STRUCTURAL CHARACTERISATION OF NICKEL - COBALT SPINEL-RELATED OXIDES OF $Ni_xCo_{3-x}O_4$ ($0 \leq X \leq 1.2$) PREPARED BY FOUR DIFFERENT ROUTES USING XRD, FTIR, UV-VIS-NIR AND XPS.

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Abstract

Four analytical techniques, i.e. X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), ultraviolet-visible-near infrared reflectance spectroscopy (UV-vis-NIR), X-ray photoelectron spectroscopy (XPS) and four different synthesis methods, i.e the sol gel routes pechini and propionic acid route, thermal decomposition of nitrates and coprecipitation of hydoxides, have been used to characterise Ni – Co mixed oxides $Ni_xCo_{3-x}O_4$ ($0 \leq x \leq 1.2$). XRD patterns show that the oxides crystallise in cubic spinel phases with a unit lattice parameter, which increases with x and closely linked to the preparation method. The UV-vis-NIR reflectance patterns confirm the two mixed valence ionic distribution. IR spectra exhibit strong peak characteristics of pure spinel. XPS study shows that there are possibly structural differences as ions site occupation or types of spinel form in compounds prepared by different methods.

Introduction

Substituted spinel cobalt oxides such as $Fe_xCo_{3-x}O_4$, $Zn_xCo_{3-x}O_4$, $Mn_xCo_{3-x}O_4$, $Ni_xCo_{3-x}O_4$ are attracted materials due to their outstanding electrochemical, catalytic, optical and magnetic properties (Yoon *et al*., 2005; Hinklin *et al*., 2008; Hamdani, Singh, & Chartier, 2010). They can be used in many industrial applications as negative electrode lithium-ion batteries (Qin *et al*., 2010; Chtouki *et al*., 2013), anodic electrochromic materials in smart windows devices (Xia *et al*., 2008), catalytic combustion of hydrocarbons (Chtouki *et al*., 2013; Guilhaume & Primet, 1994), catalysts in a number of heterogeneous chemical processes such as oxidation (Jiang, Ma & Li, 2012; Kim *et al*., 2000; Wei *et al*., 2010), etc. Among these materials nickel cobalt oxides ($Ni_xCo_{3-x}O_4$)

have received great interest due to their low cost, non-toxicity, chemical stability, low electrical resistivity and desired electrochemical properties.

Works have been done on electrochemical properties of $Ni_{0.4}Co_{2.6}O_4$ oxide synthesised by sol gel via propionic acid method (Guene *et al.*, 2005) and compared electrophysical properties such as porosity and electrical conductivity of binary nickel cobalt oxides $Ni_xCo_{3-x}O_4$ ($0 \leq x \leq 2.5$) prepared by the four methods (Guene *et al*., 2007).

In the study, the use of different techniques to synthesise $Ni_xCo_{3-x}O_4$ in powder form was reported. Some of them were sol-gel processes (Wei, Chen & Tang, 2007), thermal decomposition (Shi *et al*., 2001) and co-precipitation method (Karthikeyan, Kalpana & Renganathan, 2009). However,

very few studies focused on the relationship between the preparation methods, the electrochemical and or the electrophysical properties of these oxides. It is well known that the preparation methods affect the texture properties, the specific surface area and consequently the electrocatalytic properties of oxides (Marco *et al*., 2000; Ponce *et al*., 1999; Singh *et al*., 2000; Luisetto, Pepe & Bemporad, 2008).

Herein, the four different methods to prepare mixed oxides of $Ni_xCo_{3-x}O_4$ (x = 0, 0.4, 0.6, 0.8, 1, 1.2) in order to examine the relation between their structural properties, the preparation methods and underline the important parameters in this relation were investigated.

Experimental

Synthesis of the target oxides
The mixed oxides of $Ni_xCo_{3-x}O_4$ (x = 0, 0,4, 0.6, 0,8, 1, 1.2) were prepared by four different methods: Two sol-gel methods (Pechini and via propionic acid), thermal decomposition of nitrates (TDN), and co-precipitation of hydroxides (Guene *et al*., 2007).

Sol-gel
   Pechini. Approximately 20 g of citric acid was dissolved in 20 ml of glycol ethylene and the solution was heated to 90 °C for 30 min. The stoichiometric amounts of nitrates ($Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$) were added and heated to 120 °C until the formation of a viscous liquid. A vacuum evaporation of the products was carried out at 180 °C for 30 min under atmospheric pressure. The final product was thermally treated at 350 °C for 4 h to obtain the spinel phase (Liu *et al*., 1996).

   Propionic acid. The stoichiometric amounts of nitrates were dissolved in 20 ml of propionic acid. The mixture was gently heated to 120 °C to eliminate excess of propionic acid. A gel was formed which was afterwards broken by the addition of liquid nitrogen. The fine powder obtained was heated to 140 °C to eliminate excess water and thermally treated (350 °C) for 4 h to get the spinel phase of the mixed oxides (Ponce *et al*., 1999)..

Thermal decomposition of nitrates
   The stoichiometric amounts of hexahydrates cobalt and nickel nitrates dissolved in water of crystallisation by soft heating were placed in an oven for 24 h at 90 °C to evaporate all the water. The mixture was then calcinated at 140 °C. The blackish solid obtained was thermally pre-treated for 4 h at 200 °C. A final heat treatment at 350 °C for 4 h was realised to get the spinel phase phase (Hamdani, Singh & Chartier, 2010; Gautier, Restovic & Chartier, 1989).

Co-precipitation of hydroxides
   The metallic salts $Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ were dissolved in distilled water. An excess of 3*M* KOH solution was added, drop-wise, in order to co-precipitate the hydroxides. The solvent was evaporated and the precipitate washed with distilled water, and dried at 100 °C for 12 h and finally treated at 350 °C in an oven for 24 h (Ponce, Zelada & Gautier, 1990).

Characterisation
   X-ray diffraction pattern, I R and UV-vis-NIR spectra. All X-ray powder diffraction patterns were realised using a Siemens D

500 diffractometer using CoKα radiation (λ = 0.1789 nm) anti-cathode and a Ni filter at scanning rate of 0.05° s^{-1}, 2θ varying from 10° to 80°. The unit lattice parameter of the spinel structure *a* was determined using a least-square programme on the basis of the observed interplanar d-spacing and Miller indexes hkl (in agreement with data in the ASTM Powder Diffraction File JCPDS-ICDD 37-878).

Infrared spectra were obtained using a Brucker Multipare CT 25000 spectrometer coupled with an Avatar 320 FT IR apparatus. The reflectance UV-vis-NIR spectra were carried out using a lambda 9 Perkin–Elmer spectrometer. An integration sphere of 60 mm diameter was used as standard detection system. Barium sulfate was the neutral material used inside the sphere due to its high diffusing power.

XPS studies

XPS data were recorded with a VG ES-CALAB 250 analyser using Al Kα1.2 monochromatic radiation (hν = 1486.6 eV). All the spectra were taken at 40 eV pass energy for specific region and 150 eV for general ones; they were recorded at take-off angles of 90°. All binding energies (BE) were calibrated against the C1s (C-C/C-H) signal centered at 285 eV. The base pressure inside the spectrometer during analysis was typically below 2.10-8 mbar.

Results and discussion

X-ray diffraction patterns

The X-ray diffractograms of $Ni_xCo_{3-x}O_4$ displayed in Fig.1 shows that all the oxides cristallised as cubic spinel phases spatial FD3m, confirmed by the presence of the
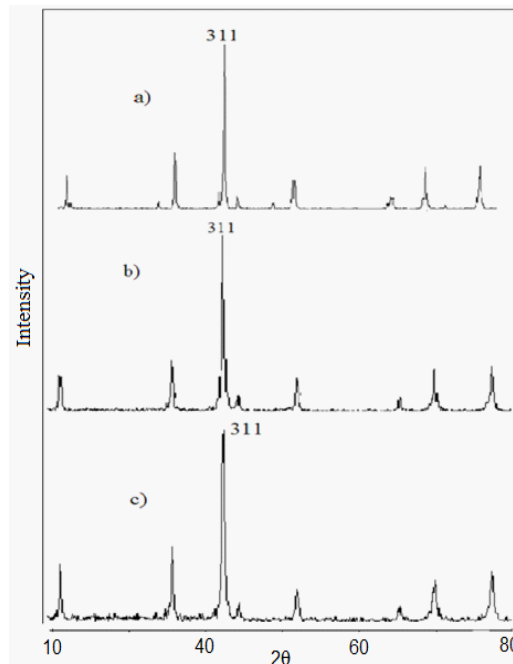

Fig.1. X-ray diffractogram of a) Co3O4 at 350°C (prepared by Pechini process), b) Ni0.4Co2.6O4 at 350°C (prepared by sol gel via propionic acid) and c) NiCo2O4 at 350°C (prepared by TDN).

different peaks belonging to this structure, and in particular the characteristic 311. They were taken for all the 24 synthesised oxides but only three representatives are presented (Fig.1).

The crystallographic lattice parameters *a* were determined as a function of the composition and of the preparation method. The calculated cubic cell parameter *a* indicates a good agreement with ASTM card (a Co_3O_4 = 0,8084 nm and $a_{Ni}Co_2O_4$ = 0,8128 nm) [JCPDS- ICDD 9-418 et 2-1O74)].

Fig. 2 shows that the cell parameters increase with x. The increase of *a* can be associated relatively to the Co^{3+} substitution in octahedral sites by Ni^{2+}. For the same value of x, it can be seen that the cell parameter of the cubic spinel lattice increases from the
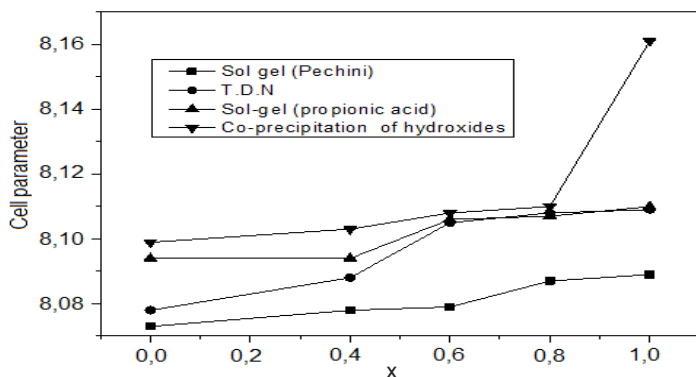
Fig. 2. Variation of the cell parameter with Ni content x for the different preparation routes.

The different preparation methods do not have influence on the IR spectra. The peak positions were shifted slightly to the lower side for the Ni-containing oxides and for the same preparation method compared to Co_3O_4.

Fig. 4 show the UV-vis NIR reflection spectra of i) Co_3O_4 and ii) $Ni_{0.8}Co_{2.2}O_4$ (prepared by the four methods). A broad bulk peak between 1200 and 1500 nm (Nkeng *et al.*, 1995) was observed. The peak is related to the non-stoichiometry and to the charge transfer between Co^{2+} and

Pechini synthesis method to the co-precipitation of hydroxides method in the order; sol gel (Pechini) < T D N < sol gel (propionic acid) < co-precipitation of hydroxides. The introduction of Ni leads to an expansion in the ionic radius of low spin Ni^{3+}, which is slightly larger than the low spin Co^{3+} (Serebrennikova & Birss, 1997).

IR reflectance and UV-vis-NIR spectra

FTIR spectroscopy is used as a powerful tool to provide supplementary on the nature of metal oxides (Melendres *et al.*, 1998). The spectra of the mixed oxide were taken in I.R. mid domain (400 – 4000 cm^{-1}). All the spectra of Co_3O_4, $Ni_{0.4}Co_{2.6}O_4$, $Ni_{0.6}Co_{2.4}O_4$, $Ni_{0.8}Co_{2.2}O_4$, $NiCo_2O_4$ and $Ni_{1.2}Co_{1.8}O_4$ were taken. Fig. 3 shows comparative spectra of i) Co_3O_4 and one of these cobaltites and ii) $Ni_{1.2}Co_{1.8}O_4$. In the analysis, two high-frequency intense bands appear in about 570 and 660 cm^{-1} regions. These two bands correspond to the metal-oxygen stretching from tetrahedral and octahedral sites, respectively, are characteristic of pure spinel crystals (Serebrennikova & Birss, 1997; Basahel *et al.*, 2010; Alizadeh-Cheslilagli *et al.*, 2012).
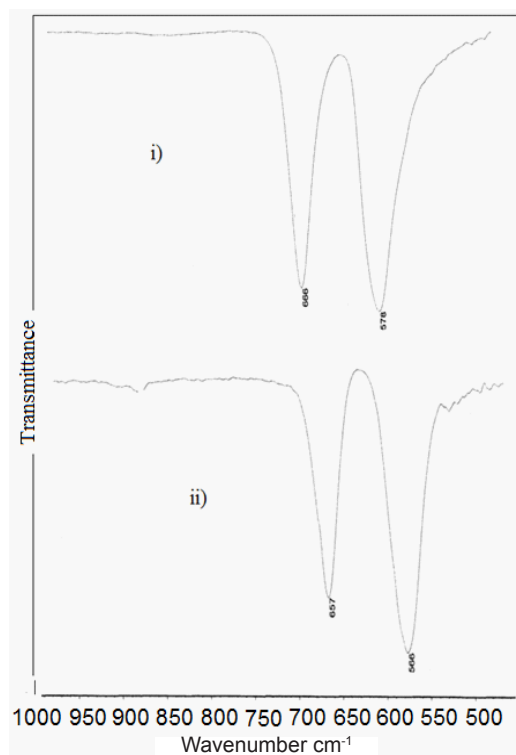

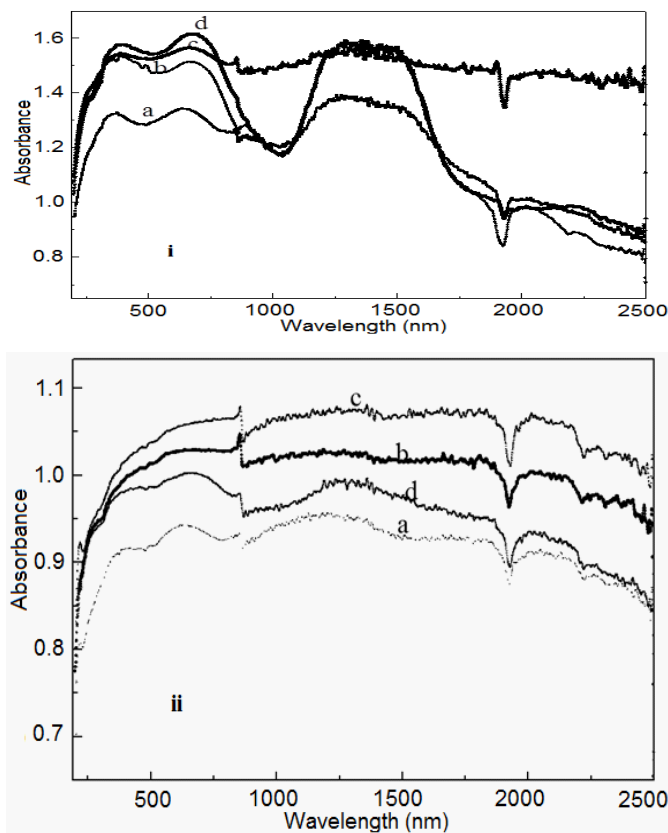Fig. 3. IR spectra of mixed oxides prepared by sol gel via propionic acid: a) Co_3O_4 and b) $Ni_{1.2}Co_{1.8}O_4$.

Fig. 4. UV-vis-NIR reflectance spectra of: i) Co_3O_4 and ii) $Ni_{0.8}Co_{2.2}O_4$ prepared by a) Sol gel (propionic acid), b) TDN, c) Co-precipitation of hydroxides, d) Pechini.

of Co_3O_4 were visible for all the compositions (except for propionic acid compound at 1200 nm). The same phenomenon was observed for the two other preparation methods but only for x = 0.4 and 0.6. This could mean that these compounds are mixtures of Co_3O_4 and another Co-Ni spinel. The corresponding RX diffractograms do not show any evidence of this, which is foreseeable as the spinels always have the same diffractogram, only very slightly modified, as the composition x changes.

In Fig. 4i the similarity between the absorption spectra of Co_3O_4 confirms that compounds of identical structures were obtained even if the second bulk peak (in the case of Co_3O_4 prepared by co-precipitation of hydroxides) is less important owing to the fact that these compounds are less crystallised.

Co^{3+} (Nkeng *et al.*, 1995). The substitution of part (even small) of Co by Ni leads to the total disappearance of the second bulk peak in all the spectra. However, the general aspect of $Ni_xCo_{3-x}O_4$ patterns are similar and remain the same for all substitution degrees and for the four methods of synthesis. Spectra similar to those previously found by Nkeng *et al.* (1995) and Lefez *et al.* (1996) for $NiCo_2O_4$ (obtained as thin films by spray pyrolysis or by sputtering) are not found with these powder compounds. Nevertheless, for the sol-gel compounds, very weak peaks at around 600 and 1200 nm and similar to that

pounds are less crystallised.

XPS studies

XPS spectra for Co 2p, Ni 2p and O 1s were taken to further elucidate surface chemical compositions and electronic properties. All the compounds prepared by Pechini method ($0 \leq x \leq 1$) were studied, according to their specific electrocatalytical properties. A comparative study between compounds for the four different methods of synthesis was carried out thereafter.

For all the metallic ions, the $2p_{3/2}$ and $2p_{1/2}$ spectra present two peaks; a main one and
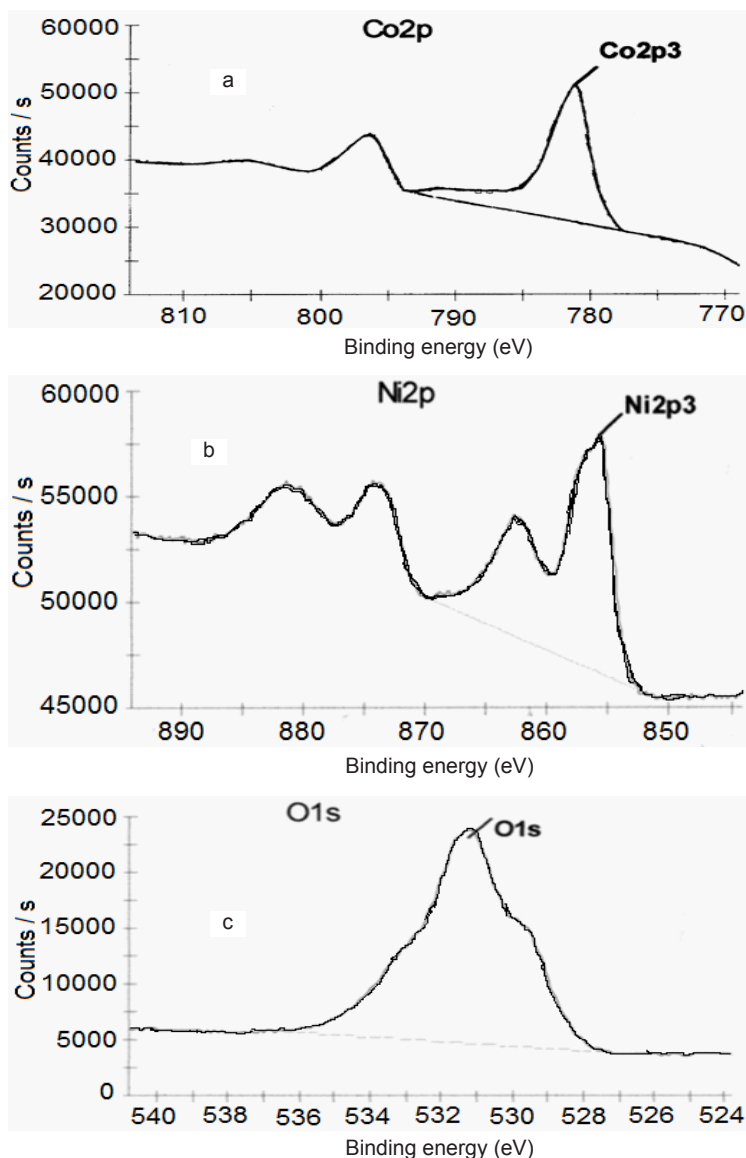
Fig. 5. XPS spectra of mixed oxide powders $Ni_xCo_{3-x}O_4$ (Pechini): a) Co 2p, b) Ni 2p and c) O 1s.

786.7 and 802.9 eV were observed (Kim *et al.*, 2000; Ding *et al.*, 2014). The very flat and weak satellite structure found to the high binding energy side of the $2p_{3/2}$ and $2p_{1/2}$ transitions indicated that few Co^{2+} cations occupy octahedral sites in the samples spinel lattice and the majority of cobalt found in the octahedral sites Co^{3+} (Kim *et al.*, 2000; Roginskaya *et al.*, 1997; Lacomi *et al.*, 2011).

The Ni 2p spectra show main peaks of binding energies centered at around 856.2 and 873.8 eV (Fig. 5b), indicating clearly that the nickel was in divalent oxidized state (Roginskaya *et al.*, 1997; Lu *et al.*, 2012). Two shakeup satellites peaks occurred at around 862.1 and 881.4 eV. The shakeup satellite peak centered at 862.1 eV contained both Ni^{2+} and Ni^{3+} species (Marco *et al.*, 2000; Garg, Basu & Ganguli, 2014). The Ni is presented as Ni^{2+} in octahedral sites at the surfaces of the compounds. Spectra of the other compounds prepared by Pechini present similar forms, and point out that nickel appears to be present predominately
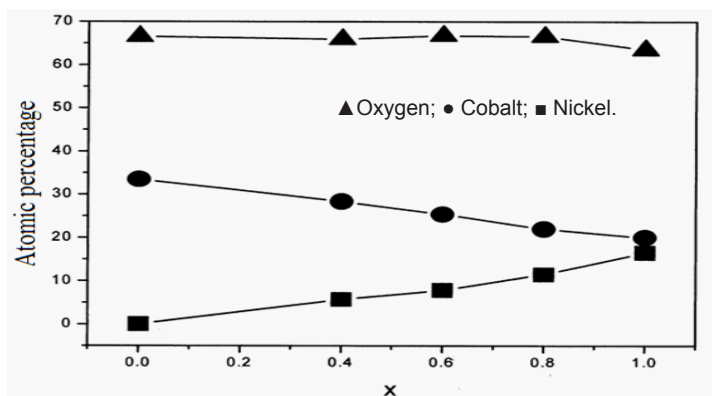
a satellite. Fig. 5a shows Co 2p spectra of samples. Two peaks centered at about 781 and 796.1 eV corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$ and characteristics of Co^{3+} and Co^{2+} bonds, and two shakeup satellites at about

Fig. 6. Variation of the different constituents of mixed oxides $Ni_xCo_{3-x}O_4$ as a function of x.

as Ni^{2+} on the surface.

The O 1s spectra, presented in Fig. 5c, show a main peak at 531.2 eV and two shoulder form peaks at 529.2 and 533 eV. The component at 529,2 eV is typical of metal-oxygen bonds (Marco *et al.*, 2000; Jimenez *et al.*, 1995). Contribution located at 531.2 eV has been associated with oxygen ions in low coordination at the surface with small particle size (Jimenez *et al.*, 1995). Component at 533 eV, finally, can be attributed to hydroxyl groups or defect oxygen (Marco *et al.*, 2000).

From the analysis, the most likely structure for the Pechini products is the spinel structure which can be expressed as Co_{1-x}^{2+} $Co_x^{3+}[Co^{3+}Ni_x^{2+}Ni_{1-x}^{3+}] O_4$ (0 < x < 1) (the cations within the square bracket are in octahedral sites, and the outside ones occupy the tetrahedral sites) (Ding *et al.*, 2014; Garg, Basu & Ganguli, 2014).

The comparative study of compounds for the four different methods demonstrates that ,the structures of these different spectra are similar, and points out that the differences between the compounds are small and does not concern composition but rather intrin-

sic or structural properties. For compounds prepared by thermal decomposition of nitrates and co-precipitation of hydroxides, a small shift of the Ni and Co peaks is noted. The main peak of the Ni $2p_{3/2}$ spectra shows two peaks situated at binding energies of 853.5 eV and 855.2 eV. The Ni $2p_{1/2}$ peak spectra appear at 870.7 eV and 872.3 eV. These binding energies are in good agreement with those of Ni 2p transitions well-defined surface of NiO (Lacomi *et al.*, 2011; Nydeggar, Couderc & Langell, 1999).

The Co 2p binding energies at 779.5 eV and 794.5 eV, and the $2p_{3/2}$ and $2p_{1/2}$ of 15.0 eV separation width suggest that the majority of Co found in octahedral sites are low spin Co^{3+} (Roginskaya *et al.*, 1997). This may represent a difference in the spinel-like surface that forms on the $Ni_xCo_{3-x}O_4$ prepared by thermal decomposition of nitrates, and co-precipitation of hydroxides compared to products prepared by sol gel methods. These variations in binding energy can be interpreted as a change in site occupancy.

A plot of the different constituents of the spinels, as a function of x, is shown in Fig. 6. The results showed that the oxygen composition is more or less constant but higher than expected due, probably, to adsorbed species, namely surface OH groups.

Conclusion

Four different methods have been used to synthesise nickel cobaltite $Ni_xCo_{3-x}O_4$ ($0 \leq x \leq 2.5$). The structural properties of the syn-

thesised products were examined by several characterisation techniques. XRD, FTIR and UV-vis-NIR investigations suggest the formation of pure cubic spinel phase in all cases for the composition up to 1.2. For the same value of x, the lattice parameter depends on the preparation method.

XPS studies show that nickel and cobalt surface cations are distributed between tetrahedral and octahedral sites. Ni^{2+} and Co^{3+} species are predominant in octahedral sites for sol-gel compounds (mainly Pechini compounds). The cation surface repartition can differ in oxides prepared by the two other methods. It can be concluded that there are some structural differences induced by the preparation methods. Sol gel process (especially Pechini) is an attractive method for synthesising mixed oxides because of the enhancement of their specific active surface areas, principal characteristic of the texture properties.

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