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# Preparation and powder characterization of spinel-type $Co_xNiMn_{2-x}O_4$ ($0.2 \leqslant x \leqslant 1.2$) by the ethylene glycol–metal nitrate polymerized complex process

P. Durán[a,*], J. Tartaj[a], F. Rubio[a], C. Moure[a], O. Peña[b]

[a]*Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, Camino de Valdelatas s/n, 28049, Madrid, Spain*
[b]*Chimie du Solide et Inorganique Moleculaire, UMR 6511, CNRS, Université de Rennes I, Institut de Chimie de Rennes, 35042 Rennes cedex, France*

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**Abstract**

$Co_xNiMn_{2-x}O_4$ ($0.2 \leqslant x \leqslant 1.2$) spinel-type powders were prepared by auto-combustion of ethylene glycol–metal nitrate polymerized gel precursors, and the thermal behaviour of the different samples was independent of the chemical composition. The formation of a pure spinel-type phase, with no intermediate compounds, was attained from the burning of the polymerized gel precursor and subsequent calcining at 600–700 °C. The formation and the microstructural evolutions of the spinel-type phase have been studied by Fourier transform infrared (FTIR) spectroscopy, simultaneous thermogravimetric and differential thermal analysis (TG/DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Powder characteristics such as particle size and specific surface areas of the calcined powders were dependent of the chemical compositions. In the same way, the crystalline structure of the synthesized spinel-type phases were strongly dependent of the Co content.


*Keywords:* $Ni(Co,Mu)_2O_4$; Powders-chemical preparation; Spinels

## 1. Introduction

Complex spinel oxides based on transition metals such as Co, Ni and Mn are of significant interest from both a fundamental point of view because of their structural and unusual magnetic properties and, on the other hand, owing to their technological applications as negative temperature coefficient (NTC) thermistors for temperature measurement and control. The magnetic properties are widely determined by the distribution of cations located between the tetrahedral (A) and the octahedral (B) sites of the spinel structure ($AB_2O_4$).

In view of the changes of crystal structure on cooling high temperature sintered samples, the cation distribution has been found to be affected by several factors and, between them, the preparation and thermal history are two of the most important. In order to obtain single-phase cubic spinel oxide, Abe et al.[1] proposed a new method for the Co–Ni–Mn ternary system. Firstly the region of single-phase cubic spinel-type in the ternary system was studied, and then the oxide compound was oxidized at the temperatures where the spinel structure is stable.[2,3] The study was restricted to the compositions in which the Mn/Co/Ni molar ratios were 2/4/0 and 4.5/0/1.5. Given that the cubic spinel phase is unstable at high temperature, a better processing method would be desirable to sinter the NTC materials at moderate temperatures with a high densification level avoiding, thus, the segregation phases phenomenon present on cooling in high temperature sintered samples. In such a way de Vidales et al.[4] carried out an alternative preparation route using the coprecipitation of the Co, Ni and Mn cations with *n*-butylamine. The as prepared powders were highly sinterable, and dense bodies (96% of the theoretical density) at a temperature as low as 1000 °C were attained. Other preparation methods using the evaporation to dryness of the nitrates or coprecipitation have also been proposed.[5,6]

* Corresponding author. Tel.: +34-91-735-5854; fax: +34-91-735-5843.
*E-mail address:* pduran@icv.csic.es (P. Durán).

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In this paper we tried to synthesize at low-temperature cubic spinel single-phase in the Co–Ni–Mn oxides ternary system using a (presumably) cation chelating organic compound as the ethylene glycol. The study of the complex polymeric (chelates) decomposition, thermal evolution, powders morphology and structural characterization by FTIR, DTA/TG, X-ray diffraction, and SEM and TEM observations on the as prepared powders have been carried out.

## 2. Experimental procedure

A series of mixed oxides $Co_xNiMn_{2-x}O_4$, where $0.2 \leqslant x \leqslant 1.2$, were prepared. In the present work, the compositions $Co_{0.2}$ $Ni_{1.0}$ $Mn_{1.8}$, Co0.6 $Ni_{1.0}$ $Mn_{1.4}$, and $Co_{1.2}$ $Ni_{1.0}$ $Mn_{0.8}$ referred to as 218, 614 and 2118, respectively, were prepared. The powders of Co $(NO_3)_2{\cdot}6$ $H_2O$, (15.768 g), $Ni(NO_3)_2$ $6H_2O$, (13.135 g), and $Mn(NO_3)_2$ $4H_2O$ (9.068 g), in the case of the 218 compositions, were dissolved in 20 ml of distilled water. To the aqueous solutions of metal nitrates was added concentrated nitric acid (65%) (20 ml) by stirring at room temperature. Then ethylene glycol (EG) (80 ml) to make a gel was added by stirring. This gel will be referred to as 218-0, and that heated at 60–80 °C for 16 h referred to as 218-80. We obtained, thus, a viscous gel which was dried at 130 °C for 24 h and referred to as 218-130. For comparison, a blank solution of pure ethylene glycol,EG, was used. After drying the gel was fired at 750 °C in air for 6 h. The same preparation path was used for the 614 and 1218 spinel compositions, using the required chemical equivalents in each case.

The decomposition and reaction processes of the dried polymeric gel were analysed by simultaneous thermogravimetric and differential thermal analysis TG/DTA (model STA 409, Netzsch) in the temperature range from room temperature to 1000 °C in air with a heating rate of 10 °C/min. To study the phase transformation, crystallization and sinterability of the derived powders, the complex polymeric gel were decomposed at various temperatures for 2 h. The complex polymeric gel and derived powders were also analysed by Fourier transform infrared (FTIR) spectroscopy (model Perkin-Elmer 1760 X). The crystallization and microstructure of the oxide powders were characterized with an X-ray diffractometer (XRD) (model D-5000, Siemens) using Cu $K\alpha$ radiation. A scanning electron microscope (SEM) (model SEM 950, Karl Zeiss), and a transmission electron microscope (TEM) (model Hitachi H-7000) were used to study the morphology of the calcined powders. The specific surface areas of the oxide powders was measured by the single-point Brunauer–Emmet–Teller (BET) method using $N_2$ gas (model MS-16, Quantachrome Corp.).

## 3. Results

Fig. 1 shows the TG/DTA curves for the different prepared compositions. During the heating of the dried polymeric gel between room temperature and 1000 °C, several thermal features takes place leading to a better knowledge of the spinel formation reaction mechanism. The TG curve of Fig. 1(a) shows for all the compositions two well-defined weight loss steps. In the first one a continuous loss of about 33 wt.%, between room temperature and about 250 °C, took place. Such a weight loss can be related with the drying process of the polymeric gel. In the second weight loss step, above 250 °C, a drastic weight loss of about 30% more occurred. This second weight loss takes place in a very narrow temperature range, and indicates that an auto-combustion occurs during the decomposition of the metal nitrate–ethylene glycol polymerized complex dried gel. Above that temperature the weight loss remained constant.

In the temperature range in which the total weight loss took place, i.e., between room temperature and about 340 °C, the DTA curve of the Fig. 1(b) shows five thermal effects. A smooth and broad endothermal effect, between room temperature and about 230 °C, followed by an exothermic peak with its maximum at 260 °C, associated with a shoulder at about 262.5 °C, were present. A new and strong exothermic peak at 300 °C and its associated shoulder at about 340 °C were also present in the DTA curve. It may be noted that apparently no weight loss accompanies the two last exothermal effects.

From the whole of the above thermal features, the reaction mechanism leading to the formation of the spinel-type $Co_xNiMn_{2-x}O_4$ phase would be carried out in three well established steps, (i) in the first one the drying of the polymerized gel with the probable formation of an EG–nitrate–metal polymerized complex is produced, (ii) in the second one an auto-combustion of the nitrate–metal–ethylene glycol followed by the oxidation of the evolved gases takes place and, finally, (iii) in the third step, a reaction and crystallization of the decomposed nitrate–metal–ethylene glycol polymeric dried gel to form the spinel-type phase takes place. The no weight loss accompanying the strong exothermic effect occurring at this third stage supported the above contention.

In order to support such a belief, different samples of the polymeric gel were heated to different temperatures, which coincided with the completion of the most important TG steps and DTA features. FTIR spectroscopy, XRD, SEM, and TEM microscopy observations characterized the as obtained powders.

Fig. 2 shows the XRD patterns of the 218 composition samples fired at 263, 300, 342, 400, 500, 640 and 750 °C for 2 h. When the polymeric gel was decomposed

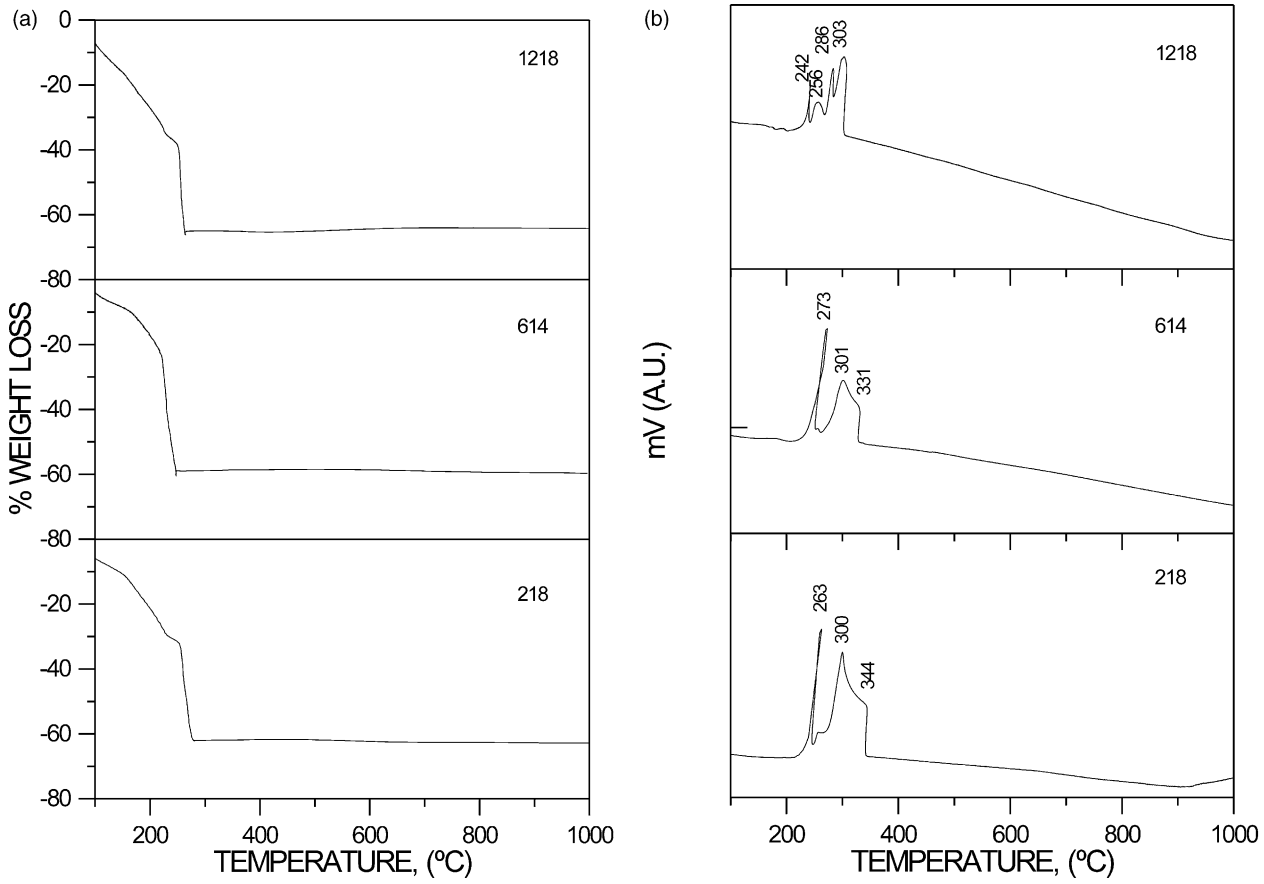


Fig. 1. (a) TG and (b) DTA curves for the 218, 614 and 1218 spinel polymeric gel precursors.

at 263 °C some peaks (rather broad bands) attributed to the spinel-type structure $(Co_xNi_yMn_z)O_4$, were present. XRD reflections centered at 35.7, 43.4 and 63.2 in $2\theta$ confirmed such a statement. All peaks of the samples fired at 400 °C were completely indexed as the spinel-type manganite, but those fired below 260 °C could not be indexed as the spinel-type manganite. Therefore, it is considered that the exothermic peak at about 300 °C was caused by the crystallization of the spinel-type manganite. As the temperature treatment increased the larger the peak intensity and narrower the peaks suggesting, thus, that the spinel-type crystalline phase became more perfect. In agreement with literature data, the crystallographic data for the spinel phases synthesized at 850 °C were evaluated as the following: $a=0.8372$ and $a=0.8323\pm0.0001$ nm, according to a cubic symmetry, Fd3m space group and $Z=8$, for the 218 and 614 spinel compositions, and $a=0.5835$ and $c=0.8423\pm0.0001$ nm according to a tetragonal symmetry, I41/amd space group and $Z=4$, for the 1218 composition. When compared with a conventional solid-state reaction, using the nitrate-metal ethylene glycol process strongly lowered the spinel-phase synthesis temperature.

Fig. 3 shows the FTIR spectra of the as prepared EG–metal nitrate–water–nitric acid solution 218-0 and of its decomposition products at selected temperatures. The IR spectrum of the 218-0 solution without heat-treatment was quite complex but a broad absorption band at about 3400 $cm^{-1}$ attributable to the stretching vibration of the hydrogen-bonded OH groups, was present. The absorption band at 2930–2870 $cm^{-1}$ is attributed to the stretching vibration mode of the $CH_2$ group of which low intensity can be attributed to a probable partial oxidation of ethylene glycol. An absorption band at about 1650 $cm^{-1}$ can be due to the stretching vibration of the free O–H group of water. The carboxylate anion ($COO^-$) stretching is also shown by the appearance of a small absorption band at 1730 $cm^{-1}$ and the strong absorption band at 1338 $cm^{-1}$.[7] The bands located at 1455, 1080–1030 and 885 $cm^{-1}$ indicate the presence of nitrate ions in the polymeric gel. After the heat-treatment at 80 °C no appreciable changes were observed in the IR spectrum, but new absorption bands at about 1600, 1417, 1065 and 650–554 $cm^{-1}$ were present. These new absorption bands seem to correspond to the C=O groups, carboxylate anions, and metal–oxygen bonds in the complex gel structure. An intensity decreasing or increasing in the absorption bands correspponding to the $CH_2$ groups and the O–C=O group, respectively, was also observed. After 24 h standing time at 130 °C, the presence of an absorption band at 775 $cm^{-1}$ could

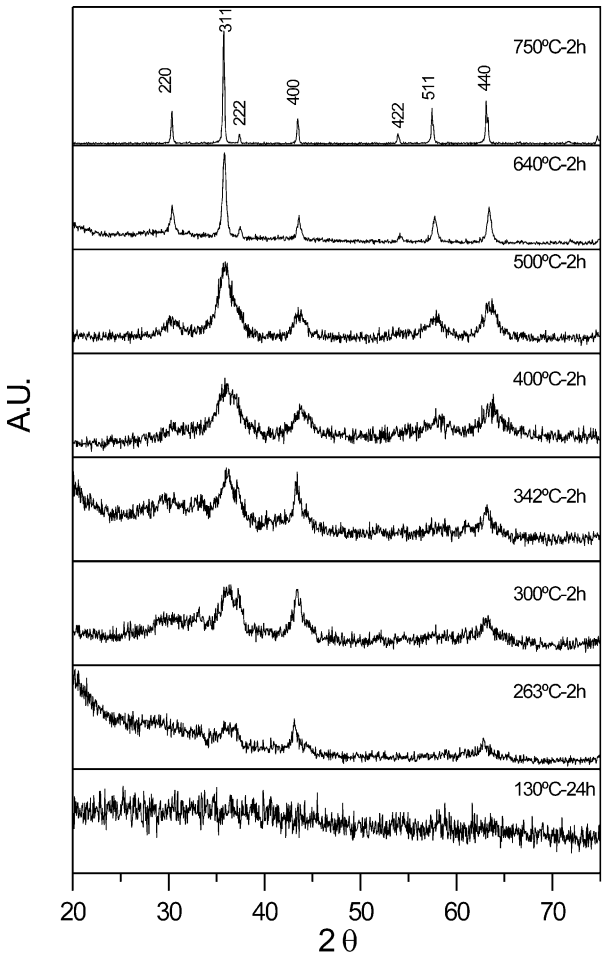


Fig. 2. XRD patterns showing the phase evolution in the 218 polymeric gel dried at 130 °C, and then calcined at the indicated temperatures.

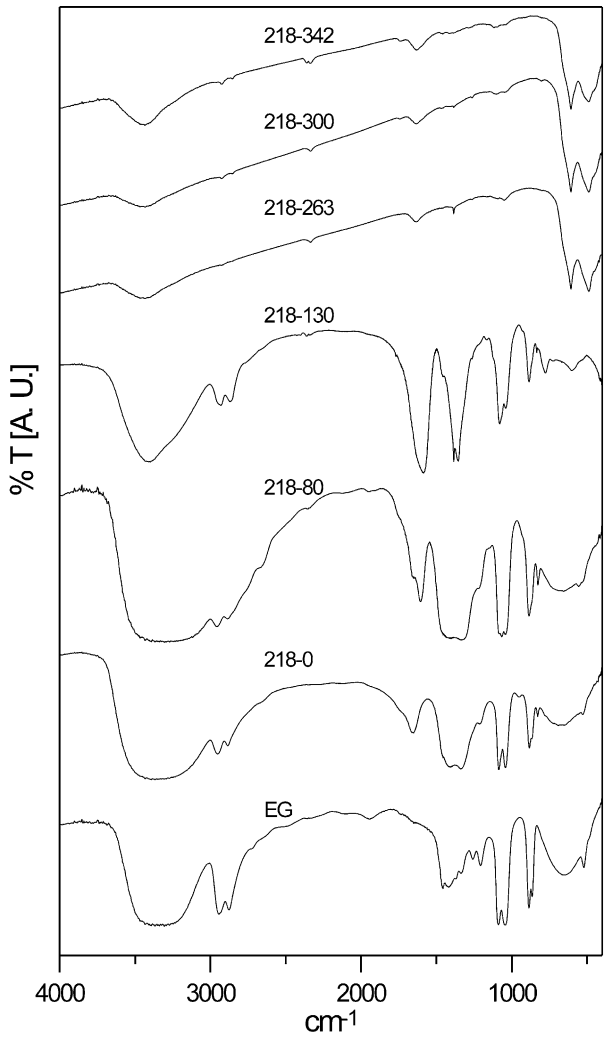


Fig. 3. FT-IR transmission spectra of the 218 polymeric gel before heating and heated at the indicated temperatures. EG is the IR spectrum of the pure ethylene glycol.

be attributable to the existence of some formate (oxalate?) ions, although such an assumption was not confirmed by the XRD results. Finally, the absorption band at about 600 $cm^{-1}$ can be attributed to the presence of metal–oxygen bonds in the complex gel structure. When the polymeric gel was heated at 263 °C, the intensity of the bands at 2930–2870 $cm^{-1}$ diminished or disappeared, indicating the total oxidation of the ethylene glycol. The absorption bands corresponding to the carboxylate and carboxylic acid groups (–COO) and (–COOH) still remained. After heating at 300 °C, i.e., at the completion of the total weight loss, all the previously mentioned absorption bands have practically disappeared, and only strong absorption bands at about 500 and 600 $cm^{-1}$ due to the metal–oxygen bonds were observed.

Fig. 4(a)–(f) shows representative SEM photographs of the polymeric gel calcined at different temperatures. In a general sense, the powders calcined at 263 °C showed the morphology of hardened round hollow spherical agglomerates containing pores and voids caused by the scaping gases during the violent combustion process, as shown in Fig. 4(a)–(c). Fig. 4(d)–(f) show the microstructure of the spherical agglomerates surfaces, after heating at 400 °C, in which the primary spinel phase particle can be observed. The individual particles were a few tens of nanometer in size with a high agglomeration state, larger in the case of the 614 spinel composition. The powder morphology of the polymeric gel calcined at 400 °C, i.e., after the completion of the weight loss, were made of agglomerates of about the same size and shape of those calcined at lower temperatures. Each one of these agglomerates, which were much larger than the crystal size, consisted of nanometric particles, i.e., smaller than 100 nm in the case of the 218 spinel composition. In the case of the 614 spinel composition the particles were submicronic in size, i.e., some particle growth took place at that calcining temperature. The BET specific surface areas of

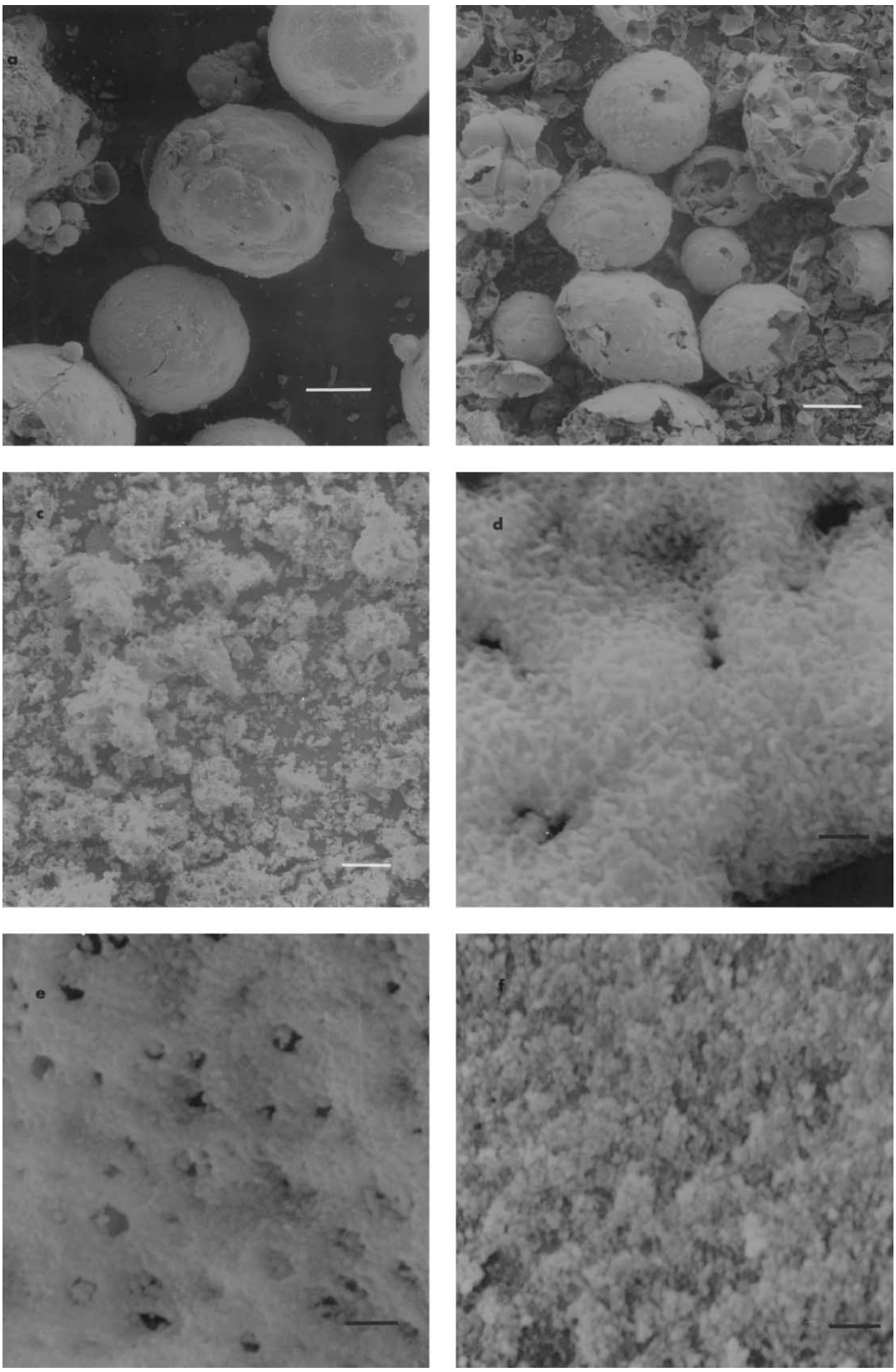


Fig. 4. SEM micrographs of the 218, 614, and 1218 polymeric gel precursors calcined at 263 °C, (a) to (c), and microstructure of the polymerized gel precursors calcined at 400 °C, (d)–(f) (bar = 50 and 0.5 μm, respectively).

the powders calcined at 400 °C ranged from about 35 $m^2 g^{-1}$ in the case of the 218 composition up to 12 $m^2 g^{-1}$ for the 1218 composition.

Transmission electron microscopy (TEM) studies made on powders calcined at 400 °C are shown in Fig. 5(a)–(d), and revealed that the agglomeration state was much lower in the case of the 218 sample than in the other two spinel-type compositions. The lattice substructure of the cubic spinel crystallites were also observed by TEM, as shown in Fig. 5(d), and the

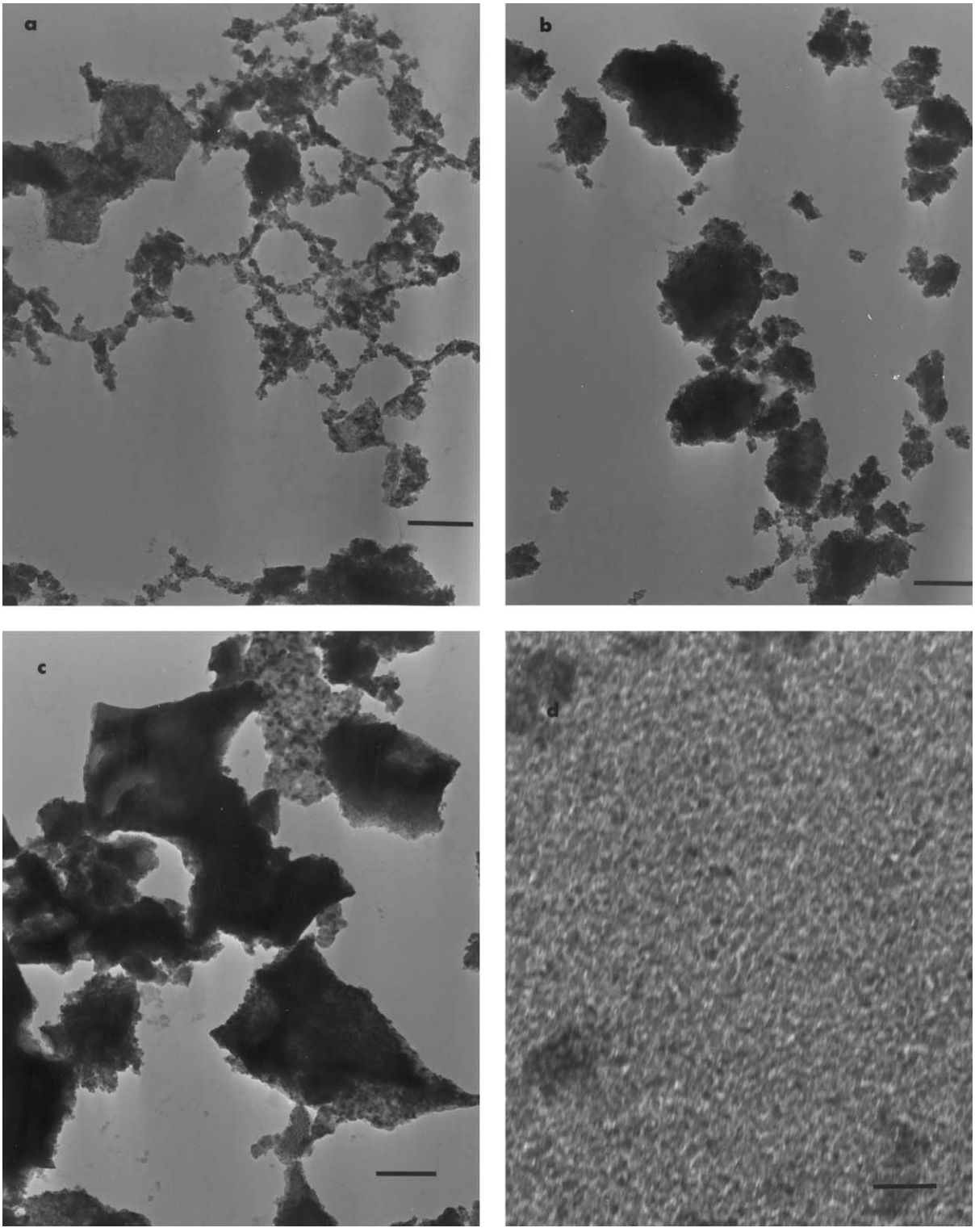


Fig. 5. TEM micrographs of the 218, 614 and 1218 polymeric gel precursors calcined at 400 °C, (a)–(c), showing the different agglomeration state of the calcined powders, and (d) showing the interconnected internal porosity (bar = 0.5 and 0.07 μm, respectively).

average grain size in the case of the 218 composition was determined to be about 15 nm. In a general sense, the morphology of the agglomerates was of small primary cubic spinel-type particles with a high level of interconnected internal porosity. If we take into account the grain size as measured by TEM microscopy and the BET specific surface area values, we conclude that the particle size measured by SEM microscopy corresponded to that of an agglomerate, i.e., the grain sizes were larger than the crystal sizes because the powder particles were made of several crystallites. The crystallinity of the powder was more perfect with the temperature increasing, and the particle size also increased up to 18 and 35 nm at 500 and 640 °C, respectively.

## 4. Discussion

A simple and low cost preparation process, comparatively with other chemical preparation methods, leading to the low-temperature formation of single-phase in the spinel series $(Co_xNiMn_{2-x})O_4$, by using cheap organic and inorganic reagents as metal nitrates, nitric acid, and ethylene glycol, is proposed. Contrarily to the Pechini method[8] in which carboxylic acid groups as chelating end groups are to exist in the organic solution, in the used ethylene glycol process, firstly proposed by Anderson et al.,[9] it is believed that during the preparation of the polymeric gel at 80 °C and further drying at 130 °C, the ethylene glycol is, at least, partially oxidized by the nitrate ions leading to the formation of carboxylic acid groups ($HCOO^-$) and/or (–COO–COO–) which can then act as the chelating end groups.[10,11] From the DTA/TG results in Fig. 1, it seems to be that an auto-combustion process accompanied by a strong exothermic reaction in a very narrow temperature range, takes place during the decomposition of the partially oxidized ethylene glycol–metal nitrate dried polymeric gel, leading to the formation of the spinel-type single- phase at low temperature. It is also assumed that such an auto-combustion was catalysed by the nitrate ions, and took place as consequence of the reaction between the metal nitrate and the formed carboxyl groups through an oxidation–reduction process. According to our XRD studies, see Fig. 2, the heat-treatment of the polymeric gel at 80 and 130 °C did not show the presence of any crystalline peaks corresponding to the formation of formate or oxalate salts, as reported by Chen et al.[10] and Wang et al.[12] Although it does not preclude the mentioned salt formation but our results indicate that, in the present experimental conditions, we are in the presence of a complex amorphous compound in which the nitrate ions are required to remain in the dried gel to preserve charge balance.[13] As the temperature was increased to about 700 °C, crystalline powders of the corresponding cubic or tetragonal spinel-type single-phase were attained.

From our FTIR spectroscopy studies, see Fig. 3, the almost disappearance of the absorption bands attributed to the $CH_2$ stretching vibration in the 2780–2930 $cm^{-1}$ region, supported the above statement for a partial oxidation of the ethylene glycol. Furthermore, the spectroscopy FTIR analyses also revealed new changes between the spectra of dried gel and the ceramic precursor. For example, the shift of the O–H absorption band at 3399 $cm^{-1}$ to higher wave numbers and the appearance of a new absorption band at 1630 $cm^{-1}$, associated with the carboxylic groups, leads to assume that some interaction of the metal ions with the O–H groups and maintained chemically bound in the complex polymer amorphous structure has, probably, occurred. Thus, a metal–ion stabilization mechanism similar to that operating in the Pechini method,[8,15] but not necessarily the same, could have taken place. A plausible explanation would be a trapping phenomenon within the ethylene glycol–cation nitrates network structure of the complex polymer, in which some of the cations are coordinated to the formed $COO^-$ groups and, on the other hand, the other cations will be coordinated (stabilized?) to the hydroxyl groups.[14–16] The non-existence of chelating groups in the initial polymerized complex gel help to such an interpretation.

Experimental lattice parameter (a) values, measured on the here obtained cubic spinel-type single-phase, were found to be dependent on the Co cation concentrations and decreased as the Co concentration was increased. If we take into account that the ionic radii of the $Co^{3+}$ is 0.685 Å, $Mn^{3+}$ is 0.72 Å, and that of the $Ni^{2+}$ ions is 0.83 Å, it seems reasonable to assume a replacement of the larger $Mn^{3+}$ ions by the smaller $Co^{3+}$ ions in both the tetrahedral A and octahedral B sites of the cation sublattices, with the corresponding decreasing in the lattice parameters.[6] To a first approximation we consider that, in the present experimental conditions, the formed $Mn^{3+}$ and $Co^{3+}$ cations are located in both the tetrahedral A and octahedral B sites, and all the $Ni^{2+}$ cations were in the octahedral B sites within the cubic spinel structure. On this assumption a cation distribution as $(Co^{3+}_{0.2-x+y}Mn^{3+}_{0.8-y+x})_A$ $(Ni^{2+}Co^{3+}_{x-y}Mn^{3+}_{1-x+y})_BO_4$ for the 218 cubic spinel-type compositions could be advanced. On the other hand, if the semiconducting properties of these NTC materials imply the existence of $Mn^{3+}$ and $Mn^{4+}$ ions in the octahedral B sites, then a new cation configuration, as for example $(Co^{3+}_{0.2-x+y}Mn^{2+}_{0.2-y+x})_A$ $(Ni^{2+}Co^{3+}_{x-y}Mn^{3+}_{0.2-2x+2y}Mn^{4+}_{0.8-y+x})_B$ $O_4$, could also be proposed. The way in which these cations are substituted will give a measure of the stability of the spinel-type phase.[17] The knowledge of the true preferability of the cation occupation on both tetrahedral A and octahedral B sites is a study which is now in progress.

After calcining at different temperatures it was demonstrated, based on our SEM/TEM results as shown in Figs. 4 and 5, that the morphology, crystal size, and specific surface areas of the calcined powders were dependent of the chemical composition (Co content?). These results indicate that some differences in the internal structure of the prepared polymeric gels are to exist.

## 5. Conclusions

The ethylene glycol process has been successfully used to the low-temperature (600–700 °C) preparation of nanosized single-phase of the spinel series ($Co_x$-$NiMn_{2-x}$)$O_4$, where $0.2 \leqslant x \leqslant 1.2$. It is stated that during the polymerization process of the precursor solution containing ethylene glycol, nitric acid, and metal nitrates at 80 °C, a partial oxidation of the ethylene glycol takes place giving rise to the formation of carboxylic acid groups. The metal cations would be in this manner trapped within the network complex polymeric gel coordinated to the $COO^-$ groups and or stabilized via interaction with the hydroxyl groups remaining in the aqueous solution. No formate or oxalate compounds were detected after polymerization, and the precursor solution, after drying at 130 °C, led to the formation of an amorphous $CoNiMnNO_3$–$(EG)\times H_2O$ powder precursor. The spinel-type single-phase was formed via an auto-combustion at about 250 °C of the partially oxidized ethylene glycol–metal nitrate dried gel precursors. The precursor decomposed completely into the spinel-type phase above 300 °C based on the DTA/TG results. XRD studies showed that nanosized ($Co_x$-$NiMn_{2-x}$)$O_4$ crystalline powder with pure spinel-type structure was attained with increasing calcination temperature between 600 and 700 °C. The powder morphology studies, as observed by SEM and TEM, showed that particle size and specific surface areas of the spinel-type calcined powders were dependent of the Co content.

The crystalline structure of the synthesized spinel-type phase had a cubic symmetry for the compositions ($Co_{0.2}NiMn_{1.8}$)$O_4$ and ($Co_{0.6}NiMn_{1.4}$)$O_4$ and tetragonal symmetry for the ($Co_{1.2}NiMn_{0.8}$)$O_4$ composition, and a significant decreasing of the cubic cell volume took place as the Co content increased.

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