Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.9 No.4, 2017

www.iiste.org

# Preparation and Characterization of Spinel $NiCr_2O_4$ by Co-precipitation Method

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## Abstract

Nickel chromite ($NiCr_2O_4$) was prepared by Co-precipitation method from an aqueous solution containing nickel (II) nitrate, chromium (III) nitrate followed by calcination at 650°C for 6h. The materials were characterized in detail by X-ray powder diffraction technology (XRD), FTIR spectroscopy and Differential temperature analysis DTA. Muller indexes (hkl) were calculated for the production, and it was clear that, the compound crystallized according to cubic lattice with following parameter $a=8.3169A^{\circ}$, $Z=8$, $V=575.3\ A^{\circ 3}$ . The space group of symmetry is Fd3m. The IR Spectroscopy Encourage our results during the bonding vibrations of Cr-O, Ni-O. The thermal characteristic shows four endothermic effects.

**Keywords:** Nickel chromite, Co-precipitation, Spinel.

## 1. Introduction

Transition metal Chromites possessing spinel structure ( an important class of mixed metal oxides) with formula of $MCr_2O_4$ ( M=Co, Ni, Zn , Ca or others) can be described as cubic, closely-packed arrangement of oxygen atoms, and $M^{+2}$ and $Cr^{+3}$ ions can occupy either tetrahedral (A) or octahedral (B) sites [1]. The unit cell contains 32 anions forming 64 tetrahedral interstices and 32 octahedral interstices; of these 8 tetrahedral and 16 octahedral sites are occupied by cations . These are called (A) and (B) sites respectively. The general formula of compounds with spinel structure is $AB_2O_4$ the unit cell of an ideal spinel is shown in figure 1.

Such materials have widespread use and attracted the attention of some investigators as good catalysts for some industrial reactions for example $NiCr_2O_4$ [2].

The spinel materials can be prepared by many methods such as solid-state reaction of metal oxides at high temperatures [3]. In the wet chemical process, the powders are synthesized in liquid systems by means of Co-precipitation [4], Microemulsion , Citrate-nitrate gel combustion [5], Sol-gel [6] , Sol-spray processes, polymeric gel , and Hydrothermal processes [7] . In the present work, we tried the synthesis of nickel oxide chromite spinel by Co-precipitation method, this method is based on the stoichiometric mixing of aqueous solutions of nitrates of $Cr^{3+}$ and of divalent Mn, Co, Ni, Cu, Zn, Mg, Ba etc. In the concentrations required for the chromite composition and their simultaneous precipitation in the form of hydroxides by $NaOH/NH_4OH$ this is followed by filtration, washing and calcination of the products to form the oxide. The structure and the size of the particles can be accurately controlled by altering the pH and/or temperature of the solution. By this method, chromite particles with a narrow size distribution may be obtained with high purity [4].

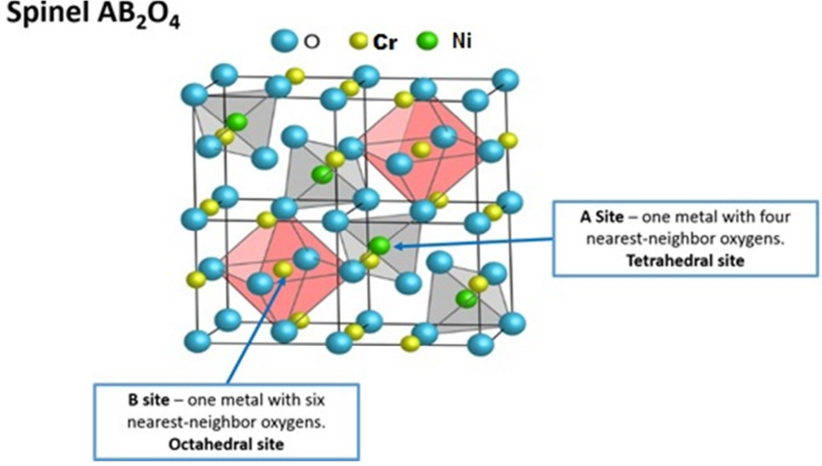

Figure1. The unit cell of an ideal spinel structure

## 2. The goal of the research:

The synthesis of Nickel chromite way joint precipitation from Nickel and chromium nitrate salts, and The study of crystalline and structural characteristics in general, and to find the temperature of synthesis and the appropriate conditions for it, such as PH and concentration of aqueous solutions of metal nitrate entering the process.

## 3. Chemicals used for preparation:

High purity materials were used for analytical goals:

- Chromium nitrate (99%) $Cr(NO_3)_3.9H_2O$
- Nickel nitrate (99%) $Ni(NO_3)_2.6H_2O$
- Ammonium hydroxide $NH_4OH$

## 4. Practical section:

### 4.1. Sample preparation and method of synthesis:

The catalyst was prepared by co-precipitation method [4]. A mixture is consisting of solutions of nickel nitrate and chromium nitrate were taken in appropriate mole ratios and the mixture was heated to 70-80°C. To this hot mixture a 15% ammonia solution was added drop wise with constant and uniform stirring to maintain a constant pH of 6.5–8. The precipitate was maintained at this temperature for 2 h and aged for one day. The precipitate was filtered, washed and dried at 150°C for 24 h and calcined at different temperatures starting from 500°C until 750°C for 6 h.

The weights of the raw materials used in account out of the molar weights of raw materials according to the following equation:

$$\boldsymbol{Ni(NO_3)_2.6H_2O + 2Cr(NO_3)_3.9H_2O\ +\ 8NH_4OH\ \rightarrow NiCr_2O_4\ \ + 8NH_4NO_3 + 29\ H_2O}$$

Table1. Shows the weights of the raw materials used and calculated in accordance with the previous equation, and weights required were calculated on the basis that the composite output desired amount equal to 5gr. Table shows size of distilled water to be affixed in accordance with the solubility of salt for the preparation of solutions according to the concentrations required

Table1.Weights of the raw materials and size of distilled water.

| | Salts | |
|---|---|---|
| | $Ni(NO_3)_2.6H_2O$ | $Cr_2(NO_3)_3.9H_2O$ |
| salt mass(gr) | 6.4702 | 17.7991 |
| added distilled water volume (ml) | 6.8708≈7ml | 13.69≈14 |

### 4. 2. Results and discussion:

### 4.2.1 Powder X-Ray Diffraction:

Powder X-ray Diffraction (XRD) is one of the primary techniques used by solid state chemists to characterize materials [8]. Powder XRD can provide information about crystalline structure in a sample even when the crystallite size is too small for single crystal X-ray diffraction, purity of the substance, transition to different phases, lattice constants and presence of foreign atoms in crystal lattice**.** The XRD patterns of the samples were taken using diffraction device X-Ray Powder Diffractometer from a company (Philips-PW-1840) using radiation source ($\lambda$=I.5406A°)**.** XRD patterns of the sample at different baking temperatures are shown as follow.

Figure2. Shows the XRD pattern of $NiCr_2O_4$, which prepared by a chemical precipitation method and calcined at 600°C for 6 hours

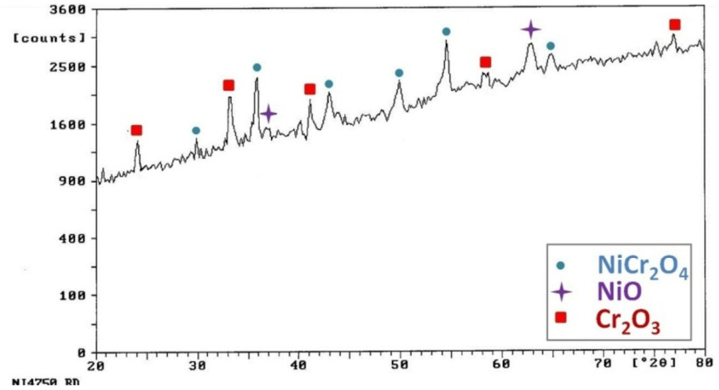

Figure2. X-ray diffraction pattern of the incomplete output in wholesale $Cr_2O_3$-NiO scheme (T = 600°C)

Note from the former diagram the appearance of some peaks belonging to the desired compound was manufactured with residue tops (low intensities) of raw materials which are oxides. These peaks belonging to preliminary oxides decrease with follow-up synthesis process and the desired compound tops look more severe until we get to the synthesis of a single phase**.**

The following chart shows the yaw values Nickel chromite compound prepared in a manner common deposition and that resulted when the follow-up increase in temperature reached up to 650°C, and has been fixed for six hours, see Figure 3.

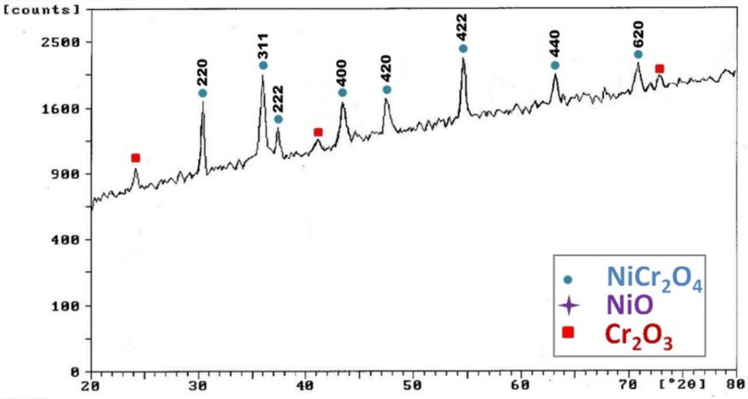

Figure3. X-ray diffraction pattern of the compound resulting $NiCr_2O_4$ scheme (T = 650°C)

The peaks of XRD pattern of the sample was analyzed by matching with standard ICDD No.: 01-075-1728 data file. At the end of the current calculations we notice that the compound corresponds to the pattern of cubic symmetry and all the Muller indexes (hkl) values for all the peaks are consistent with this pattern of crystallization, which is consistent with the following equation [8]:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Table2. Shows diffraction angle, inter planar distance and Muller indexes that calculated from XRD pattern.

Table2. Diffraction angle, inter planar distance and Muller indexes

| 2Θ | Θ | $I/I_0$ | d | $1/d^2$ | hkl |
|---|---|---|---|---|---|
| 30.42 | 15.21 | 90% | 2.9360 | 0.1160 | 220 |
| 35. 9 | 17.95 | 100% | 2.4994 | 0.1600 | 311 |
| 37.45 | 18.725 | 20% | 2.3994 | 0.1737 | 222 |
| 43.555 | 21.7775 | 37% | 2.0762 | 0.2320 | 400 |
| 47.565 | 23.7825 | 33% | 1.9101 | 0.2741 | 420 |
| 54.07 | 27.035 | 59% | 1.6947 | 0.3482 | 422 |
| 63.285 | 31.6425 | 25% | 1.4683 | 0.4639 | 440 |
| 70.98 | 35.49 | 19% | 1.3268 | 0.5681 | 620 |

The basic cell size was calculated for cubic crystalline by the following equation:

$$\mathbf{V = a^3}$$

Then experimental density of the material resulting in a manner flask density (picknometer) was measured for three times in a row and took the average value for them $\rho_E$. Depending on the material's density number of formulas in a single crystalline cell Z was calculated according to the following equation:

$$\rho = \frac{MZ}{N_a V}$$

Where M molecular weight of the material, N Avogadro number, V basic cell measured one size $(cm)^3$ [1]. Thus we find that:

$$Z = \frac{N_a . V . \rho}{M} = 7.6005 \approx 8$$

Following the method of rounding we found out that Z = 8, and therefore we can write the general formula for the content of the basic cell as follows: $Ni_8Cr_{16}O_{32}$

The results obtained are presented in Table 3.

Table3. Lattice constant, basic cell size, Z and density

| lattice constant a (A°) | basic cell size v $(A°)^3$ | experimental density $\rho_E$ $gr/cm^3$ | Z | Theoretical Density $\rho_t$ $gr/cm^3$ |
|---|---|---|---|---|
| 8.316956 | 575.2985 | 4.98 | 8 | 5.24 |

It is necessary to point at the fact that the heating up of the compound Nickel chromite to a higher degree of 750°C leads to the disintegration of the raw materials as shown Figure 4.

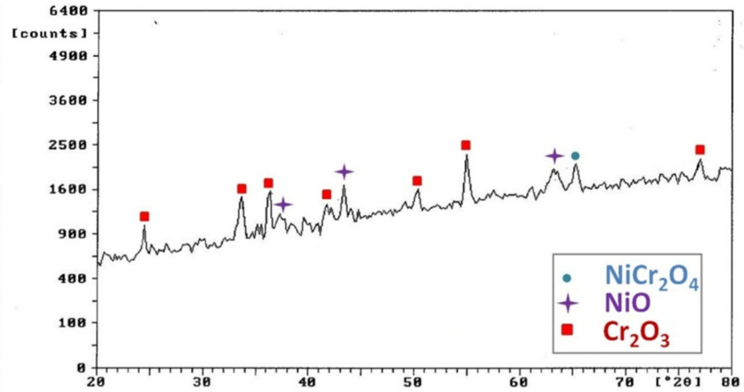

Figure4. X-ray diffraction pattern of the compound resulting $NiCr_2O_4$ scheme (T = 750°C)

### 4.2.2 Fourier Transform Infrared Spectroscopy:

FTIR Spectroscopy is an analytical technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic [1].

The Figure 5.  Shows the infrared spectrum sample Nickel Chromite burned at degree 650°C

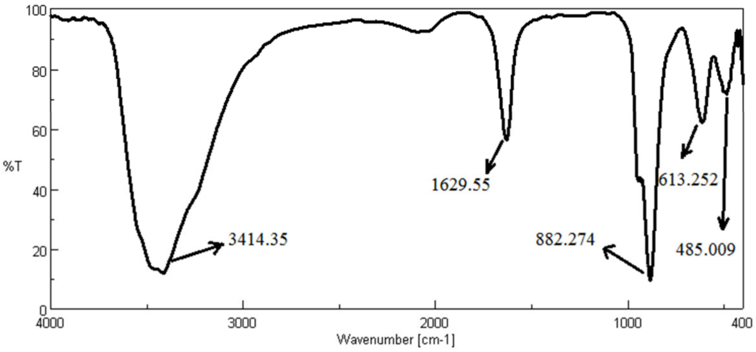

Figure5. FTIR spectra of $NiCr_2O_4$

Where it appears from the spectrum that there are five-absorption values, the first absorption at the value 3414 $Cm^{-1}$, which is due to vibration stretching of the pound OH and the second at the value 1629.55 $Cm^{-1}$, which is due to bending vibrational mode of the interlayer water molecules. The bands at 882.274 $Cm^{-1}$and 613.252$cm^{-1}$ back to vibration stretching of the pound Cr-O and The last band at 485.009 $cm^{-1}$ back to Ni-O bond.

### 4.2.2 Thermal analysis:

The study of the thermal behavior of the resulting compound gave the following curve, which includes four absorption peaks (Endothermal effects). See Figure 6.

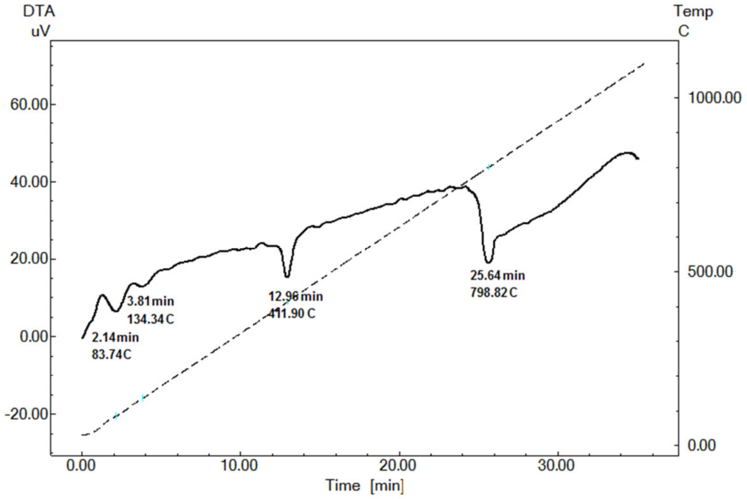

Figure6. DTA curve (differential thermal analysis)
of the compound $NiCr_2O_4$

The endothermic effect at degree 134.34°C and 83.74°C  indicating a loss of water molecules that are absorbed from the surrounding medium experience, and the thermal effect at the degree 798.82°C shows the composite $NiCr_2O_4$ turned into a developed,  noncrystallised amorphous.

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