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Facile fabrication of porous La doped ZnO granular nanocrystallites and their catalytic evaluation towards thermal decomposition of ammonium perchlorate
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The present article encompasses the synthesis of pure and La doped ZnO for thermal catalytic decomposition of Ammonium Perchlorate (AP). In the studied mesoporous materials, the lowering of Higher Temperature Decomposition (HTD) of AP was observed by 105°C in presence of ZnO. Targeted further lowering of HTD in presence of dopant La was insignificant due to reduction of BET surface area of the catalysts.

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Abstract:

The present article expresses synthesis, characterization and catalytic activity of pure and La doped ZnO (La-ZnO) towards thermal decomposition of Ammonium Perchlorate (AP). The catalytic materials (La-ZnO) with 0 to1.00 % of doped La were synthesized by simple co-precipitation method and thoroughly characterized by several spectroscopic techniques like FT-IR, XRD, UV-Visible, PL, SEM-EDS and BET analysis. The XRD pattern of synthesized materials displayed wurtzite ZnO structure

and the SEM images of the materials showed granular morphology where gradual increase in particle size and crystallite size was observed to be increased with increase in doped La concentration. The BET surface area of the materials was 28.203 to 15.830 m²/g and exhibited mesoporous nature. In catalytic studies for thermal decomposition of AP, the pure ZnO catalyst offered single stage decomposition of AP along with lowering high-thermal decomposition (HTD) temperature of AP by 105 ^oC. However, La doped ZnO showed slightly lower activity due to promotion of NO formation in oxidation of ammonia generated on initial decomposition of AP and decrease in BET surface area.

Keywords: La doped ZnO, Porous granular nanocrystallites, Thermal decomposition, Ammonium perchlorate

1. Introduction:

Ammonium perchlorate (AP) is a widely used oxidizer in composite solid propellants (CSPs) and contributes more than 60% of the total weight of a CSP. The combustion behavior of the AP-based CSP can be optimized by controlling parameters like particle size and thermal behavior of AP. [1-5] The enhancement of burning rate of propellant can be achieved by either reducing the particle size of AP or decreasing its thermal decomposition temperature (TDT). In order to enhance thermal decomposition properties of AP by reducing its higher decomposition temperature (HDT), a broad spectrum of transition metal oxide (TMO) catalysts like Co₃O₄, NiO, Fe₂O₃, TiO₂, CuO and CoO [6-12] have been employed by researchers. The lower the HTD temperature, the shorter is the propellant ignition delay time and the higher is the burning rate. [13] The two proposed mechanisms to reduce HDT of a CSP by added TMO catalyst in a minute amount (up to 5 % of wt of AP) includes formation of easily melting eutectics between metal oxides and AP [12]; and generation of *Vo*-related defects to release oxygen for enhanced burning rate.[14]

The excellence of ZnO as a promising TMO catalyst, even at industrial scale, is attributed to its exceptional reactivity, non-toxicity, low cost, versatile formation and thermal stability. [15-16] Recently, various nanostructures of ZnO have been focused as catalysts for thermal decomposition of AP and found to be very effective in lowering HTD of AP. Various modified synthetic methods are found to be effective to get superior physical and catalytic properties of ZnO. In current literature, Fazli et al. have reported bioactive egg shell membrane aided

synthesis of ZnO [17], whereas, Zeng et al. have demonstrated the exposed (2-1-1-0), (001), (0-0-0-1) facets of ZnO for lowering HTD and activation energy for AP combustion. [18-20] In addition to this, Wu et al.have coated ZnO on carbon black [21] to further reduce the HTD of AP. In another distinguished effort, Zeng et al. [22] have also reported ZnO/AP shell-core nanocomposites prepared by liquid deposition method to overcome the agglomeration of metal oxide (MOX) nanocatalysts on mechanically mixing with AP. The sodium carboxymethyl cellulose as a crystal growth modifier was utilized by Feng Gao et al. [23] and Yin et al. [24] to afford hollow and broccoli-like superstructures of ZnO respectively with advanced catalytic activity. Hydrothermally processed Twin-Cones [14] and gas-growth method synthesized nanospheres of ZnO are also reported in literature. Apart from pure ZnO as a catalyst, researchers have also studied N-doped ZnO [25-26] and NiO-ZnO composites [27-28] for synchronized catalytic effect of two transition metal ion centers. Also, there are few reports where ZnO nanoparticles are used as additives in AP-HTPB based CSPs to evaluate their effect on thermal and ballistic properties of propellants. [29-30]

The noble metal incorporated ZnO nanohybrids are equally noteworthy as it is found to enhance photocatalytic efficiency of ZnO. M. Zahouily et al. have synthesized mesoporous Ag/ZnO quasi-spherical nanohybrid material using simple and green route *via* sodium alginate media. [31] In an another highlighting work, Y. Li et al. have successfully synthesized Au ZnO hybrid nanoparticles with hexagonal pyramid-like structure exhibiting superior photocatalytic efficiency than pure ZnO nanocrystals. [32]

Doping with rare earth elements provides enhanced optical properties of ZnO materials and Lanthanum (La) doped ZnO (La-ZnO) materials shows excellent gas sensitivity and photocatalytic activity. [33] Also, there are some distinguished reports on use of copper-rare earth metal oxide (REMO) composite catalysts for oxidation of NH_3 . [34-37] The mechanism of thermolysis of AP consists formation of adsorbed and gaseous NH_3 and $HClO_4$ by proton transfer which react by radical reactions producing N_2 , H_2O along with oxides of chlorine and nitrogen. [38] Moreover, Singh et al. [38] and Patil et al. [39] have exhibited significant lowering of TDT of AP by using rare earth metal oxide (REMO) catalyst as a consequence of ability of the REMO to further oxidize ammonia to N_2 .

Taking into consideration the merits of both ZnO and REMO in advanced AP degradation applications, herein we report the synthesis and catalytic application of pure and lanthanum-doped ZnO (La-ZnO) towards the thermal decomposition of the ammonium perchlorate with reduced HTD value.

2.0 Experimental:

2.1 Materials:

Zn(OAc)₂²H₂O and La(NO₃)_{3.}6H₂O (Analytical Grade, Merck India Ltd.) were used as Zinc and Lanthanum sources respectively. Pottasium hydroxide (KOH) was procured from Merck India (Analytical Grade). The AP used without any further processing or purification in this study and was provided by the High Energy Materials Research Laboratory, India. All solvents were used for this work were of Analytical Grade, purchased from Thomas Baker, India.

2.2 Preparation of catalysts:

The simple co-precipitation method was used to prepare pure and La doped ZnO (La-ZnO) materials from their hydroxide precipitates. The required volumes of 1M zinc acetate dihydrate and 1M lanthanum nitrate hexahydrate were stirred in 250 ml beaker to get a 100 ml volume of cationic solutions. Further, 100 ml 1M potassium hydroxide solution was added to these

solutions to get a final volume 200 ml of thoroughly mixed solutions. The white precipitates of hydroxide precursors were filtered under vacuum using Whatmann filter paper No.42 by giving five to six washings of distilled water, dried and consequently ground to fine powders. The precursors were finally calcined at 400°C (temperature obtained from thermal studies which are not shown here) in a muffle furnace for 6 Hrs. The pure and La-ZnO nanocrystallites with different mole % composition of La were obtained as shown in **Table 1**. The pure ZnO was obtained as a white coloured material, whereas increasing % of La in doped materials led to gradually enhanced pale yellow colour.

Entry	1M La(NO ₃) _{3.} 6H ₂ C ml	$\begin{array}{c} 1M\\ Zn(OAc)_2 H_2O\\ ml\end{array}$	1 M KOH ml	Desired Composition (Mol % of La in ZnO)
1.	0	100	100	pure ZnO
2.	0.10	99.90	100	0.10 % La-ZnO
3.	0.25	99.75	100	0.25 % La-ZnO
4.	0.50	99.50	100	0.50 % La-ZnO
5.	0.75	99.25	100	0.75 % La-ZnO
6.	1.00	99.00	100	1.00 % La-ZnO

Table 1 Preparation of pure and La doped ZnO (La-ZnO) materials

2.3 Measurements and characterizations:

The pure ZnO and La-ZnO materials were characterized by FTIR spectroscopy using Shimadzu FTIR-8400 spectrometer equipped with KBr beam splitter in the wavenumber range of 4000-400 cm⁻¹ at a resolution of 4 cm⁻¹. X-ray diffraction (XRD) measurements were conducted by Bruker AXSD-8 Advance X-ray diffractometer with monochromatic CuK_a radiation with λ =1.5406 A°. Scanning electron micrograph-electron dispersion spectroscope, SEM-EDS JEOL JSM-6360A

was used for morphology and elemental analysis of the materials. Photoluminescence (PL) spectra were recorded on Shimadzu RF-5301PC instrument and UV-Vis spectrophotometer (UV-1601, Shimadzu) was used to study absorbance of the materials. The specific surface area and the pore size distribution estimated from nitrogen physisorption isotherms at liquid nitrogen temperature on a Quantachrome Version 3.01 BET instrument.

2.4 Catalytic activity towards thermal decomposition of AP:

The catalytic activity of the synthesized materials was studied towards thermal decomposition of AP. In order to study catalytic roles of pure and La doped ZnO samples on AP decomposition, the catalyst and AP were premixed in a mass ratio of 1:100 respectively for the TG-DTA analysis using SDT Q600 V20.9 Build 20 instrument at HEMRL, Pune. The heating rate of 10° C/min in N₂ atmosphere with flow of 100 ml/min was maintained within temperature range of 30 to 650°C.

3.0 Results and Discussion:

3.1 FTIR analysis:





The FTIR spectra of pure and La doped ZnO are demonstrated in **Fig. 1**. In FTIR spectra, frequency bands below 500 cm⁻¹ are usually recognized as metal-oxygen stretching. The FTIR spectra of synthesized materials exhibited two metal-oxygen stretching frequency bands at 424 cm⁻¹ and 481 cm⁻¹, which were clearly seen in 0.50, 0.75 and 1.00 % La-ZnO indicating presence of Zn-O and La-O bonding. Along with these expected metal oxygen IR bands, the additional IR bands were observed at 1354, 1526, 2335 and 3458 cm⁻¹, which were attributed to C-O bending in acetate species, C-O bending of CO₃²⁻, symmetric-asymmetric stretching, C=O stretching vibrations of acetate species and –OH stretching [40-41]. These additional IR bands revealed the presence of adsorbed acetate, carbonate species and hydroxide ions on material surface.

3.2 XRD analysis:



Fig. 2 XRD pattern of pure and La doped ZnO

The XRD pattern of synthesized pure and La doped ZnO are displayed in Fig. 2. All the two theta (2 θ) values of the peaks obtained were clearly matched with 100, 002, 101, 102, 110, 103, 200, 112, 201, 004 and 202 planes of the reference XRD-pattern of wurtzite ZnO structure indexed as JCPDS No. 36-1451. The presence of doped La in ZnO was ascertained by Bragg's angle shifting of 101 plane towards the higher 2 θ value by 0.2° from pure ZnO to 1.00 % La-ZnO. These observations from XRD-patterns confirmed that the pure and doped ZnO was obtained in wurtzite crystal structure. The average crystallite size of the diffracted materials was determined using Debye Scherrer's equation using the full-width at half-maximum data at the diffraction peak of the wurtzite 101 plane. [42-43] The calculated average crystallite size for the pure ZnO, 0.10, 0.25, 0.50, 0.75 and 1.00 % La-ZnO were found to be 30.13, 32.26, 34.95,

39.72, 41.62 and 44.82 nm respectively. The average particle size was found to gradually increase with incorporation of the La in pure ZnO material.





Fig. 3 UV-Visible spectra of pure and La doped ZnO

The UV-Visible spectra of the synthesized materials showed a bathochromic shift in absorption maxima of pure ZnO with increase in mole % of La in La-ZnO materials as shown in **Fig. 3**. The pure ZnO showed absorption maxima at 325 nm, whereas 0.10, 0.25, 0.50, 0.75 and 1.00 % La-ZnO have showed the absorption maxima at 357, 359, 365, 367 and 370 nm respectively. This gradual increase in absorption maxima was in correlation with increase in La % of composition which illustrated the role of La as optical responsive centers in La-ZnO. The band gap energies of the materials were calculated by formula 1250 nm / absorption maxima in nm. The obtained band gap energies (Eg) for pure ZnO, 0.10, 0.25, 0.50, 0.75 and 1.00 % La-ZnO were found as 3.85, 3.57, 3.50, 3.42, 3.41 and 3.38 eV respectively.



Figure 4. Band gap energies (Eg) of pure and La-doped ZnO materials from TAUC plots The band gap energies (Eg) of the materials were also evaluated by using Tauc equation by plotting $(\alpha h \upsilon)^2$ in $(eV \text{ cm}^{-1})^2$ vs. Energy (h \upsilon) in eV as shown in Fig. 4. The Eg values were estimated using Tauc's plot by extrapolating the linear portion of the plot of $(\alpha h \upsilon)^2$ vs. photon energy. [42-43] The Eg values for pure ZnO, 0.10, 0.25, 0.50, 0.75 and 1.00 % La-ZnO were found to be 3.84, 3.50, 3.48, 3.42, 3.40 and 3.37 eV, which are in good agreement with the

earlier calculated values. Thus, the higher % La in material composition led to reduced band gap energy of the semiconducting material and hence possible photocatalytic activity in sunlight.

3.4 Photoluminescence spectroscopy:





The photoluminescence (PL) spectra for pure and La doped ZnO at excitation wavelength 300 nm are demonstrated in **Fig. 5**. At this excitation wavelength, the pure and La-doped ZnO materials showed relatively weaker UV emission peaks at around 390 nm and 370 nm respectively. These peaks were corroborated to the near band edge (NBE) emission originated by recombination of the free excitons of ZnO. [44]

Along with these emission bands, all the materials have also showed the yellow green emission bands at 509 nm which were obtained by deep level (DL) defect emission related to oxygen vacancies in ZnO lattices. The green yellow emission band of 1.00 % La-ZnO was of the highest intensity and also was found to be 1.7 times stronger than that of pure ZnO. The intensity of this green yellow emission band was observed to be enhanced with increased La % in materials which denotes enhancement in oxygen vacancy or defect in doped materials. [45]

3.5 SEM-EDS analysis:

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The SEM images of pure and La doped ZnO spotted homogeneous granular morphology of the materials with substantial porosity, indicating the uniform doping of La in doped materials as shown in **Fig. 6**.



Fig. 6 SEM images of pure ZnO (a), 0.10 %La-ZnO (b), 0.25 %La-ZnO (c), 0.50 %La ZnO (d), 0.75 %La-ZnO (e) and 1.00 %La-ZnO (f)

The marginal agglomeration observed in 0.75 and 1.00 % La-ZnO (e-f) may be attributed to their higher level defects arised due to higher La content. The crystallite size of all the studied materials was observed in a range of 40 to 130 nm attributed to low temperature synthesis of these materials.

Fig. 7 represents the size distribution histograms which were derived by extracting the size of hundred particles from the SEM images of pure and La doped ZnO nanostructures using image J processing software. Each histogram is fitted by a Gaussian curve. According to these histograms the average particle size of ZnO nanoparticles in pure ZnO was 25.00 nm. The particle size was also found to be enhanced on doping of La. The average particle size for 0.10,

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0.25, 0.50, 0.75 and 1.00 % La-ZnO were found to be 26.60, 30.30, 34.58, 38.17 and 41.71 nm respectively. Indeed, the nanoparticle size is found to be bigger than the crystallite size, suggesting that particles can be formed by one to several crystallites. [43]



Fig. 7 Particle size distribution histograms of pure and La-doped ZnO materials

The EDS elemental analysis of synthesized materials showed the presence of La in doped materials. The observed La % in 0.10, 0.25, 0.50, 0.75 and 1.00 % La-ZnO were found to be 0.07, 0.14, 0.41, 0.56 and 0.71 % respectively. This increase in La % was in agreement with the added La³⁺ concentrations while getting their hydroxide precursors. The observed differences in La % from theoretical and observed values may be attributed to loss of La during washing of hydroxide precursor and also heating these precursors during calcination stages.

The representative EDS spectra for pure ZnO and 1.00 % La-ZnO are shown in **Fig. 8** and the EDS spectra for all the materials are given in supplementary data (S1).



Fig. 8 EDS spectra of pure and 1.00 % La-ZnO

The EDS-element mapping of Zn, O and La elements demonstrated uniform distribution of doped element La in synthesized materials. Element mapping confirmed the homogeneity of the materials obtained by simple co-precipitation process as shown in **Fig. 9**.



Fig. 9 EDS-element mapping of Zn, O and La elements in pure ZnO (a), 0.10 %La-ZnO (b), 0.25 %La-ZnO (c), 0.50 %La -ZnO (d), 0.75 %La-ZnO (e) and 1.00 %La-ZnO (f). Inset: uniform distribution of La

3.6 BET surface area measurements:

The N_2 sorption isotherms of pure ZnO and 0.10%, 0.25%, 0.50%, 0.75% and 1.00% La-ZnO materials are as shown in **Fig. 10**.



Fig. 10 Nitrogen adsorption (lower)-desorption (upper) isotherms of pure and La-ZnO materials. Inset: the corresponding BJH pore size distribution

The Brunauer–Emmett–Teller (BET) method was used to evaluate the specific surface areas and the pore size distribution curves were generated by the Barrett-Joyner-Halenda (BJH) model from the desorption and adsorption branches of the isotherm. [46] For the synthesized pure ZnO, 0.10, 0.25, 0.50, 0.75 and 1.00 % La-ZnO samples, the specific surface area values were found to be 28.203, 26.600, 21.907, 20.499, 16.884 and 15.830 m²/g respectively. These observations are in corroboration with the SEM images where the gradual agglomeration of the materials was observed with increase in doped amount of La. However the pore size (radius) of all the materials was observed to be 1.8 to 1.9 nm revealing mesoporous nature of these materials. All the samples obeyed the isotherm type III with hysteresis loops of different sizes according to the IUPAC classification. [47]

3.7 Catalytic activity of Pure and La doped ZnO towards thermal decomposition of AP:

The as-prepared porous ZnO and La-ZnO materials with different percentages of La were explored as catalysts to study their effect on thermal decomposition of AP. The role of these catalysts was evaluated in terms of TG-DTA analysis of premixed AP with 1 % mass basis of catalysts.

At a heating rate of 10° /min in N₂ atmosphere, the TG curve of bare AP showed two step decomposition (**Fig. 11**), exhibiting low-temperature decomposition (LTD) with 29 % wt loss at 300 ^OC and complete high-temperature decomposition (HTD) at 394[°]C. The observed LTD and HTD were in well agreement with the values reported as 298[°]C and 397[°]C by Zeng et al.[20] The LTD process is a heterogeneous process, proposed to include a proton transfer in the AP subsurface to yield NH₃ and HClO₄. The further adsorption of NH₃ and HClO₄ in the porous structure proceeds towards final decomposition of HClO₄ to HCl and O₂, and oxidation of NH₃ to N₂ as shown in **Scheme 1**. However, the HTD process purely involves the oxidation of NH₃ to N₂ by HClO₄ in the closed sample pans.[14]



Scheme 1. Schematic representation for thermal decomposition of AP



Fig. 11 TG curves of AP in absence and presence of pure and La doped ZnO catalysts More interestingly, under identical conditions the added ZnO catalyst exhibited a single step decomposition of AP in TG analysis with merged HTD and LTD value of 289°C. This outcome clearly indicated that ZnO has a definite role to play to reduce the decomposition temperature by

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105 °C. This promoted decomposition of AP may be attributed to the porous morphology of ZnO nanocrystallites providing higher contact surface to facilitate the AP decomposition.



Fig. 12 DTA curves of AP in absence and presence of pure and La doped ZnO catalysts The DTA curves of pure AP in absence of catalyst and in presence of 1 % mass basis of different catalysts (pure and La doped ZnO) at a heating rate of 10°C/min are shown in **Fig. 12.** The pure AP on thermal decomposition showed an endothermic peak at 241°C, which were attributed to the transformation of AP crystal from orthorhombic to cubic phase. [30] The two more exothermic peaks were observed in pure AP at 300 and 394°C corresponding to its lowtemperature decomposition (LTD) and high-temperature decomposition (HTD) respectively. The thermal decomposition of AP in presence of 1% mass basis of pure ZnO and La-ZnO catalysts exhibited the similar endothermic peaks as that of bare AP at 240-245°C for transformation of

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AP crystal from orthorhombic to cubic phase. However, La doped ZnO catalysts showed slight increase in decomposition temperature of AP where the HTD values for 0.10, 0.25, 0.50, 0.75 and 1.00 % La-ZnO were found to be 290°C, 290°C, 292°C, 293°C and 294°C respectively. The observed increase in HTD was also evidenced in DSC plots of AP decomposition as shown in **Fig. 13**. The pure AP showed two stage decomposition with LTD 294 °C and HTD of 398 °C. The addition of 1% catalysts showed the similar HTD values as that of DTA plot for ZnO, 0.10, 0.25, 0.50, 0.75 and 1.00 % La-ZnO as 287°C, 290°C, 291°C, 291°C, 294°C and 294°C respectively.



Fig.13 DSC curves of AP in absence and presence of pure and La doped ZnO catalysts This slight increase in HTD values on increasing La content indicates that La has played a retarding role to decrease the catalytic activity of pure ZnO by promoting the formation of NO instead of N_2 in further oxidation of NH₃. These outcomes were in agreement with the results

obtained by Hung et al. [33] during selective catalytic oxidation of ammonia over La doped CuO. The selectivity for the NO by-product was reported up to 41% than N₂ production (up to 30%) with 97% NH₃ conversion. The slight higher HTD for La doped ZnO may be the consequence of the further energy consumption for final oxidation of NO to N₂. [48] Another important factor which played a comprehensive role to this increase in HTD is decrease in surface area of the catalysts from 28.203 to15.830 m²/g for ZnO to 1.00 % La-ZnO catalyst. However, there is a need of further comprehensive studies to identify the precise reason for observed negative catalytic effect of La in La-ZnO on the basis of actual estimation of gaseous decomposition products.

Conclusions:

The La doped ZnO materials were synthesized by simple co-precipitation method. The IR spectra of pure and doped ZnO showed remarkable bands at 424 cm⁻¹ and 481 cm⁻¹ for metaloxygen bonding and also ascertained the presence of adsorbed acetate, carbonate and hydroxide species on catalyst surface. The XRD pattern of ZnO and La-ZnO revealed the wrutzite crystal structure and the presence of La doped ZnO was ascertained by shifting of Bragg's angle towards higher 20 value by 0.20°. The calculated average crystallite size for the pure ZnO to 1.00 % La-ZnO were found to be 30.13 to 44.82 nm respectively. The UV-Visible spectra of the materials confirmed that the La acts as UV-absorption centers leading to bathochromic shift of absorption maxima from 325 nm to 370 nm from pure ZnO to 1.00 % La-ZnO were found to be 3.84, 3.50, 3.48, 3.42, 3.40 and 3.37 eV. The PL spectra of the doped materials showed enhanced DL defects and oxygen vacancy which was reflected from intensified yellow green emission bands. The SEM images of the materials showed the porous granular nature and particle size of about 40-150 nm. The % La observed from EDS analysis was in well agreement with the expected values in respective compositions. The EDS-element mapping demonstrated uniform distribution of doped element La in synthesized materials. The BET specific surface area values were found to be decrease on La incorporation from 28.203 to15.830 m²/g for pure ZnO and 1.00 % La-ZnO respectively. In catalytic application, when pure ZnO was added in 1% amount, reduced the HTD of AP by 105°C. In La doped ZnO, the marginal increase in HTD than pure ZnO catalyst from 289°C to 294°C was observed which is due to promotion of NO formation than N₂ while final oxidation of NH₃.

Declarations of interest: none

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Facile fabrication of porous La doped ZnO granular nanocrystallites and their catalytic evaluation towards thermal decomposition of ammonium perchlorate R. M. Jagtap¹, D. R. Kshirsagar², V. H. Khire², S. K. Pardeshi^{1*}
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Research Highlights

- Mesoporous, granular nanocrystallites, Wrutzite structure for pure and La doped ZnO
- Band gap energy were reduced by La in doped materials
- Higher La content showed higher crystallite size, particle size, lower surface area
- Two stage decomposition of AP turns single stage in presence of pure and doped ZnO
- Lowering in HTD of AP by 105 °C using ZnO which further reduced by La doping