Exploring Lanthanum Sulphide Characteristics For Its Physical Properties

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Abstrac: The rare earth Lanthanum sulphide (La_2S_3) complex has been synthesized and characterized by X-ray diffraction (XRD),Optical Microscopy, Fourier transform infrared spectroscopy(FTIR) and Photo-luminescent measurements techniques. The synthesized samples have been doped with Europium (Eu) and Terbium (Tb) to study its physical properties. Under the photo excitation, these complexes exhibited characteristic emission similar to its metal ions. These investigations indicate that synthesized complexes have different energy levels than the doped lanthanide sulphide complexes. Presented data and detail examination of the synthesized complexes shows better characteristics than conventional Lanthanum sulphide. The properties of the undoped Lanthanum sulphide complex and doped samples were studied for exploring its possible thermoelectric applications.

Index Terms: Europium (Eu), Lanthanum sulphide (La_2S_3), Photoluminescence (PL), Terbium (Tb), Thermoelectric

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1 INTRODUCTION

His is well known that the rare earth elements have interesting physical and chemical properties. The excited states of Europium and Terbium complexes have strong fluorescence emission, large stokes' shifts, narrow emission profiles and long fluorescence lifetimes [1–4]. These have been widely used in many aspects for various physical devices [5–11]. Conversely, the application of lanthanide based luminescence suffers from serious draw-backs: The low absorption coefficients because of the f–f electronic transitions are forbidden and the efficient non-radioactive deactivation of their excited states by OAH oscillators such as water [12]. These evident problems can be avoided for the lanthanides complexes using mentioned strategies (I) addition of effective photo-sensitized ligands, (II) vibrational frequency suppression by high vibrational CAH & OAH bonds [13] and (III) forming asymmetric co-ordination structures for better transitions of electric dipoles [14,15]. Using these pathways, the lanthanide ions serves as an antenna or sensitizer. Described processes of these complexes will absorb the excitation light energy and transfer the energy from its lowest triplet state energy level (T1) to the resonance level of lanthanides [16]. Different types of Ligands like the macro-cyclic and the macro-bicyclic have been extensively used for these purposes [17–20]. This type of ligands have drawn much attention in present times, mainly due to possession of spheroidal cavities and binding sites that are hard. Hence they stabilize its complexes and shield the encapsulated ion from interaction with the surroundings[21]. Among these numerous compounds which have demonstrated their potential use in many applications [22–24], amide type compound are more popular in preparing the lanthanide complexes because they possess strong luminescent properties. It is expected that the amide type compound, which are flexible in structure and have terminal group effects [25], will shield the encapsulated lanthanide ion from interaction with the surroundings effectively, and thus help to achieve strong luminescent properties. In the present work, lanthanum sulphide complexes have been synthesized from the lanthanide nitrates using a novel ligand, 2-4-tetradecyloxybenzylidinecarbothioamide, and studied the luminescent characteristics after doping this complex with Europium (Eu) and terbium (Tb). The complexes have been studied by XRD and FTIR results. Under the photo excitation, the Eu & Tb doped complexes which exhibit the characteristic emission of corresponding lanthanide ions have been correlated with physical properties of the lanthanide complexes.

2 Materials and Methods

2.1 Experimental Characterization

4-n-tetradecyloxybenzaldehyde [26] and 2-4-tetradecyloxy benzylidinethiosemicarbazide[27],[28] were as prepared according to the literature methods. Other chemicals were obtained from commercial sources and used without further purification. The La^{+3} ion was determined by EDTA titration using xylenol-orange as an indicator. Carbon, nitrogen and hydrogen were determined using an Elemental Vario EL. FTIR was recorded in the 4000 – 200 cm^{-1} range using KBr pellets on a Nicolet Nexus 670 FTIR spectrometer. XRD measurements were carried out on Philips Xpert MPD X-Ray Diffractometer having 2θ range from 5 to 70. Photoluminescence Spectra were obtained on SHIMADZU RF 6000 spectrofluorophotometer equipped with Xenon lamp as an excitation source at room temperature. ^1H NMR spectra were measured on a Varian Mercury 300 spectrometer in d-DMSO solution, with TMS as internal standard. Fluorescence quantum yields were determined by using eosin solution (U = 0.190 in water) as standard for the Eu^{3+} complex, and quinine sulphate (U = 0.558 in 0.5 mol cm^{-3} H_2SO_4) for the Tb^{3+} complex.

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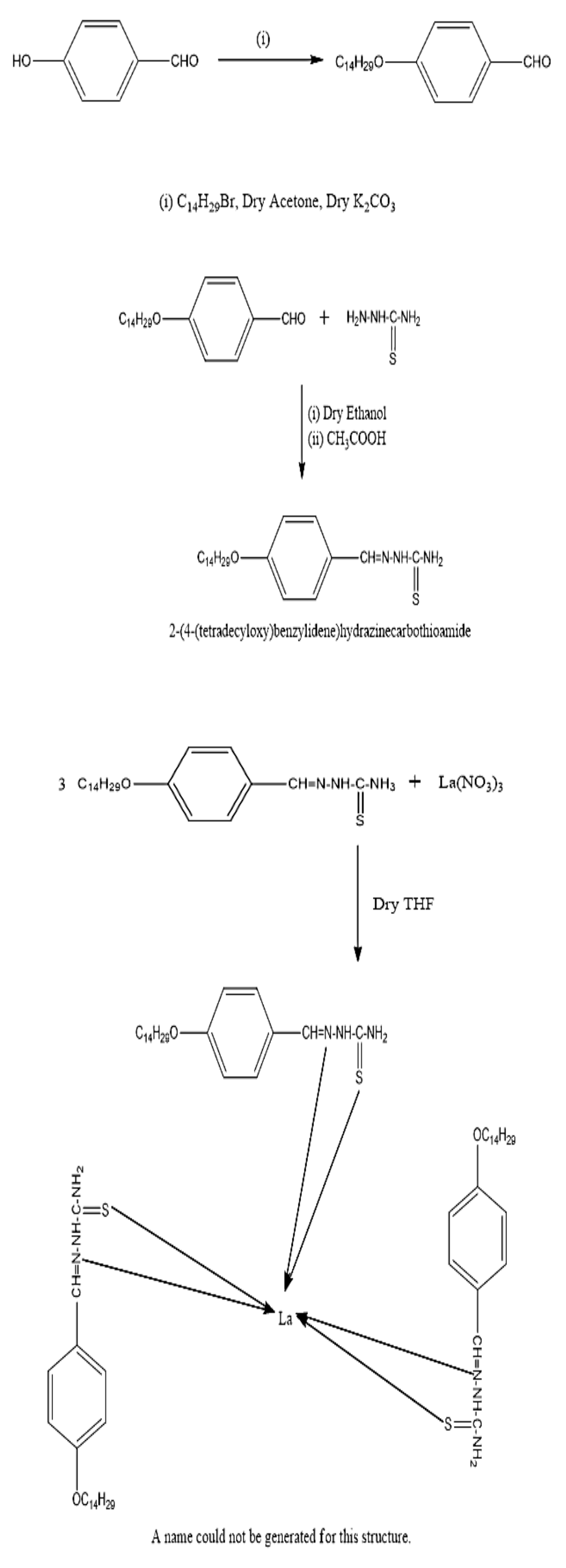
2.2 Procedure

(a) Synthesis of 4-n-Tetradecyloxybenzaldehydes: These were synthesized by alkylation of 4-hydroxybenzaldehyde using the reported method of Vyas and Shah [31]. 0.1 Mole 4-Hydroxybenzaldehyde, 0.15 mole of anhydrous K_2CO_3 and 0.15 mole of corresponding 1-bromoalkane were added to 60 ml dry acetone. The mixture was refluxed on water bath for 10 to 12 hours. Completion of the reaction was checked by TLC (70% Ethyl acetate-hexane). The whole mass was added to cold water and was extracted with ethers. Ether extract washed with 5% solution of NaOH(aq) (25 ml x 3), water (25 ml x 3), brine and was then dried over anhydrous Na_2SO_4. Reaction mass was purified by column chromatography using silica (100-200 mesh size) and 10% ethyl acetate-hexane as eluent furnished the product. Yield: 59-64%.

(b) 4-n-tetradecyloxybenzylidinethiosemicarbazide synthesis :
The corresponding 0.1 Mole of thiosemicarbazide was dissolved in dry ethanol. The solution was added drop wise to the round bottom flask containing 0.1mole of 4-n-decyloxybenzaldehydes [a], which was previously dissolved in ethanol and few drops of acetic acid. After mixing them the content of the flask heated under reflux for 6-8 hours. The crude product was repeatedly crystallized from the ethanol. Yield in general is 40-45% and M.P is 92–94 °C. The Elemental Analysis results for $C_{22}H_{37}ON_3S$ were found to be: C- 67.5; H-9.4; N- 10.74 S- 8.18 whereas the Observed results are found to be: C- 67.61; H- 9.36; N- 10.71, S- 8.16%. 1H NMR spectrum (400 MHz) results are: δ 0.88 (t,3H,-CH_3), 1.2-1.4 (m, 22H, 11 x -CH_2-), 1.76(quant. 2H, Ar-O-C-CH_2-) 3.90-4.08 (m, 2H, of Ar-O-CH_2-), 7.06 (m, 2H of ArH), 7.83 (d, 2H, ArH), 8.54 (s, 1H-CH=N-), 2.0(-NH) ,8.56 (-NH_2).

(c) Synthesis of the lanthanide complex [Tris {4-n-Tetradecyloxybenzylidinethiosemicarbazide} lanthanum]: A mixture of the 4-n-tetradecyloxybenzylidinethiosemicarbazide ligand (0.6 mmol) in dry MeoH solvent mixture was stirred for 10 min at room temperature, following which a dry THF solution of $La(No)_3.6H_2O$ (0.2 mmol) was added drop wise, and the reaction mixture was stirred subsequently for 48h. The precipitates formed were filtered off, washed with MeoH , dried over anhydrous Na_2SO_4 and purified by ethanol. After the successful synthesis of Lanthanum sulphide complex as shown in step (c), a further procedure was followed for preparing doped Lanthanide complex. $Eu(No)_3.6H_2O$ (0.01 mmol) and $Tb(No)_3.6H_2O$ (0.01 mmol) were added as dopant sources respectively during the procedure shown in step (c) to obtain the doped Lanthanum sulphide complexes. Analytical data and values of the complexes are given. All the complexes are near to white colour powders and stable in air.



3 RESULT AND DISCUSSION

Experiment and characterization has been performed by standard instrumental setup and procedure as given in previous section for the further discuss.

3.1 Infrared spectra

IR peaks as shown in Fig 2 for the complexes are reported here. The complexes have IR spectra, of which the characteristic bands have similar shifts (see Table 1), suggesting a similar coordination structure of complexes.

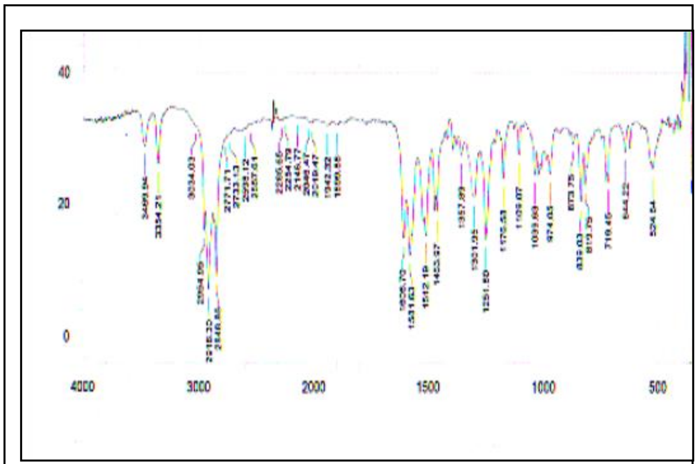


Fig. 2. Infrared spectra for the La2S3 complex

The IR spectrum of the free ligand L shows bands at 3469(N-H), 2916(C-H), 1606(CH=N), 1581(C=N), 314(Ln-N), 227(Ln-S), which are attributable to the stretch vibration of the azomethine group [CH=N] and (C=N), respectively. In the complexes, the low-energy band remains unchanged, but the high-energy band red shifts to about 1606 cm^{-1} (v = 38 cm^{-1}) as compared to its counterpart for the "free" ligand, thus indicating that only the nitrogen atom of [CH=N] takes part in coordination to the lanthanide ions. The characteristic frequencies of the coordinating nitrate groups (C_{2v}) appear at ca 1484 cm^{-1} (v_1), 1300 cm^{-1} (v_4), 1045 cm^{-1} (v_2) and 812 cm^{-1} (v_3), and the difference between two strongest absorptions (v_1 and v_4) of the nitrate groups is about 180 cm^{-1}, clearly establishing that the NO^{-3} groups in the solid complexes coordinate to the lanthanide ion as bidentate ligands [30,31]. Additionally, no bands at 1380, 820 and 720 cm^{-1} in the spectra of complexes indicates that free nitrate groups (D_{3h}) are absent. In addition, broad bands at ca. 3395 cm^{-1} indicate that water molecules are existent in the complexes, confirming the analysis results.

3.2 X-Ray Diffraction spectra

The XRD patterns are shown in Fig. 3 for La_2S_3 powders and found that samples can be indexed as cubic phase (JCPDS 25-1041). These XRD patterns prepared by the describe method of lanthanide complex consist of γ-La_2S_3. The results show that the samples have a better crystallization and resembles to the lanthanum structure having γ phase.

TABLE 1

FTIR PEAKS OF LANTHANUM SULPHIDE COMPLEX

Compounds	N-H	(CH=N)	C=N	C-H	La-N	La-S
Lanthanum Sulphide Complex	3469	1606	1581	2916	314	227
Eu Doped Lanthanum Sulphide Complex	3470	1605	1582	2915	315	225
Tb Doped Lanthanum Sulphide Complex	3468	1604	1580	2914	316	226

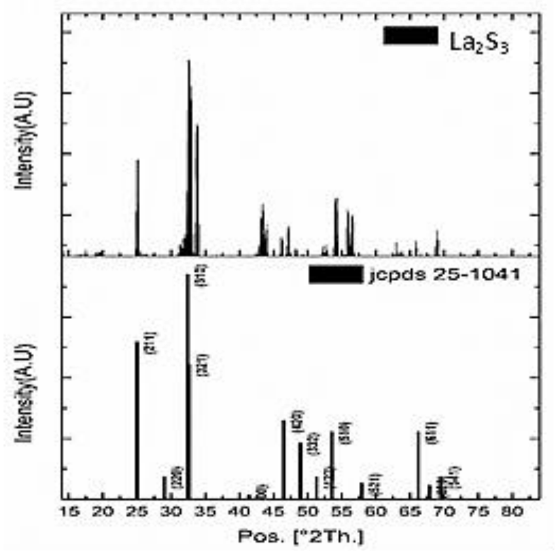


***Fig. 3**. X-ray Diffraction pattern for La_2S_3 complex*

3.3 Morphology

As shown in Fig. 4 morphological image of doped La_2S_3 of prepared samples consist of mainly mixed particles as seen from the images. In accordance with XRD peaks and analysis further it is seen that the phase of La_2S_3 is in the stoichiometric composition. Based on the morphological results, the better atmosphere condition can be investigated to find the effect of decomposition temperature on the powder preparation.

***Fig. 4.** (a) Optical image of doped Lanthanum sulphide complex (b) Magnified image of doped Lanthanum sulphide complex*

3.4 Photoluminescence

The luminescent properties of the Lanthanum sulphide complex and doped Lanthanum sulphide complexes with Eu and Tb were investigated. The excitation and emission spectra were recorded at room temperature under laboratory conditions. The Fig. 5 shows properties for Eu & Tb doped Lanthanum sulphide complexes. For the undoped sample, there is no significant change in emission peaks. For the doped samples the excitation wavelength is found to be 246 nm. Under this excitation, the strong emission peaks for doped sample are observed at 398 nm and 470 nm respectively. The excited state is independent of the doped complexes which is similar to other lanthanide structures.

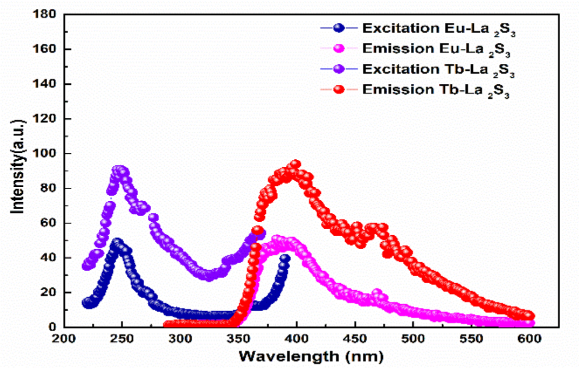


Fig. 5. *The Photoluminescence emission spectra for doped Lanthanum sulphide*

Further, the thermoelectric properties for the γ-phase of the doped Lanthanide were similar with reported materials. It is interesting to characterize temperature dependent analysis for its behavioural understanding. The thermoelectric measurement in the temperature range of 250 ̊K to 800 ̊K are found to have the values of 30 uVK^{-1} to 80 uVk^{-1} for lanthanide complex which are in accordance with reported values by other researchers [Michihiro ohta, et.al 2005].

4 CONCLUSION

In the present results and discussion, the novel Lanthanum sulphide with doped Eu and Tb can form a stable solid complex. These Lanthanide complexes are confirmed by XRD pattern and IR spectra of as prepared and doped samples. It is noteworthy that the characterization of these complexes demonstrates stoichiometric composition. Thus, the lanthanum complex could be effectively synthesized and characterized by instrumental analysis. The luminescent properties of the Eu and Tb doped complexes were investigated and they exhibit the characteristic luminescence of Europium and Terbium ions. The state of energy level indicates that the doped Lanthanide matches better to the energy level of the prepared lanthanide complex. It indicates that the exited state of the efficient ions can absorb and transfer energy to the lanthanide complexes. Also, thermoelectric exploration shows that these complexes can be used for possible thermo power applications.

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