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**INDO AMERICAN JOURNAL OF
PHARMACEUTICAL SCIENCES**Available online at: <http://www.iajps.com>**Research Article****LANTHANUM OXIDE NANO PARTICLES SYNTHESIS AND
THEIR LUMINESCENT PROPERTY****Mohd Syeed Shah¹ and Ghulam Mohammad Jan²**¹ Department of Chemistry, Amar Singh College, Srinagar J& K (India)² Department of Chemistry, Govt. Degree College for Boys, Anantnag, Jammu & Kashmir
(India)**Abstract:**

Novel photo luminescent materials were prepared from the reaction containing two steps: first preparation of complex $[La(acacen)(NO_3)(H_2O)]$ (where acacen= acetylacetonatoethylenediamine. Then the precursors were calcination. In first step, complex synthesized using a methanolic solution of $La(NO_3)_3$ and acetylacetonatoethylenediamine. Through the oxygen functionality was evidenced by the sharp enhancement of laser induced luminescence and the appearance of peaks in specific regions of the spectra of the lanthanides. Raman spectroscopy indicated that the acacen maintained its structure within the material and verified the complexation with the lanthanide by TEM demonstrated the coverage of the acacen surface by the lanthanide. Although some limited work has been published on europium and acacen. This is the first study encompassing the majority of the luminescent lanthanides, taking full advantage of their capabilities including advanced electronic structure, raman and visible luminescence in a variety of colors.

Keywords: luminescent, Raman spectroscopy, TEM,**Corresponding Author:****Mohd Syeed Shah,***Department of Chemistry,**Amar Singh College,**Srinagar J& K (India).**E Mail: prof.m.syed@gmail.com*

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INTRODUCTION:

The use of lanthanides as probe ions and signal transducers in sensing applications is widely accepted, as they can often provide sensitivity in the parts per trillion ranges and lower [1]. Lanthanides comprise the largest naturally occurring group in the periodic table, and their similarities arise from a resemblance in the electronic configurations of the elements which consists of the xenon levels, filled 6s sublevel, and a varying amount of electrons occupying the 4f sublevel. Generally, the optical absorption and emission spectra of the ions formed by the triply charged free lanthanide ions consist of very narrow lines (0.1 nm-0.01 nm). Quantum mechanical calculations have indicated that the energies and the radial extensions of the 4f eigenfunctions dramatically drop at the beginning of the lanthanide series so that the maxima of the 4f eigenfunctions no longer exceed those of the 5s and 5p eigenfunctions [2]. Thus, the 4f orbitals are not the outermost shell, but are largely shielded from the external environment by the filled 5s and 5p shells. Since these 4f orbitals are shielded, the electrostatic field in lanthanide complexes, induced by coordinating ligands causes only small perturbations in the 4f electrons energy levels. As a result, the lanthanides within the complex retain their semi "atomic" nature which gives the characteristic narrow bands observed in lanthanide emission and excitation spectra [3,4]

These narrow features often result in analyses which are both selective and sensitive. The spectral position and intensity of these features are dependent on the environmental symmetry of the lanthanide complex [5]. As a result of this unique chemistry, lanthanides have been used for a variety of purposes such as catalysts, optical components, alternatives to radioisotopes, and as scientific probes for a wide variety of phenomena including probes of temperature [6,7] and structure (both electronic and crystalline) [8,9]. Trace analysis techniques based on lanthanide spectroscopy have also found application for detection of many compounds often at parts per trillion (ppt) levels or lower [10-12].

Complexation by organic ligands was found to significantly enhance the luminescence intensity of the tripositive lanthanide, Ln(III) ions [1]. This enhancement was explained by a ligand to metal energy transfer mechanism [12]. The proposed mechanism indicates that when an excited triplet state of a coordinating ligand overlaps an excited lanthanide electronic level, the lanthanide luminescence is effectively pumped by the large cross section molecular absorbance of the ligand,

rather than by the weak lanthanide absorbance. This process is believed to be much more efficient than direct absorption of light by the lanthanide since the lanthanides themselves exhibit low molar absorptivity's. Proper ligand choice is therefore crucial in the preparation of lanthanide complexes.

acacen was selected as a coordinating ligand for the lanthanides because of its unique structural, electronic and optical properties [13], as well as its high mechanical strength [14]. The complexation with acacen would allow the lanthanide to be incorporated into a wide range of materials including field emission displays, sensors[15], thin film transistors , touch panels [31], electrodes for optoelectronic devices , fuel cells , solar cells, and batteries . acacen was chosen over graphene because the intrinsic oxygen was needed to coordinate with the lanthanide. Limited studies have addressed the luminescence properties of acacen [16-17]. However, the success has been limited by a lack of uniformity in treatment techniques and the inability to make materials that are strongly luminescent. The ability of graphene to quench the luminescence of fluorescent dyes has also been reported . Lanthanides, on the other hand, have unique and strong luminescence properties. Combining the luminescence properties of lanthanides with the structural properties of acacen was a natural step towards the creation of luminescent acacen materials.

EXPERIMENTAL:**Material and characterization**

All chemicals and solvents were reagent grade or better, obtained from Merck, and used without further purification. Infrared spectra (4000–250 cm⁻¹) of solid samples were taken as 1% dispersion in KBr pellets using a JASCO FT-IR 460 PLUS. Transmission Electron Micrographs were obtained by placing small amount of powder into a vial of Methanol and ultrasonicated them using a Branson B-12 80 watt ultrasonic cleaner for 5 minutes. Once the particles were suspended, a small amount of liquid was drawn off using a pipette and placed dropwise onto a holey carbon film copper TEM grid purchased through SPI Supplies and allowed to air dry on clean filter paper. Prior to use, the holey carbon film TEM grids were pre-cleaned with de-ionized water to remove as much adsorbed silicon and other detritus from SPI Supplies manufacturing process. Raman samples were analyzed on an aluminum substrate using a Jasco NRS-3000 (Jasco Inc. Easton, MD) at 229 nm, 532 nm, and 785 nm. Samples were analyzed using a 2400 groove/mm grating with slits set to 100 microns and integration

times between 20-30 seconds depending on the sample.

Synthesis of [La (acacen) (H₂O) (NO₃)₃]

Synthesis of [La (acacen) (H₂O) (NO₃)₃] to a methanolic solution (10 ml) of La (NO₃)₃ (0.1 M) was added drop wise aqueous solution acetylacetonatoethylenediamine (0.1 M). The resulting solution was stirred at 55–60°C for 2h. The solid (desired product) was collected by suction filtration, washed with MeOH solution, then air dried (Yield %34). Anal. Calc: C, %32. 22; H, %5.86; N, %9. 4). Found: C, 32.12; H, 5.73; N, 9.54. IR (KBr, cm⁻¹): 3419 and 2928 ν(CH), 1644 ν(N-O), 1530-ν(C=C) and ν(C=N), 3454 i(O-H), 1303 ν(conjugated NO₃⁻), 900 ν(C-O)[18]

Synthesis of nanoparticles La₂O₃

Lanthanum oxide nanoparticles were prepared from [La (acacen) (H₂O) (NO₃)₃] using the physical method. First 1.0 g of compound dissolved in oleic acid solution (5mL) as a surfactant, then calcinated at 600°C and 900°C for 4h, to get La₂O₃ nanoparticles respectively. The final products were collected and washed with distilled water and absolute ethanol several times, dried in air and kept for further characterization [18].

RESULT AND DISCUSSION:

As expected, the europium samples exhibited the greatest intensity (visibly red/orange) and interpretation of its spectral line patterns was easiest (based on number of peaks). Europium benefits from being 1 electron short of a half full shell making it easy for it to accept the electron for strong energy transitions. The conversion from europium oxide to lanthanum nitrate was confirmed spectroscopically by a comparison with the spectra published by Buezli and Yersin [19]. Europium samples were evaluated using excitation wavelengths of 465.8 nm, 472.7 nm, 488.0 nm, and 514.5 nm. Excitation at 465.8 nm was determined to have the highest luminescence intensity and give the best peak resolution, confirming previously published results [5]. Complexation between the lanthanide and acacen was determined by spectral changes and increased luminescence when compared with the luminescence of the lanthanide and the acacen by themselves. The lanthanum acacen sample with the highest luminescent intensity was that prepared with 1.5 g of europium nitrate. The sample prepared with 0.5 g showed no spectral difference from the acacen sample. This trend of highest luminescence for the complexes prepared 1.5 g of lanthanide nitrate was followed for all the lanthanides examined in this study, and it was these samples that were chosen for full characterization.

TEM images were also collected for the lanthanum acacen. High resolution analysis of the lanthanum acacen particles shows limited acacen crystallinity. EDS data collected on the sample found the expected lanthanum, oxygen, and carbon. The X-ray mapping illustrated the strong correlation of the europium being bound to the acacen particles. The lower magnification TEM images for the terbium acacen particles sample showed the acacen present as mostly planar flakes. The high magnification TEM indicated that the particles exhibited good crystallinity of the lanthanum as the atomic lattice features of the acacen particles were clearly visible. The EDS spectra confirmed the presence of terbium, oxygen, and carbon in the sample while X-ray mapping showed the uniform coverage of the terbium on the acacen particles.

Raman analysis was performed on each of the lanthanide nitrates, the lanthanide acacen materials and the acacen oxide itself. The raman was primarily used to verify the binding of the acacen with the lanthanide. The raman spectra also confirmed the acacen maintained its structure within the lanthanide based materials as indicated by the bands at 1400 cm⁻¹ (D band) and 1600 cm⁻¹ (G band) region of the spectra. The raman spectra of the terbium species. In addition to the acacen characteristics, the raman also indicated that there is still evidence of some residual nitrate co-ordinated within the materials.

CONCLUSION:

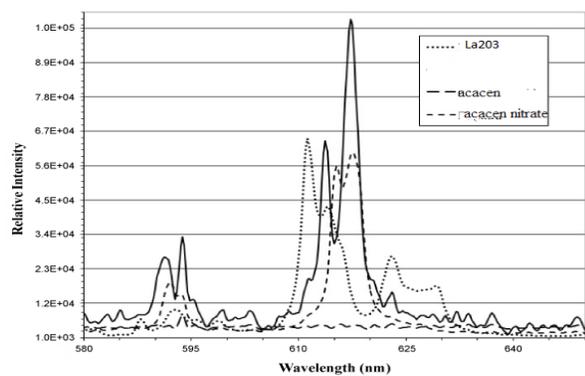
The ability to co-ordinate luminescent lanthanides with acacen has been established, providing a new set of building blocks for future generations of nanomaterials. The combination of mechanical strength and electronic properties provide by the acacen enhanced by the strong luminescence and magnetic properties of the lanthanides will provide materials for sensors and displays that can be incorporated into fabrics, battery materials and fuel cells with built in residual life indicators, and many other applications. The inclusion of several lanthanides in this study will allow the materials to be much more tunable to color, and magnetism that provide a wider range of chemical applications that could expand the fields of supramolecular chemistry.

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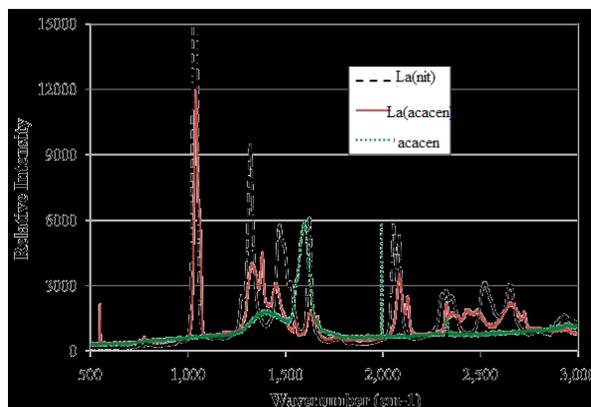
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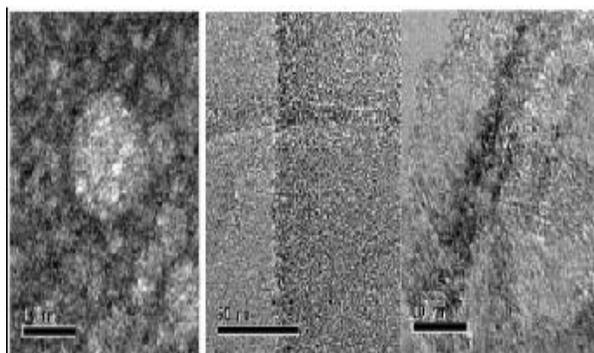
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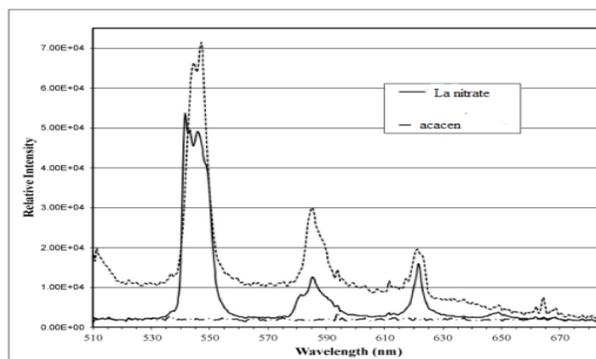
(a)



(b)



(c)



(d)

- (a) Spectra of the La, acacen , and the La(acacen) showing the changes that occur with co-ordination. The La and acacen are shown on the right axis for better comparison. Excitation wavelength 488 nm.
- (b) Spectra of the La(nit), and the (acacen) showing the changes that occur with co-ordination. The La and acacen are shown on the right axis for better comparison. Excitation wavelength 514 nm.
- (c) TEM images of (rt) La, acacen, La₂O₃(ctr) acacen
- (d) Raman images of La (nitrate), acacen and La acacen