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Preparation and Gas Sensitive Electrical Characteristics of Cobalt Doped Nickel Ferrites

Than Than Swe[*], Aye Aye Lwin[**], Win Kyaw[***]

Abstract

Cobalt Doped Nickel ferrites with the general formula $Ni_{1-x}Co_xFe_2O_4$ (x = 0.0, 0.1 and 0.2) were prepared by self-combustion method. The combustion powders were heat-treated at 1000°C for 30 min. Structure of the samples were investigated by X-ray powder diffraction (XRD). XRD patterns were collected in the diffraction angle range 10° - 70°. The gas sensitive electrical resistances of the as-prepared sample pellets were observed in acetone. It was observed that the gas sensitivity depends on the concentration of Co.

Keywords **–** $Ni_{1-x}Co_xFe_2O_4$, self-combustion**,** XRD, gas sensitive electrical resistances, acetone**.**

1. Introduction

Spinel-type oxides with a general formula of AB_2O_4 are important mixed oxides in gas sensors, and have been investigated for the detection of both oxidizing and reducing gases [1]. In particular, nickel ferrite as a p-type semiconducting oxide has show to be a good sensor to detect oxidizing [2]. The semiconductor gas sensors offer good advantages with respect to other gas sensor devices (such as spectroscopic or optic systems), due to their simple implementation, low cost and good reliability for real-time control systems [4, 5].

The self-combustion method was used for preparation because the followings two advantages [6]:

(1) heat generated in the exothermic reaction accelerates the process and

(2) the resulting as-prepared powder is fine grained with grain size smaller than that of the starting powders.

In the present study, Nickel ferrite doped with small amounts of Cobalt was prepared by self-combustion method and investigated as gas sensor. In an attempt to improve the sensitivity and nanoparticles of Nickel ferrite have been partly replaced with Co on place of Ni and Fe, respectively.

2. Aim

This paper mainly deals with the preparation and gas sensitive electrical characteristics of $Ni_{1-x}Co_xFe_2O_4$ for the application of gas sensing materials.

3. Experimental Details

Nanocrystalline $Ni_{1-x}Co_xFe_2O_4$ (x = 0.0, 0.1 and 0.2) were prepared by self-combustion method. Analytical Reagent (AR) grade $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.9H_2O$ were used as the raw materials. NH_4OH was used as the fuel. The starting materials were weighed with desired stoichiometric compositions and mixed each others. The obtained precursor solution was heated on a hot plate room temperature (29°C) to 100°C for 1 h. Then, a quick combustion was taken as the calcination of metal hydroxides and the reaction between metal oxides. The combustion powders were pressed into disk shape pellets and subjected to thermal treatment at 1000°C for 30 min **in vacuum chamber**. Fig 1 shows the flow diagram of the sample preparation process.

[*] Dr, Associate Professor, Department of Physics, Yadanabon University

[**] Dr, Associate Professor, Department of Physics, Loikaw University

[***] Dr, Associate Professor, Department of Physics, Pyay University

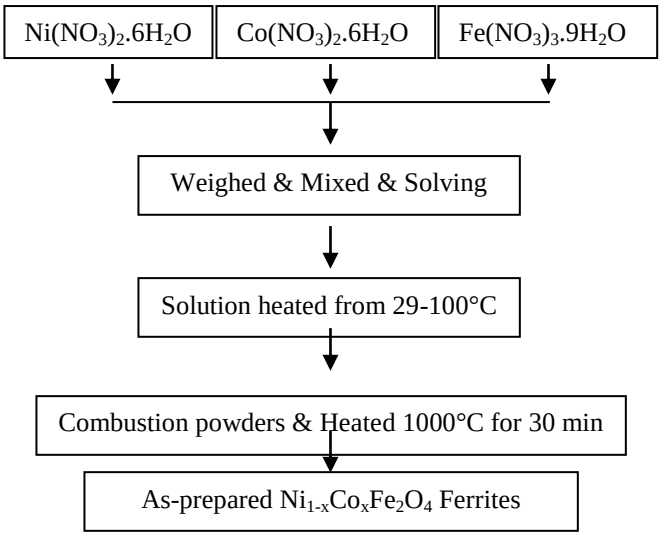

Fig. 1 Flow diagram of the sample preparation procedure

The XRD spectra of the Cobalt Doped Nickel ferrites, $Ni_{1-x}Co_xFe_2O_4$ (x = 0.0, 0.1 and 0.2) are investigated by X-Ray Diffractometer in this work. The "*d*" values are determined using the CuK_α radiation with wavelength of 1.54056 Å. Each diffracted ray is recorded as a peak. The peak heights are roughly proportional to the rays' intensity. The diffraction patterns of specimens are identified by using Materials Data Inc. data library. The initial "*d*" spacing is determined using a second derivative peak search algorithm, followed by careful editing of the raw data to improve the position accuracy and to resolve ambiguous lines. The electrical resistances of the samples were observed in the ambient condition (air atmosphere) and acetone atmosphere condition. The electrical resistances of the samples were measured by using MASTECH digital multi-meter.

4.Results and Discussion

Phase Identification

Characteristics of any solid materials depend on its structure. Crystalline solid especially depends on its crystal structure. X-ray diffraction method can be used to investigate the structure of solid materials. Powder X-ray diffraction patterns of $Ni_{1-x}Co_xFe_2O_4$ (x = 0.0, 0.1 and 0.2) samples are shown in Fig 2(a – c). The observed XRD lines were identified by using standard JCPDS data library files of Cat. No. 86-2267> Trevorite – $NiFe_2O_4$ for x = 0.0 sample and Cat. No. 86-2267> Trevorite – $NiFe_2O_4$ and Cat. No. 22-1086> $CoFe_2O_4$ – Cobalt Iron Oxide for x = 0.1 and
x = 0.2 samples. According to XRD patterns, the samples belong to cubic structure at room temperature. The lattice parameters are evaluated by using crystal utility of the equation $\frac{\sin^2\theta}{(h^2+k^2+l^2)}=\frac{\lambda^2}{4a^2}$, where (hkl) is the Miller indices, λ is the wavelength of incident X-ray (Å), θ is the diffraction angle of the peak (°) and *a* is the lattice parameter (Å). The obtained average lattice parameters are listed in Table 1. Variation of the lattice parameters with the dopant concentration of Co is shown in Fig 3. The lattice parameters of the samples increased with increase in concentration of Co due to the ionic substitution of Co on Ni in the lattice sites. It can be simply explained that the ionic radii of Co^{2+} and Ni^{2+} are 0.82 Å and 0.78 Å, thus when the increase in dopant concentration of Co^{2+} on divalent cation sites of Ni^{2+}, then the lattice parameters of the unit cell of undoped $NiFe_2O_4$ increased.

The crystallite sizes of each of the samples were estimated by using the Scherrer formula, $D = 0.9\lambda/B\cos\theta$, where *D* is the crystallite size (nm), λ is the wavelength of incident X-ray

(Å), θ is the diffraction angle of the peak under consideration at FWHM (°) and B is the observed FWHM (radians). The obtained average crystallite sizes are tabulated in Table 1. The crystallite sizes are in the range 51.4843 nm – 73.5475 nm and it indicates the nanosized $Ni_{1-x}Co_xFe_2O_4$ (where x = 0.0, 0.1and 0.2) ferrites or it can be said that the nanocrystalline materials. Variation of the crystallite sizes with the dopant concentration of Co of the samples is shown in Fig 3. It was found that the crystallite size of the samples decreased with the dopant concentration of Co.

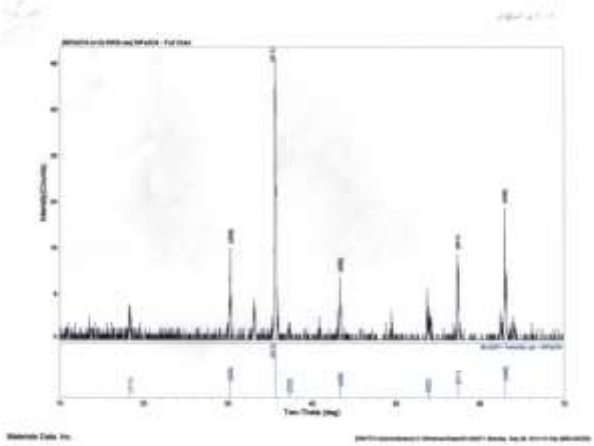

Fig 2.(a) XRD pattern of $Ni_{1-x}Co_xFe_2O_4$ (where x = 0.0)

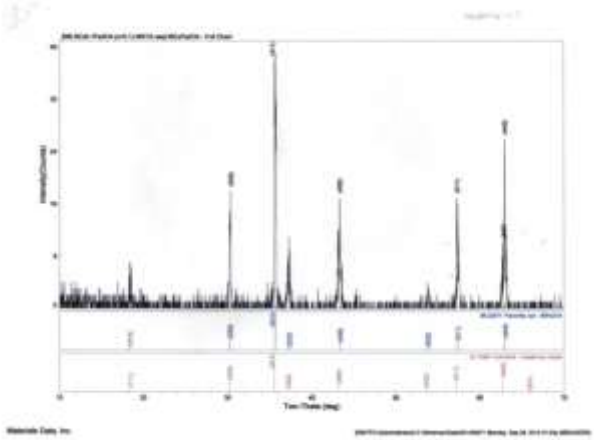

Fig 2.(b) XRD pattern of $Ni_{1-x}Co_xFe_2O_4$ (where x = 0.1)

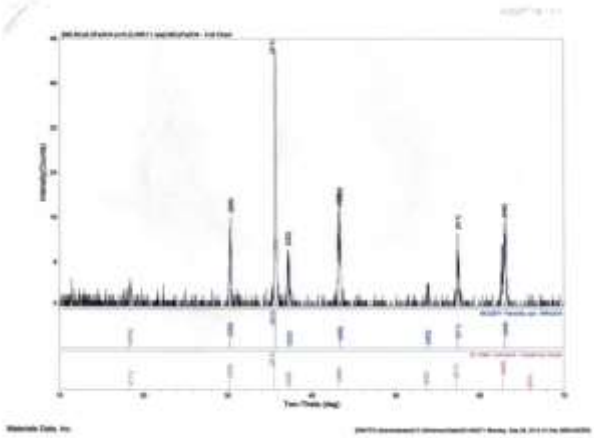

Fig 2.(c) XRD pattern of $Ni_{1-x}Co_xFe_2O_4$ (where x = 0.2)

Table 1 The lattice parameters and crystallite sizes of $Ni_{1-x}Co_xFe_2O_4$ (where x = 0.0, 0.1 and 0.2) ferrites

x	Obs. *a*=*b*=*c* (Å)	Cal. *a*=*b*=*c* (Å)	*D* (nm)
0.0	8.3450	8.3450	73.5475
0.1	8.3474	8.3474	70.0537
0.2	8.3532	8.3495	51.4843

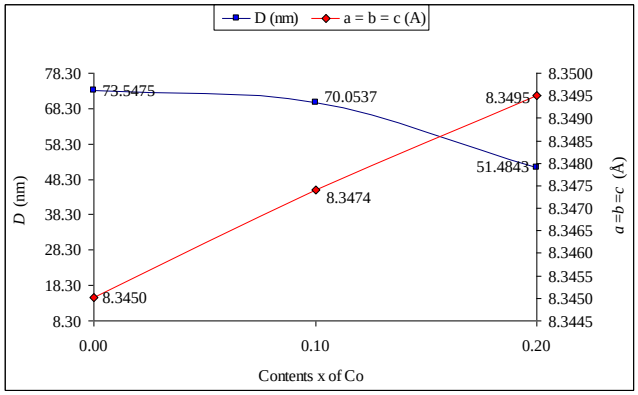

Fig 3. Variations of the lattice parameters and crystallite sizes of $Ni_{1-x}Co_xFe_2O_4$ ferrites with the concentration of Co

Gas Sensitive Electrical Resistance Study

The gas-sensing responses of $Ni_{1-x}Co_xFe_2O_4$ (where x = 0.0, 0.1 and 0.2) ferrites to the reducing gas likes acetone (CH_3COCH_3) at ambient temperature were analyzed for the applications of acetone gas sensing materials. Gas response electrical resistances of the samples in the acetone atmosphere after the exposure times of 3 min and 5 min are depicted in Fig 4(a – c) and Fig 5(a – c) respectively. It was found that the electrical resistances of $Ni_{1-x}Co_xFe_2O_4$ (x = 0.0) in air (STP) atmosphere greater than electrical resistances in acetone atmosphere. The electrical resistances, however, of $Ni_{1-x}Co_xFe_2O_4$ (x = 0.1 and 0.2) ferrites in air atmosphere smaller than electrical resistances in acetone atmosphere. The sensitivities of the samples are listed in Table 2. The acetone gas sensitive process of the samples can be discussed as follow:

The reducing gas R acting on the $Ni_{1-x}Co_xFe_2O_4$ surface can be described as

$R\ (gas) \leftrightarrow R\ (ads)$

$O^{2-}\ (ads) + e^- \leftrightarrow 2O^-\ (ads)$

$R\ (ads) + O^-\ (ads) \leftrightarrow RO\ (ads) + e^-$

In the absence of R, electrons are removed from conduction band of the sample by the reduction of O_2, resulting in the formation of O^- species and consequently the resistance of $Ni_{1-x}Co_xFe_2O_4$ sensor increases. When R is introduced, it reacts with O^- (ads) to form RO, and electrons enter the conduction band of $Ni_{1-x}Co_xFe_2O_4$ leading to decrease of resistance.

The reactions involved during the acetone (CH_3COCH_3) sensing are summarized below (taking O^- and ethanol (C_2H_5OH) for example):

$CH_3COCH_3\ (g) + O^-\ (ads) \rightarrow CH_2COCH_2^-\ (ads) + H_2\ (g)$

$CH_2COCH_2^-\ (ads) \rightarrow CH_2COCH_2\ (g) + e^-$.

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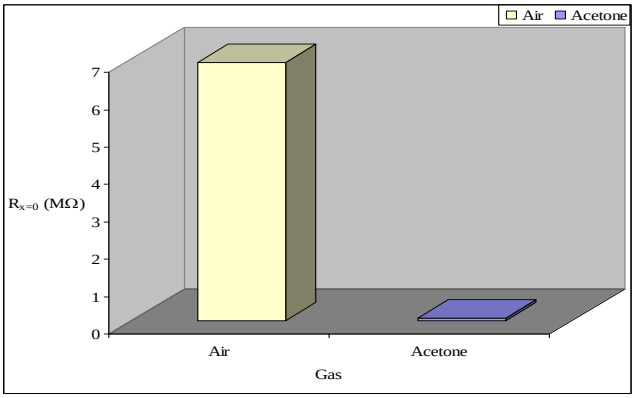
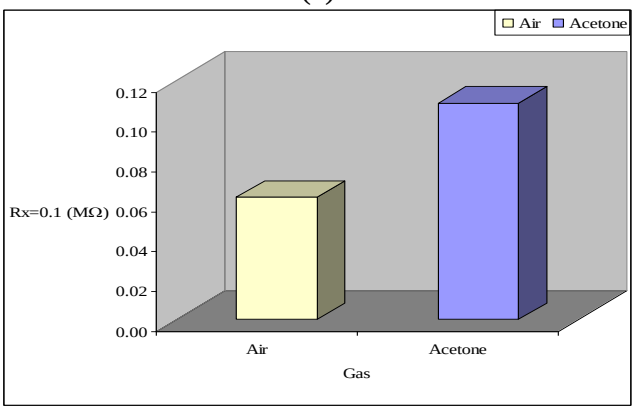


(a)



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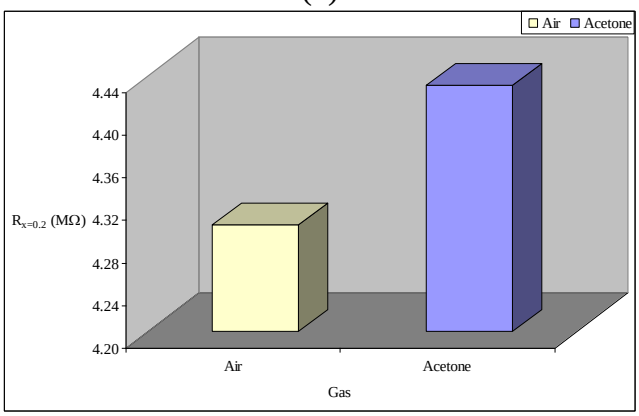
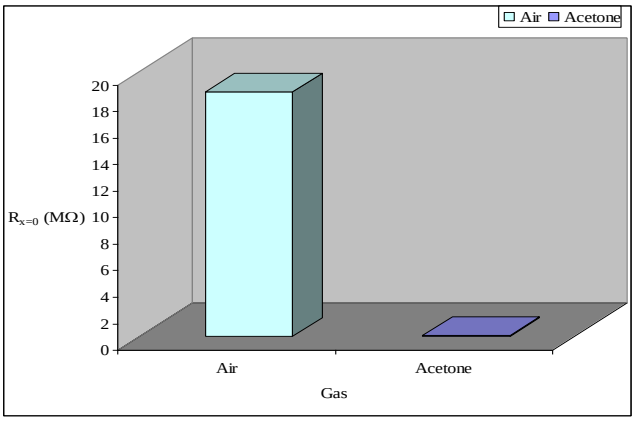


(c)

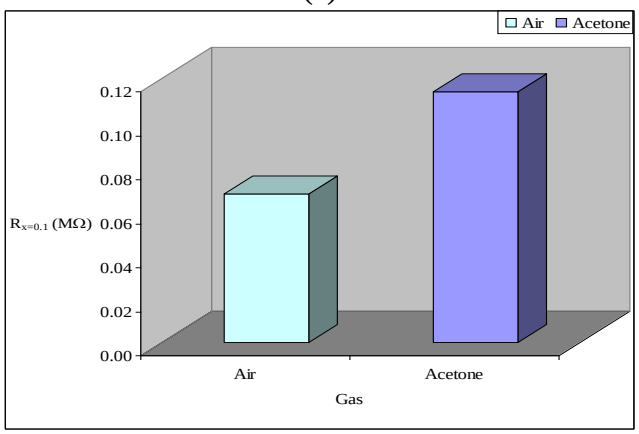
Fig 4. Gas response electrical resistances of $Ni_{1-x}Co_xFe_2O_4$ (a) x=0.0, (b) x=0.1 and (c) x=0.2 ferrites in air and acetone atmospheres after 3 min exposure time

Table 2. Sensitivities of the $Ni_{1-x}Co_xFe_2O_4$ (where x = 0.0, 0.1 and 0.2) samples after 3 min and 5 min in acetone atmosphere

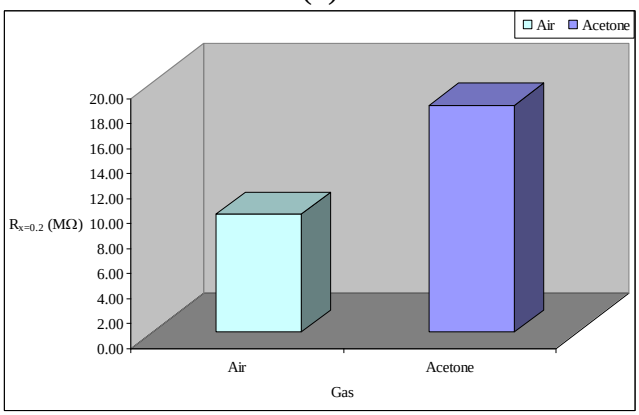
x	$S_{3\ min}$ (%)	$S_{5\ min}$ (%)
0.0	99.02	99.62
0.1	76.59	68.58
0.2	46.82	98.35



(a)



(b)



(c)

Fig 5. Gas response electrical resistances of $Ni_{1-x}Co_xFe_2O_4$ (a) x=0.0, (b) x=0.1 and (c) x=0.2 ferrites in air and acetone atmospheres after 5 min exposure time

5.Conclusion

Nanocrystalline $Ni_{1-x}Co_xFe_2O_4$ (where x = 0.0, 0.1 and 0.2) samples were successfully prepared by self-combustion method and their structural analysis and gas response electrical property were reported by using XRD and gas sensitive electrical resistance measurements. The X-ray diffraction patterns indicated the single-phase spinel type cubic crystalline materials. The lattice parameters are increased with increase in dopant concentration of Co on Ni. It indicated that the presence of Co^{2+} ions causes appreciable change in the structural properties of $Ni_{1-x}Co_xFe_2O_4$. The obtained average crystallite sizes are in the range 51.4843 nm – 73.5475 nm and it showed the nanocrystalline materials. From the acetone gas response measurements, the investigated materials can be used for acetone gas sensing materials.

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