

A Green-Chemical Approach for the Synthesis of Cobaltate Spinel MCo_2O_4 [M= Mg And Ni] Under Microwave Assistance

R. Yuvasravana^{ab}, P. P. George^{a*}, N. Devanna^b

^{ab}Research scholar, Department of Chemistry, Madanapalle Institute of Technology and Science, Madanapalle, Andhra Pradesh, India.

^{a*}Assistant professor, Department of Chemistry, Madanapalle Institute of Technology and Science, Madanapalle, Andhra Pradesh, India.

^bDirector and Professor, Department of Chemistry, Jawaharlal Nehru Technological University Anantapur, Anantapur, Andhra Pradesh, India.

ABSTRACT: The benefits of utilizing fruit peel extract for the synthesis of nanoparticles have great impact on green nanotechnology. The objective of the present study was to explore the effects of pomegranate peel extract as fuel in the microwave mediated green synthesis of MCo_2O_4 , [M= Mg and Ni] nanoparticles. MCo_2O_4 [M= Mg and Ni] nanoparticles are synthesized from their metal salts by microwave assisted solvothermal synthesis using pomegranate peel extract as fuel. The pomegranate peel extract consists of complex polyphenolic molecules that reduces the metal salts into metal oxides and also rearranges the oxides into corresponding hetero metallic oxide spinel structures. The nanoparticles synthesized have been characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) UV-Vis spectroscopy and photoluminescence (PL) spectroscopy. No impurities are detected either in PXRD, FTIR and EDX, and this indicates the purity of the sample. The green protocol which involve microwave combustion route for synthesis spinels is rapid and economical method as it does not use any hazardous chemicals as reducing or stabilizing agents.

KEYWORDS: MCo_2O_4 nanoparticles. Pomegranate peel extract. Antioxidants. Electron microscopy. Green synthesis.

I. INTRODUCTION

Rapid technological advancement along with the depleting traditional energy resources demand urgent attentions on smarter production, usage and storage of energy. Super capacitors, a class of energy storage devices attracted more and more attention in recent years [1]. Lithium-ion batteries are one of the most promising type of energy storage devices, that have attracted more attention due to their long life cycle, high-power capability, and fast charge and discharge rates; they are mostly used in energy storage, mobile communication devices, portable and stationary electronics [2]. Commercially graphite is used as anode material with a theoretical capacity of 372 mAhg^{-1} . Researchers have focused on studying alternate metal oxides as next-generation anode materials which show good capacity, rate capability and long life [3]. Cobalt oxide spinel (Co_3O_4) in different particle forms of nanowires, nanosheets, thin films and nanofibers were investigated and they showed reversible capacities ranging between $600\text{--}900 \text{ mAhg}^{-1}$ [4,5]. Wherein cobalt oxide spinel one of the Co atom is replaced by other ternary metal ions to form a heterometallic oxide spinels such as MCo_2O_4 (M = Zn, Mn, Cu, Fe, Ni, Mg) [6–12]. In recent reports, few oxide systems showed a reversible capacity of $850\text{--}1000 \text{ mAhg}^{-1}$ for $ZnCo_2O_4$ [6], 827 mAhg^{-1} for $FeCo_2O_4$ [10], 745 mAhg^{-1} for $CuCo_2O_4$ [11], 900 mAhg^{-1} for $MnCo_2O_4$ [13] and $850\text{--}900 \text{ mAhg}^{-1}$ for $NiCo_2O_4$ [12,14]. $MgCo_2O_4$, which comes under metal cobalt oxide family, has been synthesized by green chemical method. Previously $MgCo_2O_4$ has been synthesized under hydrothermal method followed by calcination at $400 \text{ }^\circ\text{C}$ [15], molten salt method [1], oxalate

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decomposition method and electro spinning technique [3], solution combustion synthesis and coprecipitation [16]. NiCo₂O₄ has been synthesized under microwave assistance method [17-18] and hydrothermal approach [19]

In the present study, MCo₂O₄ spinels are synthesized under green chemical approach by using pomegranate fruit peel extract as fuel. MCo₂O₄ spinels are synthesized in house hold microwave oven by solvent combustion process.

II. EXPERIMENTAL SECTION

2.1. Materials

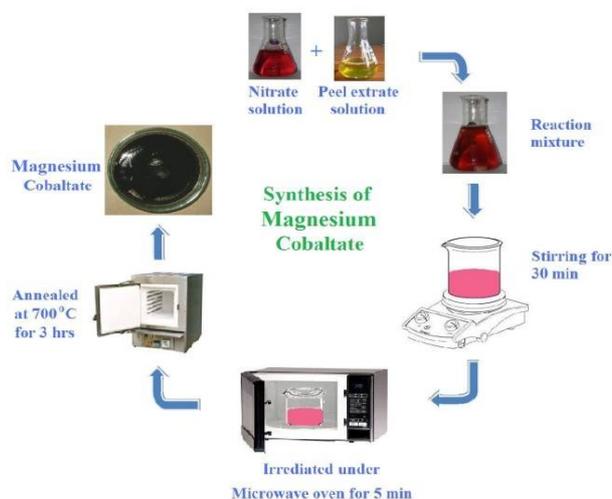
Magnesium nitrate, nickel chloride and cobalt nitrate (97% purity) were used as the starting material, (Merck chemicals, India) and were used as received without any further purification. The pomegranate (*Punica granatum*.) fruits were collected from local fruit market, Madanapalle, Andhrapradesh.

2.2. Preparation of the Plant Extract

The *pomegranate* (*Punica granatum*) fresh peels were washed thoroughly with distilled water to remove unwanted dust and they were dried in shade. 20g of pomegranate fruit peel was weighed again with distilled water and added in 100 ml of distilled water in 250 ml Erlenmeyer flask and boiled on a gas burner for 15 minutes, cooled and filtered using filter paper, the filtrate thus obtained is used as aqueous fruit peel extract for synthesis of nanoparticles.

2.3. Synthesis of Metal Cobaltates

Stoichiometric ratio of magnesium nitrate and cobalt nitrate (1:2) are dissolved in 50 ml distilled water in 250 ml beakers. Then 5 ml of fruit peel extract was added to the nitrate solution, the reaction mixture solution was stirred for 15 minutes using a magnetic stirrer. The solution was then irradiated under microwave radiation using a house hold microwave oven for about 5 minutes, with break at every 60 sec to avoid wastage of the solution by spilling. Initially solution underwent boiling, dehydration and decomposition by releasing gases leaving dry flakes like solid behind. This dry solid was washed several times with water and ethanol for its purity and annealed in muffle furnace at 700 °C for about 3 hours. Same procedure is repeated for NiCo₂O₄. The pomegranate fruit peel extract obtained as a result of extraction procedure was examined under UV-Vis spectroscopy by using Jasco UV-670 spectrophotometer and the results obtained were similar to those published by Wenjuan Qu et.al [20, 21].



Scheme 1. Synthesis of Magnesium Cobaltate

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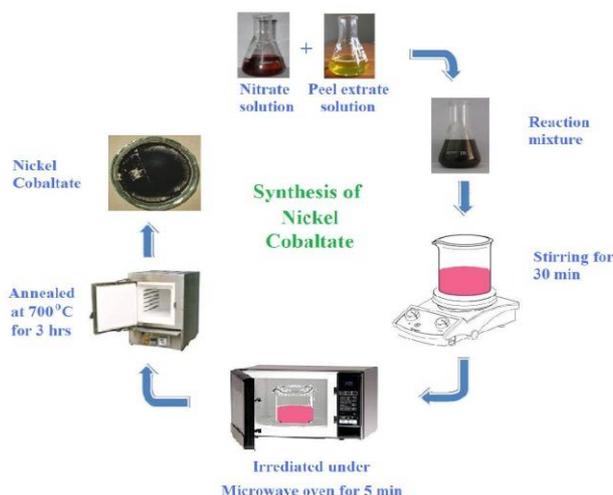
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Synthesis of magnesium cobaltate is presented in Scheme 1. Mixture of magnesium and cobalt nitrates give a red colored solution and on addition of light yellow colored peel extract, it turns to dark greenish red colored solution. The reaction mixture is stirred for 30 min and then irradiated under microwave to obtain a reddish brown flakey residue, it is washed and annealed at 700 °C for 3 hours in a muffle furnace. Finally a pure crystalline black colored magnesium cobaltate spinel is formed.

Synthesis of nickel cobaltate is described in Scheme 2. In general, cobalt nitrate is in red color and nickel chloride is green in color, hence the mixture of these metal salts give greenish red colored solution. Pomegranate fruit peel extract is light yellow in color, hence, on mixing of peel extract to metal salt solution it turns into dark solution, indicating that reaction is initiated. On microwave irradiation of this dark solution give rise to a reddish brown flakey residue. This residue is washed and then annealed in muffle furnace at 700 °C for 3 hours, as a result of annealing pure crystalline black colored nickel cobaltate spinel is formed.



Scheme 2. Synthesis of Nickel Cobaltate

The total yield of magnesium and nickel cobaltate was estimated to be 60 % and 70 % respectively. The synthesis of nanoparticles by the green protocol method requires neither the use of any hazardous chemicals or a surfactant for the preparation of samples. The as-prepared samples are annealed at 700 °C to enhance its purity by thermally decomposing the plant remains from sample.

III. CHARACTERIZATION

The Bruker D8 diffractometer was used for recording PXRD patterns of samples with Cu K α radiation for 2 θ values ranging from 10 to 80°. The scanning electron microscope, Ziess-SEM instrument was used for morphological characterisation of the metal cobaltates, the samples were coated with gold sputtering for the better visibility of surface morphology. FT-IR spectra of samples in KBr pellets were collected for determination of surface functional groups by Jasco FT/IR-4200 infrared spectrophotometer in transmittance mode wavelength ranging from 400 to 4000 nm. The optical measurements were performed using a UV-VIS-NIR diffuse reflectance spectrophotometer, Jasco UV-670 spectrophotometer at room temperature, the wavelength ranges from 200 to 900 nm. The photoluminescence measurements were performed on a Jasco spectro fluorometer FP-6300 at room temperature.

IV. RESULTS AND DISCUSSION

4.1. Powder X-ray Diffraction (PXRD) Analysis

The Bruker D8 diffractometer at Vellore Institute of Technology, with Cu $K\alpha$ radiation is used for recording XRD patterns for the samples at 2θ values ranging from 10 to 80° . The XRD pattern are analysed to study the crystallinity of the sample and phase identification for MCo_2O_4 , [M= Mg and Ni] spinels as it is shown in Figures 2a-b. All the diffraction peaks can be perfectly indexed to face-centered cubic spinel-structure. The diffraction peaks for $MgCo_2O_4$ are observed at 2θ of 19.21° , 31.38° , 37.04° , 38.75° , 44.99° , 55.82° , 59.53° and 65.39° that are associated to the (111), (220), (311), (222), (400), (422), (511), and (440) planes respectively, and these planes can be correlated to the cubic phase of $MgCo_2O_4$ with JCPDS card No. 81-0667 (space group $Fd\bar{3}m$). The diffraction peaks at 2θ 42.82° and 62.03° are also observed and can be attributed to the planes (200) and (220) respectively of MgO phase (JCPDS data file no. 71-2179) which are formed due to high temperature annealing at $700^\circ C$ for 3 hours where a little amount of magnesium is oxidised. The diffraction peaks for $NiCo_2O_4$ are observed at 2θ of 19.10° , 31.36° , 36.92° , 38.62° , 44.87° , 55.67° , 59.35° and 65.24° that are associated to the (111), (220), (311), (222), (400), (422), (511), and (440) planes, respectively, and these planes can be correlated to the cubic phase of $NiCo_2O_4$ with JCPDS card No. 20-0781 (space group $Fd\bar{3}m$). The diffraction peaks at 2θ 43.33° and 62.86° are also observed and can be attributed to the planes (200) and (220) respectively of NiO phase (JCPDS data file no. 65-2901) which are formed due to high temperature annealing at $700^\circ C$ for 3 hours where a little amount of nickel is oxidised. Also the average crystallite size of the samples was calculated from diffraction pattern using Scherrer formula, as demonstrated below

$$L = \frac{0.94\lambda}{\beta_{1/2} \cos \theta}$$

Where L is the average crystallite size (\AA), λ is the X-ray wavelength (0.154 nm), θ is the diffraction angle, and β the peak position and the FWHM (full-width at half maximum). The average crystallite size is found to be 45 ± 2.5 nm for $MgCo_2O_4$ and 52 ± 2.5 nm for $NiCo_2O_4$.

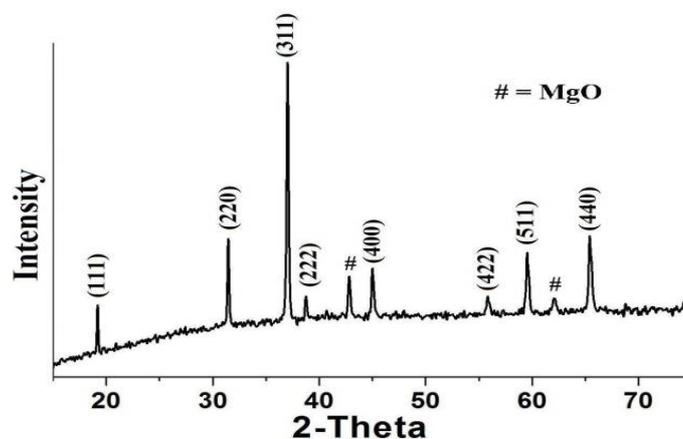


Figure 2a. XRD patterns of of $MgCo_2O_4$ spinels

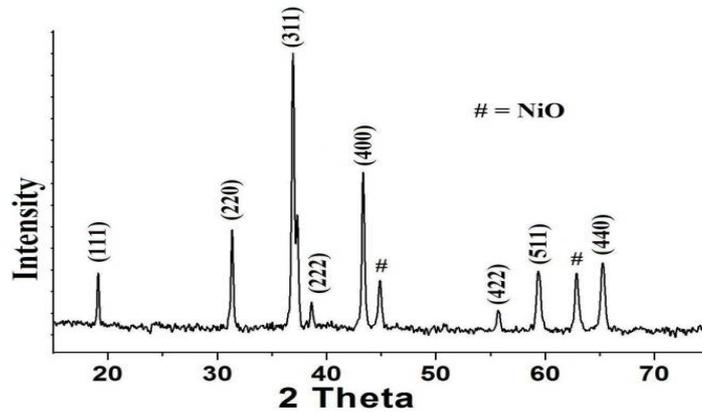


Figure 2b. XRD patterns of of NiCo_2O_4 spinels

4.2. Scanning electron microscopy (SEM) studies

The surface morphology of MgCo_2O_4 spinel nanoparticles are illustrated in Figures 3a. From SEM images it is observed that the spinel particles have nearly spherical like agglomerated structures with diameters ranging from less than 100 nm to nearly 600 nm and are eventually distributed in the form of small particles and large agglomerates. Agglomerated structures are formed as a result of cold welding between small particles and also because of the high temperature annealing at 700 °C. The size of agglomerated MgCo_2O_4 nanoparticles of this work are in better morphology compared to that of synthesized in solution combustion (SCS) method by Nunzio Russo and his co-workers [16]. Solution combustion (SCS) method involves heating of solution containing metal nitrates and glycine in a oven, where glycine is used as the fuel, whereas the current microwave assistance method involves pomegranate fruit peel extract as fuel and microwave irradiation for five minutes. Precursor solution containing fruit peel extract and metal nitrates react to form complex matrix on microwave irradiation, followed by the formation of MgCo_2O_4 samples at the end, this confirms that addition of fruit peel extract may have influenced the size of nanoparticles.

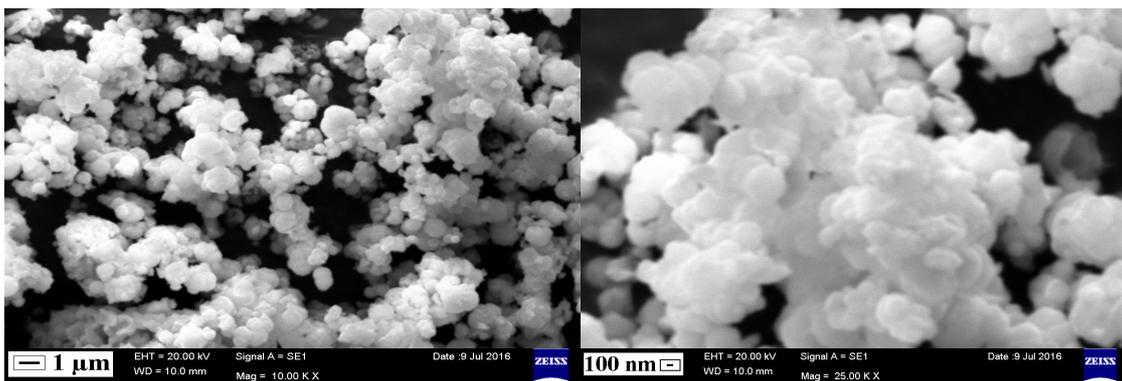


Figure 3a. SEM image of MgCo_2O_4

The surface morphology of NiCo_2O_4 spinels nanoparticles are illustrated in Figures 3b. The size of resulting NiCo_2O_4 nanoparticles seems to be slightly smaller than NiCo_2O_4 nanoparticles synthesized by microwave irradiation method (MIM) by Umesh T. Nakate [22]. Nakate's method involves no plant materials and is a simple precipitation process where the aqueous NaOH solution is added to the aqueous metal chlorides mixture solution to obtain NiCo_2O_4 precipitate and this precipitated solution is irradiated under 350 W microwave oven for 30 minutes. Whereas the current microwave assistance method involves the addition of pomegranate fruit peel extract to metal salt solution and is irradiated under microwaves for five minutes. Precursor solution containing fruit peel extract and metal nitrates react

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to form complex matrix on microwave irradiation, followed by the formation of NiCo₂O₄ samples at the end, this confirms that addition of fruit peel extract may have influenced the size of nanoparticles.

It is well known that the morphology of the samples can be varied based on the preparation procedure. Hence in this work microwave application emerges as significant method in the reduction of reaction time and pomegranate fruit peel extract arises as a better fuel than glycine in producing MgCo₂O₄ and NiCo₂O₄ spinel particles with good morphological structures.

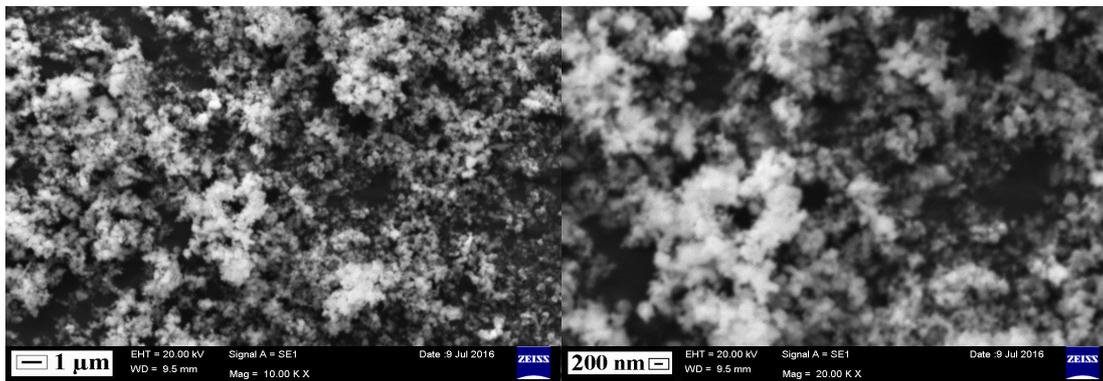


Figure 3b. SEM image of NiCo₂O₄

4.3. Energy dispersive X-ray spectroscopy (EDX) analysis

Elemental analysis and chemical characterisation of MgCo₂O₄ spinel are predicted using energy dispersive X-ray spectroscopy (EDX). Figure 4a shows the EDX spectra of MgCo₂O₄. In the spectra the elements are showing their weight and atomic percentages as follows, magnesium has 5.57 and 7.14, cobalt has 64.16 and 33.91, oxygen has 30.27 and 58.95 respectively.

Elemental analysis and chemical characterisation of NiCo₂O₄ spinel are predicted using energy dispersive X-ray spectroscopy (EDX), Figure 4b shows the EDX spectra of NiCo₂O₄. In the spectra the elements are showing their weight and atomic percentages as follows, nickel has 30.85 and 18.74, cobalt has 44.89 and 27.17, oxygen has 24.26 and 54.09 respectively.

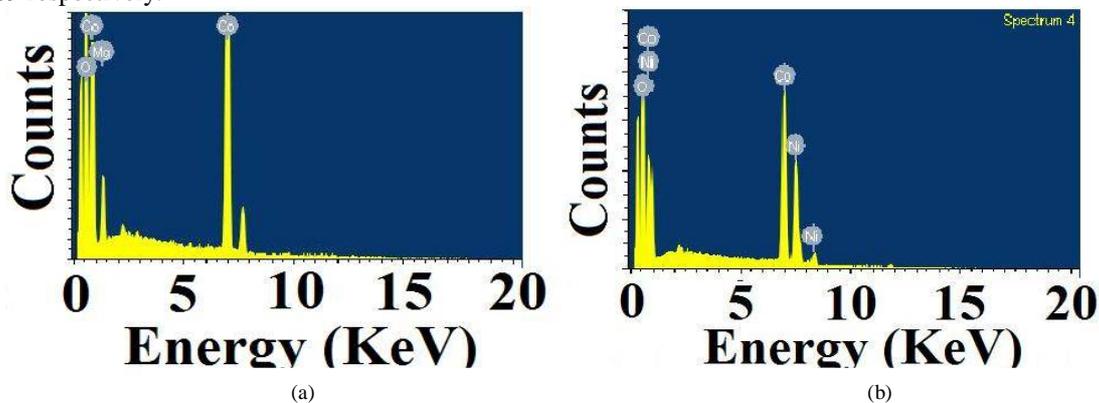


Figure 4. EDX image of (a) MgCo₂O₄ (b) NiCo₂O₄

4.4. Fourier transform infrared (FT-IR) analysis

The FT-IR spectra of $MgCo_2O_4$ are shown in Figures 5a-b and were recorded in the frequency range from 400 – 4000 cm^{-1} . In the spectra, no specific peaks are observed in the range of 1000 to 4000 cm^{-1} . It indicates that organic impurities or any other impurities are absent in both of the sample. In FT-IR spectra the range 400–1000 cm^{-1} are assigned to the metal–oxygen stretching frequencies. Figure 5a shows that $MgCo_2O_4$ exhibits three sharp peaks centered at 654, 532 and 441 cm^{-1} respectively and can be assigned to Co–O–Mg, Co–O and Mg–O as such metal – oxygen stretching and bending vibrations.

From Figure 5b FT-IR spectra of $NiCo_2O_4$ exhibits two peaks centered at 651.9 and 551.6 cm^{-1} respectively and they are related to the, Co–O and Ni–O stretching and bending vibration. The FT-IR values can be supported by that of the FT-IR values of $NiCo_2O_4$ nanoparticles synthesized by microwave irradiation method (MIM) by Umesh T. Nakate [22] and that of the $NiCo_2O_4$ nanoparticles synthesized under CTAB surfactant assistance [17].

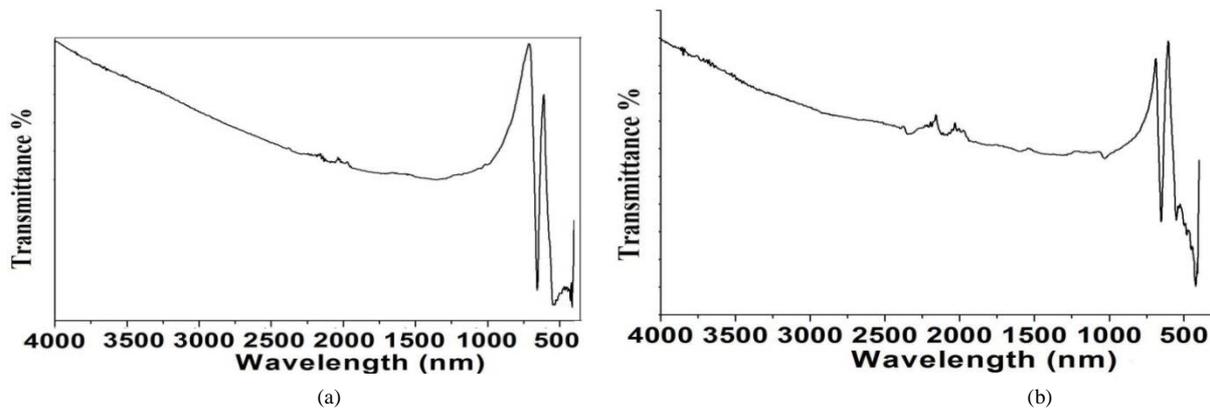


Figure 5. FT-IR image of (a) $MgCo_2O_4$ (b) $NiCo_2O_4$

4.5. Optical properties

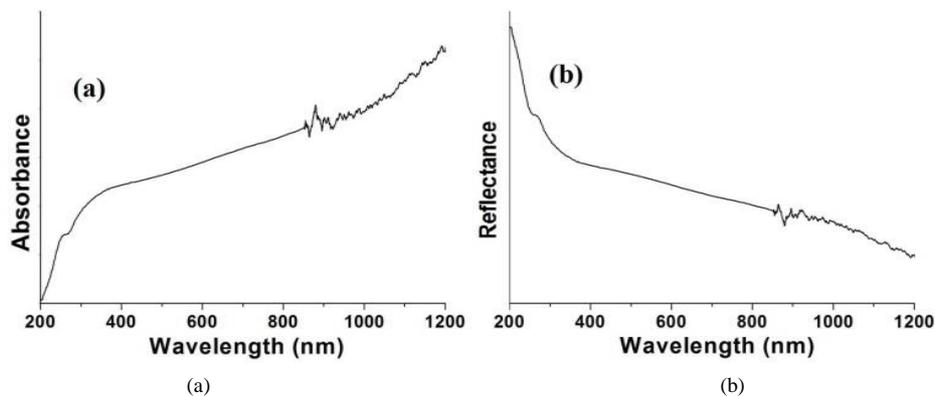


Figure 6: (a) UV-Vis spectra of $MgCo_2O_4$ (a) absorbance spectra (b) reflectance spectra

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The optical studies for MgCo_2O_4 are performed using a Jasco UV-670, a UV-VIS-NIR diffuse reflectance spectrophotometer and the reflectance spectra was recorded at room temperature. Metal cobaltates are mostly dark in color and rarely exhibit d-d electron transitions, hence we see no absorption bands in the UV-Vis absorbance spectra of MgCo_2O_4 , even then a sharp peak can be seen at 880 nm in the absorbance spectra. MgCo_2O_4 is a normal spinel and dark colored compound that is because Mg^{+2} ion is tetrahedrally coordinated and have completely filled d-orbital and Co^{+3} ion have completely half-filled d-orbital, hence they rarely exhibit d-d electron transitions. Figure 6a shows the typical UV-Vis absorbance spectra of MgCo_2O_4 nanoparticles and shows UV-absorption peak at 880 nm. UV-Vis reflectance spectra are recorded to estimate the optical band gap of MgCo_2O_4 nanoparticles and is shown in Figure 6b.

Figure 6c shows the typical UV-Vis absorbance spectra of NiCo_2O_4 nanoparticles and shows UV-absorption peak at 334 nm. UV-Vis reflectance spectra are recorded to estimate the optical band gap of NiCo_2O_4 nanoparticles and is shown in Figure 6d.

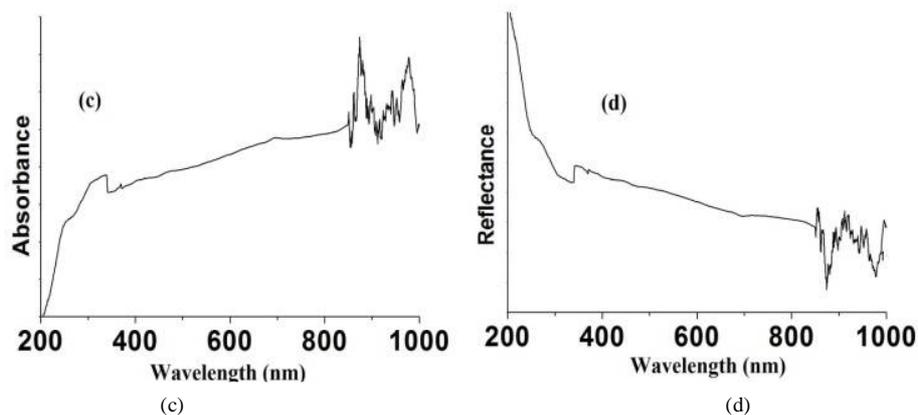


Figure 6. UV-Vis spectra of NiCo_2O_4 (c) absorbance spectra (d) reflectance spectra

The band gap is determined by relating diffuse-reflectance (R) of the samples with the Kubelka-Munk function $F(R)$ in the equation $F(R) = (1-R)^2/2R$ and the energy intercept plot of $(F(R)*hv)^2$ versus hv is plotted which yields the $E_{g, dir}$ for a direct-allowed transition, when the linear regions are extrapolated to the zero ordinate, one can get the band gap of the sample. Hence by this method, the band gap is calculated for MCo_2O_4 , [$M = \text{Mg}$ and Ni] nanoparticles and the band gap is found to be 1.45 eV for MgCo_2O_4 and 1.44 eV for NiCo_2O_4 and hence are represented in Figure 7a and 7b respectively. The decrease in optical band gap indicates the good conductivity of MCo_2O_4 due to the presence of half-filled d-orbital of Co^{+3} ions and also indicates the increase in crystal size of MCo_2O_4 nanoparticles. From the quantum confinement the increase in crystal size, band gap energy exhibits a decreasing trend. Thus the results from UV-Vis reflectance spectra are in good agreement with that of XRD results.

Fruit peel extract of pomegranate consists of polyphenols such as gallic acid, punicalagin and ellagic acid as reported by Wenjuan Qu et.al. [20]. These fruit peels are naturally available, non-polluting and non-toxic, thus fruit peel extract as active ingredient, enables synthesis of nanoparticles at low cost. Microwave radiation, dehydrates and decomposes the solution into flake like residue, washed and annealed to give MCo_2O_4 [$M = \text{Mg}$ and Ni] nano spinels. Fruit peel material is completely decomposed and removed in the form of carbon related by-products, either in microwave or at the annealing process, resulting magnesium cobaltate and nickel cobaltate nano spinels.

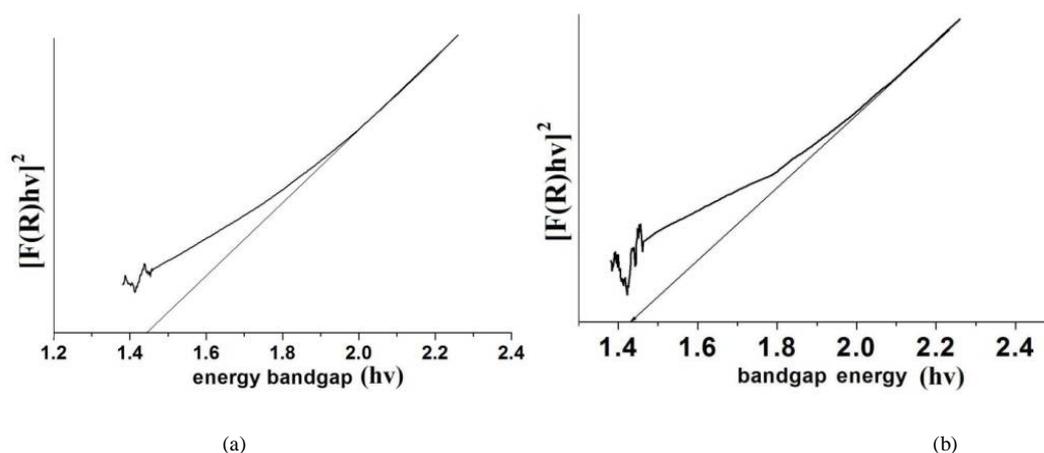
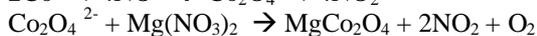
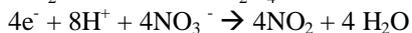


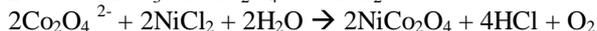
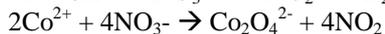
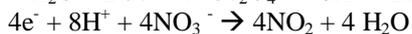
Figure 4. Bandgap energy of (a) $MgCo_2O_4$ (b) $NiCo_2O_4$

The reaction mechanism of spinel preparation can be described as follows.

For $MgCo_2O_4$



and for $NiCo_2O_4$



V. CONCLUSIONS

In this work MCo_2O_4 [M = Mg and Ni] nanoparticles are synthesised under microwave assistance by using pomegranate fruit peel extract as fuel and obtained anticipated results. The pomegranate fruit peel extract promotes the formation of nanoparticles at room temperature and no other harmful chemicals are used except that of metal salts and fruit peel extract. This microwave assistance method is more reliable, can be performed in simple and easy steps and gets the results within a short duration. The MCo_2O_4 [M = Mg and Ni] nanoparticles formation were confirmed by PXRD, FT-IR and SEM. The band gap values calculated from reflectance spectra of UV-VIS-NIR diffuse reflectance spectrophotometer, ranges between 1.44 eV and 1.45 eV. Thus, this work provides a simple and convenient method for the preparation of transition hetero metallic oxides like MCo_2O_4 [M = Mg and Ni] and this synthetic route can be further used for the synthesis of other hetero metallic oxides.

REFERENCES

- [1]S.G. Krishnan, M.V. Reddy, M. Harilal, B. Vidyadharan, I.I. Misnon, M.H.A. Rahim, J. Ismail, R. Jose, "Characterization of $MgCo_2O_4$ as an electrode for high performance supercapacitors", *Electrochim Acta.*, Vol.161, pp.312- 321, 2015.
- [2]L. Zhang, Q. Tang, X. Chen, B. Fan, K. Xiao, S. Zhang, W. Deng, A. Hu, "Self-assembled synthesis of diamond-like $MnCo_2O_4$ as anode active material for lithium-ion batteries with high cycling stability", *J. alloys. Comp.*,doi.org/10.1016/j.jallcom.2017.06.124, 2017.
- [3]D. Darbar, M. V Reddy, S. Sundarajan, and R. Pattabiraman, "Anodic electrochemical performances of $MgCo_2O_4$ synthesized by oxalate decomposition method and electrospinning technique for Li-ion battery application", *Mater. Res. Bull.*, Vol.73, pp.369 – 376, 2016.

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 6, Issue 6, June 2017

- [4]M.V. Reddy, G.V. Subba Rao, B.V.R. Chowdari, "Metal oxides and oxysalts as anode materials for Li ion batteries", Chem. Rev., Vol.113, pp.5364 – 5448, 2013.
- [5]J. Cabana, L. Monconduit, D. Larcher, M.R. Palacin, "Beyond intercalation-based Li-ion batteries: the state of the art and challenges of electrode materials reacting through conversion reactions", Adv. Mater., Vol.22, pp.E170–E192, 2010
- [6]M.V. Reddy, K.Y.H. Kenrick, T.Y. Wei, G.Y. Chong, G.H. Leong, B.V.R. Chowdari, "Nano-ZnCo₂O₄ material preparation by molten salt method and its electrochemical properties for lithium batteries", J. Electrochem. Soc., Vol.158, 12, pp.A1423 - A1430, 2011.
- [7]P. Lavela, J.L. Tirado, C. Vidal-Abarca, "Sol-gel preparation of cobalt manganese mixed oxides for their use as electrode materials in lithium cells", Electrochim. Acta., Vol.52, pp.7986 – 7995,2007.
- [8]J.F. Li, S.L. Xiong, X.W. Li, Y.T. Qian, "A facile route to synthesize multiporous MnCo₂O₄ and CoMn₂O₄ spinel quasi-hollow spheres with improved lithium storage properties", Nanoscale., Vol.5, pp.2045 – 2054,2013.
- [9]M.V. Reddy, C. Yu, F. Jiahuan, K.P. Loh, B.V.R. Chowdari, "Molten salt synthesis and energy storage studies on CuCo₂O₄ and CuO•Co₃O₄", RSC Adv., Vol.2, pp.9619 – 9625,2012.
- [10]Y. Sharma, N. Sharma, G.V. Subba Rao, B.V.R. Chowdari, "Studies on Spinel Cobaltites, FeCo₂O₄ and MgCo₂O₄ as Anodes for Li-ion batteries", Solid State Ionics., Vol.179, pp.587 – 597,2008.
- [11] R. Alcantara, M. Jaraba, P. Lavela, J.L. Tirado, "NiCo₂O₄ Spinel: First Report on a Transition Metal Oxide for the Negative Electrode of Sodium-Ion Batteries", Chem. Mater., Vol.14, pp.2847 – 2848,2002.
- [12] C. Huang, Y. Chien, C. Shih, and H. Chang, "Crystal structure and dielectric properties of Ca (Mg 1 / 3 Nb 2 / 3) O 3 – (Ca 0.61 Nd 0.26) TiO 3 at the microwave frequency", Mater. Res. Bull., vol. 63, pp. 1–5, 2015.
- [13] L. Li, Y.Q. Zhang, X.Y. Liu, S.J. Shi, X.Y. Zhao, H. Zhang, X. Ge, G.F. Cai, C.D. Gu, X.L. Wang, J.P. Tu, "One-dimension MnCo₂O₄ nanowire arrays for electrochemical energy storage", Electrochim. Acta., Vol.116, pp.467 – 474,2014.
- [14] J. Xu, L. He, W. Xu, H. Tang, H. Liu, T. Han, C. Zhang, Y. Zhang, "Facile synthesis of porous NiCo₂O₄ microflowers as high-performance anode materials for advanced lithium-ion batteries", Electrochim. Acta., Vol.145, pp.185-192,2014
- [15] H. Zhao, L. Liu, X. Xiao, Z. Hu, S. Han, Y. Liu, D. Chen, X. Liu, "The effects of Co doping on the crystal structure and electrochemical performance of Mg(Mn₂ – xCo_x)O₄ negative materials for lithium ion battery", Solid State Sci., Vol.39, pp.23,2015.
- [16] M.A. Zamudio, S. Bensaid, D. Fino, and N. Russo, "Influence of the MgCo₂O₄ Preparation Method on N₂O Catalytic Decomposition", Ind. Eng. Chem. Res., Vol.50, pp.2622-2627,2011.
- [17] G.A. Babu , G. Ravi, Y. Hayakawa, "Microwave synthesis and effect of CTAB on ferromagnetic properties of NiO, Co₃O₄ and NiCo₂O₄ nanostructures", Appl. Phys. A, Vol.119, pp.219–232,2015.
- [18] Y. Lei, J. Li, Y. Wang, L. Gu, Y. Chang, H. Yuan, and D.X. Rapid, "Rapid Microwave-Assisted Green Synthesis of 3D Hierarchical Flower-Shaped NiCo₂O₄ Microsphere for High-Performance Supercapacitor", ACS Appl. Mater. Interfaces, Vol.6, pp.1773–1780,2014.
- [19] M. Zhou, F. Lu, B. Chen, X. Zhu, X. Shen, W. Xia, H. He, X. Zeng, "Thickness dependent complex permittivity and microwave absorption of NiCo₂O₄ nanoflakes", Materials Letters, Vol.159, pp.498–501,2015.
- [20] W. Qu, P. Li, J. Hong, Z. Liu, Y. Chen, A.P. Breksa III and Z. Pan, "Thermal stability of liquid antioxidative extracts from pomegranate peel", J Sci Food Agric., Vol.94, pp.1005,2014.
- [21] R. Yuvasravana, P.P. George, "A Green Protocol for Synthesis of MAI₂O₄, [M ¼ Cu and Co] Spinel Under Microwave Irradiation Method", Int. J. Nanosci., Vol.15, pp.1650033,2016.
- [22] U.T. Nakate, S.N. Kale, "Microwave assisted synthesis and characterizations of NiCo₂O₄ nanoplates and Electrical, magnetic properties", Materials Today: Proceedings, Vol.3, pp.1992–1998,2016.