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

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Abstract

Spinel-type powders of composition $Co_xNiMn_{2-x}O_4$ ($0.2 \leq x \leq 1.2$) were prepared by auto-combustion of ethylene glycol–metal nitrate polymerized gel precursors. 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, the structural evolution of the spinel-type phase, and calcined powder characteristics have been studied by using different techniques, having found that the properties were strongly dependent of the chemical composition. Sintering of the $Co_xNiMn_{2-x}O_4$ powders have been studied by both the constant rate of heating (CRH) and the conventional ramp-and-holding methods. Density increased with the increasing of the Co content, and theoretically dense bodies (≥99.9% of the theoretical density) with submicronic average grain sizes were obtained at a temperature as low as 1050 °C for 6 h in the case of the $Co_{1.2}NiMn_{0.8}O_4$ composition. Above that temperature, a slow bloating phenomena as consequence of the evolution of oxygen gas with the corresponding decreasing in density, and the beginning of an exaggerated grain growth in the sintered samples was present. Microstructure of the sintered samples has also been studied.

Keywords: Spinels; Powder processing; Sintering

1. Introduction

Thermistors with negative temperature coefficient (NTC), are most often complex spinel oxides based on transition metals such as Co, Ni, and Mn. On the other hand, they are of significant interest from both a fundamental point of view because of their structural and unusual magnetic properties and owing to their technological applications for temperature measurement and control. The electrical and 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–O 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 the-

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oretical 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.[5–7]

In the present 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 powders morphology and structural characterization by FTIR, DTA/TG, X-ray diffraction, BET specific surface areas, and the particle size distribution of the calcined powders by the sedimentation technique have been carried out. The sintering behaviour by the constant rate of heating (CRH) method of $Co_xNiMn_{2-x}O_4$ samples and SEM and TEM microstructure are reported.

2. Experimental procedure

A series of mixed oxides $Co_xNiMn_{2-x}O_4$, where $0.2 \leq x \leq 1.2$, were prepared. In the present work, the compositions $Co_{0.2}Ni_{1.0}Mn_{1.8}O_4$, $Co_{0.6}Ni_{1.0}Mn_{1.4}O_4$, and $Co_{1.2}Ni_{1.0}Mn_{0.8}O_4$ referred to as 218, 614, and 1218, respectively, were prepared. The powders of $Co(NO_3)_2{\cdot}6H_2O$ (15.768 g), $Ni(NO_3)_2{\cdot}6H_2O$ (13.135 g), and $Mn(NO_3)_2{\cdot}4H_2O$ (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%) (10 ml) by stirring at room temperature. Then ethylene glycol (EG) (80 ml) to make a gel was added by stirring. This gel and those heat-treated at 60–80 °C for 16 h, and that dried at 130 °C for 24 h will be referred to as 218–0, 218–80, and 218–130, respectively. For comparison, a blank solution of pure ethylene glycol, EG, was used. After drying the gel was fired at 750 °C in air for 2 h. The same preparation pathway 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, as well as the crystallization, morphology and sinterability of the calcined powders were analyzed by the above-mentioned techniques. A more detailed description of the preparation process and powder characterizations was made elsewhere.[8]

The sintering behaviour of the spinel-type samples was studied, on the calcined powders isopressed at 200 MPa, with a dilatometer (Model 402E/7, Netzsch, Germany) in a still-air atmosphere at a constant rate of heating (CRH) of 5 °C/min. On the other hand, isopressed pellets were also sintered in air under isothermal conditions at 900–1200 °C for 6 h. The heating and cooling rates were 2 °C/min. The density of the sintered samples was measured by the Archimedes method in water. Microstructure of the sintered samples was observed with a transmission electron microscope (TEM) on the gold-coated surfaces, and the average grain size was determined by the linear intercept method.

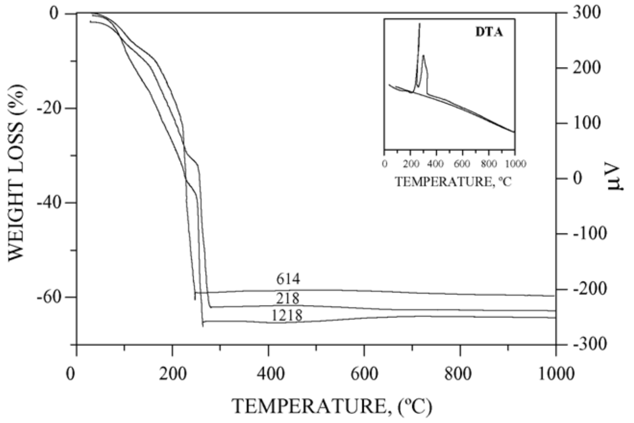

Fig. 1. TG curves for the 218, 614 and 1218 spinel polymeric gel precursors. Insert represents the DTA curve for the 614-spinel composition.

3. Experimental results

3.1. Study of the precursor thermal behavior

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. As it is shown the TG curves revealed several thermal features leading to a better knowledge of the spinel formation reaction mechanism. In the temperature range in which the main weight changes took place, i.e., between room temperature and about 600 °C, the DTA curve showed five thermal effects in al the compositions. For simplicity, only that corresponding to the 614 composition is shown in the insert of Fig. 1. From the whole of the above thermal features, the overall combustion reaction in air could be represented as follows:

$$m[(Co_{0.2}NiMn_{1.8})(NO_3)_2{\cdot}H_2O]_s + n[HOCH_2\text{–}CH_2OH]_l$$
$$\rightarrow [mN_2 + 2nCO_2 + (m+2n)H_2O]_g$$
$$\uparrow + m[(Co_{0.2}NiMn_{1.8})O_4]_s$$

3.2. The formation of the $Co_xNiMn_{2-x}O_4$ spinel-type crystal structure

In order to support such a belief, different samples of the polymeric dried gel were heated to different temperatures, which coincided with the completion of the most important TG steps and DTA features. X-ray diffraction (XRD), FTIR spectroscopy, SEM, and TEM microscopy observations characterized the as obtained powders.[8] As the temperature treatment increased the larger the peak intensity and narrower the peaks suggesting, thus, the spinel-type crystalline phase became more perfect. In agreement with literature data, the crystallographic data for the well crystallized spinel phases synthesized at 850 °C for 4 h were evaluated as the following: $a = 0.8372$, and $a = 0.8323 \pm 0.0001$ nm, according to a cubic symmetry, $Fd3m$ space group and $Z = 8$, for the 218 and 614 spinel compositions, and $a = 0.5835$ and $c = 0.8423 \pm 0.0001$ 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 ethylene glycol–metal nitrate process strongly lowered the spinel-phase synthesis temperature.[8]

3.3. Morphology and characterization of the spinel-type powders

In a general sense, all the powder compositions 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. 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. The BET specific surface areas of the powders calcined at 750 °C ranged from about 5 $m^2 g^{-1}$ in the case of the 218 composition up to 9.5 $m^2 g^{-1}$ for the 1218 composition. These results indicated a high sinterability of the spinel-type calcined powders. A study, by the sedimentation technique, of the particle size distribution revealed that the measured average particle (agglomerate) size, ranged from about 2 μm for 218 and 1218 powder compositions up to 5 μm in the case of the 614 composition.

3.4. Sintering behaviour of the $Co_xNiMn_{2-x}O_4$ oxides

A sintering study of the $Co_xNiMn_{2-x}O_4$ fine particle was carried out by compacting the powders isostatically at 200 MPa. After compaction, the density of the green compacts was very similar being these of 48.5, 47, and 50% of the theoretical density for the 218, 614, and 1218 powder samples, respectively.

Fig. 2 shows the linear shrinkage (A) and linear shrinkage rate (B) under the CRH sintering conditions of 218, 614, and 1218 samples, in air. From the broad sintering range shown in the three samples it can be assumed as representative a solid-state sintering process in all cases. Although the powders had been calcined at the same conditions (750 °C for 2 h), the 218 sample exhibited a lower onset temperature of rapid densification due to its smaller agglomerate size. However, the 1218 sample showed the highest densification rate and reached its end density at a significantly lower temperature than the two other samples. Furthermore, the linear shrinkage rate demonstrate clearly only one sintering event in the case of the 218 and 1218 samples, while the corresponding curve for 614 sample has two sintering events. The linear shrinkage rate of the 614 sample also has a broader feature and the densification rate is lower than for the 218 and 1218 samples, which indicates a much more sluggish densification, i.e., higher sintering temperatures are required for those powder samples with larger average particle (agglomerate) size. On the other hand, it must be emphasized that the highest densified body at the lowest temperature was achieved for the 1218 composition, i.e., for the composition with the higher Co content. Therefore, it seems that the Co content promoted an increase in the shrinkage rate and shifting the maximum shrinkage rate to lower temperatures.

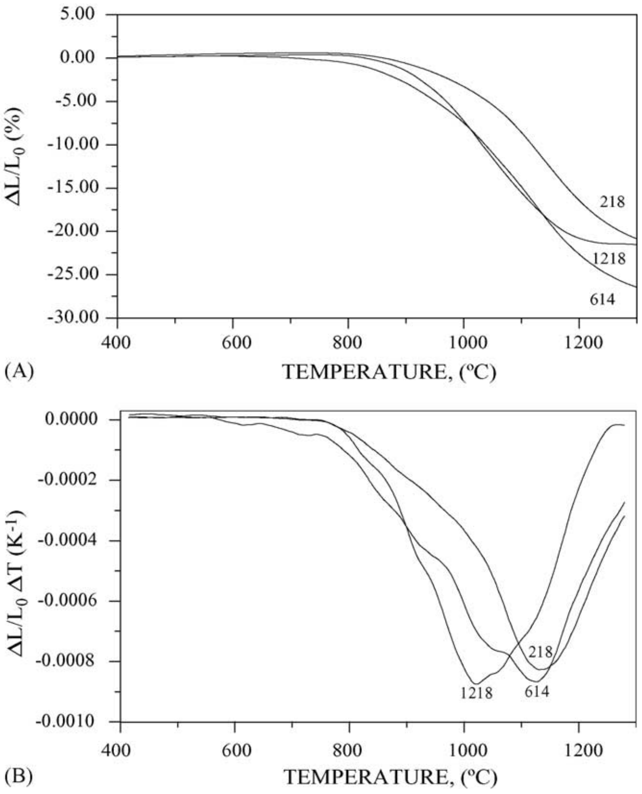

Fig. 2. CHR curves: (A) linear shrinkage, (B) linear shrinkage rate.

Fig. 3 shows the relative density of the sintered samples under isothermal sintering conditions in the temperature range of 900–1200 °C. The holding time at each temperature was 6 h. From this figure, two well-established densification regions are to exist. The first one up to 1050 °C, in which the density rapidly increases and the second one, above that temperature, with a decreasing in density as the temperature increases. The 1218 powder composition reaches a relative density as high as 99.9% of theoretical density at only 1050 °C against a 96 and 92% in the case of the 218 and 614 powder compositions, respectively. Above that temperature the relative density decreased for all the compositions but such a decreasing was higher in the case of the 1218 composition, 13%, against 7 and 8.5% in the case of the 218 and 614 compositions, respectively, i.e. the higher is the Co content the larger is the density decreasing. Such a sintering behaviour is believed to be due to an oxygen losses consequence of the reduction of Co^{3+} and Mn^{4+} cations to Co^{2+} and Mn^{3+} cations, respectively.[9,10]

Average grain size decreases as the Co content increases, i.e., for the same sintering temperature, for example at

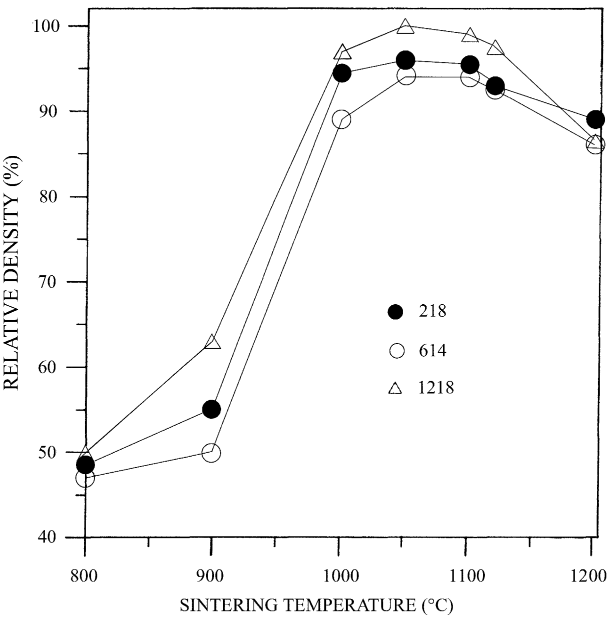

Fig. 3. Temperature dependence of the relative density after 6 h of isothermal sintering for the three spinel compositions.

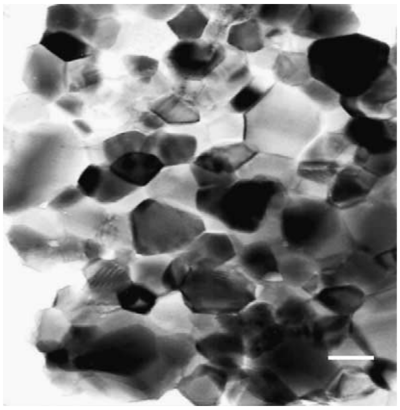

Fig. 4. TEM micrographs of 1218 spinel composition sintered at 1100 °C (bar = 1 μm).

1130 °C, the average grain size was about 4, 2.5, and 2 μm for the 218, 614, and 1218 sintered samples, respectively. The exaggerated grain growth present at temperatures higher than 1130 °C indicated a very high mobility of grain boundaries. In order to detect the presence of a possible cobalt oxide boundary film, TEM analysis of the microstructure on the 1218 sample sintered at 1100 °C was performed, as shown in Fig. 4. No liquid phase film could be observed at the present experimental conditions confirming, thus, that the densification process up to or below that temperature is typical of a solid state sintering.

4. 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 $Co_xNiMn_{2-x}O_4$, where $0.2 \leq x \leq 1.2$. The precursor solution, after drying at 130 °C, led to the formation of an amorphous $CoNiMnNO_3$-EG·$x$$H_2O$ powder precursor. The spinel-type single-phase was formed at about 260 °C via an auto-combustion of the partially oxidized ethylene glycol–metal nitrate dried gel precursors, and nanosized $Co_xNiMn_{2-x}O_4$ crystalline powder with pure spinel-type structure was attained with increasing calcination temperature between 600 and 700 °C. Both the powder morphology and the crystalline structure were strongly dependent of the Co content.

Near fully dense spinel-type ceramic bodies (99.9% of theoretical density) with Submicronic grain sizes could be achieved at temperatures as low as 1050 °C for 6 h. The fast densification can be an attributable to a change in the intermediate-stage sintering mechanism of $Co_xNiMn_{2-x}O_4$ samples as the Co content increases. Above about 1130 °C, a rapid grain growth with entrapment of pores occurred. Oxygen gas release from the reduction of Co^{3+} and Mn^{4+} to Co^{2+} and Mn^{3+}, respectively, and the high mobility of the grain boundaries were, probably, the cause for the high temperature desintering phenomenon.

Acknowledgments

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