Asian Journal of Chemistry Vol. 19, No. 6 (2007), 4831-4836

Synthesis and Characterization of Antimony Oxide Doped Cobalt Oxide by Rheological Phase Method

ABDOLALI ALEMI*, ALIAKBAR KHANDAR and FATEMEH EKHTIARY KOSHKY
Department of Inorganic Chemistry, Faculty of Chemistry
University of Tabriz, Tabriz, Iran
Fax: (98)(411)334892; E-mail: aa_alemi@yahoo.com; mc2242707@yahoo.com

Antimony doped cobalt oxid nanoparticles with composition $Sb_xCo_{3-x}O_4$ ($0 \leq x \leq 0.024$) were synthesized by rheological phase reaction and pyrolysis method. The products were characterized by X-ray powder diffraction, fourier transform infrared spectrum, scanning electron microscope, thermogravimetric analysis and simultaneous differential thermal analysis. Calcination of the precursor at 500ºC resulted in the formation of antimony doped cobalt oxide nanoparticles of 45 nm in crystal size. Effect of calcination temperature on antimony doped Co_3O_4 crystal size was discussed.

Key Words: Nanoparticles, Spinel, Antimony oxide, Cobalt oxide, Rheological phase reaction method.

INTRODUCTION

The preparation of nanocrystalline oxides is expected to be of fundamental importance in the development of solid-state, catalyst and gas sensors with improved performances. Transition metal oxides have many applications due to their interesting properties[1,2]. Among these oxides, spinel type Co_3O_4 displays unique electronic and chemical properties. Co_3O_4 is an important ceramic oxide with electrochemical[3], magnetic behaviour[4] and catalytic applications[5]. In general, there are many methods of preparation of cobalt oxide, *e.g.*, chemical spray pyrolysis[6], chemical vapour deposition[7] and sol-gel[8].

In the present study, an attempt is being made to synthesize nanosized Co_3O_4 by rheological phase reaction and pyrolysis method. The rheology phase reaction method is a process of preparing compounds or materials from a solid-liquid rheological mixture. The solid reactants were fully mixed and made up by adding a proper amount of water or other solvents to a solid-liquid rheological body in which the solid particles and liquid substances were uniformly distributed. After reaction under suitable experimental conditions (temperature commonly 80-100ºC), the product was obtained[9].

The aim of this work is to prepare antimony doped cobalt oxide ceramics by rheology phase reaction method. A set of complementally investigation methods has been used to characterize the ceramics structural analysis has been evaluated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The Co_3O_4 particles doped with Sb_2O_3 with different sizes can be obtained at different pyrolysis temperature.

EXPERIMENTAL

Antimony doped cobalt oxide spinel were prepared by using analar grade $C_2H_2O_4\cdot2H_2O$, $Co_2(OH)_2CO_3$ and Sb_2O_3 in the composition range of XSb_2O_3-(50-X)$Co_2(OH)_2CO_3$-50$C_2H_2O_4\cdot2H_2O$ where (X = 0.25, 0.5, 0.75 and 1 % mol). All the chemicals were weighed by using Shimadzu AW220 balance and mixed by grinding and the rheological body was prepared with a proper amount of water. Then, it was reacted at 80ºC for 3h and dried in an oven at 100ºC for 2 h.

The precursor was pyrolyzed at temperature range of 500-800ºC for 6 h in air and the antimony doped cobalt oxide ceramics in black colour were obtained. The X-ray diffraction measurements were carried out with D5000 Siemens with Cu-K_α line of wavelength $\lambda = 1.541$Å at the scanning rate of 2º/min and 2θ was varied from 16 to 70º. The FTIR transmission spectra in the region 4000-400 cm^{-1} were recorded for all the samples using FTIR Tensor27 by KBr pellet technique. Thermogravimetry/differential thermal analysis (TG/DTA) were performed by using a shimadzu DTG 60AH thermal analyzer at heating rate of 10ºC/min in air. The scanning electron microscope images were performed by means of LEO440i microscope.

RESULTS AND DISCUSSION

X-Ray diffraction: The XRD patterns in the whole composition range ($0 \le x \le 0.024$), exhibit a good definition of the diffraction lines (Fig. 1). No parasitic phases were detected making possible to index the single phase to a cubic spinel structure with Fd3m symmetry.The major peak in all XRD spectra was found to correspond to the (311) crystallographic plane. A monotonic decrease in the d-spacing values as the antimony content increased was evident[10]. When the precursor was pyrolyzed over 500ºC, the black powders were obtained. The data of XRD confirm that the powder is antimony doped Co_3O_4 with spinel type structure without any impurity phases (Fig. 2). Higher temperature treatment results in sharper diffraction peaks, indicating increase of particle size of antimony doped Co_3O_4. In order to estimate the size of crystallites, the Scherer method was applied to the (311) peak. The crystallite size has been evolved with temperature from 41 nm (heated at 500ºC for 6 h) to 54 nm (heated at 800ºC for 6 h).

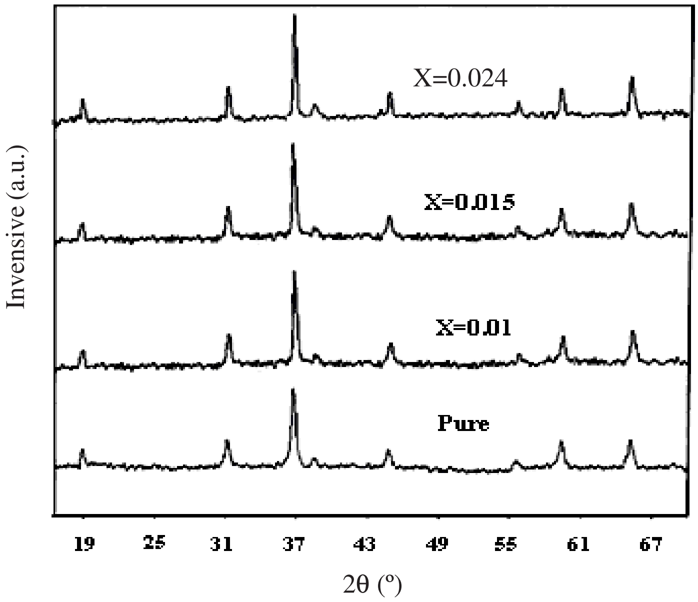


Fig. 1. X-ray diffraction of pure and antimony doped Co_2O_3 calcined at 500°C

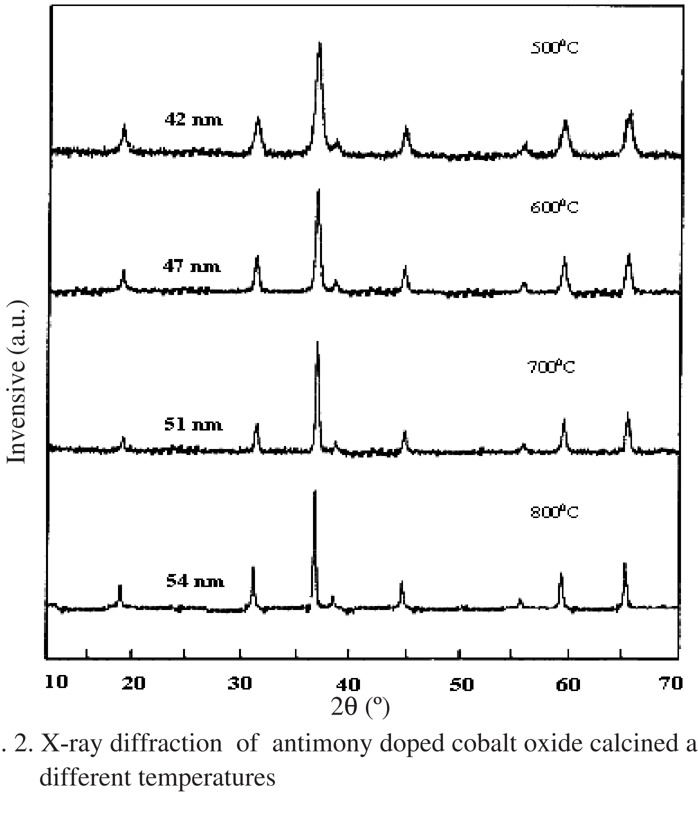


Fig. 2. X-ray diffraction of antimony doped cobalt oxide calcined at different temperatures

Thermal analysis: The TG/DTA curves of the sample (with x = 2.4 mol % Sb) are shown in Fig. 3. Two steps can be observed: (i) from room temperature to 917.10ºC (weight low = 0 %) and the sample is stable. (ii) from 917.10 to 959.54ºC the sample start to loss the weight and the most-loss occurred in the temperature 936.70ºC. The actual mass % loss is 6.32 %. Possible mechanism of the thermal decomposition may be deduced as follows:

$$Sb_{0.024}Co_{2.976}O_4 \rightarrow Sb_{0.024}Co_{1.976}O_2 + CoO + \frac{1}{2}O_2$$

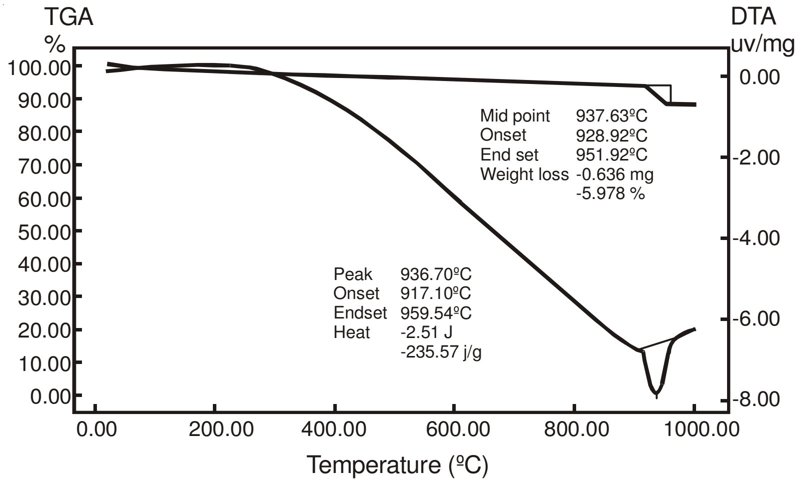


Fig. 3. DTA and TG curves of antimony doped cobalt oxide in air

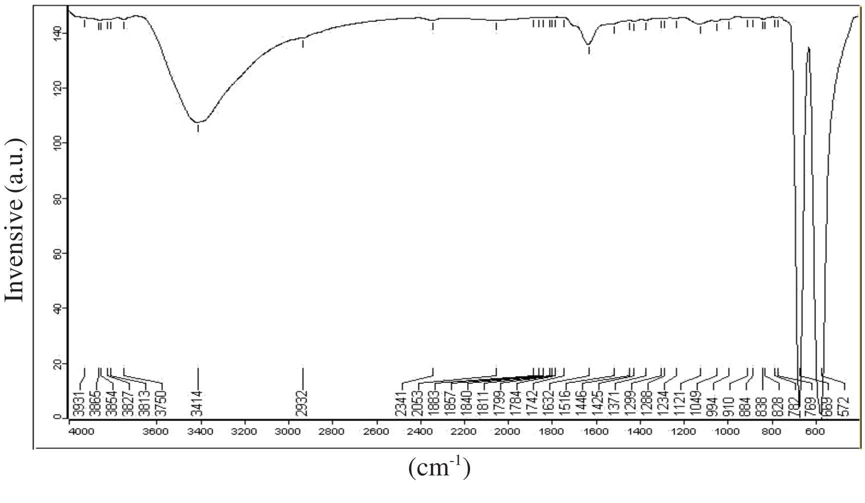
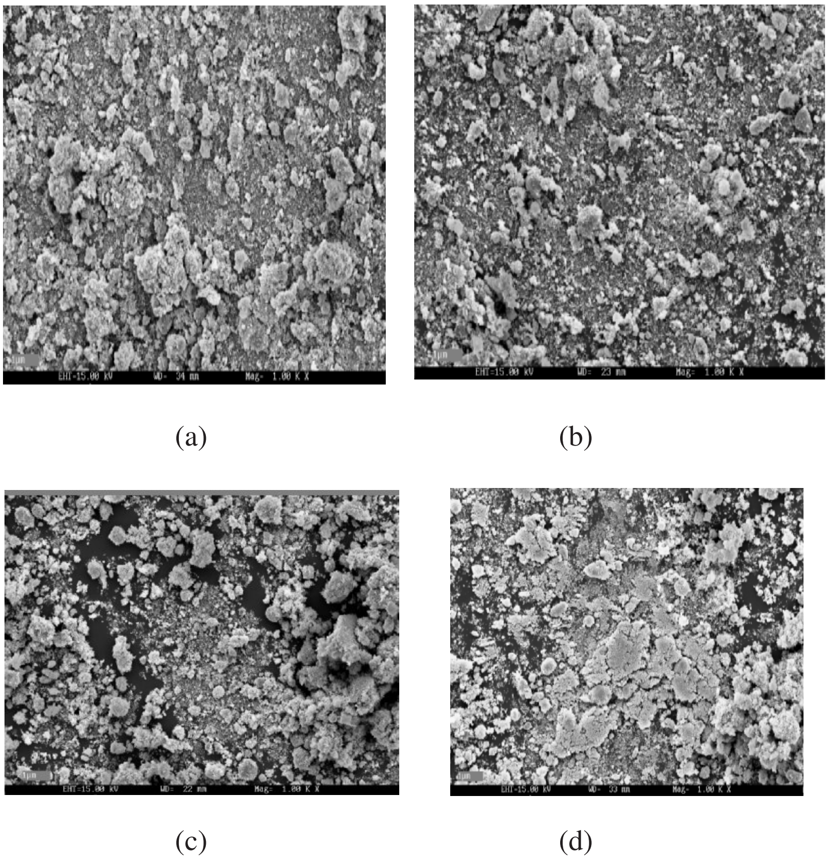


Fig. 4. FTIR spectra of $Sb_{0.02}Co_{2.98}O_4$ nanoparticles

FTIR analysis: Fourier transition spectra of the antimony doped cobalt oxide is shown in Fig. 4. All the absorption bands were assigned to those of the spinel structure and seems that in the spectra containing different concentration of antimony oxide the structure is not changed. The detected new bands at 850-680 cm^{-1} correspond to presence of Sb in compounds. It seems that the amount of Sb_2O_3 involved in the formation of antimony doped Co_3O_4 was too small to be detected by X-ray diffraction.

SEM analysis: The morphologies of the final dark powders are given in Fig. 5. SEM investigation reveals that the particle sizes of the samples prepared at 500ºC for 6 h in air are distributed uniformly. Investigation of the particle size and shape of Co_3O_4[11] and its doped systems prepared by solid state reaction and sol-gel method shown that the rheological phase reaction method is the best and lead to the formation of ultrafine spherical particles.



(a) (b)

(c) (d)

Fig. 5. SEM images of (a) Pure; (b) $Sb_{0.01}Co_{2.99}O_4$; (c) $Sb_{0.015}Co_{2.985}O_4$ (d) $Sb_{0.024}Co_{1.976}O_4$ calcined at 500°C in air

Conclusion

Antimony doped cobalt oxide nanoparticles have been successfully synthesized by the rheological phase reaction. The phase of the prepared product is identified by XRD. The line width analysis are consistent with an average crystalline size of *ca.* 45 nm. The SEM study showns the ultrafine spherical particles with homogenous distribution. Upon thermal analysis at 936.70ºC antimony doped Co_3O_4 nanoparticles could be converted to $Sb_{0.024}Co_{1.976}O_4$, CoO nanoparticles.

ACKNOWLEDGEMENT

This study has been supported by the Council of University of Tabriz, Tabriz, Iran.

REFERENCES

1. W.F.S. Spear and D.S. Tamhuser, *Phys. Rev.*, **B7**, 831 (1993).
2. R.N. Singh, J.F. Koenig, G. Poillerat and P. Chartier, *J. Electroanal. Chem.*, **241**, 314 (1981).
3. G.X. Wang, Y. Chen, K. Konstantinov, J. Yao, J.H. Ahn, H.K. Liu, S.X. Dou, *J. Alloys Compd.*, **340**, 5 (2002).
4. S.A. Makhlouf, *J. Magn. Magn. Mater.*, **246**, 184 (2002).
5. S. Weichel and P.J. Moller, *Surf. Sci.*, *399*, 219 (1998).
6. R.N. Singh, J.F. Koening, G. Poillerat and P. Chartier, *J. Electrochem. Soc.*, **137**, 1408 (1990).
7. S. Sakamoto, M. Yoshinaka, K. Hirota and O. Yamaguchi, *J. Am. Ceram. Soc.*, **80**, 267 (1997).
8. U. Morales, A. Campero and O. Solorza-Feria, *J. New Mater. Electrochem. Syst.*, **2**, 89 (1999).
9. D. Zhan, X. Zhou, Y. Zhang and K. Zhang, *Thermochim. Acta*, **428**, 47 (2005).
10. E. Rios, P. Chartier and J.-L. Gautier, *J. Solid State Sci.*, 267 (1999).
11. Z. Yuan, F. Huang, C. Feng, J. Sun and Y. Zhou, *Mater. Chem. Phys.*, **79**, 1 (2003).

(*Received*: 25 September 2006; *Accepted*: 28 April 2007) AJC-5630