

# Synthesis of nanosized zinc and magnesium chromites starting from PVA–metal nitrate solutions

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**Abstract** In this article, we present a detailed study regarding the preparation of nanosized zinc and magnesium chromites starting from a 4% poly(vinyl)alcohol (PVA) aqueous solution and metal nitrates. The controlled thermal treatment of these solutions has permitted the isolation of an intermediary solid product, used as precursor of the preferred mixed oxides: zinc and magnesium chromites. The as-obtained precursors were characterized by FT-IR spectrometry and thermal analysis. FT-IR spectrometry has evidenced the disappearance of the  $\text{NO}_3^-$  anions at 140 °C, due to the redox interaction with PVA. The thermal decompositions of the synthesized precursors were different, as resulted from both thermal analysis and FT-IR spectrometry. Thus, while ZnCrPVA precursor decomposes up to 400 °C with formation of zinc chromite, the precursor MgCrPVA decomposes up to 500 °C, with formation of  $\text{MgCrO}_4$  as intermediary amorphous phase. By thermal decomposition of  $\text{MgCrO}_4$  at 500 °C, weakly crystallized  $\text{MgCr}_2\text{O}_4$  powder is obtained. The obtained chromite powders consist of fine nanoparticles with diameters ranging from 10 to 30 nm at 500 °C; on raising the annealing temperature to 1000 °C, chromite particles become octahedral, with diameter up to 500 nm, but with no sign of sintering.

**Keywords** Polyvinyl alcohol · Chromites · Thermal decomposition · Precursor · FT-IR

## Abbreviations

PVA Polyvinyl alcohol  
FT-IR Fourier transformed infrared spectroscopy  
XRD X-ray diffractometry  
SEM Scanning electron microscopy

## Introduction

The synthesis of metal chromites with spinel structures is a subject that acquired keen researcher interest from early times because of their technological applications [1]. In the last decade, the synthesis of tailored ultrafine microstructure allowed the obtaining of solids with new electronic/atomic structure. These fine ceramic materials (<100 nm) have reached high technological levels in various fields of applications because of their properties (high elastic modulus, high hardness, general refractoriness, and low relative density) being much improved over those of conventional ceramics (>10  $\mu\text{m}$ ). Thus, the synthesis of fine ceramic powders with uniform composition is desirable in the improvement of existing ceramics [2].

Various chemical methods were developed for the synthesis of pure, single-phase, mixed oxide powders with controlled powder characteristics. Some of these chemical routes even have a tendency to result in other phases, along with the preferred mixed oxide. Polyvinyl alcohol (PVA) has been in use since 1999 for the synthesis of several mixed oxides, either by polymerization and burning of the as-resulted gel [3, 4], or by evaporation from solutions [5],

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or by combustion [1]. In the literature, several PVA-based synthesis methods of nanocrystalline mixed oxides powders were reported. PVA-assisted sol–gel processes can result in uniform, monophasic, and even nanosized particles for many multicomponent oxides such as spinels ( $\text{NiFe}_2\text{O}_4$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{CoFe}_2\text{O}_4$ ) [6, 7].

The PVA-based synthesis methods consist usually of one-step thermal treatment of the metal nitrate–PVA solution, or of gelation, followed by calcinations. These methods allow the obtaining of the preferred mixed oxide spinels at lower temperatures and for shorter calcinations durations [6]. A big advantage of the PVA's presence in the system is the carbonaceous residue that results by its thermal decomposition, acting as a surfactant for the oxides particles, thus preventing their aggregation. PVA acts not only as a metal-chelating agent thereby inhibiting the segregation of metals during heating [1, 7], but also as a fuel which provides heat through combustion during calcinations of the precursor. Another interesting feature is that the nitrate ions provide an in situ oxidizing environment for the decomposition of PVA [6].

In our previous studies, we have synthesized several simple and mixed oxides [8, 9] starting from metal nitrates and different organic polyols. We have established that when the solution of metal nitrates in PVA is heated in the range of 70–120 °C, a redox reaction takes place, resulting in its oxidation to polycarboxylates that coordinate to the metal cations forming isolable coordination compounds. The isolation of these products and their controlled thermal decomposition may allow a higher control over their particle size and morphology, apart from the known advantages of the PVA's presence in the system besides the metal nitrates.

In this article, we present a detailed study regarding the preparation of nanosized zinc and magnesium chromites starting from a 4% PVA aqueous solution and the mixture of metal nitrates. The controlled thermal treatment of these solutions has permitted for the isolation of intermediary solid products, used as precursors of the preferred mixed oxides: zinc, and magnesium chromites. The as-obtained precursors were characterized by FT-IR spectrometry and thermal analysis. The evolution of the system with the temperature of the thermal treatment was studied by both FT-IR and XRD techniques. The obtained metal chromites at different temperatures were characterized by SEM microscopy.

## Experimental

### Materials and preparation method

The amounts of metal nitrates ( $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{M} = \text{Mg}$ ,  $\text{Zn}$ ) necessary to obtain 3 g of  $\text{MCr}_2\text{O}_4$  were dissolved in

the corresponding volume of 4% PVA solution (PVA Merck,  $M = 60,000 \text{ g/mol}$ ) to have a molar ratio PVA (monomer): $\text{NO}_3^- = 2:1$ . The obtained clear solutions were heated in a stove at 100 °C, until they became a gel, and then gradually heated further up to 150 °C, when the reaction started, with emission of brown nitrogen oxides. The mass reaction was kept at this temperature for 5 h; fluffy products were obtained in all cases. The obtained precursors were named according to the metal nitrates involved as  $\text{MgCrPVA}$ —the precursor of magnesium chromite and  $\text{ZnCrPVA}$ —the precursor of zinc chromite. These products were grinded, thermally decomposed at 350 °C when the primary oxidic system is formed, and further annealed at temperatures of 500 and 1,000 °C.

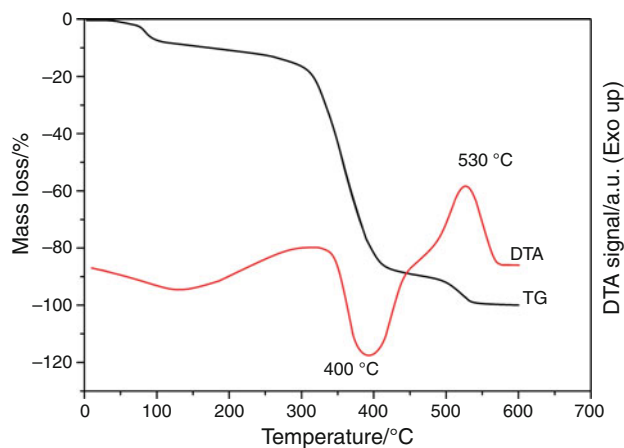
In order to establish the evolution of the oxidic system with the annealing temperature, we have also synthesized in the same manner the corresponding oxides of the metals involved ( $\text{Zn}(\text{II})$ ,  $\text{Mg}(\text{II})$ , and  $\text{Cr}(\text{III})$ ). Thus, each of these metal nitrates, ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), was mixed with the corresponding volume of 4% PVA solution, for the same molar ratio PVA (monomer): $\text{NO}_3^- = 2:1$ . The resulting solutions were thermally treated as shown in case of  $\text{MCrPVA}$  solutions. The as-obtained precursors named  $\text{MgPVA}$ ,  $\text{ZnPVA}$ , and  $\text{CrPVA}$  were characterized by FT-IR spectrometry and thermal analysis. All precursors were annealed at different temperatures (350, 500, and 1,000 °C), and the obtained products were characterized by FT-IR spectrometry, X-ray diffractometry, and SEM microscopy.

### Characterization methodology

Thermal analysis was performed on a 1500D MOM Budapest Derivatograph. The heating was achieved in static air, up to 500 °C, with a heating rate of 5 °C/min, on Pt plates using  $\alpha\text{-Al}_2\text{O}_3$  as inert material. The synthesized powders were characterized by FT-IR spectrometry with a Shimadzu Prestige FT-IR spectrometer, in KBr pellets, in the range 400–4,000  $\text{cm}^{-1}$ . Phase analysis was achieved with D8 Advance-Bruker AXS diffractometer, using the  $\text{Mo-K}_\alpha$  radiation ( $\lambda_{\text{Mo}} = 0.7093 \text{ \AA}$ ). SEM images were recorded on a Quanta 3D FEG (FEI) microscope.

## Results and discussions

In this study, we investigated the evolution of the mixed metal nitrate–PVA in aqueous solution during heating; a redox reaction took place between PVA and  $\text{NO}_3^-$  ions with emission of brown nitrogen oxides, leading to homogenous and fluffy solid products, which are precursors of the preferred simple or mixed oxide.



**Fig. 1** TG and DTA curves for PVA thermally treated at 150 °C

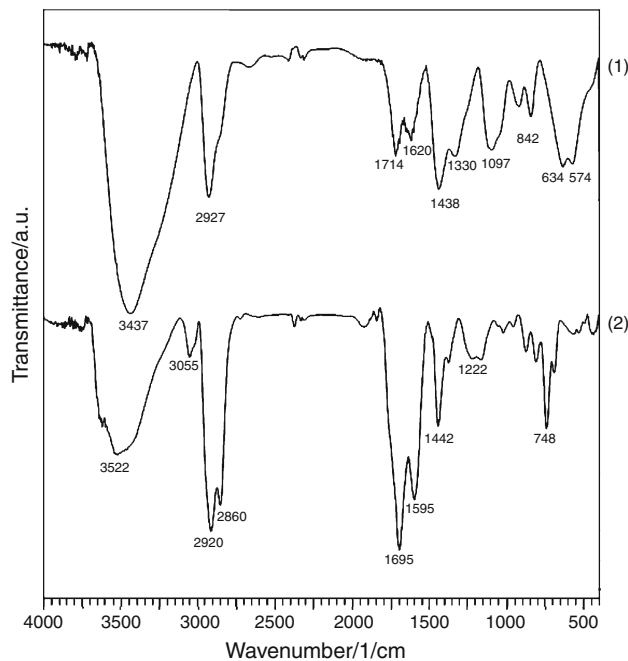
In order to confirm that the thermal evolution of PVA in the metal nitrate–PVA solution is a result of the redox interaction with the nitrate ions, we studied first the thermal behavior of PVA solution. Figure 1 presents the thermal curves (TG and DTA) for the PVA samples obtained from 4% PVA solution by thermal treatment for 4 h at 150 °C.

The as-obtained PVA was brownish in color, and probably suffered an enhanced dehydration. According to Senkevich et al. [10], the possible chemical processes that occur on heating PVA in air (up to 200 °C) are both the elimination of alcohol groups (dehydration) and the oxidation or etherification of these groups. This means that the thermal decomposition will be different compared to the PVA thermal degradation which takes place in four steps according to the literature [11]: water desorption (50–100 °C), partial dehydration with formation of polyene (200–300 °C), polyene degradation (300–400 °C), and thermo-oxidation of carbonized residue (500–600 °C).

As expected, both thermal curves evidence only three steps of thermal decomposition on the PVA.: The first step, up to 100 °C, corresponds to the endothermic process of desorption of physically absorbed water. The second step, in the range 300–400 °C, associated to a strong endothermic effect, correspond to the polyene decomposition in the position at the tertiary carbon atom to form macroradicals followed by decomposition with the formation of poly-conjugated aromatic structures.

The third step corresponds to the combustion of the carbonaceous residue, evidenced by the exothermic effect registered in the range 500–600 °C and the absence of a residue at 700 °C.

Figure 2 presents the FT-IR spectra of PVA heated at 150 °C [spectrum (1)] and annealed at 350 °C [spectrum (2)]. Spectrum (1) of PVA heated at 150 °C exhibits the absorption bands characteristic for water and –OH associated by H-bonds in the range of 3,200–3,600  $\text{cm}^{-1}$ , bands that are due to deformation vibration in –OH groups in

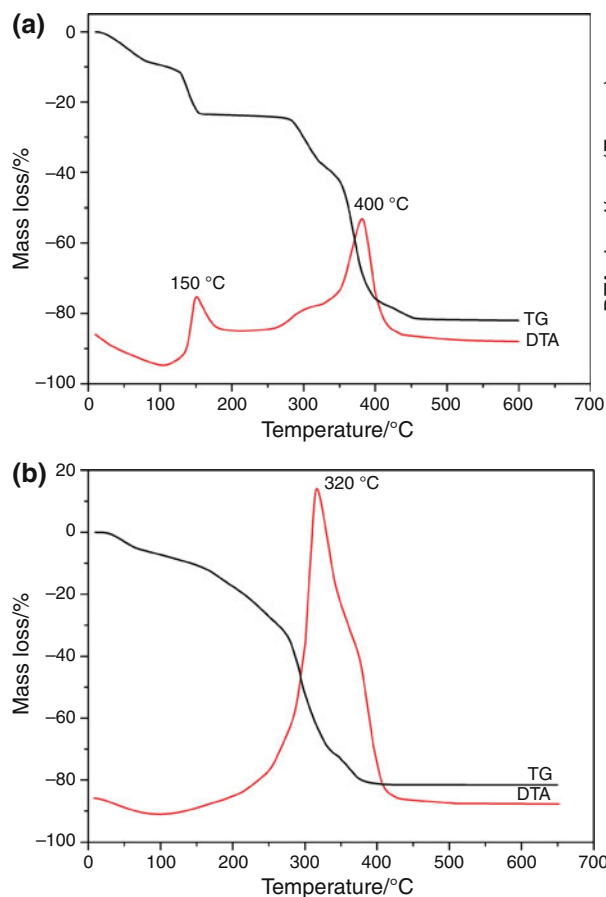


**Fig. 2** Fourier transformed infrared spectra of PVA obtained by heating the 4% aqueous solution at 150 and 350 °C

alcohols at 1,400–1,340  $\text{cm}^{-1}$ , and bands for –C–OH bond for secondary alcohols at 1,125–1,085  $\text{cm}^{-1}$  [12]. Thus, the absorption bands with maximum at 1,087 and 1,330  $\text{cm}^{-1}$  can be attributed to O–H deformation and C–O valence bond vibrations of secondary alcohols to which PVA belongs.

After heating at 350 °C [spectrum (2)], we can see an increase of band intensities in the frequency region 1,750–1,550  $\text{cm}^{-1}$ , which are characteristic of the stretching vibrations of C=C and C=O groups, because of the thermal oxidation of PVA [10]. The appearance of a new absorption band with maximum at 3,055  $\text{cm}^{-1}$  can be attributed to valence C–H vibration in CH=C group in IR spectrum (2) of PVA annealed at 350 °C. It testifies for isolated and conjugated carbon–carbon double bonds formation in polymer chain. The bands in the regions of 1,300–1,000  $\text{cm}^{-1}$  (the stretching vibrations of alcohol C–O groups and in-plane deformation vibrations of –OH groups) and 700–500  $\text{cm}^{-1}$  (mainly due to the torsion vibrations of hydroxyl groups) which noticeably become decreased in the sample annealed at 350 °C characteristic to –OH bond vibrations are no longer present. Appearance of bands with maximum at 700–760  $\text{cm}^{-1}$  can be attributed to deformation C–H bonds' vibrations in *trans*- and *cis*-conformations of –CH=CH– polymer chain fragments [13].

By introducing the metal nitrates in PVA aqueous solution and heating at 150 °C, both thermal curves and FT-IR spectra show significantly changes. Figure 3 presents the TG and DTA curves of the sample ZnPVA (a) and

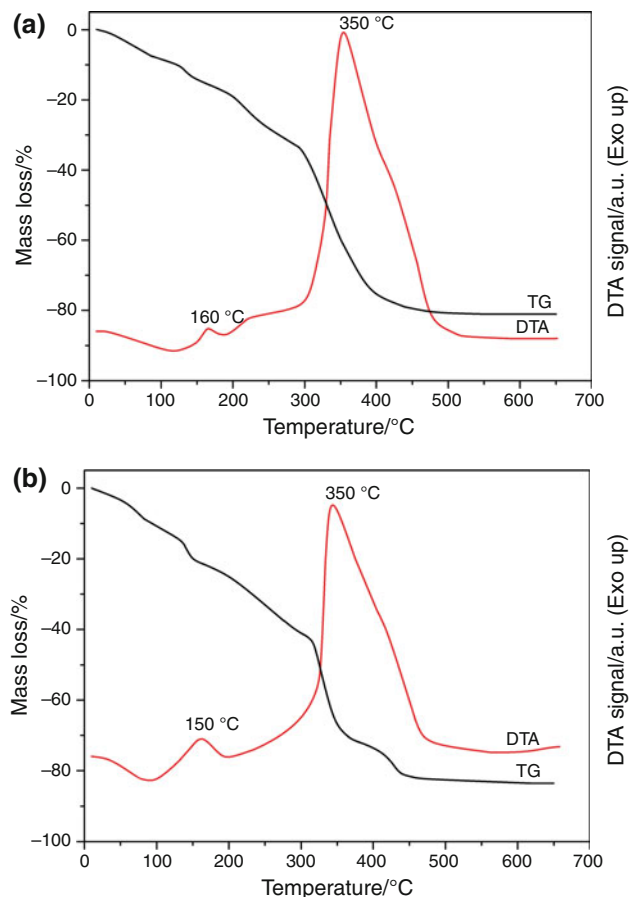


**Fig. 3** TG and DTA curves of **a** ZnPVA and **b** CrPVA powders obtained by heating the corresponding metal nitrate–PVA solutions at 150 °C

CrPVA (**b**) obtained by heating the aqueous-PVA–metal nitrates solution at 150 °C.

In these cases, the thermal behaviors of the powders are quite different from the one of simple PVA heated at the same temperature. In case of powder ZnPVA (Fig. 3a), several mass losses are visible on TG curve. Interesting is the second step, registered in the range 140–170 °C, with a visible exothermic effect on DTA which corresponds to the unfinished redox reaction that takes place between zinc nitrate and PVA. This is a confirmation of the supposed redox interaction between metal nitrates and PVA. The product of this interaction is a compound which thermally decomposes in the range 300–400 °C with an exothermic effect. No carbonaceous residue results from this oxidative decomposition, as confirmed by the absence of an exothermic effect between 500 and 600 °C.

In case of CrPVA powder, the redox reaction between chromium nitrate and PVA is complete. Thus, no exothermic process takes place in the range 100–200 °C. The decomposition of this product takes place in the range



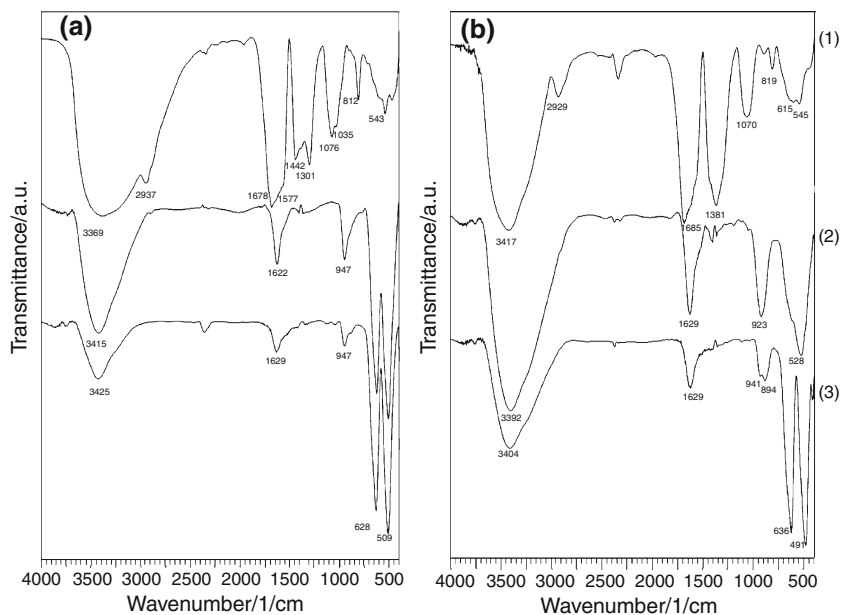
**Fig. 4** TG and DTA curves of the chromite precursors obtained by heating the corresponding metal nitrates–PVA solutions at 150 °C: **a** ZnCrPVA and **b** MgCrPVA

250–400 °C with a strong asymmetric exothermic effect, revealing a superposition of exothermic processes.

In case of MgPVA sample, there were neither interactions nor emission of nitrogen oxides. In this case, the sample was gradually heated up to 300 °C when it burned (with explosion). Thus, in this case the intermediary precursor could not be obtained. Taking into account the difference between the electronic configurations and the ability of forming coordination compounds of chromium and zinc as transitional metals and of magnesium (representative metal), we can conclude that, in case of transitional metals, the redox interaction of the corresponding nitrates with PVA may be initiated (promoted) by the formations of some coordination compounds with PVA and with its oxidation products.

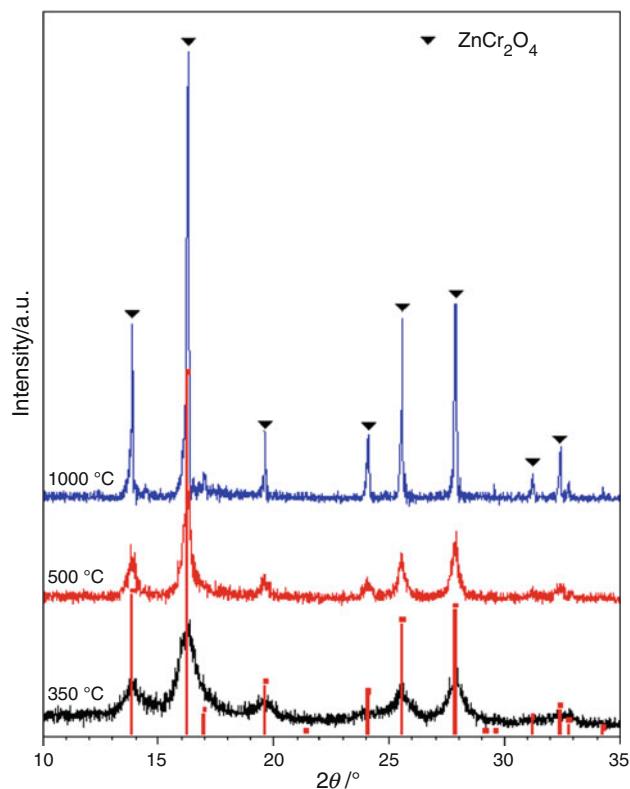
Surprisingly, when M(II) nitrate is mixed with chromium nitrate, the nature of the M(II) metal is not so important, with the behaviors of both powders ZnCrPVA and MgCrPVA being similar. The TG and DTA curves of the binary powders are presented in Fig. 4a, b.

**Fig. 5** Fourier transformed infrared spectra of the samples **a** ZnCrPVA and **b** MgCrPVA thermally treated at 150 °C (1) and annealed at 350 °C (2) and 500 °C (3)



It results from the evolution of thermal curves that after the elimination of physically adsorbed water; in both cases, a small mass loss is registered around 150 °C, corresponding to an exothermic effect, which most probably is the redox reaction of bivalent metal nitrate with PVA. This process is more visible in case of  $M(II) = Mg$  (Fig. 4b). It is possible due to the presence of  $Cr(III)$  to catalyze the redox reaction between  $Mg(NO_3)_2$  and PVA. The main decomposition stage, corresponding to the oxidative degradation of the organic part, takes place differently: in a single, strongly exothermic, step in the range of 300–400 °C in case of ZnCrPVA sample, whereas in case of MgCrPVA sample, the thermal decomposition takes place in two steps of 300–400 and 400–450 °C. It is possible that in the later case (MgCrPVA) is an intermediary decomposition product to form; it was evidenced in literature [14] that, by thermal decomposition of some precursor containing  $Mg(II)$  and  $Cr(III)$  magnesium chromate forms at lower temperatures, which further decompose at around 500 °C to amorphous magnesium chromite. This hypothesis was confirmed, as well by results obtained from FT-IR analysis.

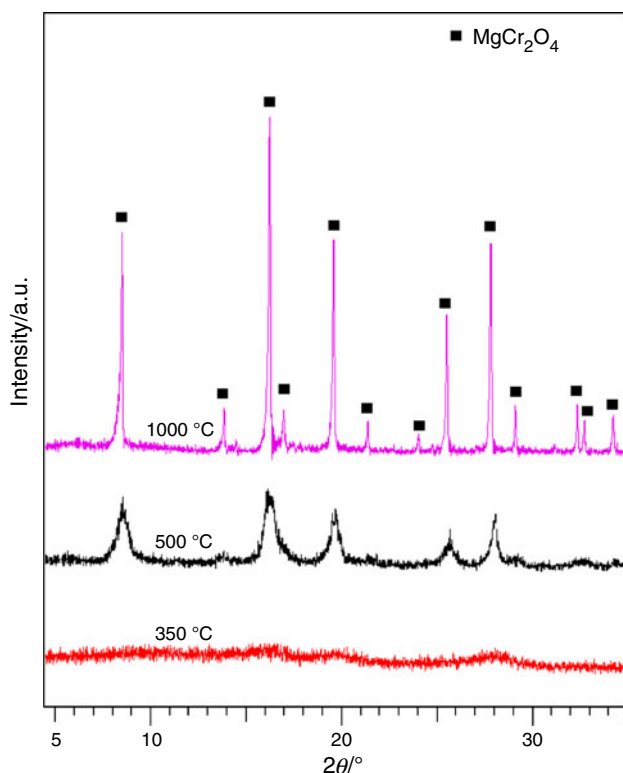
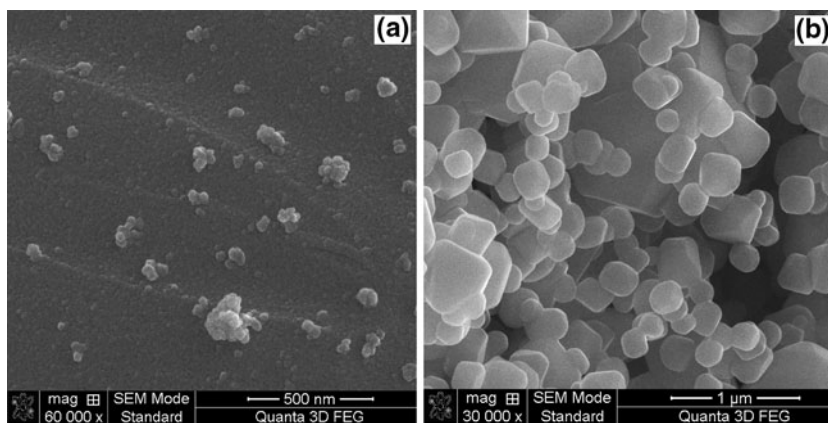
Figure 5a presents the FT-IR spectra of the sample ZnCrPVA as-obtained at 150 °C and thermally treated at 350 and 500 °C. FT-IR spectra of the product ZnCrPVA obtained at 150 °C are quite different from the one of simple PVA heated at the same temperature (Fig. 2, spectrum (1)). Thus, the bands in the range of 2,000–1,000  $cm^{-1}$  corresponding to C=O, C–O, and –C–OH vibrations have higher intensities, and their relative intensities are different in case of ZnCrPVA (Fig. 5a, spectrum (1)), compared to simple PVA (Fig. 2, spectrum (1)). The large band within the range of 1,500–1,700  $cm^{-1}$  includes two different bands. The band



**Fig. 6** X-ray diffractometry patterns of the powders obtained by annealing the precursor ZnCrPVA at different temperatures

located at 1,680  $cm^{-1}$ , corresponds probably to the C=O bonds formed by oxidation of secondary C–OH groups from PVA. This band is much stronger compared with the simple PVA at 150 °C, because of the interaction with  $NO_3^-$  as oxidant. The second band located at 1,577  $cm^{-1}$  can be

**Fig. 7** Scanning electron microscopy images of  $\text{ZnCr}_2\text{O}_4$  powder obtained by  $\text{ZnCrPVA}$  precursor calcination at **a** 500 °C and **b** 1,000 °C



**Fig. 8** X-ray diffractometry patterns of the powders obtained by annealing the precursor  $\text{MgCrPVA}$  at different temperatures

assigned to asymmetric vibrations of the  $\text{-COO}^-$  groups, while the band at  $1300\text{ cm}^{-1}$  can be assigned to symmetric vibrations of the  $\text{-COO}^-$  groups formed by the oxidation of terminal  $\text{C-OH}$  groups of PVA and by possible oxidative degradation of PVA in the presence of a strong oxidizing agent, i.e.,  $\text{NO}_3^-$ . Previous study regarding the product on heating the solution of PVA-metal nitrates has evidenced the presence of metal carboxylates formed in situ during thermal degradation of PVA [2].

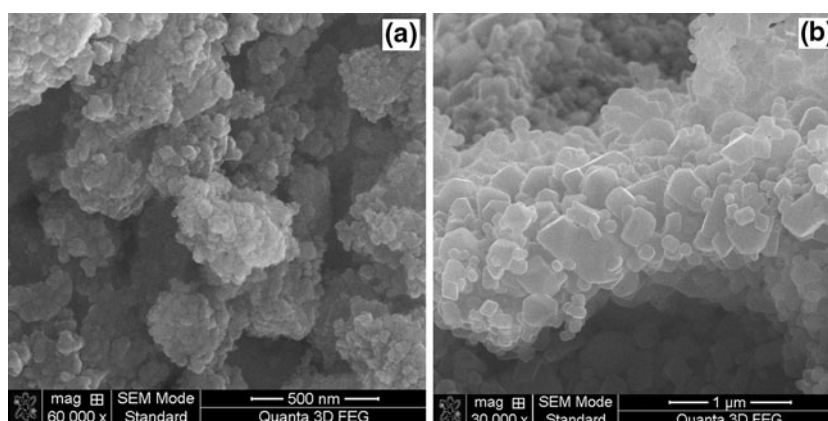
After annealing of the precursor at 350 °C for 3 h, the thermal decomposition of the organic part is complete, unlike in the case of simple PVA (Fig. 2, spectrum (2)).

The corresponding FT-IR spectrum (2) exhibits only bands of the physically adsorbed water ( $3,415$  and  $1,620\text{ cm}^{-1}$ ) and bands characteristic to the  $\text{M-O}$  bonds in spinels ( $\sim 620$  and  $\sim 510\text{ cm}^{-1}$ ) [15] suggesting that  $\text{ZnCr}_2\text{O}_4$  is already formed at this temperature. The band located at  $947\text{ cm}^{-1}$  may be assigned to  $\text{Cr(VI)-O}$  bond vibrations, due to some traces of  $\text{CrO}_3$ , which usually turns to  $\text{Cr(III)}$  around 400 °C. In case of the powder annealed at 500 °C, this band is very weak, confirming our supposition.

In case of  $\text{MgCrPVA}$  precursor, the evolution with the annealing temperature is quite different (Fig. 5b). Spectrum (1) of the as synthesized precursor (at 150 °C) show a very strong band at  $1,685\text{ cm}^{-1}$ , characteristic to  $\text{C=O}$  bond vibration. This band is asymmetrical, and so may include also the band characteristic to  $\text{-COO}^-$  asymmetric vibrations. The  $\text{-COO}^-$  symmetric vibrations, generates a characteristic band located in the IR spectra usually in the range of  $1,300\text{--}1,400\text{ cm}^{-1}$  [16]. The maximum of this band located in our case is at  $1,381\text{ cm}^{-1}$  and may overlap with the band of  $\text{NO}_3^-$  present in the system, in this case. We cannot conclude in this case that  $\text{Mg(II)}$  ions interact with PVA and its oxidation products, to form coordination compounds.

After calcinations at 350 °C, the FT-IR spectra no longer evidence the presence of an organic part. Still, there are no bands characteristics to the spinel  $\text{MgCr}_2\text{O}_4$  either. In this case, a strong band appears at  $923\text{ cm}^{-1}$ , characteristic to  $\text{Cr(VI)-O}$  bond vibrations, and another strong band with minimum at  $570\text{ cm}^{-1}$ , characteristic to  $\text{Mg-O}$  bond vibrations. In the sample annealed at 400 °C the same bands appears but the band characteristic to  $\text{Cr(VI)-O}$  vibrations is shifted to  $890\text{ cm}^{-1}$ , confirming the formation of  $\text{MgCrO}_4$  [14, 17]. It is possible, according to these FT-IR data, to have an  $\text{MgCrO}_4$  intermediary phase, besides  $\text{CrO}_3$ , formed during  $\text{MgCrPVA}$  precursor decomposition. When the precursor  $\text{MgCrPVA}$  is annealed at 500 °C, the band at  $941\text{ cm}^{-1}$  decrease in intensity, and two sharp bands located at  $636$  and  $497\text{ cm}^{-1}$  appear, because of the formation of  $\text{MgCr}_2\text{O}_4$  as a result of  $\text{MgCrO}_4$  thermal decomposition. Thus, FT-IR data are in agreement with thermal analysis data.

**Fig. 9** Scanning electron microscopy images of  $\text{ZnCr}_2\text{O}_4$  powder obtained by  $\text{ZnCrPVA}$  precursor calcination at **a** 500 °C and **b** 1,000 °C



The evolution of the crystalline phases with the annealing temperature was studied in both systems by X-ray powder diffraction. Figure 6 presents the XRD patterns of the powders obtained by annealing the precursor  $\text{ZnCrPVA}$  at 350, 500, and 1,000 °C. As resulted from FT-IR study, in this case, the spinel  $\text{ZnCr}_2\text{O}_4$  phase crystallizes (JCPDS file No. 01-1123 [18]) starting with 350 °C, as sole crystalline phase. The crystallization degree increases with the annealing temperature.

Scanning electron microscopy images of  $\text{ZnCr}_2\text{O}_4$  powders obtained at 500 and 1,000 °C are shown in Fig. 7a, b. It results from these images that the powder obtained at 500 °C is formed from fine, nearly spherical particles, with diameters between 10 and 30 nm. After annealing at 1,000 °C, the powder consists of octahedral, well-individualized particles ranging from 200 to 500 nm. There is no sign of sintering at this temperature.

In case of  $\text{MgCrPVA}$  powders (Fig. 8), after annealing at 350 °C, no crystalline phases are evidenced on the XRD pattern. This may be explained by the formation of amorphous mixture  $\text{MgCrO}_4 + \text{CrO}_3$ , as concluded from the FT-IR study. When the precursor is annealed at 500 °C,  $\text{MgCr}_2\text{O}_4$  begin to crystallize (JCPDS file No. 10-0351 [18]) as sole phase, with low crystallization degree. The crystallization degree significantly increases while increasing the annealing temperature to 1,000 °C.

Scanning electron microscopy images of  $\text{MgCr}_2\text{O}_4$  powders (Fig. 9a, b) show that the resulting particles are smaller than  $\text{ZnCr}_2\text{O}_4$  particles, but more agglomerated at both temperatures.

## Conclusions

A PVA-based synthesis method was successfully used to obtain fine  $\text{ZnCr}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$  powders. The interaction between PVA and  $\text{NO}_3^-$  ions was evidenced, with formation of some coordination compound between the metal cations involved and the oxidation products of PVA. The isolation

of these products used as precursors for the preferred chromites allows for a better control of the synthesis process and thus, a better control of chromites particle size. The thermal behavior of the synthesized precursor was different. Thus, while  $\text{ZnCrPVA}$  precursor decomposes up to 400 °C with formation of zinc chromite, the precursor  $\text{MgCrPVA}$  decomposes up to 500 °C, with formation of  $\text{MgCrO}_4$  as intermediary amorphous phase. By thermal decomposition of  $\text{MgCrO}_4$  at 500 °C, weakly crystallized  $\text{MgCr}_2\text{O}_4$  powder is obtained. The obtained chromites powders consist of fine nanoparticle with diameters ranging from 10 to 30 nm at 500 °C; on increasing the annealing temperature to 1,000 °C, chromites particles become octahedral, with diameters up to 500 nm, but with no sign of sintering.

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