

**TWO DAYS NATIONAL LEVEL CONFERENCE**

**ON**

**ROLE OF  
PHYTOCHEMICALS AND  
ADVANCED MATERIALS IN  
CANCER PREVENTION  
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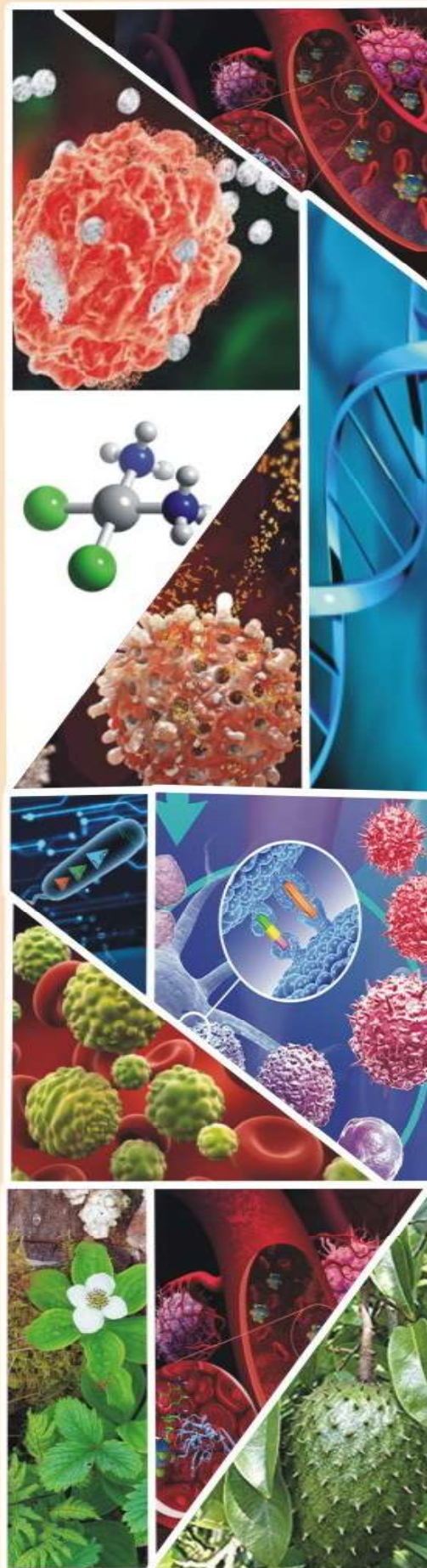


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**PG DEPARTMENT OF CHEMISTRY  
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## INTERESTING MORPHOLOGY OF La doped $\text{CuC}_2\text{O}_4$ and Na doped $\text{CuC}_2\text{O}_4$ SYNTHESISED VIA THERMAL DECOMPOSITION

POONKODI K, ATHIRA. S, AKSHAYA, V. SAJANA. M.S. and SUBHAHARINI

*PG Department of Chemistry,*

*Nallamuthu Gounder Mahalingam college, Pollachi- 642001, Tamilnadu, India*

### ABSTRACT

In the present investigation aimed to evaluate the synthesis of copper oxide nanoparticles doped with lanthanum and sodium via simple thermal decomposition. The prepared La doped  $\text{CuC}_2\text{O}_4$  and Na doped  $\text{CuC}_2\text{O}_4$  was characterized by using XRD, FE-SEM and DSC studies. The results revealed that as prepared nanoparticles are shifted to left from that of copper oxalate. Lanthanum ( $1.06\text{\AA}$ ) and sodium ( $1.02\text{\AA}$ ) ions are of higher radius than copper ion ( $0.73\text{\AA}$ ). Replacing a cation with a dopant of smaller or larger ionic radius can change inter-planar spacings that can induce lattice strain/stress, may shift diffraction peak position. The morphology of the as prepared powder showed different structure like, flowers, rods and spongy with the diameter of 2-3 $\mu\text{m}$  and DSC studies revealed that  $\text{CuC}_2\text{O}_4$  is stable up to 540K and then decomposes exothermically to form copper oxide, which is a single step process. The analysis of residue obtained after the decomposition by chemical, XRD confirms the formation of metallic copper,  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ .

**Keywords:** La doped  $\text{CuC}_2\text{O}_4$ , Na doped  $\text{CuC}_2\text{O}_4$ , DSC, FE-SEM

### 1. INTRODUCTION

In recent years, the development of new technologies has increased the demand for methods for the preparation of transition metal nanosized particles which are used in electronics and the production of composite materials. The thermal decomposition of many transition metal oxalate yields homogenous oxide nanoparticles. The thermal decomposition of oxalate ligand based compounds is relatively complicated due to their reduction property and variable coordination modes to stabilize a broad variety of complexes. The thermal decomposition of metal oxalates strongly depends on the reducible property of the metallic cation involved [1-3].

Copper oxalate is believed to have unusual anti ferromagnetic properties and is also a potential precursor material for the production of copper (II) oxide ( $\text{CuO}$ ) and  $\text{Cu}$  particles. Due to the fact that the precipitation processes provide the possibility of controlling the chemical and physical properties of the final products, the sparingly soluble oxalate systems are widely used as precursors in the synthesis of nanomaterials and high- temperature superconductive ceramic materials, containing  $\text{CuO}$ . Copper oxides have applications in thin-film oxygen pressure sensors, as a binder in pastes for thick-film microelectronic circuits, as a p-type semiconductor and they exhibit luminescence [4].

Doping introduces point defects such as vacancies, interstitials, and impurity atoms in the solid, compression generates active dislocations and grain boundaries due to plastic deformation caused to the solid. We, therefore, interested in doping of metal ions to copper oxalate so as to get doped copper oxides nanoparticles via thermal decomposition. The kinetics of the thermal decomposition of inorganic materials could be markedly increased by pre treatments, by the shortening of the induction period followed

by an overall decrease in time needed to complete the reaction.

Publications concerning metal ion doped copper oxide nanoparticles via thermal decomposition of oxalate precursor, are still incomplete. Therefore lanthanum and sodium doped copper oxide nanoparticles via thermal decomposition of oxalate precursor could be worthwhile investigating.

## 2. MATERIALS AND METHODS

Synthesis of copper oxalate, sodium doped copper oxalate, lanthanum doped copper oxalate and their thermal decomposition to yield respective oxides.

### 2.1. MATERIALS REQUIRED

**CHEMICALS:** Analar grade copper nitrate tri hydrate [Cu (NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O], sodium nitrate (NaNO<sub>3</sub>), lanthanum nitrate (La(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O), oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. 2H<sub>2</sub>O), Sodium oxalate and Lanthanum oxalate (Merck ) with purity assay  $\geq 99.9\%$  were used.

### 2.2. PREPARATION OF COPPER (II) OXALATE

Copper (II) oxalate was synthesized by co-precipitation of dilute aqueous solution (30% of Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O by adding oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O solutions) with a warming and stirring. The resultant solutions was stirred for another four hour .The reacted solutions was kept for some time to settle the precipitate, then filtered off and washed several times with distilled water frequently with ethyl alcohol and air dried in an oven kept at 40<sup>0</sup>C and was used for the characterization and thermal analysis.

### 2.3. PREPARATION OF Na AND La DOPED COPPER (II) OXALATE

10 g of above prepared copper oxalate was dissolved in 230 ml of ammonium hydroxide in a 500 ml beaker. 10 ml of a solution containing 1 mole % Na<sup>+</sup> are added to the solution so as to achieve a total volume of 240 ml. The beaker containing the solution was covered by using a clean uniformly perforated paper and stirred for 1 hour and allowed for slow crystallization. The resultant solution is then filtered off and washed several times with distilled water frequently with ethyl alcohol and air dried in an oven 313 K. the same procedure was repeated for La<sup>3+</sup> (1 mole%) doped copper oxalate.

### 2.4. CHARACTERIZATION TECHNIQUES

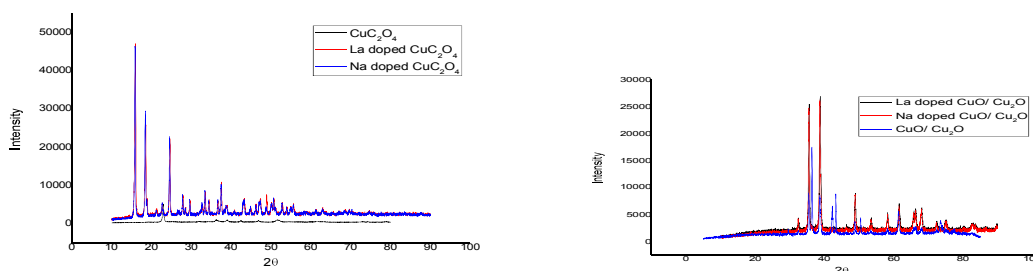
The X- ray diffraction (XRD) measurements of the samples were performed on a RIGAKU MINI FLEX -600 X-ray diffraction spectrophotometer using Cu K $\alpha$  (1.5418Å) radiation. The differential scanning calorimetric (DSC) measurements of the samples was performed on a Mettler Toledo DSC822e. The operational characteristic of the DSC system are: atmosphere: flowing air at a flow rate of 20 mL min<sup>-1</sup>; sample mass: 5 mg; sample holder: platinum. Samples were subjected to control heating, in the range 303 – 648 K at a heating rate of 10 K min<sup>-1</sup>. Morphological analysis was done on ZEISS Gemini SEM - Field Emission Scanning Electron Microscope. The elemental analysis was done on the EDX instrument by AMETEK materials analysis division.

### 3. RESULTS AND DISCUSSION

#### 3.1. XRD STUDIES

The structural characteristics of copper oxalate and its doped oxalates with sodium and lanthanum was investigated by XRD. These studies reveal that both the copper oxalate and its doped oxalates are highly crystalline. The relative crystalline sizes are determined from the XRD line broadening using the Scherrer equation:  $d = 0.9\lambda/\beta\cos\theta$  where  $d$  is the crystallite size,  $\lambda$  is the wavelength used in XRD ( $1.5418\text{\AA}$ ),  $\theta$  is the Bragg angle,  $\beta$  is the pure diffraction broadening of a peak at half height, i.e., broadening due to crystallite dimensions.

The size of the oxalates was estimated to be  $23.9\ \mu\text{m}$  according to the Scherrer equation which indicates the micro crystalline nature of particles. The XRD analysis when compared with the standard data (JCPDS No.21-0297) reveals the presence of a cubic phase. The most intense peak in all of these mixtures is that of copper oxalate at about  $2\theta = 22.9^\circ$ . XRD analysis was employed to confirm the composition of decomposition products (Fig.2). In the case of pure copper oxalate decomposition, the peaks appeared clearly at  $43.3^\circ$ ,  $50.4^\circ$  and  $74.1^\circ$  degree and were attributed to the (110), (111) and (200) reflections of cubic metallic copper (JCPDS file No. 4-0836). The presence of two crystalline phase indices, monoclinic cupric oxide (CuO) and cubic cuprous oxides ( $\text{Cu}_2\text{O}$ ) was confirmed from XRD analysis. The peak position with  $2\theta$  value of  $61.3^\circ$  indexed as (220) plane, (space group Pn-3m (224), JCPDS file no. 05-0667) confirmed the formation of a crystalline cubic phase  $\text{Cu}_2\text{O}$  with a cuprite structure, while the peaks at  $35.9^\circ$ ,  $38.9^\circ$ ,  $49.1^\circ$ ,  $52.9^\circ$ ,  $58.7^\circ$ ,  $66.6^\circ$  and  $68.3^\circ$  can be assigned to (002), (111), (-202), (020), (202), (-311) and (113) planes, matches well with the values of monoclinic phase of CuO reported with the JCPDS file no. 45-0937 (space group C2/c(15)). The higher intensities at  $2\theta$  values  $35.9^\circ$  and  $38.9^\circ$  respectively indicated that the mixed phase has major proportion of CuO with the highly oriented crystalline monoclinic phase. Thus, it can be concluded that the amount of cuprous oxide is little in the decomposition. Theoretically, doping other atoms into a structure will lead to both peak shifts and changes in intensity. The lines of doped co-precipitates are shifted to left from that of copper oxalate. Lanthanum ( $1.06\text{\AA}$ ) and sodium ( $1.02\text{\AA}$ ) ions are of higher radius than copper ion ( $0.73\text{\AA}$ ). Replacing a cation with a dopant of smaller or larger ionic radius can change inter-planar spacings that can induce lattice strain/stress, may shift diffraction peak position; here it is shifted to left (Fig.1).

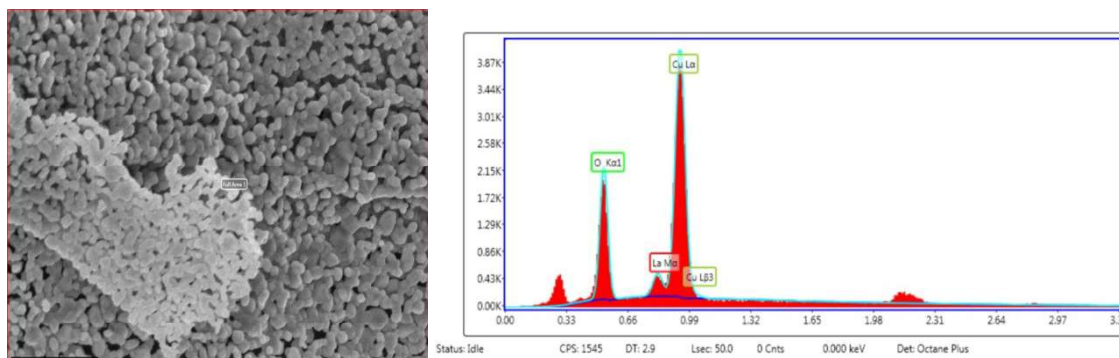


**Fig. 1** XRD pattern of  $\text{CuC}_2\text{O}_4$  and doped **Fig. 2.** XRD pattern of Copper oxide and co-precipitates

#### 3.2. EDX ANALYSIS

Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an x-ray technique used to identify the elemental composition of materials. The elemental composition and the identification of contaminants is done by EDXA analysis. Study reveal that the samples prepared is pure.



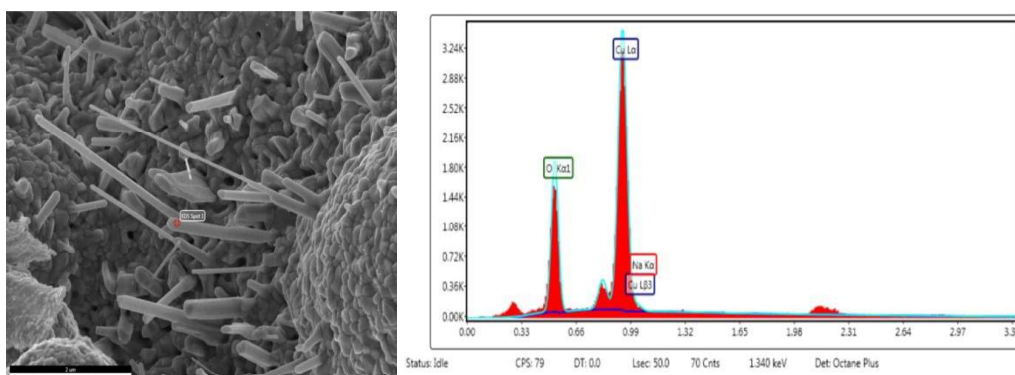


**Fig.3** Selected area for EDAX and elemental analysis of copper oxide doped with La

**Table.1&2.** Elemental analysis of La doped copper oxalates and Na doped copper oxalates

| Element | Wt%   | Atomic% | Net Int |
|---------|-------|---------|---------|
| OK      | 19.97 | 49.78   | 223.22  |
| LaM     | 0.02  | 0.01    | 0.01    |
| CuL     | 80.01 | 50.21   | 394.23  |

| Element | Weight% | Atomic% | Net Int |
|---------|---------|---------|---------|
| OK      | 20.4    | 49.97   | 192.92  |
| CuL     | 79.73   | 49.81   | 338.46  |
| NaK     | 0.13    | 0.22    | 0.63    |



**Fig.4&5.** Selected area for EDAX of copper oxide doped with Sodium

### 3.3. SEM ANALYSIS

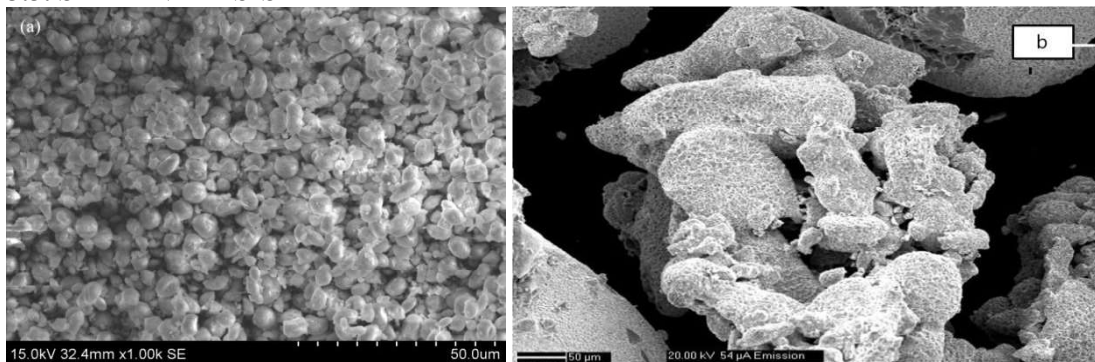


Fig.6 SEM images of copper oxalate (a) and copper oxide (b)

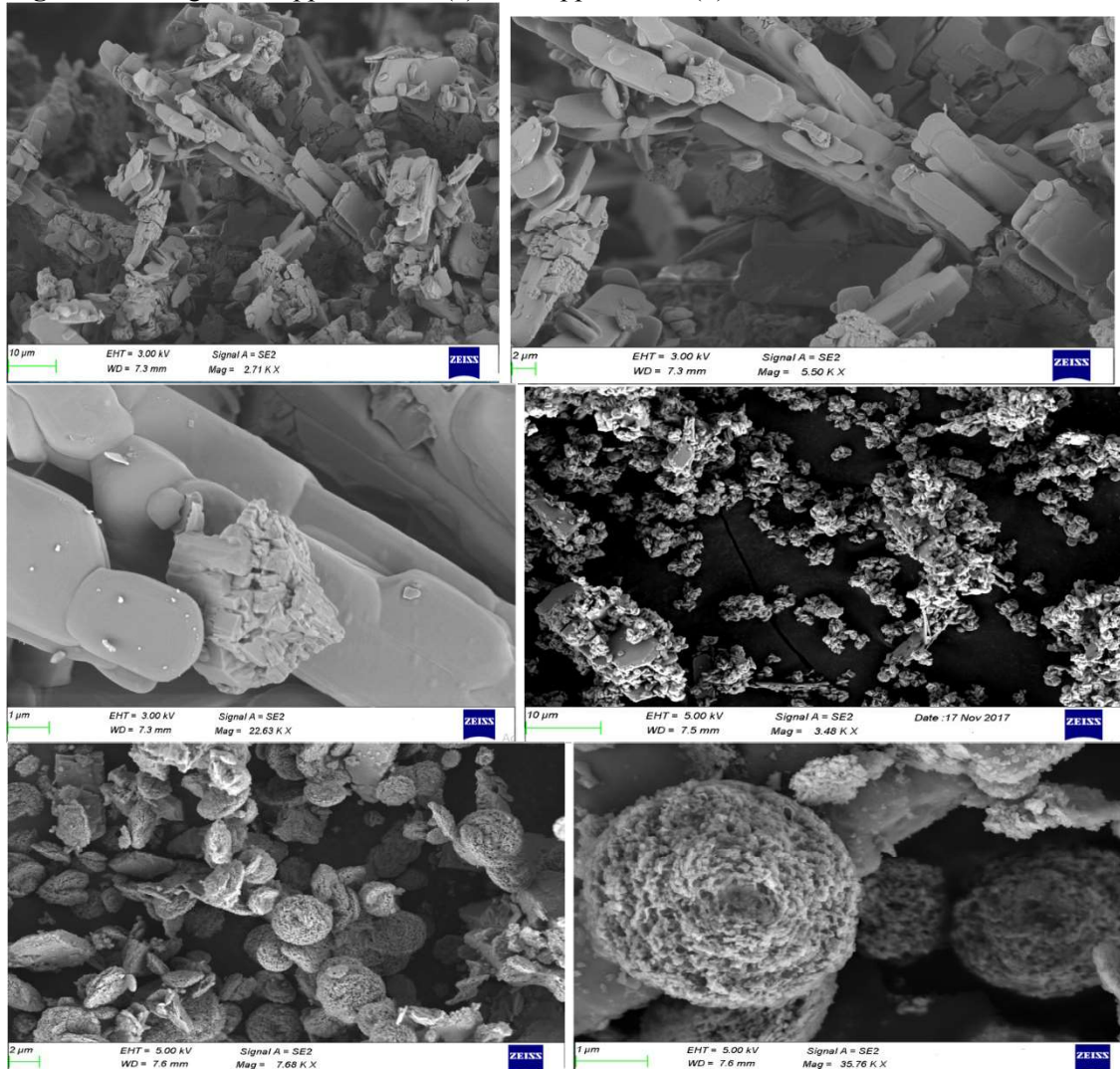
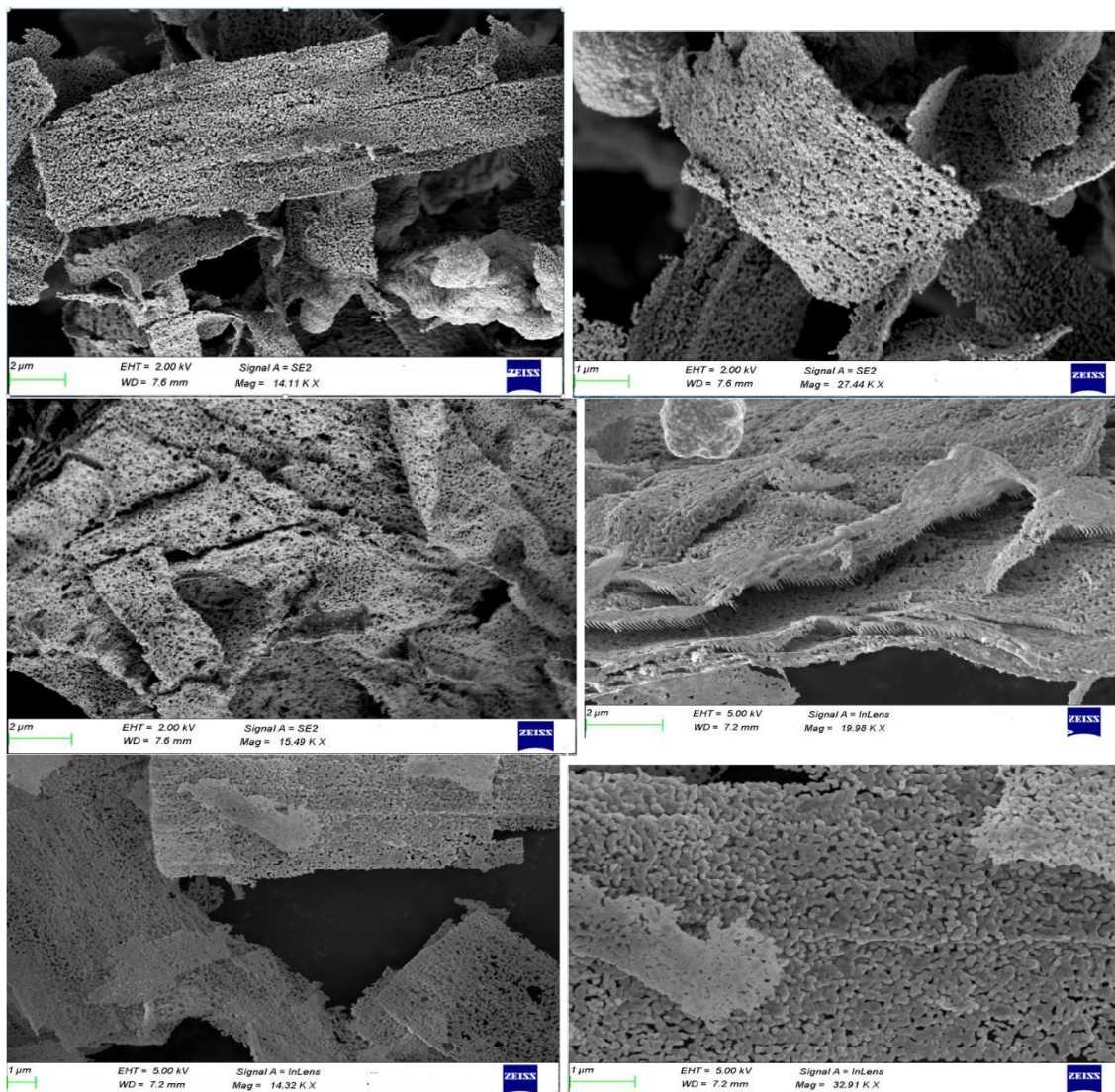
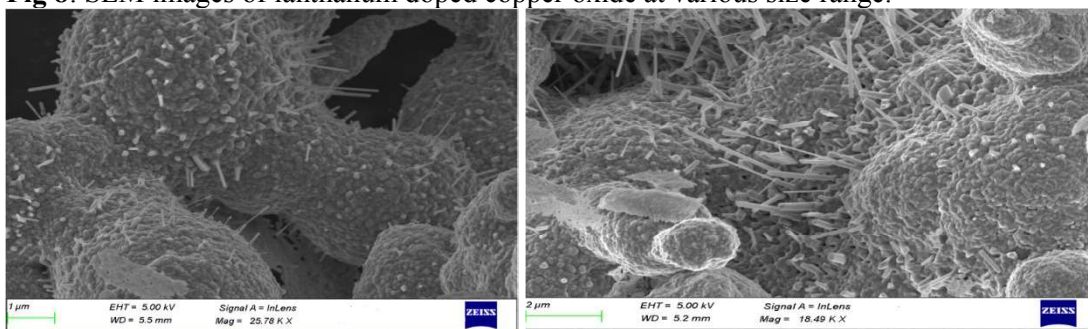


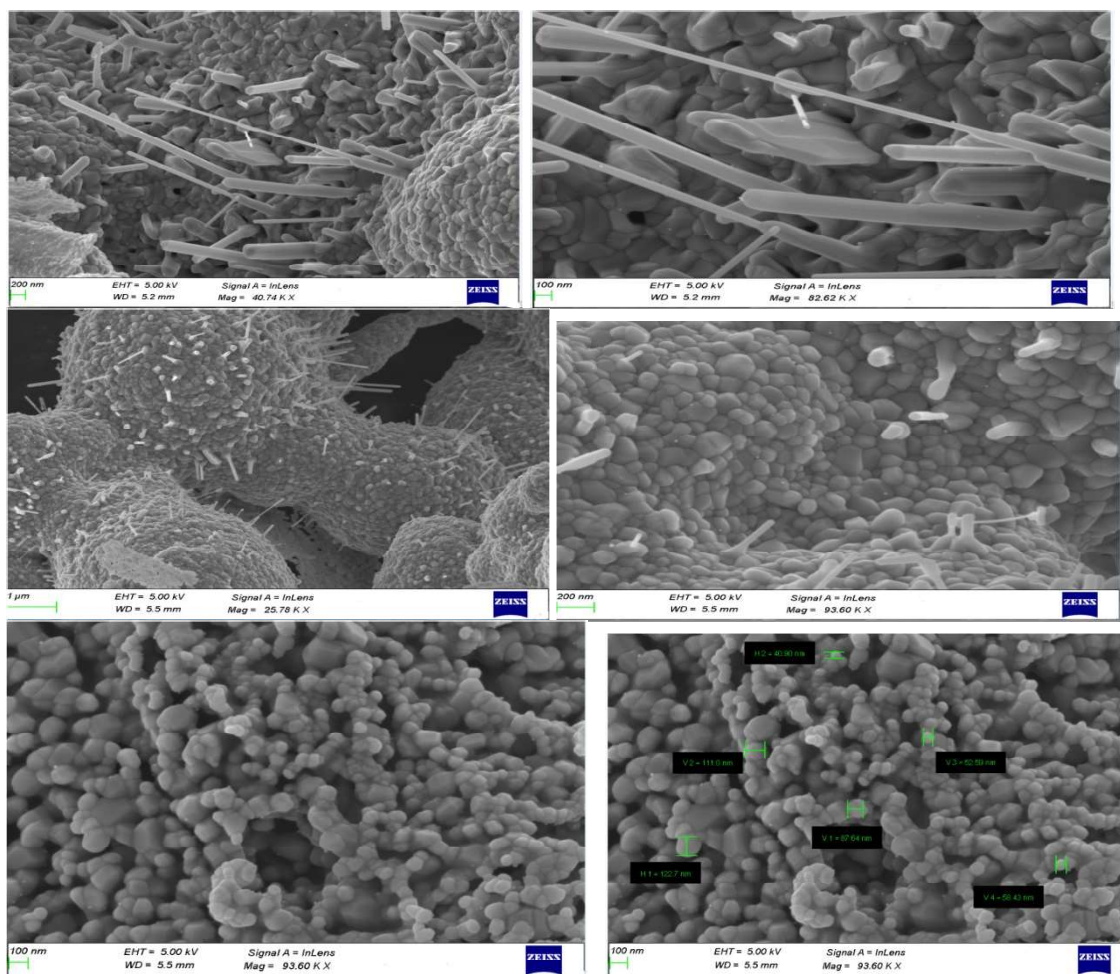
Fig. 7. SEM images of lanthanum doped copper oxalate and sodium doped copper oxalate.





**Fig 8:** SEM images of lanthanum doped copper oxide at various size range.





**Fig 9:** SEM images of sodium doped copper oxide at various size range.

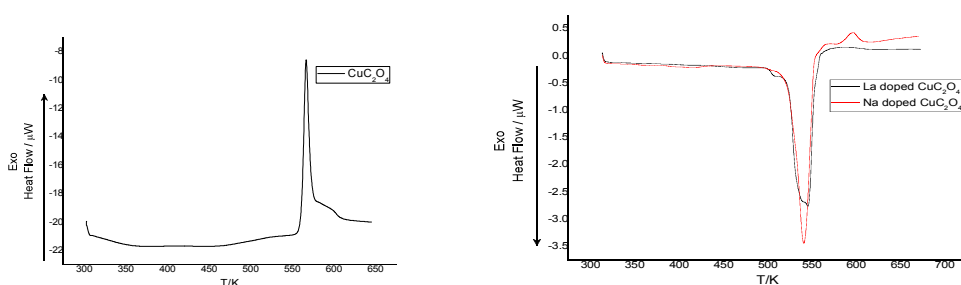
The SEM images of the synthesized copper (II) oxalate and the doped oxalates are shown in Fig. 8. These figures show the presence of crystals having different shapes and size. The SEM images of the copper oxides and the doped oxides are shown in Fig. 9. These figures show the presence of crystals having different shapes and size.

### 3.4. DSC ANALYSIS

The DSC curves obtained for the thermal decomposition of copper (II) oxalate and the doped oxalates at a heating rate of  $10 \text{ K min}^{-1}$  (shown in Fig. 11 & 12) implies that the decomposition exhibits an exothermic character. All of the samples show a sharp exothermic peak in the temperature range 540-600 K.

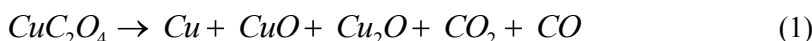
**Table.4.3** Phenomenological data of precursor oxalates from DSC

| Samples                           | Stage2 |       |       |
|-----------------------------------|--------|-------|-------|
|                                   | $T_i$  | $T_g$ | $T_f$ |
| $\text{Cu}_2\text{O}_4$           | 540    | 568   | 640   |
| La doped $\text{CuC}_2\text{O}_4$ | 490    | 545   | 576   |
| Na doped $\text{CuC}_2\text{O}_4$ | 494    | 542   | 566   |



**Fig.10.** DSC of doped copper oxalate and Sodium oxalate precursors

The phenomenological data for the thermal decomposition of all the three oxalate precursors obtained from DSC analysis are given in Table 3. From the DSC curves, it can be seen that  $\text{CuC}_2\text{O}_4$  is stable up to 540 K and then decomposes exothermically to form copper oxide, which is a single step process. The analysis of residue obtained after the decomposition by chemical, XRD confirms the formation of metallic copper,  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ . The overall reaction can be represented as



Since the decomposition of oxalate has been taken place in air atmosphere, the carbon monoxide formed is immediately oxidized by air to  $\text{CO}_2$  producing an exotherm in DSC. DSC curves, Fig 10 reveal that doped oxalate also decompose in single stage. From the thermal analysis of doped oxalate samples, it is observed that above 580 K, the oxalate precursors converted completely into metal oxide. Therefore the high quality doped copper oxides can be obtained by heat treating the coprecipitated precursors in a muffle furnace for 1 h at 580 K. Whereas pure oxalate sample require temperature, 640 K for complete conversion to oxides. Hence doping decreased the initial temperature as well as induction time.

#### 4. CONCLUSION

As prepared La doped  $\text{CuC}_2\text{O}_4$  and Na doped  $\text{CuC}_2\text{O}_4$  matches the monoclinic phase of Cu, it forms different size and shapes, and from the thermal analysis of doped oxalate samples, it is observed that above 580 K, the oxalate precursors converted completely into metal oxide. Therefore the high quality doped copper oxides can be obtained by heat treating the coprecipitated precursors in a muffle furnace for 1 h at 580 K. Hence doping decreased the initial temperature as well as induction time.

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