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Zinc doped $ZnCo_2O_4$: Wet Chemical Synthesis and Structural Analysis

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Abstract
Well established wet chemical (coprecipitation) method was successfully used to create Zn doped $ZnCo_2O_4$. Samples that have been produced and heated are structurally characterized using X-ray powder diffraction, or XRD. For the sample that was calcined at 600°C, typical diffraction peaks corresponding to the cubic $ZnCo_2O_4$ spinal structure were found. The Deby-Scherrer concept was applied to XRD data, and the crystallite size of $ZnCo_2O_4$ was calculated to be 47 nm. When Zn is mixed with $ZnCo_2O_4$ and heated to 600°C, some new peaks are formed. Investigations were conducted on the crystal size, cell parameters, R-factor, and structural characteristics of nanocomposites. The Goodness Fit factor, cell parameters, and R-factor had been examined employing Rietveld Refinement.
Keywords: *coprecipitation, XRD, Spinel*

I. Introduction

Since their remarkable properties—turned by size, magnetic properties, chemical properties, and mechanical properties—are so different from their corresponding bulk opposite numbers, nanostructured materials have found widespread application. In metal oxide semiconductors with amazing architecture, there is a significant advancement in chemical and physical properties such as optical, electrical, sensitive to gas, catalytic, magnetic stability, cost-effectiveness, and controllable training, a number of study projects have recently focused on improving self-meeting synthesizing diverse metal oxide semiconductors and implementing them into our surroundings. One of the most promising options for detecting poisonous, flammable, and combustible gases among petrol sensing components is one-dimensional (1-D) metal oxide semiconductors with a high surface-to-volume ratio and appropriate surface permeability. A lot of research has already been done on utilizing and improving these sensing residences [1-2].

Due to their wide range of applications in chemical sensors, permanent magnets, microwave radiation absorbers, drug delivery, and cancer thermotherapy, among other bioscientific endeavors, nanoparticles with recently tested spinal architectures have been found [3–4]. The last ten years have seen a significant increase in interest in binary transition metal oxides such as ZnCo2O4, NiCo2O4, CuCo2O4, and ZnFe2O4 because, for various metal cations, they exhibit alternative oxidation states with enhanced electrochemical activities due to richer redox processes [5]. Zinc cobaltate (ZnCo2O4) is a significant functional material that has a distinct spinel structure and may be easily composited with the highest amount of metallic oxides [6].Out of p-type semiconductors, $ZnCo_2O_4$ with spinal structure has been widely used as electrodes in Li-ion batteries because of its extra and advanced performance like conductivity & electrochemical [7].

To manufacture ZnCo2O4, a variety of techniques have been used, including micro-emulsion, combustion, thermal decomposition, sol-gel, co-precipitation, W/O (water in petroleum), hydrothermal, and surfactant-mediated processes [8]. Spinel ferrite (AB2O4) is widely utilised in the production of electrocatalysts, solar cells, and supercapacitors because of its high conductivity, low charge, and energetic electrochemical performance. In this example, large quantities of news of spinel ferrites, such as MnFe2O4, NiCo2O4, CoFe2O4, ZnFe2O4, etc., are mostly employed as an absorber material and exhibit excellent absorbance qualities [9–10]. Due to these properties researchers look forward to using zinc cobaltate as a wave-absorbing material. Due to low conductivity and great dielectric properties, Zn is counted as an extremely good dielectric material. At present, there are associated reports that the composite materials which are based on Zn are used as absorbing substances. The absorbing material $ZnCo_2O_4$ which possesses a complex structure has characteristics like- conduction loss, multiple reflections, resonance, loss of eddy current, and multiple scattering. The addition of Zn affects electromagnetic parameters and absorption properties significantly. $Zn/ZnCo_2O_4$ composites, one can achieve excellent absorption properties and enhance complex permittivity. As a result of adding Zn hollow spheres to Zn/ $ZnCo_2O_4$, the composites exhibit great EMW absorption properties.

So It is quite interesting to know that when Zn and $ZnCo_2O_4$ are mixed and heated at a high temperature of 700°C, the characteristic peaks of $ZnCo_2O_4$ shifted slightly toward the left, because of doping [11].
In our work we also doped Zn in $ZnCo_2O_4$ and heated the sample at 300-700°C, and no remarkable changes had observed in the characteristic peaks of $ZnCo_2O_4$.

II. Experimental

Himedia Chemicals was the source of the chemicals used. No chemical is employed that hasn't been purified. Using a magnetic stirrer, stichometric ratio of zinc nitrate and cobalt nitrate were dissolved in deionized water to create the $ZnCo_2O_4$ solution. A uniform solution was obtained after one hour of magnetic stirring. A 10 ml saturated sodium hydroxide solution was added gradually. After two hours of nonstop stirring, the precipitate was centrifuged and repeatedly cleaned with deionized water. After obtaining the $ZnCo_2O_4$ precipitate, it was added to the Zn nanopowder and agitated for two hours at 80°C using a magnetic stirrer. The final precipitate took 24 hours to dry in air. The resulting powdered particles were crushed using a mortar and pestle, and they were eventually calcined at various temperatures of 300 to 700 °C.

III. Characterization

X-ray diffraction was used to analyse the crystallites and structural behaviour of the materials. The XRD pattern was recorded using a Philips X-ray powder diffractometer equipped with a nickel filter and GIXRD geometry. Two theta, or the angle of twice-glancing, varied from 10° to 70°. Using Fullprof software's Rietveld refinement, the pattern or curve was fitted, and MAUD Software's phase matching helped match the phases.

IV. Result and Discussion

4.1. XRD Analysis

The X-Ray diffraction method is utilised to assess the $ZnCo_2O_4$ crystallite structure. The crystal composition of composites, as determined by the X-ray diffraction method, is displayed in Fig. 1. This XRD pattern illustrates the sample that was calcined at, 300°, 500°, and 700°C. The $ZnCo_2O_4$ crystal planes are consistent with the typical peaks at 31.207°, 36.771°, 44.903°(400), 59.227°(511), and 65.090°(440).(JCPDS No. 23-1390). This showed that phase $ZnCo_2O_4$ are formed during heat treatment of as-prepared materials.

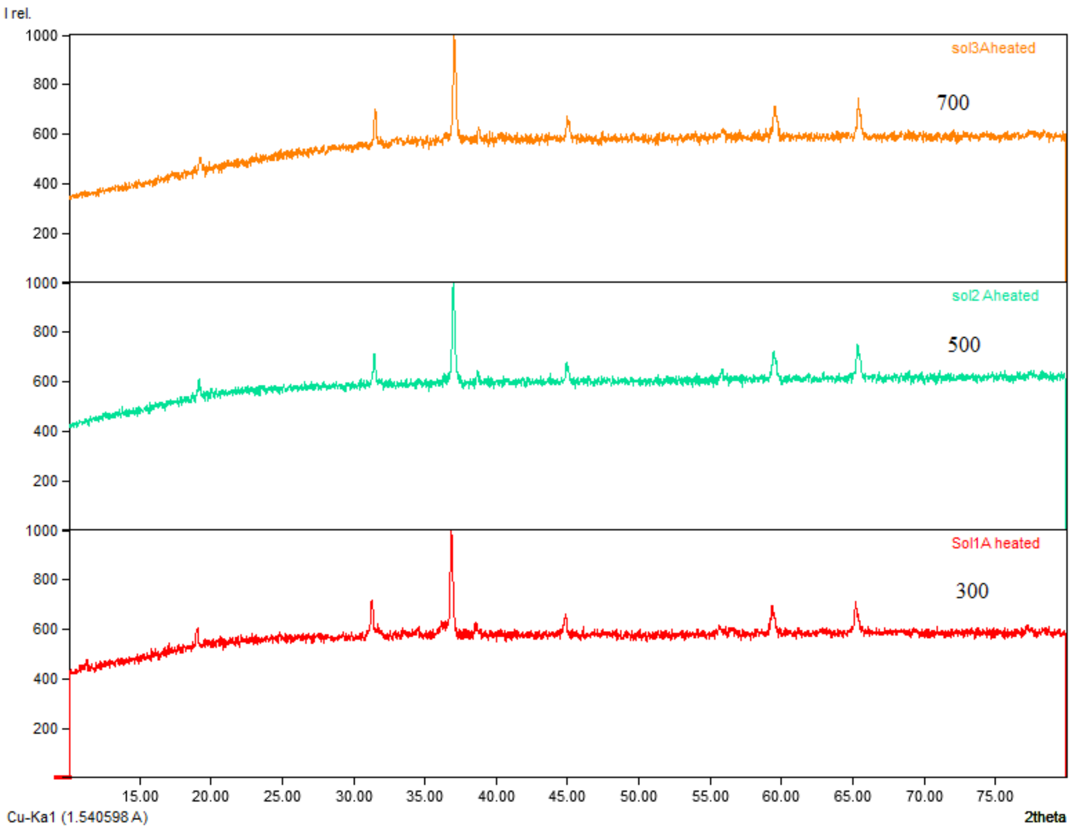

Fig. 1. XRD pattern of $ZnCo_2O_4$.

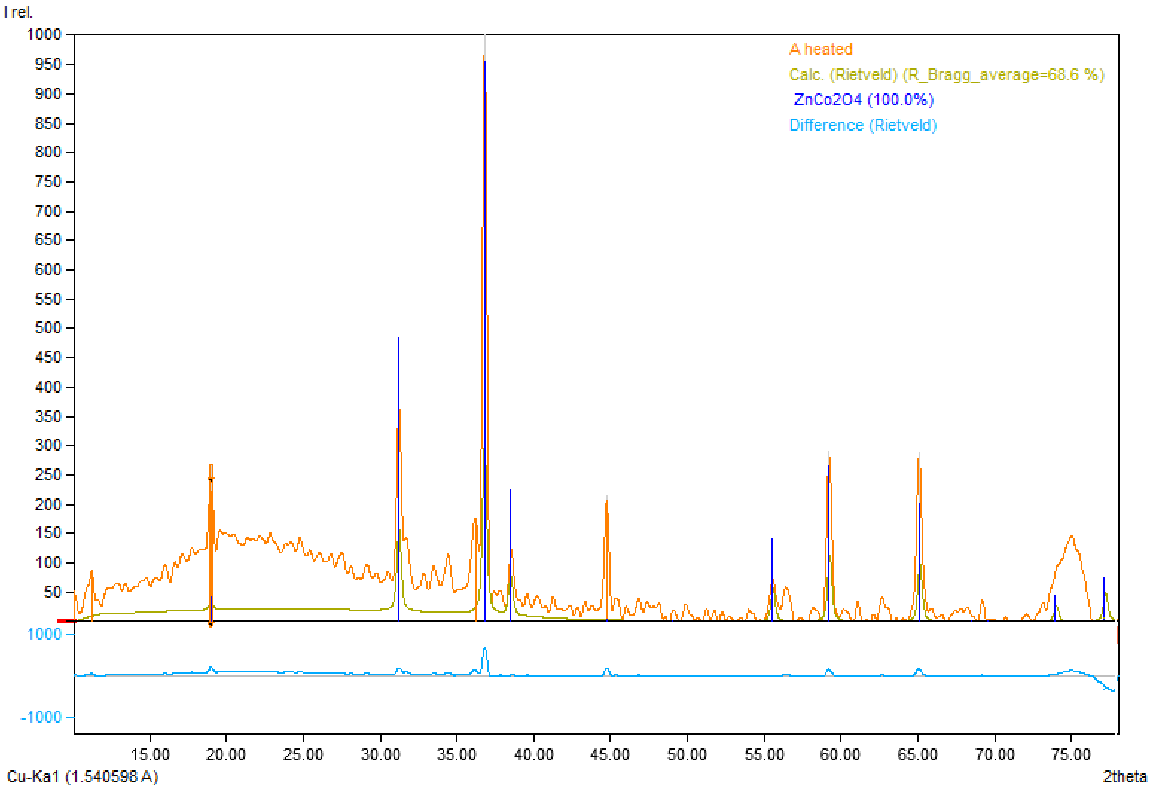

Fig. 2. XRD pattern with Rietveld refinement **of $ZnCo_2O_4$.**

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Below is Scherrer's equation for determining crystal size:-
Crystallite size = (λ*0.9)/ (Full Width Half Maxima*Cos θ)
Based on the highly intense peaks at 36.7710 and 36.2220 in Table 1, the crystallite size of $ZnCo_2O_4$/Zn can be calculated. We choose three intense peaks for both phases and crystallite size is calculated by taking the average of those peaks. $ZnCo_2O_4$, The crystal's size is determined to be 47nm [14] .

Table 1. Structural parameters of $ZnCo_2O_4$ were determined from XRD patterns.

No.	d-value	Full width half maxima	Flex width	I/Io	(hkl)	2 Theta	Size of particles
1	2.8638	0.2000	365.33	880.57	(0 2 2)	31.207	41.24
2	2.8179	0.2800	91.87	585.69	(0 1 0)	31.729	29.49
3	2.6022	0.2400	151.46	395.77	(0 0 2)	34.437	34.66
4	2.4780	0.2800	103.74	1000	(0 1 1)	36.222	29.85
5	2.4422	0.2400	432.52	924	(1 1 3)	36.771	34.89
6	2.0250	0.2400	57.27	124.23	(0 0 4)	44.903	35.82
7	1.9117	0.2000	67.49	185.12	(0 1 2)	47.523	43.41
8	1.6269	0.3200	144.14	285.70	(-1 2 0)	56.520	28.19
9	1.5588	0.2400	336.83	250.16	(1 1 5)	59.227	38.08
10	1.4773	0.3200	111.06	207.65	(0 1 3)	62.856	29.10
11	1.4319	0.2400	536.36	298.92	(0 4 4)	65.090	39.27
12	1.3795	0.2800	112.73	179.00	(-1 2 2)	67.890	34.20

4.2 Rietveld Refinement Method

In Rietveld refinement, the powder is refined using X-Ray Diffraction patterns. Parameters (atom position, orientation, and occupancy) need to be adjusted for Rietveld Refinement. Chebyshev polynomials have been used to do background correction. The Pseudo-Voigt is a tool that we use for modelling peak profile functions. The process is repeated until the chai square factor is obtained. A phase is obtained in the prepared sample that is $ZnCo_2O_4$ and the information of the space group is given in table below:

Table 2. Table for information on space group

Phase	Laue class value	Space Group no.	Bravais Lattice	Hermann-Mauguin symbol	Hall Symbol	general multiplicity
$ZnCo_2O_4$	m-3m	227	F	F d -3 m	-F 4vw 2vw 3	192

With the help of Rietveld Refinement, we evaluated Direct Cell Parameters (DCP) as well as reciprocal cell parameters (RCP). Those parameters are shown in Tables 3 and 4:

Table 3. The tabular form of DCP

Phase	α	β	γ	a	b	c
$ZnCo_2O_4$	90	90	90	8.0645	8.0645	8.0645

From Reitveld Refinement,
Value of $ZnCo_2O_4$ direct cell volume= 524.4880 $Å^3$

The parameters of reciprocal cells were as follows:

Table 4. The tabular form of RCP

Phase	α*	β*	γ*	a*	b*	c*
$ZnCo_2O_4$	90	90	90	.124000	.124000	.124000

Reciprocal cell volume value for $ZnCo_2O_4$ = .00190662 $Å^3$

Tables 5 show the values of x/a, y/b, z/c, Wyckoff position, sites of $ZnCo_2O_4$.

Table 5. atomic coordinates and isothermal parameters for phase $ZnCo_2O_4$:

Atoms	WK position	Sites	x/a	y/b	z/c
Zn	16c	.-3m	0	0	0
Co	8b	-43m	5/8	5/8	5/8
O	32e	.3m	0.387	0.387	0.387

The profile of X-ray diffraction data is fitted with the Rietveld Refinement and obtained spectra of $ZnCo_2O_4$ are shown in the figure 6.

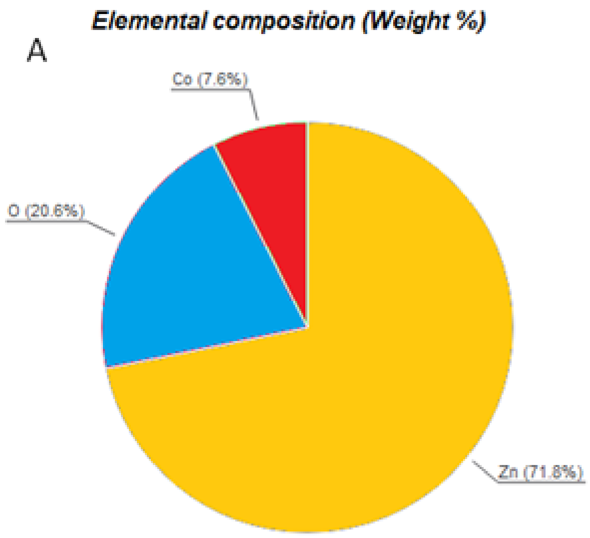

Fig. 6 (A) Elemental weight percent of Zn/$ZnCo_2O_4$ calculated by Rietveld refinement

In Tables 7 & 8, the obtained parameters like distance, angle, and symmetry of $ZnCo_2O_4$ with the help of the Rietveld refinement are shown.

Table 7. Some parameters values of $ZnCo_2O_4$

atom 1	atom 2	atom 3	symmetry operation2	symmetry operation3	d 1,2 [Å]	d 1,3 [Å]	Angle 2,1,3 [Å]
Zn	Zn	Zn	-1/4-t, -1/4-u, v	-u, -1/4+t, -1/4+v	2.8637	2.8637	60.000
	Zn	Zn	-u, 1/4+t, 1/4+v	1/4+u, -t, 1/4+v	2.8639	2.8639	60.000
	Zn	Zn	-1/4-t, -1/4-u, v	1/4+u, -t, 1/4+v	2.8637	2.8639	120.000
	Zn	Zn	-1/4+u, -t, -1/4+v	1/4+u, -t, 1/4+v	2.8637	2.8639	179.986
Co	O	O	1-v, 1/4+t, 1/4+v	1/4+x, 1/4+v, 1-u	0.1687	0.1687	109.471
	O	O	1-u, 1-t, 1-v	1/4+u, 1-t, 1/4+v	0.1686	0.1687	109.471
O	Co	O	1-u, -1/4+t, -1/4+v	3/4-t, 3/4-u, v	0.1686	0.2754	35.264
	Co	O	1-u, -1/4+t, -1/4+v	t, 3/4-u, 3/4-v	0.1686	0.2754	35.264
	O	O	3/4-t, 3/4-u, v	t, 3/4-u, 3/4-v	0.2754	0.2754	60.000
	O	O	3/4-t, u, 3/4-v	t, 3/4-u, 3/4-v	0.2754	0.2754	60.000

The goodness fit factor and R-Factors of $ZnCo_2O_4$ are given below.

Table 9. The tabular form of R_p, R_{wp}, R_{exp} of $ZnCo_2O_4$

Goodness fit factor(χ^2)	(R_p)	(R_{wp})	(R_{exp})
35.5	75.9	77.3	12.97

V. Conclusion

$ZnCo_2O_4$/Zn nanocomposite synthesis was carried out with the aid of a wet chemical co-precipitation technique. The heat treatment of the prepared sample was carried from 300°C to 700°C. As we increase the temperature above 700°C then we observe the fine peaks of $ZnCo_2O_4$ with a space group -F 4vw 2vw 3 with a cubic structure. The DCP (a,b,c) for $ZnCo_2O_4$ is 8.0645.The direct cell volume for $ZnCo_2O_4$ is 524.4880 $Å^3$. The RCP (a*, b*, c*) for $ZnCo_2O_4$ is 0.124000. The RCV values for $ZnCo_2O_4$ is .00190662 $Å^3$. The size of crystal for $ZnCo_2O_4$ is 47 nm.

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