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Co-precipitated $MnCo_2O_4$ Spinel: Physicochemical Properties and Potential Energy Storage Applications

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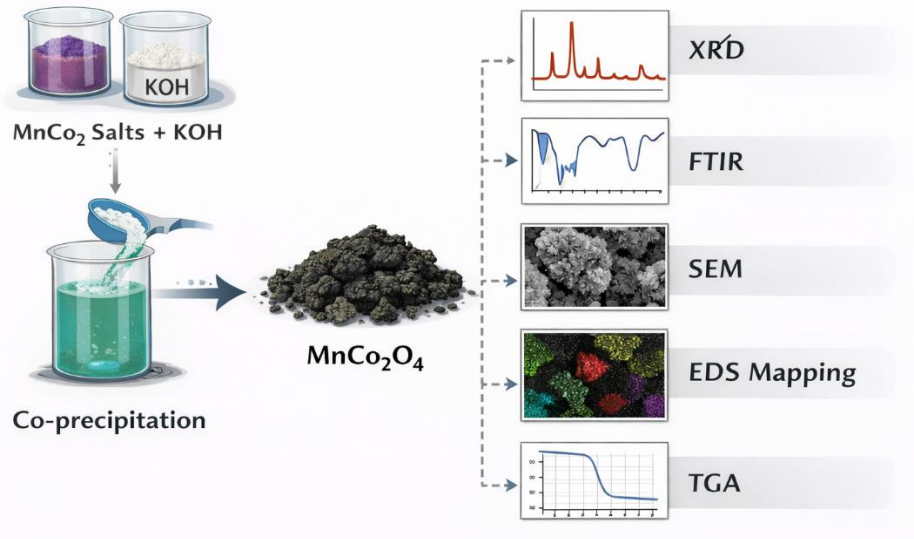
ABSTRACT: In this work, we reported a simplistic co-precipitation technique for the preparation of manganese cobaltite-$MnCo_2O_4$ material using potassium hydroxide-KOH. A comprehensive study on the properties of $MnCo_2O_4$ material was studied using characterization techniques like thermogravimetric analysis, X-ray powder diffraction, Fourier transform infrared spectroscopy-FTIR, morphology studies, and energy dispersive X-ray spectroscopy-EDS with elemental mapping. The X-ray diffraction and FTIR studies of $MnCo_2O_4$ material confirm a cubic spinel structure with an Fd3m space group. The average crystalline size was 37 nm from the Scherrer formula. FTIR analyses from lower frequency regions have also confirmed the ion locations in the spinel structure of $MnCo_2O_4$ material. Micrographs look to be in irregular shape with an agglomeration of $MnCo_2O_4$ particles. To confirm the existence of Mn, Co and O elements from EDS studies and the corresponding distribution of elements was studied by elemental mapping. Therefore, the prepared material via the simplistic co-precipitation technique may be favorable for energy storage and other practical applications.

Keywords: $MnCo_2O_4$; X-ray diffraction; Co-precipitation method; Structural; Morphological properties.

GRAPHICAL ABSTRSCT



1. INTRODUCTION

Due to their remarkable chemical and physical properties, an oxide with one or two types of cations containing spinel compounds under controlled shape and size is of great

interest for various applications including hybrid cars, portable electronic devices, memory systems, microelectronics, rockets, etc [1]. Spinel type-Manganese cobaltite-$MnCo_2O_4$ is beneficial in several application domains (supercapacitor, transportation, telecommunication, medical, and energy) owing to their elemental abundance, cost effective, and electrical behavior [2]. For the $MnCo_2O_4$, various cation distributions have been put forth in the literature [3]. These findings indicate that the preparation conditions of this material could affect the crystal phase, morphology, cation distribution, and vibrational properties.

Researchers are very interested in synthesizing the manganese cobalt oxide material via common methods including sol-gel, combustion technique, ball milling, solid-state reaction, solvothermal, mechanochemical method, hydrothermal and wet chemical. However, some of these methods are frequently used and costly, unreliable, and challenging for large-scale production. Among them, chemical techniques, co-precipitation is cost-effective and the best method due to it providing homogeneous size distribution, required surface morphology and purity.

To synthesis the manganese cobalt oxide material using the simplistic coprecipitation process. The aim is to characterize the same materials using TGA analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray spectroscopy (EDS) with mapping analysis. The struct-morphology properties of $MnCo_2O_4$ materials were investigated and tried to correlate the properties of manganese cobalt oxide with morphology and crystallite size.

2. EXPERIMENTAL

2.1. Materials

Manganese chloride, potassium hydroxide, and cobalt (II) chloride were acquired from Sigma Aldrich. The synthesis technique used deionized water, which was not further refined.

2.2. Synthesis

A simplistic co-precipitation technique was used to synthesize manganese cobalt oxide material. Each product was weighed using a weighing machine. Then, 20 ml of distilled water was added gradually while being stirred with a magnetic stirrer at a speed of 660 rpm. The last addition is KOH, which will be added gradually to the mixture. This will cause the color of the combination to shift from red to a greenish blue and precipitate was obtained as a product. The precipitated sample was centrifuged for 2:10 minutes, while the speed was preset at 9340 rpm. The samples were collected and washed with de-ionized H_2O and absolute ethanol for 5 times. Finally, the samples were dried at 100°C for 4 hours and stored for characterization.

Fig. 1 Synthesis schematic of the $MnCo_2O_4$ prepared via co-precipitation method.

2.3. Materials characterization

TGA analysis was performed at room temperature at a rate of 10 °C per minute using an N_2 atmosphere and a PerkinElmer Simultaneous Thermal Analyzer (STA). The phase identification was performed using a Panalytical-Empyrean X-ray measurement, with wavelength λ=1.54 Å at 45 kV and recorded from

10 to 80°. Standard patterns from the International Centre for Diffraction Data (ICDD) database was utilized to determine the phase. The FTIR spectra were collected over a range of 400-4000 cm^{-1} using a Nicolet, Thermo Electron Fourier transform infrared spectrometer fitted with a deuterated L-alanine triglycine sulfate (DLATGS) detector (mid-IR region). The sample's microstructure was studied by JEOL-JSM-6010LA scanning electron microscopy, at 20 keV. Secondary electron imaging was used to capture the SEM images (SEI). A double-sided adhesive carbon tape was used to secure the sample to the brass stub. Fields of the sample were kept in a high-vacuum chamber (ULVAC KIKO lnc, Japan), and micrographs of the sample were captured by InTouchScope JSM program.

3. RESULTS AND DISCUSSION

3.1. Thermal analysis

Fig. 2 displays the TGA thermogram of the synthesized manganese cobalt oxide by the co-precipitation method. From 50 to 800C, there was no considerable weight loss (ie, the TGA plot remained virtually steady) or exothermic peak. As a result, it suggests that the destruction of organic derivatives and the formation of manganese cobalt oxide as highly crystalline nature occurred at his temperature range.

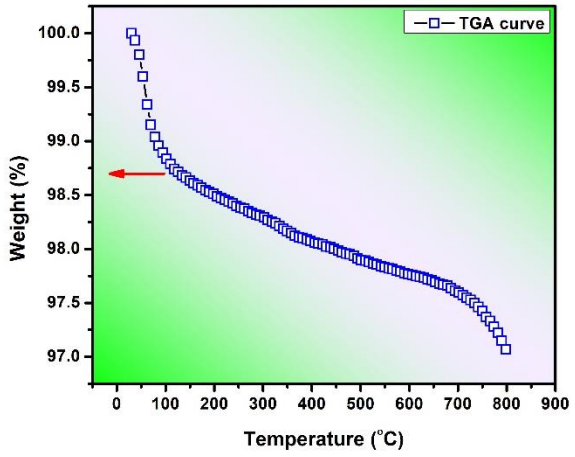


Fig. 2 TGA graph of the synthesized manganese cobalt oxide by co-precipitation method.

3.2. XRD investigation

The structural XRD analyses were utilized to investigate the phase formation of the manganese cobalt oxide by the co-precipitation method. The XRD pattern of manganese cobalt oxide at room temperature is given in Fig. 3. The 2 angles indexed to JCPDS card No. 023-1237 with (111), (220), (311), (222), (400), (422), (511), 440), (620), and (533) planes are coupled to an FCC spinel $MnCo_2O_4$ with an Fd3m space group [4]. All the XRD peaks were strong and distinct, suggesting the materials are crystalline in nature. No more phases were found within the range of the XRD. The average grain sizes, D_{avg} was calculated using the Scherrer formula [5],

$$D_{avg} = 0.9\lambda/\beta\cos\theta \quad (1)$$

Where λ denotes the X-ray wavelength (Å), D_{avg} reprents the grain size, β reprents the full width at half maximum, and θ reprents the Bragg's angle. The predicted D_{avg} for the manganese cobalt oxide material was 37 nm. This value is satisfactory when compared to other methods of synthesis of manganese cobalt oxide material [6].

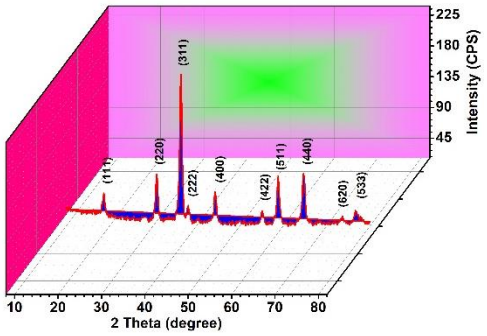


Fig. 3 XRD pattern of the synthesized manganese cobalt oxide by co-precipitation method.

3.3. FTIR studies

Fig. 4 displays the FTIR spectra that were acquired at room temperature for the nanocrystalline $MnCo_2O_4$ material spanning the wavelength range of 400–4000 cm^{-1}. In general, most prominent bands arise between 700 and 350 cm^{-1}, where intensity and wave number rely on

cation distribution in spinel-type material. For $MnCo_2O_4$, the band at 557 cm^{-1} (v_1) is allocated to the octahedral complexes, whereas the band at 656 cm^{-1} (v_2) is ascribed to the tetrahedral complexes [7]. The FTIR analyses further confirmed the ion locations in the spinel structure of the $MnCo_2O_4$ nanocrystalline material.

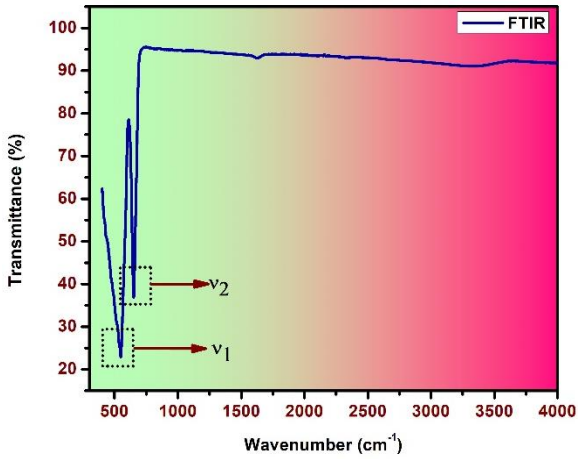
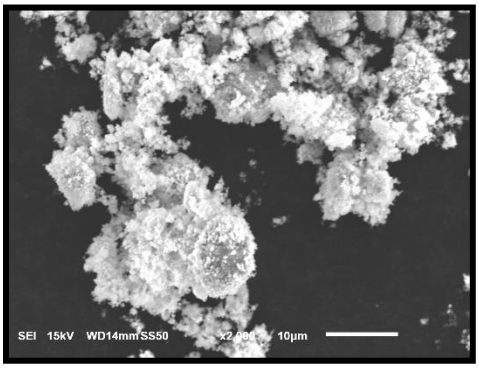


Fig. 4. FTIR spectra for the synthesized manganese cobalt oxide by co-precipitation method.

3.4. Microscopic analysis

Micrographs taken by a scanning electron microscope (SEM) of the synthesized manganese cobalt oxide are shown in Fig. 5. The $MnCo_2O_4$ material seems to be irregular in shape. This can be ascribed to the presence of particle agglomeration via magnetic interaction between them during synthesis. The particles displayed sizes between 10-70 nm [8, 11].



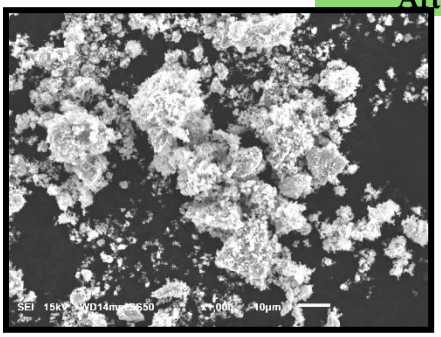


Fig. 5. SEM micrographs with 10 µm of the synthesized manganese cobalt oxide by co-precipitation method.

3.5. Energy Dispersive X-Ray, EDS analysis

The elemental analysis of manganese cobalt oxide produced by the co-precipitation method is shown in Fig. 6. Mn, Co, and O elements can be found in the EDS spectra. No other elements were presented within the EDS spectra This shows the prepared sample's purity [12].

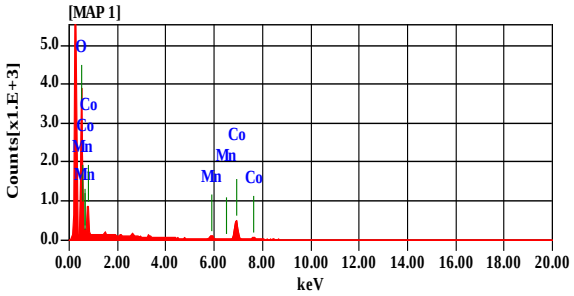


Fig. 6. EDS spectrum of the synthesized manganese cobalt oxide by co-precipitation method.

3.6. Elemental mapping analysis

Fig. 7 shows the elemental mapping analysis of manganese, cobalt, and oxygen in the manganese cobalt oxide produced by a co-precipitation process [13-15]. The constituent cations are spread uniformly throughout the entire sample.

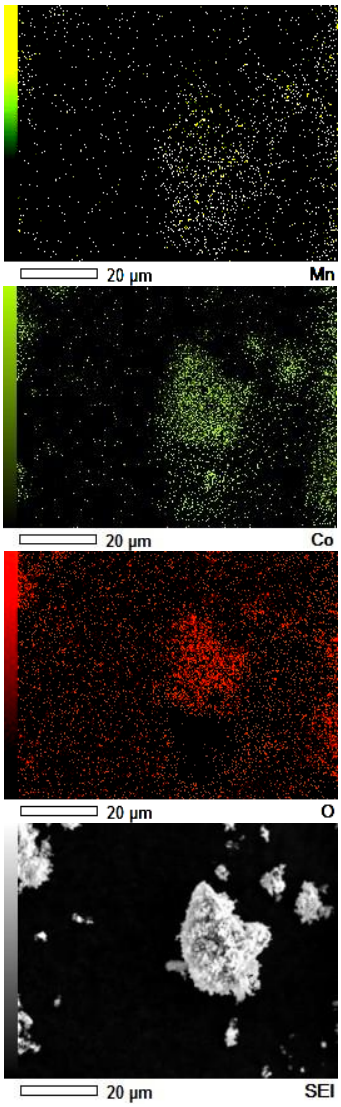


Fig. 7 Elemental mapping of the manganese cobalt oxide by co-precipitation method.

4. CONCLUSION

In conclusion, a simplistic co-precipitation technique was used to synthesize successfully $MnCo_2O_4$ material using KOH. A comprehensive study on the properties of $MnCo_2O_4$ material was analyzed by various characterizations. The X-ray diffraction and FTIR studies confirm the formation of $MnCo_2O_4$ material in cubic spinel structure form with an Fd3m space group. The calculated average crystalline size was 37 nm from the Scherrer formula. Micrographs reveal an irregular shape with an agglomeration of $MnCo_2O_4$ particles. The distribution of elements in $MnCo_2O_4$ material was confirmed from elemental mapping. Overall, the synthesized material via simplistic co-precipitation technique may be favorable for energy storage and other practical applications.

Author contributions

Tholkappiyan Ramachandran: Writing-original draft, Conceptualization, Writing-review and editing, Methodology, Investigation; **Ramesh Kumar Raji:** Writing-review and editing, Formal analysis, Methodology.

Conflicts of interest

There are no conflicts to declare.

References

[1] Babakhani B, Ivey DG, Investigation of electrochemical behavior of Mn–Co doped oxide electrodes for electrochemical capacitors. Electrochim Acta, vol. 56, pp. 4753–4762, 2011.

[2] Tholkappiyan Ramachandran, Fathalla Hamed, Ramesh Kumar Raji, Abdel Hamid I. Mourad, Room temperature ferromagnetism in garnet type Dysporisum ferrite by coprecipitation approach, Advances in Science and Engineering Technology International Conferences (ASET), pp. 1-5, 2022.

[3] H. Bordeneuve, C. Tenailleau, S. Guillemet-Fritsch, R. Smith, E. Suard, A. Rousset, Structural variations and cation distributions in $Mn_{3-x}Co_xO_4$ (0-x-3) dense ceramics using neutron diffraction data. Solid State Sci., vol. 12, pp. 379–386, 2010.

[4] G.Rekha, R. Tholkappiyan, K. Vishista, Fathalla Hamed, Systematic study on surface and magnetostructural changes in Mn-substituted dysprosium ferrite by

hydrothermal method, Applied Surface Science, vol. 385, pp. 171-181, 2016.

[5] Tholkappiyan Ramachandran, Abdel-Hamid I Mourad, Ramesh Kumar Raji, Ramachandran Krishnapriya, Nizamudeen Cherupurakal, Abdul Subhan, Yarub Al-Douri, KOH mediated hydrothermally synthesized hexagonal-$CoMn_2O_4$ for energy storage supercapacitor applications, International Journal of Energy Research, vol. 46, pp.16823-16838, 2022.

[6] Ramesh Kumar Raji, Tholkappiyan Ramachandran, M. Muralidharan, R. Suriakarthick, Muthu Dhilip, Fathalla Hamed, Vishista Kurapati, Conventional synthesis of perovskite structured $LaTi_xFe_{1-x}O_3$: A comprehensive evaluation on phase formation, opto-magnetic, and dielectric properties, International Journal of Materials Research, vol. 112, pp. 753-765, 2021.

[7] Tholkappiyan Ramachandran, Selvi Natarajan, Fathalla Hamed, The role of dysprosium levels in the formation of mixed oxidation states within spinel $MnCo_{2-x}Dy_xO_4$ nanocrystalline powders, Journal of Electron Spectroscopy and Related Phenomena, vol. 242, pp. 146952, 2020.

[8] Ahmed Alzamly, Fathalla Hamed, Tholkappiyan Ramachandran, Maram Bakiro, Salwa Hussein Ahmed, Shefaa Mansour, Sahar Salem, Nawf Saif Al Kaabi, Mohammed Meetani, Abbas Khaleel, Tunable band gap of Bi^{3+}-doped anatase TiO_2 for enhanced photocatalytic removal of acetaminophen under UV-visible light irradiation, Journal of Water Reuse and Desalination, vol. 9, pp. 31-46, 2019.

[9] R. Tholkappiyan, A. Nirmalesh Naveen, S. Sumithra, K. Vishista, Investigation on spinel $MnCo_2O_4$ electrode material prepared via controlled and uncontrolled synthesis route for supercapacitor Application, J. Mater. Sci., vol. 50, pp. 5833–5843, 2015.

[10] Ramesh Kumar Raji, Tholkappiyan Ramachandran, M Muralidharan, R Suriakarthick, M Dhilip, A Raja, Vishista Kurapati, Fathalla Hamed, P Ramasamy, Abdel-Hamid I Mourad, Twitching the inherent properties: the impact of transition metal Mn-doped on LaFeO3-based perovskite materials, Journal of Materials Science: Materials in Electronics, vol. 32, pp. 25528-25544, 2021.

[11] R Tholkappiyan, R Satheesh Kumar, L Mohamed Azarudeen, G Anand Kumar, K Vishista, Fathalla Hamed, K Vishista, Facile Synthesis of Cr–doped SrS Phosphor: An Investigations on Structural, Vibrational, Morphological and Photoluminescence Properties, Materials Focus, vol. 5, pp. 342-346(5), 2016.

[12] Raji RameshKumar, Tholkappiyan Ramachandran, Karthikeyan Natarajan, Munisamy Muralidharan, Fathalla Hamed, Vishista Kurapati, Fraction of rare-earth (Sm/Nd)-lanthanum ferrite-based perovskite ferroelectric and magnetic nanopowders, Journal of Electronic Materials, vol. 48, pp. 1694-1703, 2019.

[13] Tholkappiyan Ramachandran, Fathalla Hamed, Electrochemical performance of plate-like zinc cobaltite electrode material for supercapacitor applications, Journal of Physics and Chemistry of Solids, vol. 121, pp. 93-101, 2018.

[14] Marim Elkashlan, Vijo Poulose, Rana Zeeshan Habib, Obaida Karabala, Afnan Aldhanhani, Maryam Shakir, Heba Shaath, Tholkappiyan Ramachandran, Abdel-Hamid Ismail Mourad, Fathalla Hamed, Ruwaya Al Kendi, Thies Thiemann, Analysis of the Solid Contents of Toothpastes Available in UAE (United Arab Emirates) Markets, Journal of

Environmental Protection, vol. 13, pp. 539-556, 2022.

[15] Anifat Adenike Bankole, Vijo Poulose, Tholkappiyan Ramachandran, Fathalla Hamed, Thies Thiemann, Comparative Study of the Selective Sorption of Organic Dyes on Inorganic Materials—A Cost-Effective Method for Waste Treatment in Educational and Small Research Laboratories, Separations, vol. 9, vol. 144, 2022.