Structural and Bonding Behavior Analysis of Microwave Sintered ZnO:Co materials

D. Sivaganesh, S. Sasikumar, S. Saravanakumar, S. Asath Bahadur

Abstract*— In this present study, $Zn_{1-x}Co_xO$ (x = 0.0, 0.04 & 0.06) samples were synthesized using conventional solid state sintering process and characterized by PXRD and SEM. The structural analysis was done using Rietveld profile refinement technique. The chemical bonding features and nature between Zn and O atoms was analyzed by charge distribution studies. The bonding between Zn and O is clearly visible in the three- dimensional and two-dimensional MEM maps. One- dimensional charge density distribution analysis clearly reveals that the characteristics of the bond. MEM results were also correlated with the PXRD parameters.

Keywords*— X-ray diffraction, Rietveld Refinement, Scanning charge microscopy, Charge density distribution.

I. INTRODUCTION

In the past few decades, researchers have focused the transition metal oxides with great interest in various science and technological applications [1]. Among them, zinc oxide (ZnO) have paid enormous curiosity in the field of photocatalysis, electrocatalysis, catalysis, spintronics, opto-electronic devices, solar cells, energy storage devices and so forth owing to its peculiar properties including high photostabilty, superior chemical stability, good electrical conductivity and excellent exciton binding energy [2,3]. Due to its widespread applications, numerous researchers have been their attention for the synthesis of ZnO with various morphologies such as flower-like [4], rod-like [5], sphere-like [6], hexagonal structures [7] by various preparation routes, which includes solid states sintering [8], chemical methods [9-11], chemical vapor deposition [12] and ball milling methods [13] in order to improve their physical and chemical properties [4]. However, the aforesaid techniques have some limitations such as high temperature; high cost instruments and the obtained products were not uniform structures. Interestingly, microwave–assisted sintering (MWS) is an efficient route when compared to conventional sintering [14]. Generally, conventional sintering could generate heat transfer by radiation or conduction and heat energy is transferred from the materials surface to the core by conduction. In contrast, during MWS process, the samples could catch the microwaves itself which provide the uniform particle growth with well-defined structures [15-17]. Generally, the electrons that present in the materials play a crucial role in conductivity, luminescence, and magnetic, insulating, semiconducting and piezoelectric properties. However, lack of reports available for the investigation charge density distributions in the Zn-O unit cell under microwave irradiation. Recently, our research group have been investigated the bonding nature and mid–bond charge densities of Al doped ZnO materials.

In this regard, we tried an attempt for the fabrication of Co2+ doped ZnO tailored via MWS route and characterized by XRD and SEM analysis. Also, we have evaluated the bonding nature and mid-bond charge densities of Co2+ doped ZnO.

II. EXPERIMENTAL

A. Sample preparation

The $Zn_{1-x}Co_xO$ (x = 0.0, 0.04 & 0.06) samples were synthesized using solid state sintering process. High purity starting materials ZnO (Alfa Aesar; purity: 99.99%) & Co3O4 (Alfa Aesar; purity: 99.98%) were added with stoichiometric molar ratio and ground using ball mill for 5 h. The mixture was transferred to quartz ampoules and then sintered at 1150°C using microwave furnace. Then, the heated samples were cooled with at a rate of 50°C per hour.

B. Characterization

$Zn_{1-x}Co_xO$ (x = 0.0, 0.04 & 0.06) samples were characterized by PXRD using monochromatic Bruker (D8 advance ECO) diffractometer with CuKα (λ=1.54056 Å) radiation from 10° to 120° with scan width of 0.02°. The detailed structural analysis was also done by Rietveld refinement technique. The microstructure and surface morphological images of the materials was measured using scanning electron microscopy (SEM) (ZEISS-EVO 18).

III. RESULTS AND DISCUSSION

A. Structural analysis

The crystalline purity of $Zn_{1-x}Co_xO$ (x = 0.0, 0.04 and 0.06) was determined by powder X-ray diffraction (PXRD) data sets.

Phase pure hexagonal

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structured ZnO were identified and is compared to standard JCPDS patterns [18]. Fig. 1 shows the well-indexed observed PXRD profiles of the prepared $Zn_{1-x}Co_xO$ (x = 0.0, 0.04 and 0.06) system. The intensity of diffraction peaks is gradual decrease with the addition of Co^{2+} concentration in ZnO. In general, the X-ray intensity of diffraction patterns depends only by the scattering factor of the atoms [19]. This is mainly caused by the atomic number of Zinc is 30 and the atomic number of Copper is 27. Due to the less atomic number of Co^{2+} the X- ray intensity of the peaks decreased gradually. On the other hand, the peaks shifted towards the lower side of 2θ for x=0.04 and peaks shifted to higher angle 2θ side for x = 0.06.

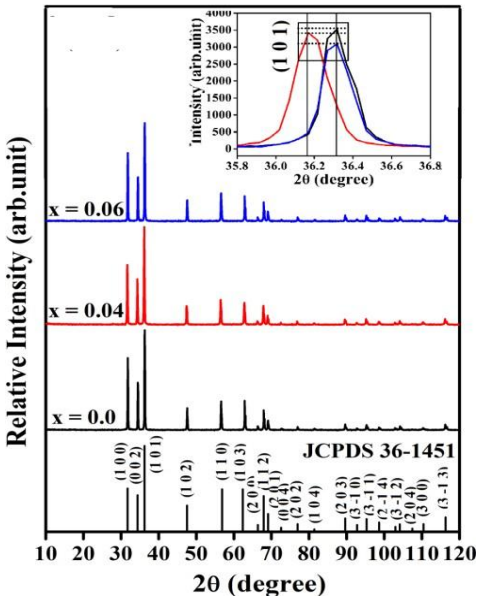
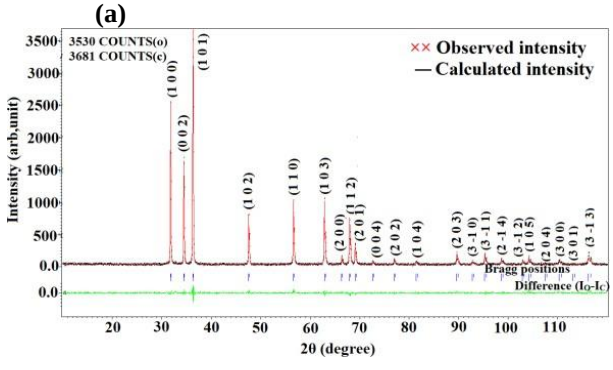


Fig. 1.PXRD patterns of $Zn_{1-x}Co_xO$ materials (x=0.0, 0.04, 0.06).

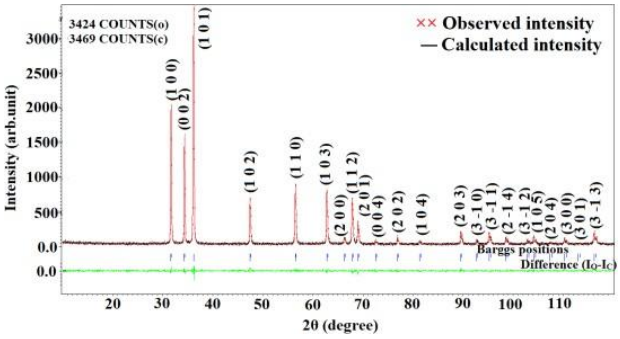
These result consistent with the cell parameter shown in Table 1. The intensity variation and the peak shifting confirm that Cobalt ions occupied the ZnO substitutional lattice site. The crystallite size of the materials is calculated by Scherrer formula [20] and the size of Zn1-xCoxO (x = 0.0, 0.04 and 0.06) materials are 14 nm, 16 nm and 14 nm respectively.

The obtained XRD data sets of $Zn_{1-x}Co_xO$ (x = 0.0, 0.04 and 0.06) samples were fitted using Rietveld refinement technique [21] by the software JANA 2006. The structure pattern was taken from wurtzite ZnO in space group of P63mc and both Zn and O at 2b Wyckoff positions, (1/3 2/3 0) and (1/3 2/3 0.375) respectively. The refined profile of $Zn_{1-x}Co_xO$ (x = 0.0, 0.04 and 0.06) are depicted in fig. 2 (a)-(c). The refined cell parameters of the samples listed in table 1.

(a)



(b)



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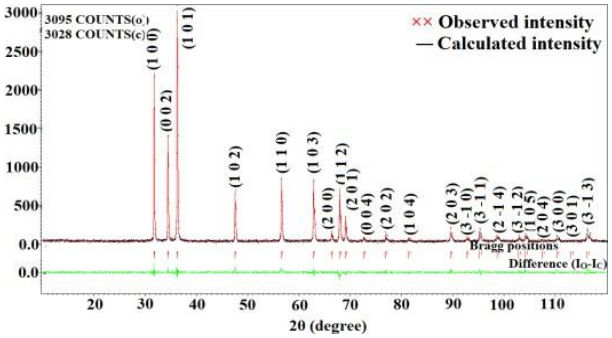


Fig. 2.Rietveld Refinement profiles of Zn1-xCoxO materials, a) x=0.0, b) x=0.04, c) x=0.06.

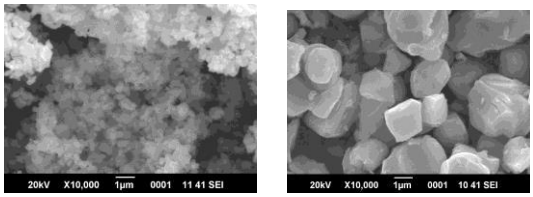
TABLE I. REFINED PARAMETERS OF THE PREPARED MATERIALS

Parameters	x=0	x=0.04	x=0.06
a=b (Å)	3.2511(9)	3.2546(13)	3.2438(42)
c (Å)	5.2049(16)	5.2113(21)	5.1927(68)
Volume (Å)	47.63(2)	47.80(3)	47.39(5)
Density (g/cm^3)	5.64	5.63	5.41
Robs(%)[a]	1.83	2.03	1.44
Rp(%)[b]	3.33	3.43	3.36
$F_{(000)}$	76	74.64	73.96
GOF[d]	1.02	1.02	1.00

B. *Microstructal studies*

The microwave sintered $Zn_{1-x}Co_xO$ (x = 0.0, 0.04 and 0.06) materials were evaluated by scanning electron microscopic images (SEM) to analyze the microstructure and surface morphological analysis and is shown in fig. 3 (a)-(c). There is an enormous change in the morphology of pure ZnO and Co2+ doped ZnO materials. Irregular hexagonal shaped morphology was observed in the pure ZnO and is shown in fig. 3(a). Fig. 3 (b) & (c) shows well dispersed and mine stone like morphology was observed. The approximate size of the particle is in the range of 1 µm.

(a) (b)



(c)

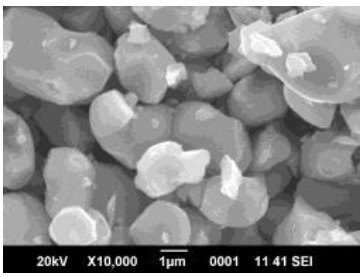


Fig. 3.SEM images of Zn1-xCoxO materials a) x=0.0, b) x=0.04, c) x=0.06.

C. Charge density analysis

The charge acquired characteristics were analyzed using the extracted structure factors. This analysis is done by maximum entropy method (MEM) [22] which is versatile software and standard method to analyze the charge density distribution inside unit cell employed by the DYSNOMIA software [23]. In this report, the charge density distributions inside unit cell is reconstructed for $Zn_{1-x}Co_xO$ (x = 0.0, 0.04 and 0.06) samples. Three-dimensional, two-dimensional and one-dimensional charge density views can be visualized by VESTA software [24].

Fig. 4 (a)-(c) show the distributions charges inside the unit cell of $Zn_{1-x}Co_xO$ (x = 0.0, 0.04 and 0.06) samples with iso-surface level 1 e/Å3. The Zinc and Oxygen atoms placed on the horizontal axis is referred by Bond 1 and the Zn-O bond along the vertical axis is mentioned by Bond 2 [17]. Fig. 5 and 6 show the two-dimensional charge density distributions drawn on (100) and (014) planes. Fig. 7 shows the bond length and charge density at the middle of the bonds which is evaluated by one-dimensional charge density profiles and the mid bond charge densities listed in table 2. It reveals that the mid-bond charge density values for 4% Co2+ doped ZnO material shows maximum value at Bond 1 and minimum value at Bond 2.

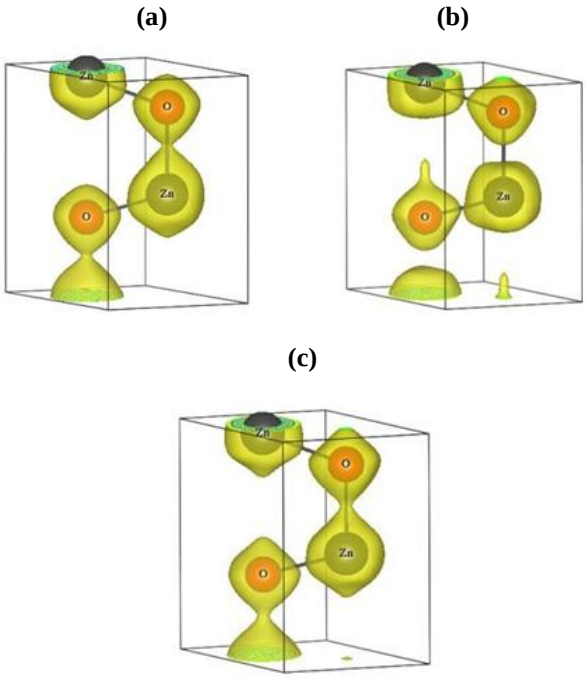


Fig. 4.3D unit cell of Zn1-xCoxO materials, a) x=0.0, b) x=0.04, c) x=0.06.

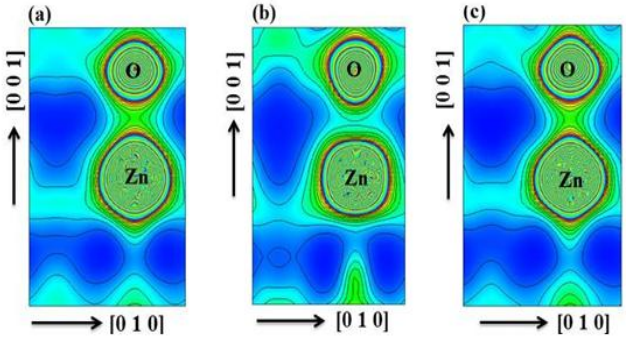


Fig. 5.2D ED maps on (100) lattice plane of Zn1-xCoxO materials, a) x=0.0, b) x=0.04, c) x=0.06.

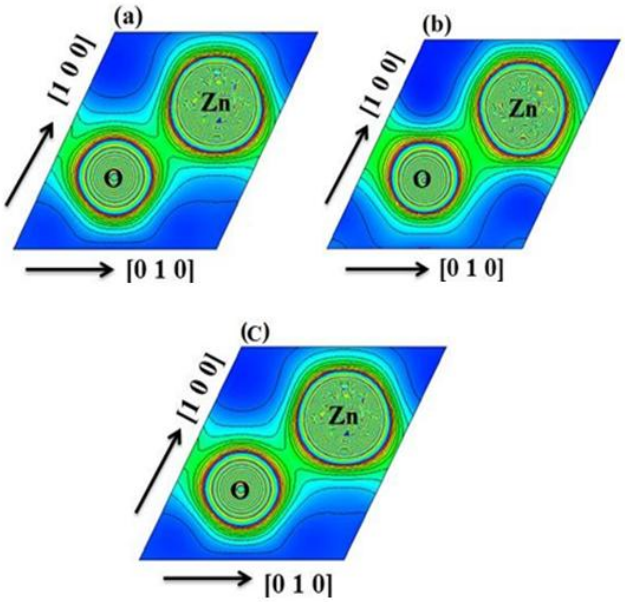
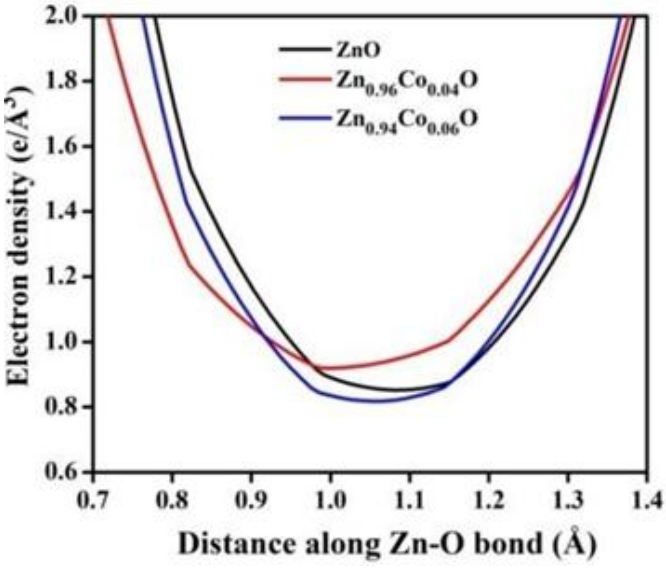


Fig. 6.2D ED maps on (103) lattice plane of Zn1-xCoxO materials, a) x=0.0, b) x=0.04, c) x=0.06.

(a)



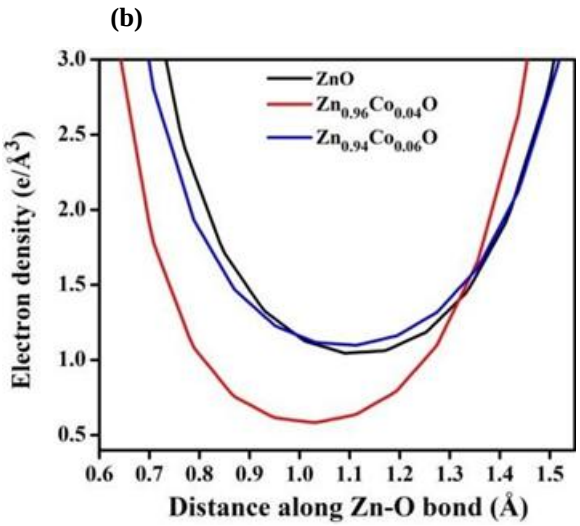


Fig. 7. 1D ED profiles of Zn1-xCoxO materials a) Bond 1, b) Bond

TABLE II. BONDING BEHAVIOR OF $Zn_{1-X}Co_XO$

Nominal Co concentration (mol %)	Bond 1		Bond 2	
	Distance of Zn-O bond	Mid bond electron density (e/ Å^3)	Distance of Zn-O bond	Mid bond electron density (e/ Å^3)
x=0.0	1.9741	0.8522	1.9919	1.0451
x=0.04	1.9704	0.9190	2.0136	0.5834
x=0.06	1.9720	0.8180	2.0127	1.1008

IV. CONCLUSION

Cobalt doped zinc oxide ($Zn_{1-x}Co_xO$ (x = 0.0, 0.04 and 0.06)) materials were synthesized using solid state sintering process by means of microwave medium. PXRD profiles confirm that the prepared systems with phase pure ZnO. The detailed structural information of prepared system was investigated by Rietveld profile refinement technique. The difference of morphologies between pure and cobalt doped ZnO samples were found in SEM measurements. Charge density distribution analyses have done in maximum entropy method and charge derived properties are consistent with PXRD data.

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