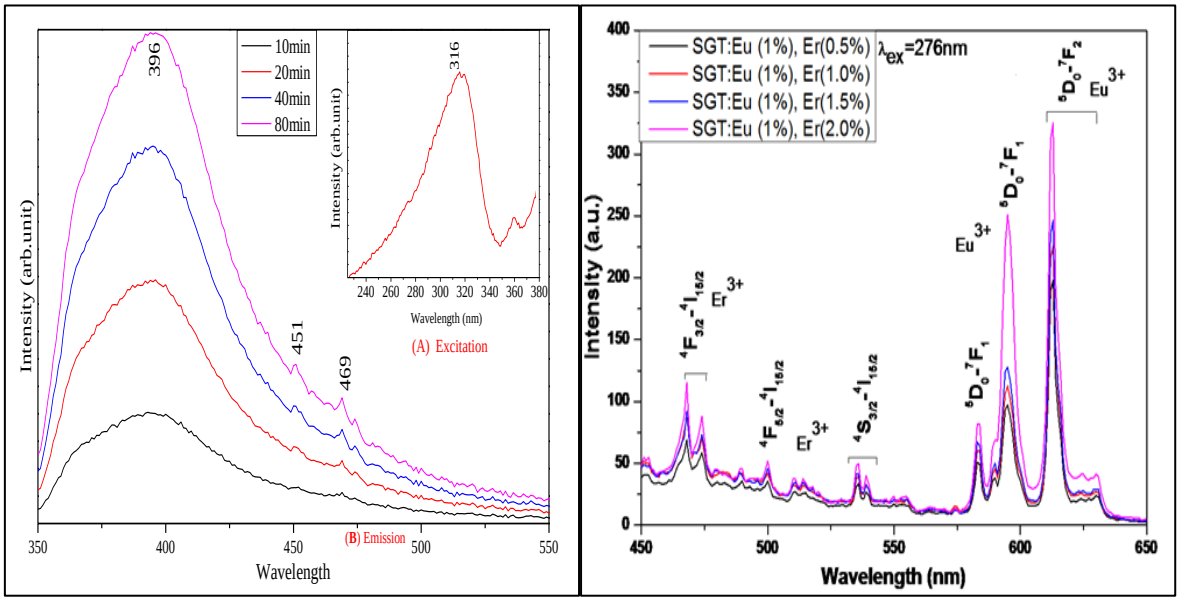

Fig. 3 (a) **Fig. 3(b)**

Figure-3 PL spectra of (a) Sr_2CeNbO_6 and (b) Sr_2GdTaO_6: 1.0 %Eu^{3+}, X% Er^{3+}

Brief Information of Proposed Chapters of Thesis

Chapter 1. Introduction

In this chapter, the basic concept of the luminescence phenomenon involved in the phosphor material will be discussed. The literature review of the perovskit materials with brief information of its phosphor application in luminescence will be explained. The objective of the thesis and the layout of thesis are explained in later part of this chapter.

Chapter 2. Synthesis Methods and Characterization Techniques

In this chapter, different synthesis methods will be explained with their principle, useful parameters, theoretical background and recent scope of the synthesis method in material science and technology. Different characterization techniques like X-Ray diffraction, Fourier Transformation Infrared Spectroscopy (FTIR), Photoluminescence and Scanning Electron Microscopy (SEM) are explained in detail.

Chapter 3. Synthesis and Photoluminescence studies of Strontium Cerium Niobate Nanophosphor

In this chapter, synthesis method and structural characterization of strontium cerium niobate oxide was explained in detail. The photoluminescence results of the prepared samples will be analysed for its applications in solid state lightning.

Chapter 4. Photoluminescence Studies of Europium doped Strontium Gadolinium Niobate Oxide

In this chapter, synthesis method and characterization of Eu^{3+} doped strontium gadolinium niobate oxide was explained in detail. The results of characterization and optical properties will be discussed in detail.

Chapter 5. Synthesis and Photoluminescence studies of undoped and Europium doped Barium Cerium Niobate Oxide

In this chapter, synthesis method and characterization of undoped and europium doped barium cerium niobate oxide was explained in detail. The results of characterization will be discussed in detail.

Chapter 6. Synthesis and Photoluminescence studies of undoped, single doped and double doped Strontium Gadolinium Tantalum Oxide

In this chapter, synthesis method and characterization of undoped and rare earth doped strontium gadolinium tantalum oxide was explained in detail. The result of

characterization and optical properties of the samples will be discussed in detail with require measurements and results.

Chapter 7. Conclusion

In this chapter, the brief summary of the outcome of the results are explained on the basis of the application of the prepared different double pervoskite phosphors.

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PROPOSED PLAN OF CHAPTERS IN THESIS

Chapter 1: Introduction and Literature Review

Chapter 2: Experimental Method and Characterization Techniques

Chapter 3: Synthesis and Photoluminescence studies of Strontium Cerium Niobate Nanophosphor

Chapter 4: Photoluminescence Studies of Europium doped Strontium Gadolinium Niobate Oxide

Chapter 5: Synthesis and Photoluminescence studies of undoped and doped Barium Cerium Niobate Oxide

Chapter 6: Synthesis and Photoluminescence studies of undoped, single doped and double doped Strontium Gadolinium Tantalum Oxide

Chapter 7: Conclusions

LIST OF PUBLICATIONS BASED ON THE RESEARCH WORK

Publications in Refereed Journals

1. Synthesis and Photoluminescence Studies of Eu(III), Er(III) Doped Strontium Gadolinium Tantalum Oxide.
   Verma Vishwnath, M.Srinivas, Nimesh Patel, Dhaval Modi, K.V.R. Murthy. Journal of Fluorescence, January 2016, Volume 26, Issue 1, pp 277–282.
2. Characterization of newly synthesized Strontium Cerium Niobate nano phosphor. M.Srinivas, **Verma Vishwnath**, Nimesh Patel, Dhaval Modi, D. Tawde, K.V.R. Murthy. Journal of Luminescence, Volume 147 (2014) 324–327.

Presentations in Conferences

1. Optical properties of Eu(III) doped strontium gadolinium niobate oxide
   Verma Vishwnath, M. Srinivas, Nimesh Patel, Dhaval Modi, and K. V. R. Murthy AIP Conference Proceedings **1731**, 110019 (2016); doi: 10.1063/1.4948040
2. Characteriztion and luminescence studies of Dysprosium Titanate by two synthesis methods, Verma Vishwnath, M. Srinivas, Dhaval Modi, Nimesh Patel, B.P. Shah, Invertis Journal of Science and Technology, Vol. 9, No. 2, 2016 ; pp. 67-71.