

Comparative Structural, Phase Evolution, and Spectroscopic Investigation of Binary and Ternary Mixed Metal Oxide Nanoparticles (Co-Cu, Co-Ni, Ni-Fe, And Co-Ni-Zn) Synthesized Via Grape Leaf Powder Calcination

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ABSTRACT

Mixed transition metal oxide nanostructures have attracted a lot of interest in science and technology because they show electronic, catalytic and magnetic behavior than single-metal oxides. In this study we compare four mixed metal oxide systems made using a green method. The samples are: ternary Co-Ni-Zn (Sample 1) binary Co-Cu (Sample 2) binary Co-Ni (Sample 3) and binary Ni-Fe (Sample 4). All of them were made using grape leaf powder from waste (*Vitis vinifera*) as a natural material to help form the structure reduce metal ions and shape the nanostructures. After that the materials were heated at 500°C to get the product. We looked at the structure crystal phases, particle size, chemical bonds and surface purity using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). The XRD results showed that the way the metal ions fit into the crystal lattice depends on their size how strongly they attract electrons and how their d-electrons arrange. In the Co-Cu and Co-Ni-Zn systems the different metal ions didn't mix well leading to phases: Co_3O_4 with CuO and Co_3O_4 with NiO and ZnO. This happened because of Jahn-Teller distortion and the tendency of the ions to separate. In the Co-Ni system, a slight XRD peak shift to 37.2° suggests the possible formation of a Co-Ni solid solution (CoNiO_2); however, this assignment remains tentative and requires quantitative phase analysis such as Rietveld refinement for confirmation. The Ni-Fe system showed reflections consistent with inverse spinel NiFe_2O_4 along with NiO and $\alpha\text{-Fe}_2\text{O}_3$; quantitative phase refinement would be needed to establish the relative phase fractions and degree of spinel formation. The average size of the particles was between 50 and 70 nanometers and this was controlled by how the metal ions moved and how crystals grew. The Ni-Fe sample had a peak at 668 cm^{-1} , which is typical for spinel ferrites showing both tetrahedral and octahedral bonding. Interestingly the materials with nickel helped burn off carbon effectively leaving very little leftover organic material. This was not the case, for the copper- or zinc-based samples. Residual carbon-oxygen bonds (1045 cm^{-1}) and surface hydroxyl groups ($3394\text{--}3423\text{ cm}^{-1}$) were still present which means the biocapping process was stable and eco-friendly. Because of these features these materials could be used in cleanup, photocatalysis and magnetic treatment applications.

Keywords: Green synthesis, Mixed metal oxides, Grape leaf powder, Phase evolution, Solid solution, Spinel ferrite, Comparative XRD and FTIR

INTRODUCTION

Transition metal oxide nanoparticles are an important group of functional nanomaterials. Transition metal oxide nanoparticles are used in different areas such as heterogeneous catalysis cleaning up environmental pollutants storing energy in pseudocapacitors detecting gases, spintronics and treating diseases in medicine. In years research has moved from simple single-component oxides like pure Co_3O_4 , NiO, CuO, ZnO or Fe_2O_3 to more

complex binary, ternary and polymetallic mixed metal oxide systems. Adding two or more transition metal cations into the same composite changes the electronic band structure changes local geometry speeds up charge transfer at interfaces and creates active sites that work better than single-metal versions.

Cobalt oxide (Co_3O_4) is a mixed-valence ($\text{Co}^{2+}/\text{Co}^{3+}$) p-type semiconductor that can change its oxidation state easily. Cobalt oxide (Co_3O_4) is very active. When it is used alone its performance is often limited by only moderate conductivity and by particles clumping together during heating. The careful addition of 3d transition metals such as copper (Cu^{2+}) nickel (Ni^{2+}) iron (Fe^{3+}) and zinc (Zn^{2+}) is a good way to shape the phase structure and improve the material. Depending on how the ion sizes match the preferred coordination patterns and the energy driving forces the mixture of metal cations can give different structures: (i) phase-separated heterostructured nanocomposites (physical mixtures) (ii) substitutional solid solutions such as CoNiO_2 or (iii) ordered spinel crystals such as NiFe_2O_4 . Understanding the basic chemical rules that decide whether phase separation, solid solution or spinel forms is essential for designing custom nanomaterials.

Typical synthesis routes such as chemical co-precipitation, hydrothermal autoclaving, sol-gel and microemulsion usually use organic solvents, toxic reducing agents like sodium borohydride or hydrazine hydrate and expensive surfactants. These methods often produce waste that can harm the environment. Because of this green biogenic synthesis using plant waste has become a cheaper and scalable option. Grape leaves (*Vitis vinifera*) are a common waste from vineyards and contain many natural polyphenols, flavonoids organic acids, tannins and terpenoids. The many hydroxyl ($-\text{OH}$) and carboxyl ($-\text{COOH}$) groups in the plant material act as chelating sites that hold transition metal cations stop them from clumping early and act as a natural template that can be removed when the material is heated in solid-state calcination.

In earlier work, we reported separately the synthesis and basic structure of Co-Ni-Zn and Ni-Fe systems in one paper and of binary Co-Cu and Co-Ni systems, in another paper. However we have not yet done a study that looks at all four systems side by side under the same synthesis conditions. This new work fills that gap.

In this study we give a comparison of four different mixed oxide systems: Co-Ni-Zn (Sample 1), Co-Cu (Sample 2), Co-Ni (Sample 3), and Ni-Fe (Sample 4).. By comparing X-ray diffraction data, the size of crystallites the rules that decide which phase appears the infrared bonding patterns and how well the organic parts burn away we show how the choice of metal cations controls the synthesis of solid-state oxides.

METHODOLOGY

Precursor Materials and Plant Matrix Preparation

All chemicals and precursors were high-grade reagents and were used as received, without extra purification.

The metal salt precursors included Cobalt(II) Chloride Hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 99% purity, Merck) Nickel(II) Chloride Hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ Qualigens) Copper(II) Sulfate Pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Merck) Zinc Sulfate Heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, Merck) and Iron(III) Chloride Hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Merck).

Deionized water was used for all washing and processing stages. Fresh mature leaves of *vinifera* were collected locally washed thoroughly with tap water followed by deionized water to remove surface debris and oven-dried at $60\text{--}70^\circ\text{C}$ for 24 hours until the weight was constant. The brittle leaves were pulverized using a mortar and pestle into an ultra-fine powder and preserved in airtight desiccators.

Solid-State Biogenic Synthesis Protocol

A solvent-free state green grinding method was used for all four systems to make sure the results could be compared properly. The amount of biomass to precursor was kept the same at 0.01 mol of each metal salt for every 20 g of ground grape leaves:

- Sample 1 (Co-Ni-Zn): 2.38 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) plus 2.38 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) plus 2.87 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (0.01 mol) mixed into 20 g leaf powder.

- Sample 2 (Co-Cu): 2.38 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) plus 2.50 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.01 mol) mixed into 20 g leaf powder.
- Sample 3 (Co-Ni): 2.38 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) plus 2.38 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) mixed into 20 g leaf powder.
- Sample 4 (Ni-Fe): 2.38 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) plus 2.70 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.01 mol) mixed into 20 g leaf powder.

Each mixture of precursor and biomass was ground hard for 25 to 30 minutes to make sure the metal ions were spread out completely in the plant material. The mixtures were dried at 80°C for 6 to 8 hours to get rid of any water on the surface. Then they were heated in an oven. The temperature was increased slowly to 200°C at 5°C per minute. Kept there for one hour to break down the plants and remove water. Then the temperature was raised to 500°C at 10°C , per minute. Held there for three hours to fully turn the material into solid oxides and make crystals. The oven was left to cool on its own. That produced very small oxide powders.

Reaction Mechanisms and Thermal Evolution

During grinding and heating oxygenated functional groups such as polyphenolic $-\text{OH}$, carboxylic $-\text{COOH}$ and carbonyl $\text{C}=\text{O}$ bind transition metal cations into organometallic complexes. When we calcine at temperatures up to five hundred degrees Celsius in air the organic backbone breaks down, by oxidation releasing gaseous CO_2 , H_2O , HCl and SO_2 . Meanwhile metal ions assemble into crystalline lattices:

- For Co-Ni-Zn (Sample 1): $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{Biomass} + \text{O}_2 \rightarrow \text{Co}_3\text{O}_4 + \text{NiO} + \text{ZnO} + \text{gaseous byproducts}$.
- For Co-Cu (Sample 2): $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{Biomass} + \text{O}_2 \rightarrow \text{Co}_3\text{O}_4 + \text{CuO} + \text{gaseous byproducts}$.
- For Co-Ni (Sample 3): $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{Biomass} + \text{O}_2 \rightarrow \text{possible Co-Ni solid solution (CoNiO}_2) / \text{Co}_3\text{O}_4 + \text{NiO} + \text{gaseous byproducts}$.
- For Ni-Fe (Sample 4): $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{Biomass} + \text{O}_2 \rightarrow \text{NiFe}_2\text{O}_4 \text{ (spinel)} + \text{NiO} + \text{Fe}_2\text{O}_3 + \text{gaseous byproducts}$.

Characterization Methodologies

Powder X-ray diffraction measurements were performed on a high-resolution automated diffractometer that uses $\text{Cu K}\alpha$ radiation with a wavelength of $1.5406 \text{ \AA}$. The instrument ran at 40 kV and 40 mA. Continuous step scans were taken from 5° to 90° in 2θ with a step width of 0.02° . Powder X-ray diffraction data were matched to JCPDS crystallographic cards for phase identification. The average crystallite size (D) was calculated using the Debye-Scherrer equation: D equals K times λ divided by β times $\cos \theta$, where K 0.94, λ is $1.5406 \text{ \AA}$ β is the full width at half maximum in radians and θ is the Bragg diffraction angle. Surface coordination organic degradation residues and metal-oxygen ($\text{M}-\text{O}$) framework vibrations were examined with an ATR-FTIR spectrophotometer, over the spectral range of 4000 to 400 cm^{-1} . Quantitative phase analysis via Rietveld refinement, along with complementary techniques such as SEM/TEM with EDS mapping, XPS, and TGA/DSC, is recommended for future work to further validate the proposed phase assignments.

RESULTS

Comparative X-Ray Diffraction (XRD) Analysis

The X-ray diffraction profiles of the four synthesized nanomaterials reveal crystallographic architectures dictated by cation compatibility and thermal reactivity. In Sample 1 (Co-Ni-Zn) diffraction reflections were recorded at 2θ values of 36.6° , 37.1° , 43.3° , 44.8° , 62.9° and 75.3° . The prominent peak at 43.3° confirms cubic bunsenite NiO (JCPDS Card No. 47-1049) While peaks at 36.6° and 44.8° index to cubic spinel Co_3O_4 (JCPDS

Card No. 42-1467). Hexagonal wurtzite ZnO is evidenced by reflections at 37.1° and 44.8° (JCPDS Card No. 36-1451). The coexistence of peaks for all three monometallic oxides without observable reciprocal lattice shifts indicates the preservation of a tri-phasic physical mixture.

In Sample 2 (Co-Cu) sharp and intense diffraction peaks appeared at 31.6° , 35.9° , 37.1° , 38.7° , 43.5° , 59.6° and 65.4° . The intense peak at 37.1° (~2845 counts) corresponds strictly to the (311) crystal plane of Co_3O_4 whereas peaks at 35.9° and 38.7° correspond to monoclinic tenorite CuO (JCPDS Card No. 48-1548). No reciprocal peak displacement was observed, validating the presence of a Co_3O_4 -CuO physical mixture without solid solution formation.

In contrast, Sample 3 (Co-Ni) displayed reflections at 36.6° , 37.2° , 43.5° , 44.8° , 62.9° and 75.3° . A small positive peak shift was recorded at 37.2° relative to pristine Co_3O_4 (37.1°). Since Ni^{2+} (ionic radius $0.690 \text{ \AA}$) possesses a size and electronic configuration close to that of Co^{2+} ($0.745 \text{ \AA}$), partial lattice substitution may be possible, and this shift is consistent with the possible formation of a Co-Ni solid solution. However, the observed shift is small, and a definitive assignment of a homogeneous CoNiO_2 substitutional solid solution cannot be made from XRD alone. Rietveld refinement, quantitative peak indexing, and complementary spectroscopic or microscopic evidence would be required to confirm this phase assignment.

In Sample 4 (Ni-Fe) diffraction peaks appeared at 31.2° , 35.6° , 37.1° , 43.3° , 53.7° , 57.3° and 62.9° . High peak intensity (~1241 counts) at 37.1° and 43.3° indexes NiO while 35.6° and 53.7° denote hematite $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS Card No. 33-0664). The reflections at 31.2° and 57.3° match the (220) and (511) planes of inverse spinel NiFe_2O_4 (JCPDS Card No. 10-0325), suggesting that solid-state interdiffusion between Ni^{2+} and Fe^{3+} produces a spinel-type phase at 500°C . However, since NiO and $\alpha\text{-Fe}_2\text{O}_3$ reflections are also present, the material appears to be a multi-phase mixture containing a spinel ferrite component. Quantitative phase analysis (e.g., Rietveld refinement) would be required to determine the relative phase fractions and the degree of spinel formation.

Debye-Scherrer calculations revealed that average crystallite sizes followed the order: Co-Ni (~50 nm) < Co-Ni-Zn (~50–60 nm) < Co-Cu (~65 nm) < Ni-Fe (~60–70 nm). The smaller crystallite sizes, in Co-Ni and Co-Ni-Zn highlight crystallite growth retardation resulting from lattice strain and multi-element steric hindrance.

Table 1. Comprehensive XRD Structural and Crystallographic Comparison of the Four Synthesized Mixed Metal Oxide Systems

System / Sample ID	Precursor Ratio	Identified Phases	Dominant Peaks (2θ)	Crystallite Size (nm)	Phase Nature	Crystallinity Level
Sample 1: Co-Ni-Zn	Co:Ni:Zn (1:1:1)	Co_3O_4 + NiO + ZnO	36.6° , 37.1° , 43.3° , 44.8°	~50–60 nm	Physical Mixture (Tri-phase)	Moderate
Sample 2: Co-Cu	Co:Cu (1:1)	Co_3O_4 + CuO	35.9° , 37.1° , 38.7° , 43.5°	~65 nm	Physical Mixture (Bi-phase)	High (~2845 counts)
Sample 3: Co-Ni	Co:Ni (1:1)	Co_3O_4 + NiO (CoNiO_2)	36.6° , 37.2° , 43.5° , 62.9°	~50 nm	Possible Co-Ni solid solution (tentative)	Moderate (~840 counts)
Sample 4: Ni-Fe	Ni:Fe (1:1)	NiO + Fe_2O_3 + NiFe_2O_4	31.2° , 35.6° , 37.1° , 57.3°	~60–70 nm	Spinel-type NiFe_2O_4 with NiO + Fe_2O_3 (multi-phase)	High (~1241 counts)

Figure 1: X-ray diffraction pattern of sample 1 (Co-Ni-Zn) mixed metal oxide nanoparticles

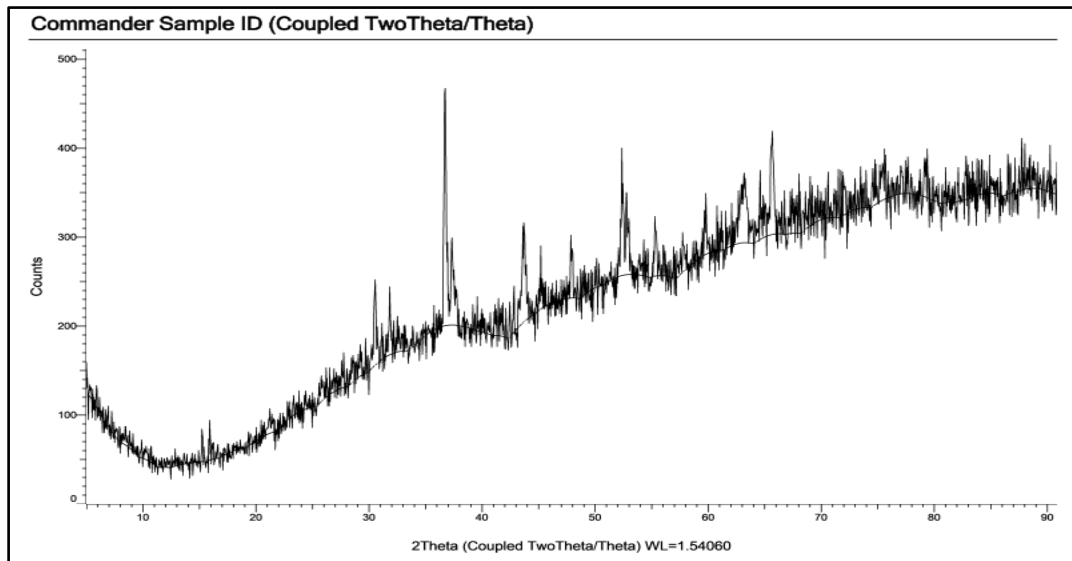


Figure 2: X-ray diffraction pattern of sample 2 (Co-Cu) mixed metal oxide nanoparticles

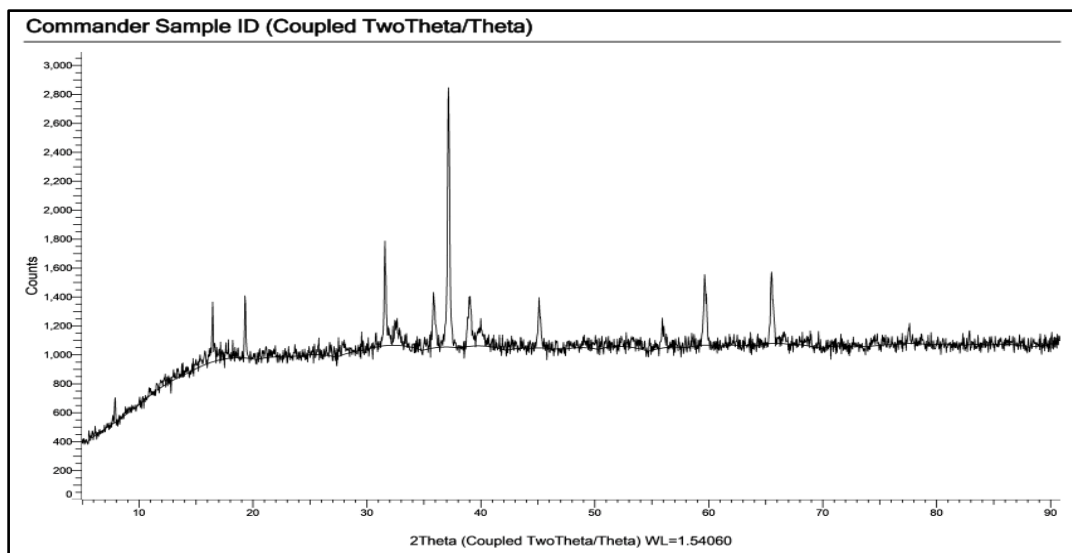


Figure 3: X-ray diffraction pattern of Sample 3 (Co-Ni) mixed metal oxide nanoparticles

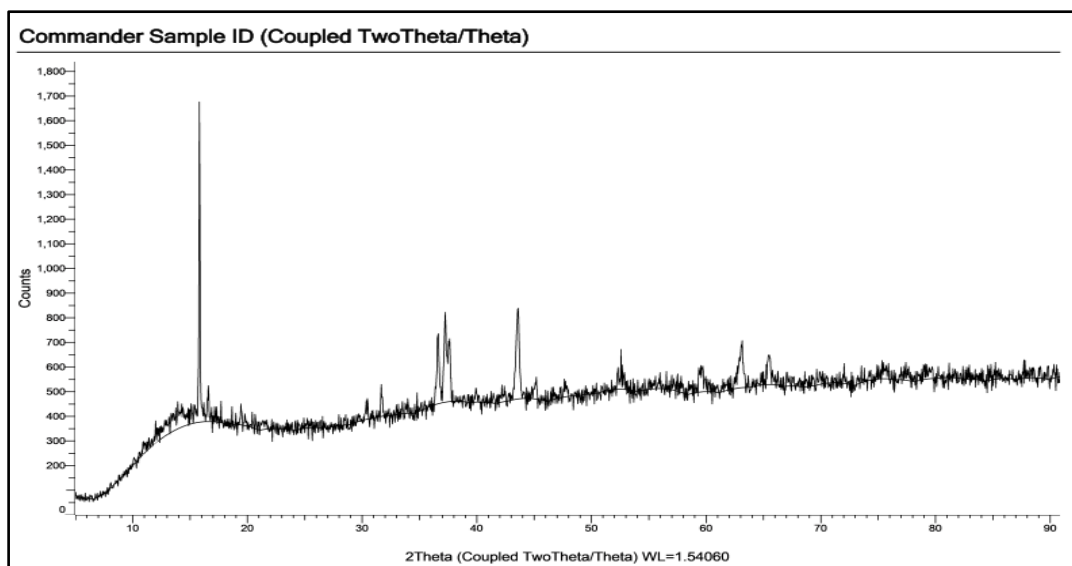
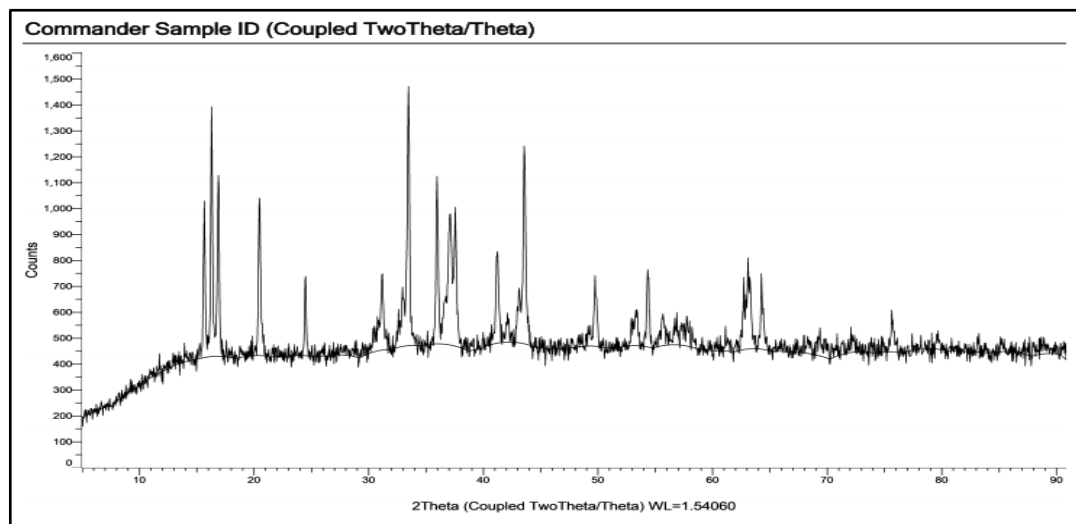


Figure 4: X-ray diffraction pattern of Sample 4 (Ni-Fe) mixed metal oxide nanoparticles



Comparative FTIR Spectroscopic Analysis

Fourier-transform infrared spectroscopy gave clues about how chemical bonds form what groups sit on the surface and how much carbon remains after burning in the four samples. In each of the four spectra we observe a strong absorption band between 3394 and 3516 cm^{-1} . This band comes from O–H groups that stick to the surface coming from water in the air and leftover phenolic hydroxyls. A middle band around 1618–1630 cm^{-1} shows bending vibrations of water molecules (H–O–H) that overlap with the ring vibrations of C=C and C=O.

The fingerprint region below 1000 cm^{-1} provides evidence that metal–oxygen frameworks are present. In Sample 1 which contains Co, Ni and Zn we observe metal–oxygen stretching peaks at 547 and 469 cm^{-1} . These peaks come from overlapping Co–O and Ni–O bonds in sites and Zn–O bonds in tetrahedral sites. For Sample 2 (Co–Cu) and Sample 3 (Co–Ni) we observe metal–oxygen absorptions at 668 and 457 cm^{-1} . These peaks are consistent with octahedral and tetrahedral oxide networks. In Sample 4 (Ni–Fe) the main peak at 668 cm^{-1} comes from the stretch of tetrahedral $\text{Fe}^{3+}\text{--O}^{2-}$. Lower peaks at 547 and 469 cm^{-1} belong to octahedral $\text{Ni}^{2+}\text{--O}^{2-}$ and $\text{Fe}^{3+}\text{--O}^{2-}$ bonds. These features are consistent with the formation of a spinel-type NiFe_2O_4 lattice, though the presence of residual NiO and $\alpha\text{-Fe}_2\text{O}_3$ should be noted.

Fourier-transform infrared spectroscopy also showed differences in how much carbon remains after burning in the four samples. Sample 1 (Co–Ni–Zn) and Sample 2 (Co–Cu) still have absorption peaks at 1385 cm^{-1} , which come from aliphatic C–H bending and surface carbonate groups and at 2926 cm^{-1} which comes from aliphatic C–H stretching. In contrast Sample 3 (Co–Ni) and Sample 4 (Ni–Fe) show no trace of those peaks. Adding nickel and iron speeds up the oxidation of material during calcination giving very pure phases. Importantly all four samples show C–O stretching peaks, between 1005 and 1093 cm^{-1} . These peaks indicate that biogenic phytochemical capping species remain on the nanoparticle surfaces stopping them from clumping.

Table 2. Systematic Cross-Comparison of FTIR Absorption Bands (cm^{-1}) and Functional Group Assignments

Vibrational Mode Assignment	Sample 1 (Co–Ni–Zn)	Sample 2 (Co–Cu)	Sample 3 (Co–Ni)	Sample 4 (Ni–Fe)	Functional Role & Implication
O–H stretching (adsorbed H_2O / –OH)	3418 cm^{-1}	3423–3516 cm^{-1}	3396 cm^{-1}	3394 cm^{-1}	Surface hydrophilic reactivity, active catalytic sites
Aliphatic C–H stretching	Absent	2926 cm^{-1}	Absent	Absent	Residual unburnt organic hydrocarbon fragments

H–O–H bending / C=O stretching	1620–1630 cm^{-1}	1618–1630 cm^{-1}	1630 cm^{-1}	1630 cm^{-1}	Adsorbed surface moisture and biogenic quinone chelates
C–H bending / Carbonate (CO_3^{2-})	1385 cm^{-1}	1385 cm^{-1}	Absent	Absent	Organic residues; extinguished by Ni/Fe catalytic burnout
C–O stretching (Phytochemicals)	1045 cm^{-1}	1005–1093 cm^{-1}	1005–1093 cm^{-1}	1045 cm^{-1}	Biogenic capping agent preserving nanostructure
M–O stretching (Tetrahedral Fe–O / Spinel)	Absent	668 cm^{-1}	668 cm^{-1}	668 cm^{-1}	Diagnostic of spinel ferrite (NiFe_2O_4) & Co–O lattices
M–O stretching (Octahedral Co–O / Ni–O)	547 cm^{-1}	Absent	Absent	547 cm^{-1}	Octahedral coordination in rock-salt/spinel
M–O stretching (Zn–O / Cu–O / Ni–O)	469 cm^{-1}	457 cm^{-1}	457 cm^{-1}	469 cm^{-1}	Sub-lattice metal-oxygen framework establishment

Figure 5: FTIR spectrum of sample 1 (Co-Ni-Zn) mixed metal oxide nanoparticles

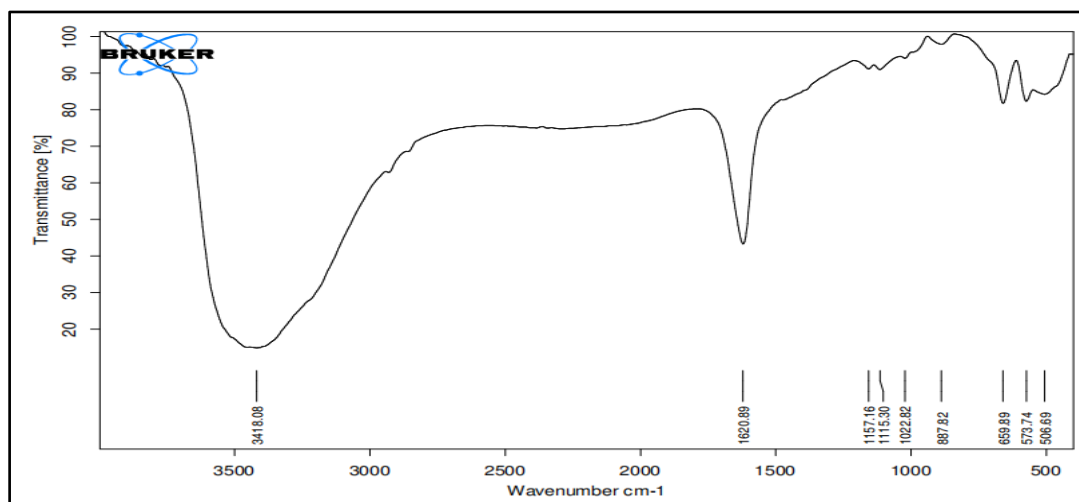


Figure 6: FTIR spectrum of sample 2 (Co-Cu) mixed metal oxide nanoparticles

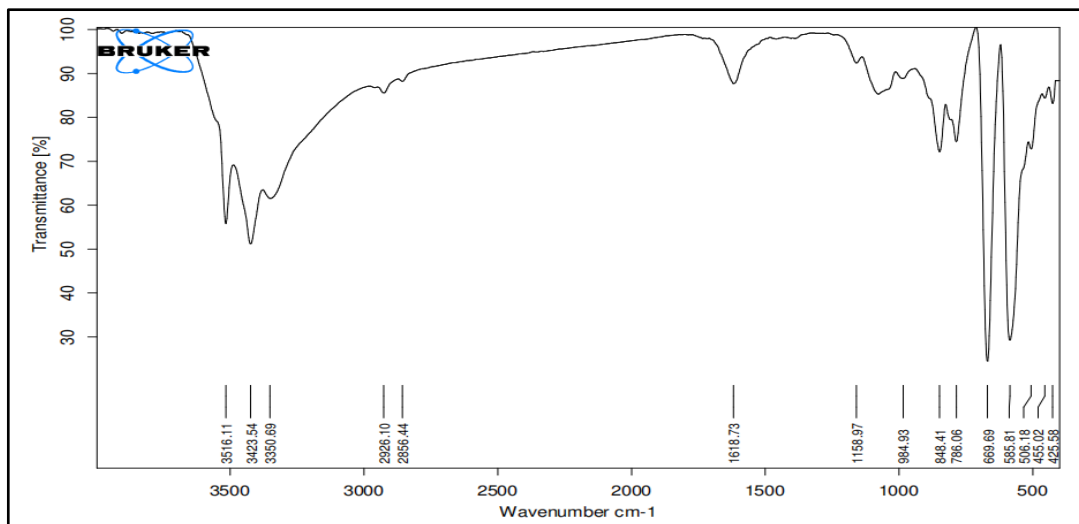


Figure 7: FTIR spectrum of Sample 3 (Co-Ni) mixed metal oxide nanoparticles

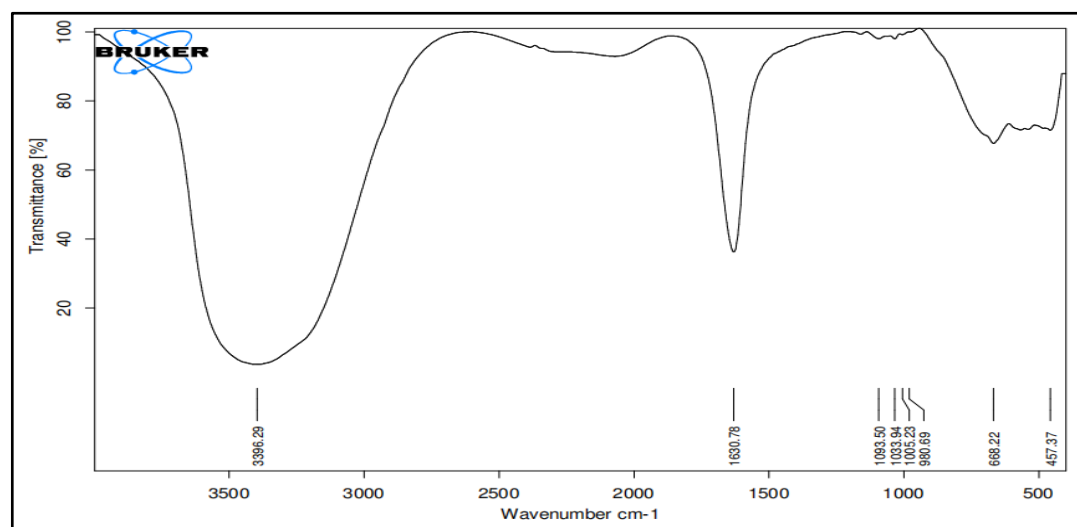
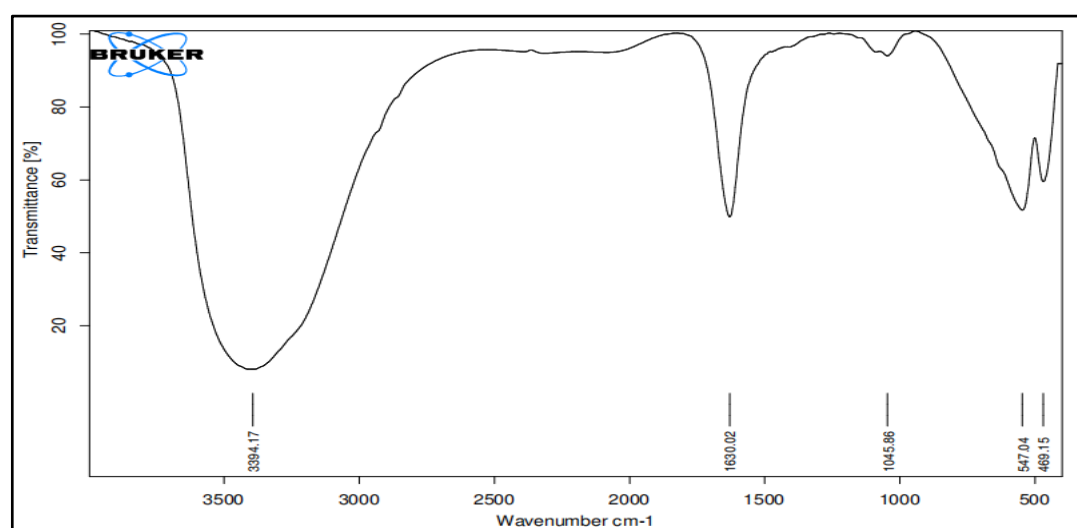


Figure 8: FTIR spectrum of Sample 4 (Ni-Fe) mixed metal oxide nanoparticles



DISCUSSION

Cation Size, Electronic Structure, and Phase Evolution Pathways

This study investigated four mixed transition metal oxide systems shows how small differences in transition metal sizes, oxidation levels and d-orbital electron setups control the final phase selection during solid-state biogenic calcination. In the Co- system (Sample 3) Co^{2+} (effective ionic size 0.745 Å in high-spin octahedral geometry) and Ni^{2+} (0.690 Å) have a very small ionic size difference (< 8%) well under the Hume-Rothery limit for a lot of solid solubility. Both cations can adopt octahedral coordination in rock-salt and spinel structures, which may allow partial substitution in the lattice. The small Bragg angle shift to 37.2° is consistent with possible Co-Ni solid solution formation, although definitive confirmation requires quantitative structural analysis.

On the other hand, the Co-Cu system (Sample 2) separates completely into cubic Co_3O_4 and monoclinic tenorite CuO . Cu^{2+} ($3d^9$ setup) has strong electronic confusion in octahedral ligand fields leading to strong Jahn-Teller distortion that stretches axial Cu–O bonds and makes cubic symmetry very unstable. As a result Cu^{2+} can't mix evenly into the cubic Co_3O_4 host lattice at 500°C forming tenorite areas. Similarly in the Co-Ni-Zn system (Sample 1) Zn^{2+} ($3d^{10}$ setup) prefers tetrahedral sp^3 hybridization forming wurtzite hexagonal ZnO while Co and Ni separate into Co_3O_4 and NiO phases because of competition among multiple cations and kinetic limits at 500°C .

In the Ni-Fe system (Sample 4) the strong thermodynamic push for spinel ferrite crystallization allows Fe^{3+} (0.645 Å) and Ni^{2+} (0.690 Å) to mix quickly creating an inverse spinel NiFe_2O_4 lattice with some leftover NiO and $\alpha\text{-Fe}_2\text{O}_3$. Fe^{3+} ions occupy both tetrahedral (A) and octahedral (B) positions in the face-centered cubic oxygen sublattice while Ni^{2+} only takes octahedral (B) sites because of high crystal field stabilization energy (CFSE). This is consistent with the FTIR peak at 668 cm^{-1} (tetrahedral Fe–O vibration) and the XRD reflections at 31.2° and 57.3° , which together support the presence of a spinel ferrite phase alongside residual NiO and $\alpha\text{-Fe}_2\text{O}_3$.

Crystallite Size. Growth Kinetics

The crystallite size order—Co-Ni (~50 nm) $\approx$ Co-Ni-Zn (~50–60 nm) < Ni-Fe (~60–70 nm) $\approx$ Co-Cu (~65 nm)—shows how important chemical composition is in limiting grain boundary movement. In the Co-Ni and Co-Ni-Zn systems multiple cation disorder and solute-drag pinning at grain boundaries greatly limit joining keeping the crystallite sizes small (50–60 nm). However in the Co-Cu and Ni-Fe systems the strong thermodynamic crystallization of tenorite CuO and spinel-type NiFe_2O_4 helps the crystals grow more making diffraction peaks and larger crystallite areas (60–70 nm).

Catalytic Biomass Decomposition and Surface Purity

A key finding from this comparison study is the difference in how organic residue is removed. In both Sample 3 (Co-Ni) and Sample 4 (Ni-Fe) there are no FTIR bands at 2926 cm^{-1} (C–H stretching) and 1385 cm^{-1} (C–H bending/carbonate) showing pure phases. Both nickel and iron substances are known oxidation catalysts that help break down biopolymers into gas CO_2 and H_2O during calcination at 500°C . However the presence of copper and zinc, in Samples 1 and 2 slows down the deep oxidation process leaving some carbonate and hydrocarbon leftovers. Still all four systems keep biogenic C–O caps ($1005\text{--}1093\text{ cm}^{-1}$) and active surface hydroxyl groups ($3394\text{--}3516\text{ cm}^{-1}$) which stop the particles from sticking together and offer many active catalytic sites.

Limitations And Scope For Future Work

The present study relies primarily on XRD and FTIR, which provide complementary but not exhaustive information on phase formation, crystallite size, and functional groups. Several conclusions, particularly the proposed Co-Ni solid solution and the extent of spinel formation in the Ni-Fe system, are based on qualitative interpretation of peak positions and cannot be fully established from these data alone. Quantitative phase analysis via Rietveld refinement would provide lattice parameters, phase fractions, and more rigorous crystallographic information. Complementary techniques such as SEM/TEM with EDS mapping (morphology, particle size, elemental distribution), XPS (oxidation states, surface chemistry), and TGA/DSC (thermal decomposition and biomass-burnout mechanism) would further strengthen the proposed phase-evolution pathways. These analyses are recommended as the focus of future work. The phase assignments presented here, especially for the Co-Ni system, should therefore be regarded as tentative until supported by such additional evidence.

CONCLUSION

This study investigated four mixed transition metal oxide systems—ternary Co-Ni-Zn (Sample 1), binary Co-Cu (Sample 2), binary Co-Ni (Sample 3), and binary Ni-Fe (Sample 4). I made these materials using an eco-friendly biogenic method that uses grape leaf powder (*Vitis vinifera*) and then heats them to 500°C .

The principal findings are summarized as follows:

- **Phase Architecture:** Cation arrangement and site preference control which phases appear. Co-Cu and Co-Ni-Zn form multi-phasic mixtures, consistent with Jahn-Teller distortion in Cu^{2+} and the tetrahedral site preference of Zn^{2+} . Co-Ni shows a small XRD peak shift to 37.2° , suggesting a possible Co-Ni solid solution, though this assignment remains tentative. Ni-Fe shows reflections consistent with a spinel-type NiFe_2O_4 phase together with NiO and Fe_2O_3 .

- **Crystallite Dimensions:** Every sample stays in the range about 50–70 nm. In Co-Ni and Co-Ni-Zn the mix of cations strains the lattice and slows grain growth keeping them around 50–60 nm. In Ni-Fe and Co-Cu fast spinel and tenorite crystallization pushes the particle size up to about 60–70 nm.
- **Spectroscopic Fingerprints:** FTIR data indicate that metal-oxygen bonds have formed, using peaks from 668 to 457 cm^{-1} . A Fe-O vibration at 668 cm^{-1} is consistent with spinel ferrite formation in the Ni-Fe sample.
- **Purity and Catalytic Burnout:** The samples that contain nickel and iron—Co-Ni and Ni-Fe—show thermal purity. They leave no traces of C–H or carbonate bands because the plant material burns off in a reaction while the sample is heated.
- **Capping Stability:** Phytochemical C–O groups are observed at 1045 cm^{-1} and water-like hydroxyl peaks from 3394 to 3516 cm^{-1} . These signals indicate that each sample retains a surface phytochemical cap.

Overall this comparison gives guidelines for choosing the right mixed metal oxide nanostructure. It supports the design of materials that can clean wastewater harvest energy from light or be used in magnetic separation.

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