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Synthesis and Characterization of $Ni_xCo_{1-x}TiO_3$ Nano-Structure

Amal M. Ibrahim[1], S. E. Kader[2] and M.M. Selim[1]

1- Surface Chemistry and Catalysis Laboratory, Physical Chemistry Department, National Research Centre, El Buhouth St., Cairo 12622, Egypt

2- Ceramics, Refractoreis and Building Materials Department, National Research Centre, El Buhouth St., Cairo 12622, Egypt

Abstract

In this study, successful synthesis of ilmenite type ternary oxide Nickel Cobalt Titanate with different composition ratios 0f Nickel and Cobalt (NixCo1-xTiO3) powders was reported. NixCo1-xTiO3 was prepared by simple solid –solid interaction of Nickel nitrate with Cobalt Nitrate and Titanium dioxide as precursors in the presence of Urea. The as prepared powders of different compositions were characterized using X-Ray diffraction spectroscopy (XRD), Transmission Electron Microscopy (TEM) , Diffuse Reflectance Spectroscopy (DRS) and their bulk densities were measured from which their porosity values were calculated. The products showed single phase X-Ray Diffraction pattern and their sizes ranged from 130nm to 175nm as revealed from Transmissions Electron Microscopy images.

Keywords: ***Nanostructure; Inorganic compounds; Chemical synthesis; X-Ray diffraction; Transmission Electron Microscope***

1. Introduction

The chemical synthesis of solid inorganic coloring materials is making an increasingly important contribution to the development and manufacture of ceramic materials. It also plays a vital role in development of fabrication techniques in ceramic industries.1 Titanium based Ilmenite – type perovskites with general formula ATiO3 (A= Pb, Ni, Fe. Co, …….) have attracted great interest over the past few decades because of the utilization of such materials in a wide range of applications such as photocatalysis, sensors, fuel cell 2-5 and also as inorganic pigments.6 Ttitanates are considered as intelligent materials due to their excellent and special electronic and optical properties as well as their chemical stability and non-toxicity.7-9 Nickel Titanate (NiTiO3) being a member of this family has a broad range of the above mentioned properties. In NiTiO3 both Ni and Ti atoms prefer octahedral coordination with alternating cation layers occupied by Ni and Ti alone.10 Ni TiO3 as well as CoTiO3 has a wide range of applications in semiconductors rectifiers,11 electrodes of solid oxide fuel cell,12 metal air barrier,13 color mixtures of surface coating and gas sensing devices.14 Nano-structured NiTiO3 can be obtained by differ wet chemistry techniques including sol gel, sole precipitation, chemical co-precipitation, combustion synthesis and hydrothermal synthesis. 15-18 In this manuscript, we report synthesis of NixCo1-xTiO3 by simple solid interaction route and the different compositions produced were characterized.

2. Experimental

2.1. Synthesis of NixCo1-xTiO3

The chemicals used in this study are analytically pure reagents and used without further purification. $Ni_xCo_{1-x}TiO_3$ systems were prepared by mixing Ni $(NO_3)_2$.6H2O and $CO(NO_3)_2$.$6H_2O$ both giving 1 molar with stoichiometric equivalent of TiO_2 and 2 equivalent of urea i.e. in molar ratio 1:1:2 from nitrate precursors, TiO_2 and urea respectively. The solid mixture of precursors was grinded well at room temperature and left to dry at 100^oC, after being cooled to room temperature the mixture fused in an oven in two steps process, 1st step at 370^oC for 2 hours and the 2^{nd} step at 900^oC for 2 hours. The samples collected represent the pure $NiTiO_3$, pure $CoTiO_3$ and also $Ni_{0.75}Co_{0.25}TiO_3$, $Ni_{0.5}Co_{0.5}TiO_3$ and $Ni_{0.25}Co_{0.75}TiO_3$.

2.2. Characterization of Samples:

The bulk densities of the produced powders were measured using Quantachrome Instrument, from which porosity values of samples were calculated. The produced powders were characterized by X-Ray diffraction spectroscopy (XRD). X-Ray Diffraction (XRD) of the products was carried out using a Shimadzu-XRD-600 X-R ay diffractometer with Cu Kα radiation anode (λ=0.15406 nm) with step size 0.026 and 2θ range from 10^o to 80^o., Transmission Electron Microscopy (TEM) images were carried out on JOEL JEM-200 x and Diffuse Reflectance Spectroscopy (DRS) was carried out using JASCO V-570 UV-Visible/NIR spectrophotometers.

3. Results and discussion:

Figure (1) shows bulk density and porosity of samples with different composition of $Ni_xCo_{1-x}TiO_3$. Bulk density as well as porosity is greatly affected by electrovalence and atomic radii of the cation atom.[19] As the electrovalence of both Ni^{2+} and Co^{2+} are the same and their atomic radii are too close to each other, it was expected that samples with different compositions have nearly the same density and porosity. But it was noticed that there is slight and gradual decrease in density as well as porosity of samples with increasing ratio of Co^{2+}. This could be devoted to the increase of density and atomic radius of Ni^{2+}.

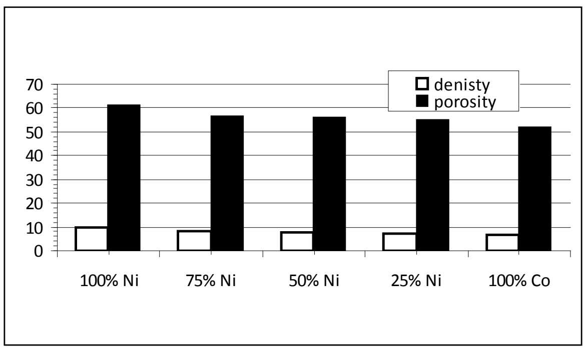

Figure (1) Bulk Density and Porosity of samples

Fig.(2) shows the X-Ray diffraction patterns of as prepared samples $Ni_xCo_{1-x}TiO_3$ with different composition of both $NiTiO_3$ and $CoTiO_3$ as the atomic size of both Ni and Co atoms are too close to each other there is no crystallographic deformation. Pattern shows pure $NiTiO_3$ (sample 1), $Ni_{0.75}Co_{0.25}TiO_3$ (sample 2), $Ni_{0.5}Co_{0.5}TiO_3$ (sample3), $Ni_{0.25}Co_{0.75}TiO_3$ (sample 4) and pure $CoTiO_3$ (sample 5).The XRD patterns revealed that the pattern of pure $NiTiO_3$, pure $CoTiO_3$ and ternary oxides are nearly single phased and in good agreement with JCPDS card files No. 89-3743 and data given in the inorganic crystal structure database (ICSD) .[20] The products are rhombohedral crystal system with lattice parameters a= 5,03A^o and c = 13.7905 A^o. The strong and narrow diffraction peaks reveal the high crystallinity of the as prepared samples. The crystallite size of the samples were calculated using Debye-Sherrers equation which is given as.[21]

$$L = 0.89\lambda / \beta \cos\theta$$

Where β is the FWHM of diffraction peak, λ is the wave length of X-ray (0.154 nm), L is the crystallite size, and θ is the Bragg peak position.

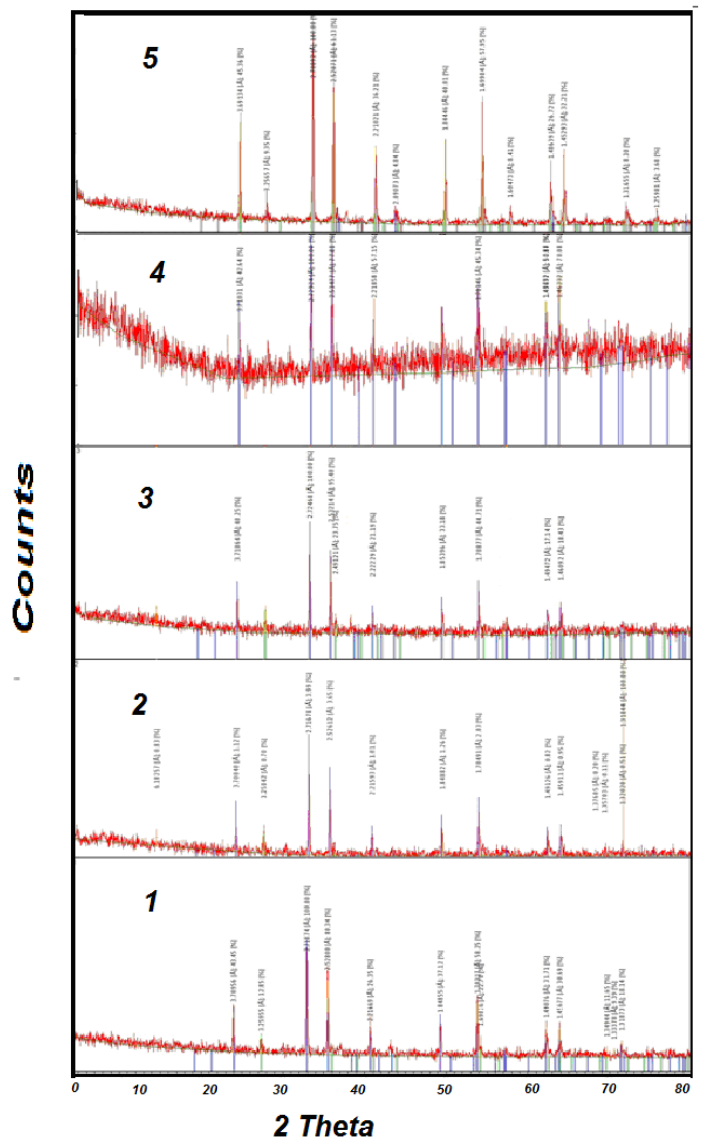

Fig. (2): XRD patterns of as prepared samples; $NiTiO_3$ (sample 1), $Ni_{0.75}Co_{0.25}TiO_3$ (sample 2), $Ni_{0.5}Co_{0.5}TiO_3$ (sample3), $Ni_{0.25}Co_{0.75}TiO_3$ (sample 4) and pure $CoTiO_3$ (sample 5).

Fig.(3) Highlights TEM images for as prepared different compositions of

$Ni_xCo_{1-x}TiO_3$. TEM images reflect heterogonous morphology of samples in both shape and dimensions, even though the predominant morphology was the hexagonal crystal structure. The particle size of the samples ranging from 130 nm to 175 nm and this is in good agreement with the crystallite size calculated from XRD.

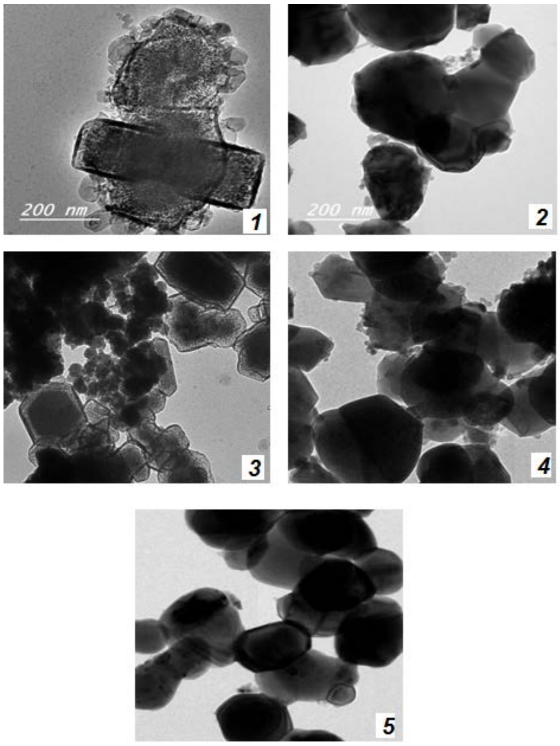

Fig. (3) TEM images of as prepared samples NiTiO3 (sample 1), Ni0.75Co0.25TiO3 (sample 2), Ni0.5Co0.5TiO3 (sample3), Ni0.25Co0.75TiO3 (sample 4) and pure CoTiO3 (sample 5)

Color is one of the most conspicuous attributes of metal titanates as one of the many uses of titanates as pigments.[22] Fig.(4) shows the DRS of the produced colored powders. The figure showing smooth curves in which the reflectance increases as the light goes from blue (~ 490 nm) to yellow (~ 590 nm) making peak at ~ 590 nm in case of pure $NiTiO_3$ as yellow powder and for samples composed from both $NiTiO_3$ and $CoTiO_3$ the figure showing splitting of the peak into two peaks at ~ 500 nm and 595 nm corresponding to green color of $CoTiO_3$ and yellow color of $NiTiO_3$. In case of pure $CoTiO_3$ one peak appeared at ~ 500 nm with almost vanishing of the other peak.

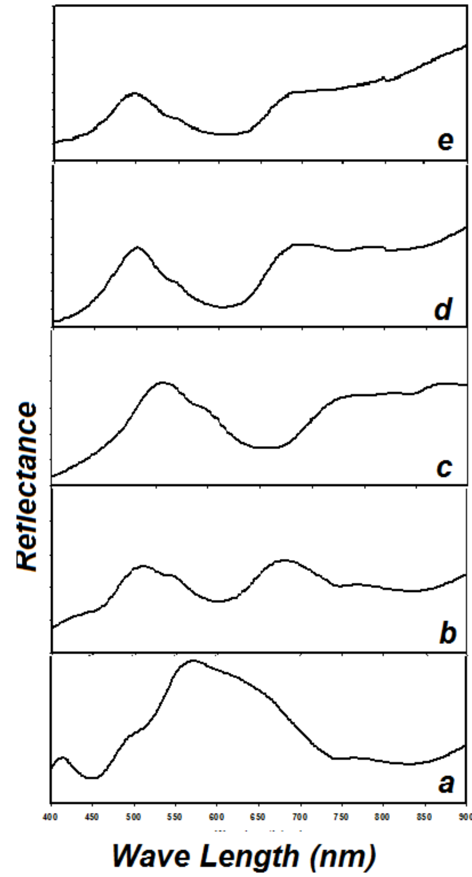

Fig. (4)
DRS of as prepared samples NiTiO3 (a), Ni0.75Co0.25TiO3 (b), Ni0.5Co0.5TiO3 (c),Ni0.25Co0.75TiO3 (d) and pure CoTiO3 (e)

4. Conclusions

Crystallographic single phase of ilmenite type ternary oxide NixCo1-xTiO3 was synthesized via simple solid-solid interaction. The reaction was carried out in the presence of urea which was assumed to be reaction promoter, reducing agent and also particle size controller. XRD pattern revealed one phase of the different composition products which is explained by the very close atomic radii of both Ni and Co atoms. The TEM images showed heterogeneous morphology of shape and dimensions. The particle sizes of the produced powder were in the range from 130nm to 175nm. DRS patterns explained the nature of green and yellow colors of the produced samples.

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