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### RESEARCH ARTICLE

#### COMPARATIVE STRUCTURAL STUDIES OF $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ CATHODE MATERIALS PREPARED BY SOL-GEL VERSUS SOLID-STATE-REACTION METHOD.

V. Kondala Rao<sup>1</sup>, N. Murali<sup>2</sup>, V. Veeraiah<sup>1</sup> and K. Samatha<sup>1</sup>.

1. Department of Physics, Andhra University, Visakhapatnam.
2. Department of Engineering Physics, Andhra University College of Engineering (A), Andhra University, Visakhapatnam.

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#### Abstract

In the present work, the layered structure oxide  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  (NCM 811) is synthesized by sol-gel auto combustion and solid state reaction methods. Microstructural and optical properties are investigated by XRD, FE-SEM with EDS, FT-IR and bonding nature studies. Characterization of the crystalline powders, phase identification, particle size examination, and morphological studies are done using XRD and FE-SEM. From FT-IR and UV-NIR studies, vibrational bands are identified in the range of 400-2000  $\text{cm}^{-1}$  representing the  $\text{MO}_2$  (M = Ni, Co & Mn) layers.

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#### Introduction:-

Lithium-ion batteries (LIBs) have been predominately applied in electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to their high energy density, long cycle life, and energy safety and good rate capability [1-5]. Some researchers have been found Ni-rich cathode materials are the power of Lithium-ion batteries superior energy density due to its high capacity and low cost [6-8]. But, these materials are so many problems are there, such as poor cycling, commercially poor thermal stability, cation mixing [9-10]. Such as these problems are rectify in cations (substitute Ni ions by Ti, Cr, Na, Zr, Mg and non-metallic ion, like F) [11-13] bulk doping (obviously increase the lithium layer spacing, resulting in rapid lithium-ion diffusion into the electrode) [14-15] and surface coating (achieve superior performances due to less unwanted surface functional groups, hydrogen fluoride (HF) scavenger and physical obstacle and conducting media for lithium-ion and electron) [16-18] have been solved these issues. Therefore, great efforts have been reported that it can cause long cycle life owing to enhanced thermal and structural stability and reduced transition metal dissolution [19-20].

Finally, in this paper, we prepared  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  (NCM-811) cathode materials prepared by two different methods such as sol-gel auto-combustion and solid-state reaction methods. Therefore, we believe that the NCM-811 cathode material is a beneficial approach for high performance and reliability of lithium-ion batteries.

#### Preparation and Characterizations

**Sol-gel auto-combustion method:** We synthesized  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  cathode materials by using the sol-gel method. A stoichiometric amount of  $\text{LiNO}_3$  (AR) and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (AR),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (AR) and  $\text{MnC}_6\text{H}_4 \cdot 4\text{H}_2\text{O}$  (AR) are dissolved in distilled water. The aqueous solution of citric acid which is acting as chelating agent is added to the mixer of the metal ion solution according to their molar ratio of 1:1. At the same time, an Ammonia solution as a precipitation agent is separately added. The reaction temperature is kept at  $80^\circ\text{C}$  and pH is

**Corresponding Author:-V. Kondala Rao.**

Address:-Department of Physics, Andhra University, Visakhapatnam.

controlled by ammonia solution to 8 ~ 9. The solutions are added together under stirring at 130°C for 10 hours, forming a sol solution. The sol solution is vaporized at 130°C till the dry gel is formed, followed by the heat treatment at 500°C for 6h in the air with a 5°C/ min heating rate to eliminate the organic residues. The powders are thoroughly ground and then sintered at 850 °C for 20 hours in the air to obtain the required compounds.

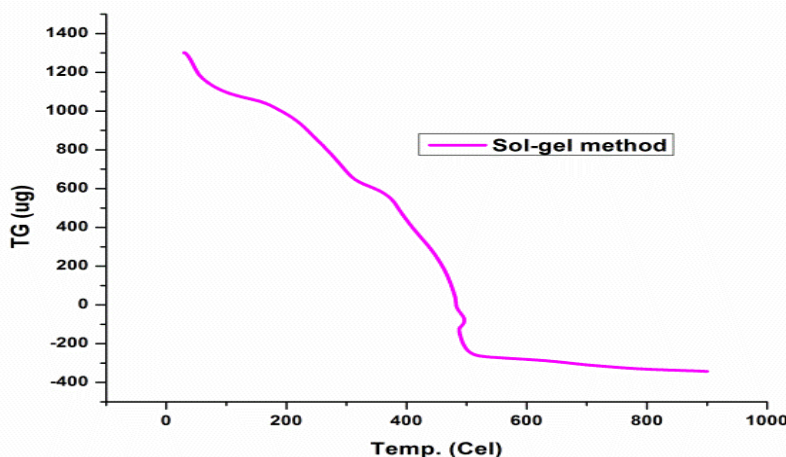
**Solid-state reaction method:** The cathode compositions are synthesized by a solid-state reaction method from stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  (Merck 99.9%) and NiO (Merck 99.9%), CoO (Merck 99.9%) and MnO (Merck 99.9%). A slight excess amount of lithium (5%) was used to compensate for any loss of the metal which might have occurred during the calcination at high temperatures. The mixture of the starting materials is sufficiently mixed and after grinding the powder it is then heat-treated in the air at 500 °C for 5 h and it is again ground and mixed, and calcined again at 750 °C for 20 h. Then, this powder was cooled at a rate of 5 °C/ min. Finally, the powder was ground and mixed, and calcined again at 850 °C for 20 h in the air using a muffle box furnace.

The powder X-ray diffraction (XRD) data of the samples are collected on a Rigaku Cu-K $\alpha$  diffractometer with diffraction angles of 20° and 80° in increments of 0.02°. The unit cell lattice parameter is obtained by the least square fitting method from the d-spacing and (hkl) values. Further, the crystal size of the sample is obtained by applying the Scherrer's equation from the XRD pattern. The particle morphology of the powders is observed using a field effect scanning electron microscopy images taken from CarlZeiss, EVOMA 15, Oxford Instruments, Inca Penta FETx3.JPG. Fourier transform infrared (FT-IR) spectra are obtained on a Shimadzu FT-IR-8900 spectrometer using KBr pellet technique in the wavenumber range between 350 and 800  $\text{cm}^{-1}$ .

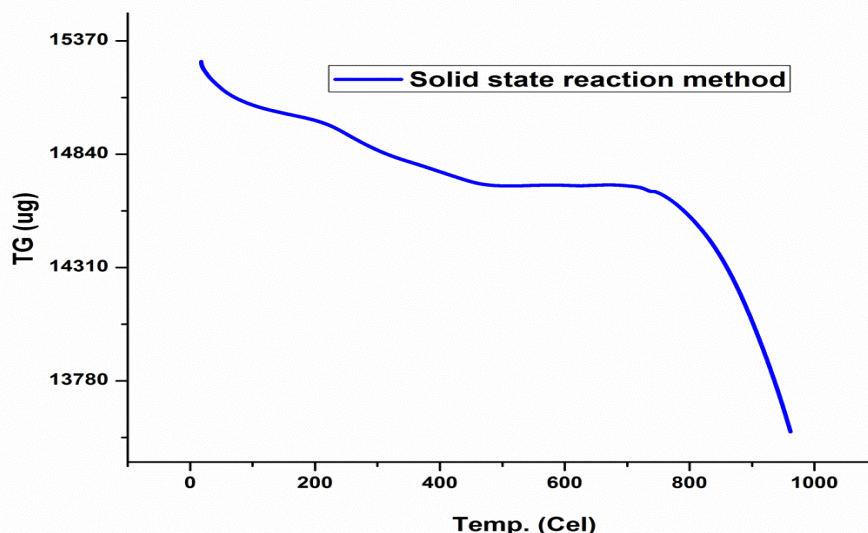
## Results and Discussions:-

### TG studies

Figure 1 represents the TG curves of  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  gel precursors synthesized by sol-gel auto combustion method using citric acid as a chelating agent. The formation of synthesized material takes place around 500°C, which is observed from the TG curve. The major weight loss (around 50%) occurs from 290–485°C, which leads to the decomposition of acetates corresponding exothermic peak appears around 485°C. After 485°C TG curves become flat which indicates that no weight loss occurs in this region; further heating only assists the crystallization event of the  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  material. Similarly, solid state reaction method the first weight loss region from 0 to 100°C corresponds to the loss of absorbed water molecules. The next weight loss region (100–290°C) indicates that the decomposition of the chelating agent. From figure 2 shown from the curves, there is an initial weight loss in the temperature range from room temperature to 310°C. This corresponds to the evaporation of methanol used during grinding to homogenize the mixture and the moisture absorbed during storage [21]. TG curve of the synthesized materials are shows significant weight loss (17.8%) between the temperatures 310°C and 570°C. This loss may be due to the decomposition of the precursors  $\text{Li}_2\text{CO}_3$ ,  $\text{NiO}_2$ ,  $\text{Co}_2\text{O}_3$  and  $\text{MnO}_2$ , and the reaction between the decomposed materials thereby to produce crystalline materials. Though,  $\text{Li}_2\text{CO}_3$  is stable in air up to 750°C and the melting point is 723°C, some studies have point out that  $\text{Li}_2\text{CO}_3$  already reacts below 300°C [22]. At the proposed temperature, the TG curve becomes more flattened, indicating stable phase is formed.



**Figure 1:-**TG/DTG curve for  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  material is prepared by sol-gel auto-combustion method



**Figure 2:-**TG/DTG curve for  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  material is prepared by solid state reaction method

### XRD studies

X-ray diffraction patterns for  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  sample is prepared by sol-gel and solid-state reaction methods are shown in Figure 3. Both XRD patterns of the powders prepared by sol-gel auto-combustion and solid-state method show X-ray peaks corresponding to  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  can be indexed to a phase-pure hexagonal structure with the space group of R3m and match well with diffraction file (JCPDS) 74-0919 [23]. The synthesized material is with no evidence of any impurities, indicating that the uniform solid solution has been formed in the compounds [24]. The crystal lattice parameters of the compounds are calculated by using the unit cell program and presented in Table 1.  $\text{LiO}_6$ ,  $\text{MO}_6$  where  $M=\text{Ni}$ ,  $\text{Co}$  and  $\text{Mn}$  occupy 3b, 3a positions and  $\text{O}$  is in the 6c position in Fig. 1. Which should be related to the larger radii of  $\text{Li}^+$  ( $0.72\text{\AA}$ ) is thus their cell volume should be expanded according to Vegard's law. We believe that this would be attributed to the decrease in the  $\text{Ni}^{2+}$  ( $0.69\text{\AA}$ ),  $\text{Co}$  and  $\text{Mn}$  (ionic radii) content caused by the charge compensation for the compound in both methods to remain in electrically neutral. The overall high-intensity ratio of the (0 0 3) and (1 0 4) peaks and the clear splitting of the (0 1 8) and (1 1 0) peaks indicate that the compounds have a good structure [25]

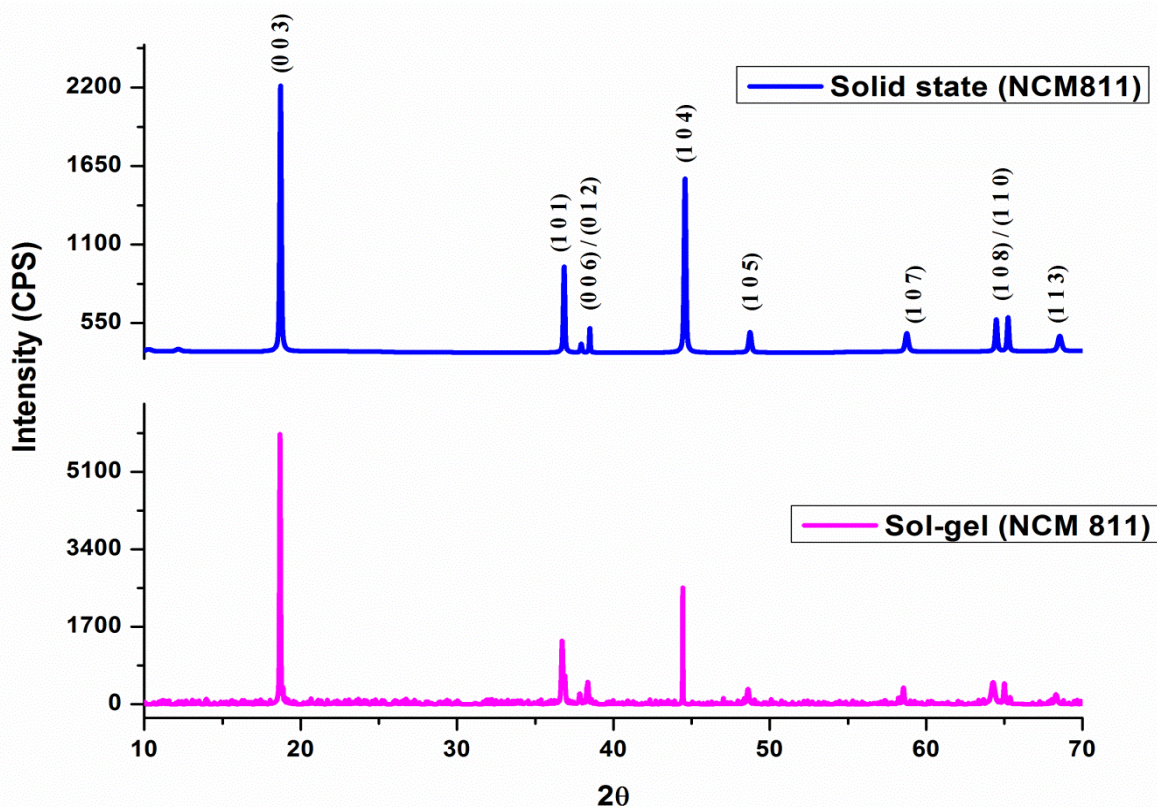
The a-axis increases linearly from 2.893 to 2.896  $\text{\AA}$  and the c-axis decreases from 14.238 to 14.23  $\text{\AA}$ . The ratio of c/a decreases from 4.922 to 4.915  $\text{\AA}$  due to the substitution of Ni ions by Co and Mn ions probably result from the severe cation mixing because it has the lowest intensity ratio of (0 0 3) to (1 0 4) peaks as given in Table 1. The unit-cell volume also increases from 103.205 to 103.371  $\text{\AA}^3$ . The crystallite sizes of the cathode powders are prepared from the sol-gel auto-combustion and solid-state reaction methods are shown in 9.8 nm and 12.67 nm. The Bragg intensity ratio of  $I(0\ 0\ 3)/I(1\ 0\ 4)$ , which is a signature of the cation-mixing and its values are 1.1602 and 1.1361. It has been reported that if this value is  $< 1.2$  for the undesirable cation mixing would occur in the lattice. The crystallite size can be estimated using Scherrer's formula given in eq. (1).

$$D = 0.9/\beta\cos\theta \quad \text{----- (1)}$$

where,  $\lambda$  is the wavelength of X-ray used, which is  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406\text{\AA}$ ), and  $\beta$  is the full width at half-maximum of the diffraction peak corresponding to  $2\theta$ . Using the above equation the sizes of the crystallites are found to be in the range of nanometer [26]. The crystallite size is measured by taking the average of three mainline widths, which are obtained from the XRD patterns. The crystallite size calculated using the Debye Scherrer's formula is listed in the table. 1.

**Table 1:-**The sol-gel and solid state reaction methods

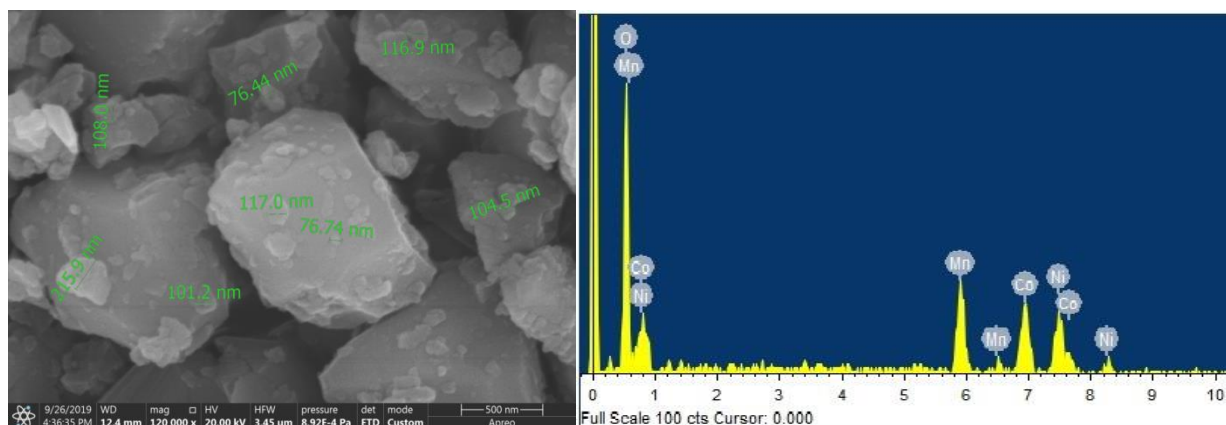
Samples	a( $\text{\AA}$ )	c( $\text{\AA}$ )	c/a	Cell volume ( $\text{\AA}^3$ )	$I_{003}/I_{104}$	R-factor ( $(I_{006}+I_{102})/I_{101}$ )	Crystallite size (nm)
NCM811 (SG)	2.875	14.336	4.921	103.31	1.67	20.6	7.43
NCM811 (SSR)	2.893	14.243	4.923	103.26	0.99	20.8	10.77



**Figure 3:-**X-ray diffraction patterns for  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  material is prepared by sol-gel auto-combustion and solid state reaction methods

#### FE-SEM with EDS studies

Figure 4 and 5 shows the FE-SEM images of the  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  compound in sol-gel auto-combustion and solid-state reaction method. Both compounds have a smooth, well-shaped and particle-agglomerated morphology [27]. The average size of the primary particle is about 500 nm and 2  $\mu\text{m}$ . These samples have the accumulation morphology, but the primary particles become well-shaped and their size increases. In this results suggest that foreign metal ion doping could improve the crystallinity of the synthesized samples. The precursor powders with spherical shape and dense morphologies were necessary to prepare the cathode powders with spherical shape and dense structure by both methods with a lithium component. Figure 3 and 4 shows the EDS spectra, qualitative results and elemental analysis that confirms the presence of Ni, Co, Mn and O in  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  cathode material. It is clearly observed that the spectra show the appropriate ratios of the elements. Lithium is not observed in the EDS spectrum because it has too low of an atomic number to be detected with EDS.



**Figure 4:-**FE-SEM with image for  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  material is prepared by sol-gel auto-combustion method

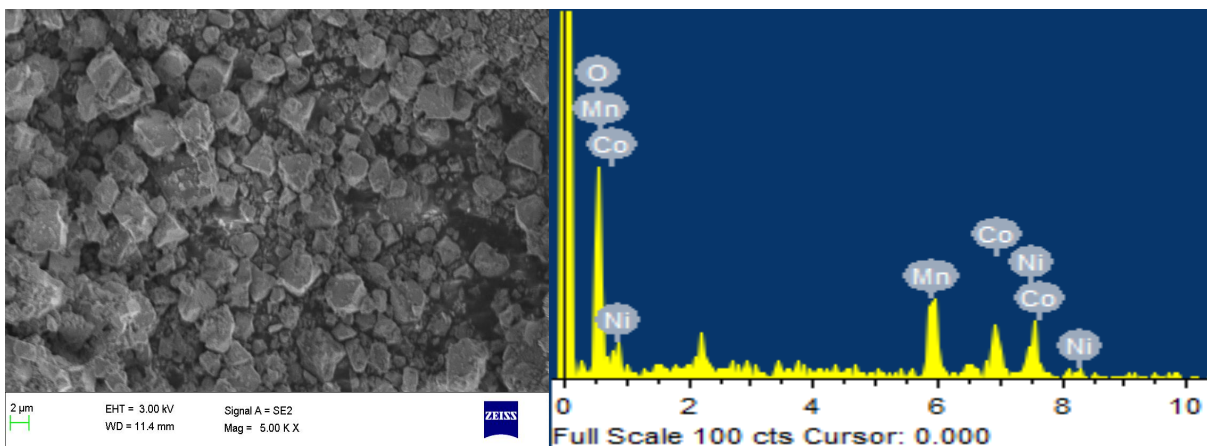


Figure 5:-FE-SEM with image for  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  material is prepared by solid state reaction method

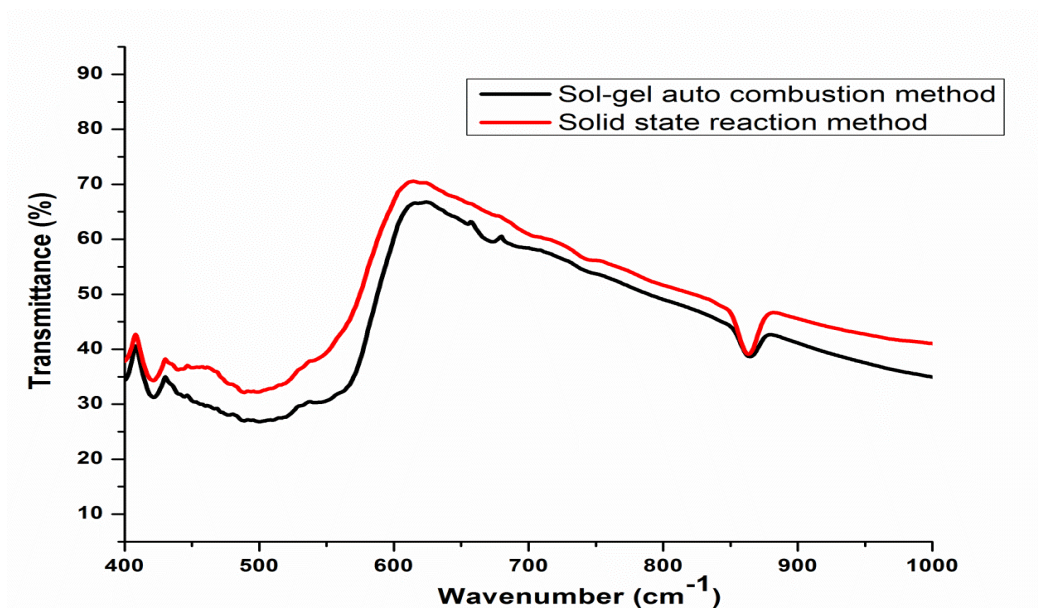


Figure 6:-FT-IR spectra  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  material is prepared by sol-gel auto-combustion and solid state reaction methods

### FT-IR studies

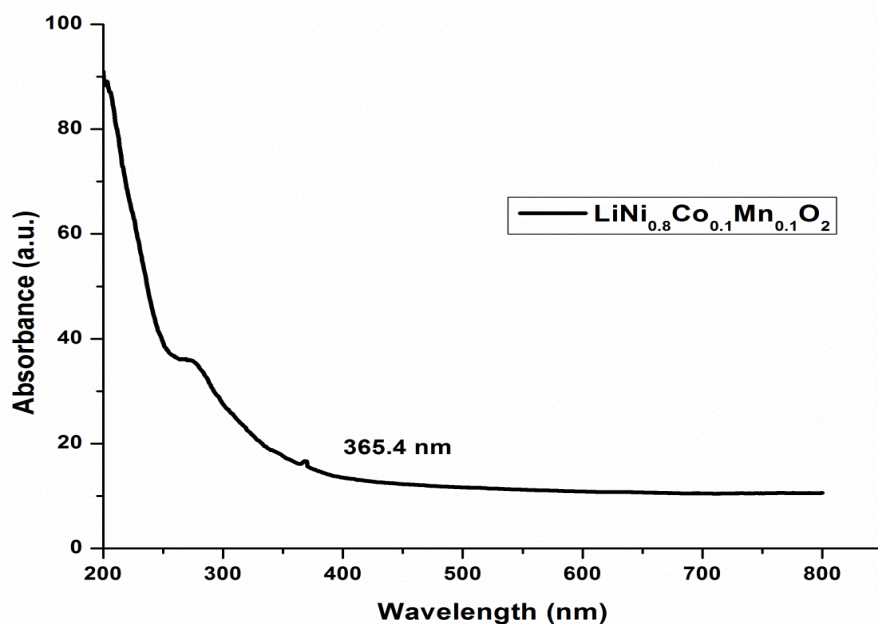
From the figure 6 represents the mode of vibrations for transition metals  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  in the  $400\text{--}1000\text{ cm}^{-1}$  region which is largely associated with the vibrations of  $\text{MO}_6$  where  $\text{M}=\text{Ni}, \text{Co}$  and  $\text{Mn}$  and  $\text{LiO}_6$  octahedral units. The peaks at  $613\text{ cm}^{-1}$  and  $614\text{ cm}^{-1}$  are listed in the table. 2 the vibration bending modes of  $\text{MO}_6$  i.e.  $\nu$   $[(\text{M}-\text{O}-\text{Li})]$ , the weak band around  $430\text{ cm}^{-1}$  is assigned for the asymmetric stretching of  $\text{Li}-\text{O}$  in  $\text{LiO}_6$  environments. The structure of the synthesized sample by the ion-exchange reaction was further characterized by FT-IR. Figure 4(b) shows the IR spectra of the synthesized sample prepared by solid state reaction method at air atmosphere. It can be seen that strong absorption peaks are observed in the region  $400\text{--}1000\text{ cm}^{-1}$ . The typical absorption peaks at  $515.2\text{ cm}^{-1}$  and  $859.4\text{ cm}^{-1}$  which are in agreement with those for  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  prepared by solid-state reaction at high temperature, are observed. The  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  crystal can be considered to be composite metallic oxidant in which Li-ion layer is sandwiched between Ni, Co and Mn and O layers.

### Optical properties

It was carried out by measuring the diffuse reflectance spectroscopy in UV-Vis range. The spectrum was taken in the range of 200-700 nm. Fig.1 shows the prepared  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  nano-powders synthesized by sol-gel auto-combustion method of the diffused reflectance spectra (absorbance as a function of wavelength). The absorption edges are homogeneous with no other band observed, which confirm that the prepared samples (both methods) are  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  layered structure. Those absorption band at around 364.5 nm to 385.5 nm may be due to the MO (M=Ni, Co and Mn) nanoparticles. The absorption edge of the bulk spinel cathode material is around 320 nm and 472 nm [31-32]. The band gap energy was calculated from the diffuse-reflectance spectra by plotting the square of the Kubelka-Munk function given as [33],

$$K = \frac{(1 - R)^2}{2R}$$

where  $K$  is reflectance transformed according to Kubelka Munk,  $R$  is reflectancy (%),  $h\nu$  is the photon energy. The  $E_g$  were measured with the help of reflectance spectra plotting graphs of  $(K \cdot h\nu)^n$  versus  $(h\nu)$ .



**Figure 1:-**UV-visible spectra of  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  material is prepared by sol-gel auto-combustion

### Conclusions:-

The layered structure material  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  is synthesized by sol-gel auto-combustion and solid-state reaction method. The cathode material resembled the hexagonal  $\alpha\text{-NaFeO}_2$  structure which was confirmed from the XRD pattern. This result strongly supports the results obtained for the preparation method is sol-gel.

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