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STABILITY STUDIES ON UNDOPED AND DOPED Mg_2TiO_4 , OBTAINED BY THE POLYMERIC PRECURSOR METHOD

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Mg_2TiO_4 was synthesized by the polymeric precursor method, was doped with 1 mol% of Mn^{2+}, Fe^{2+} or Co^{2+}. The powder precursors were characterized by TG/DTA methods. The mass loss took place in three steps. In the first one water and adsorbed gases were released while the second and third step were representative to the decomposition of the organic substance. The DTA experiments indicated the combustion as well as the decomposition and recrystallization of Mg_2TiO_4 between 800 and 1200ºC. XRD results indicated that spinel (AB_2O_4) which have been observed at 600ºC transformed to ilmenite ($MgTiO_3$) over 800ºC.

Keywords: *magnesium titanate, polymeric precursor method, spinel, thermal analysis*

Introduction

Magnesium orthotitanate, Mg_2TiO_4, is used as a heat resistor, dielectric for microwave technology, capacitor for temperature compensation and refractory material [1].

Mg_2TiO_4 is a metastable system. It can be obtained below 800°C, but it decomposes to $MgTiO_3$ and MgO on further heating [1].

Mg_2TiO_4 crystallizes in the cubic system, with a $[Mg(MgTi)O_4]$ inverse spinel structure, in which magnesium occupies both tetrahedral and octahedral sites but titanium occupies only octahedral sites. The spinel formula can be written as $(A_{1-x}B_x)^{tet}(A_xB_{2-x})^{oct}O_4$, where x is called to inversion parameter. In the present case, the spinel is named to (inverse) since x is equal to 1 [2, 3].

Spinels are complex oxides with a regular structure that consists of a FCC close-packed oxygen sublattice, in which 1/3 of the metal ions are located in tetrahedral sites and the remaining ions are in octahedral sites. Spinels are more often formed by two trivalent and one bivalent cation and can be represented as $A^{2+}B_2^{3+}O_4$. For Mg_2TiO_4, there are bivalent and tetravalent ions [3].

There are three stable phases in the MgO–TiO_2 system: $MgTiO_3$, Mg_2TiO_4 and $MgTi_2O_5$. Magnesium titanates are usually synthesized at relatively high temperatures, (1400ºC), by solid state reaction. On the other hand, the Mg_2TiO_4 spinel is obtained at much lower temperatures by chemical methods (coprecipitation, sol–gel, peroxide route). Its decomposition to $MgTiO_3$ and MgO starts at about 900ºC, with recrystallization of spinel above 1000ºC [1, 2, 4–6].

In the present study, the polymeric precursor method was used to obtain powders with better morphology and to allow a good stoichiometric control. The polymeric precursor method results in the chelation of metal cations in a polymeric network, obtained by the esterification of mixed metallic citrates with ethylene glycol [7, 8]. Then the polymeric network is heat treated, in order to obtain a high quality ceramic powder precursor.

Experimental

Titanium citrate was prepared by the addition of citric acid to distilled water, at 70ºC, followed by the slow addition of titanium isopropoxide. Gravimetric analysis was done to determine the amount of TiO_2 obtained from the citrate.

For the resin formation, citric acid and magnesium carbonate were added to titanium citrate followed by the addition of 1 mol% of manganese acetate, cobalt acetate or iron nitrate addition. 3:1 acid:metal molar ratio was used. After the complete dissolution of salts, ethylene glycol was added to the solution, keeping 60:40 citric acid:ethylene glycol mass ratio. After addition of all reagents, the solution was heated up to about 100ºC to reveal the polymerization process. Then, the first heat treatment was performed at 300ºC

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for 1 h to obtain the powder precursors, which were powdered in a mortar, and then passed through in a 200 mesh sieve. The resulted material was characterized by TGA-50 Shimadzu thermal analyzer and Shimadzu DTA-50. The experiments have been carried out from ambient room temperature to 950ºC under air atmosphere with a flow rate of 50 mL min^{-1}, at a heating rate of 10 K min^{-1}. About 10 mg sample were weighed at alumina crucibles.

Powder precursors were heat treated between 600 and 1200ºC for 60 min. The structural transformation was evaluated by X-ray diffraction (D-5000 Siemens). Diffractograms were recorded with a 0.03º step and a step time of 1.0 s, using the FeK_α target. Using XRD data, FWHM of the 100% peaks of ilmenite – peak (104) – and spinel – peak (311) were calculated. Crystallite size was calculated by Scherrer equation. The amount of ilmenite was calculated using 100% peak intensities, according to Eq. (1):

$$\mathrm{MgTiO_3}\,\% = I_{\mathrm{MgTiO_3}} / (I_{\mathrm{MgTiO_3}} + I_{\mathrm{Mg_2TiO_4}}) \qquad (1)$$

Results and discussion

In the thermogravimetric curves (TG and DTG), three decomposition events were observed for both undoped $\mathrm{Mg_2TiO_4}$ and $\mathrm{Mg_2TiO_4}$ doped with Fe, Mn or Co. The first event is related to the loss of water and some adsorbed gases. The second and third steps are related to the decomposition of organic matter [9, 10] (Figs 1 and 2).

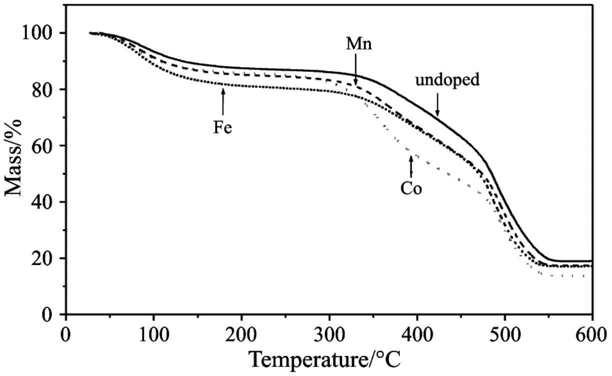

Fig. 1 TG curves of the powder precursor of undoped and doped $\mathrm{Mg_2TiO_4}$

In the DTA curves (Fig. 3) the exothermic peaks indicate the combustion of the organic material. The peak temperatures of the powder precursors of undoped and $\mathrm{Co^{2+}}$, $\mathrm{Fe^{2+}}$ and $\mathrm{Mn^{2+}}$ doped samples are 507, 514, 507 and 511ºC, respectively.

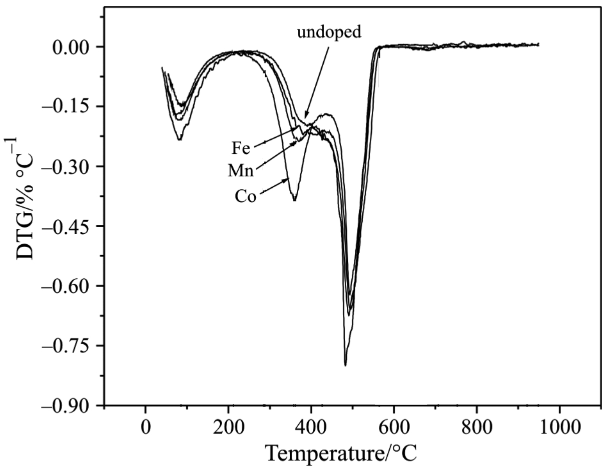

Fig. 2 DTG curves of the powder precursor of undoped and doped $\mathrm{Mg_2TiO_4}$

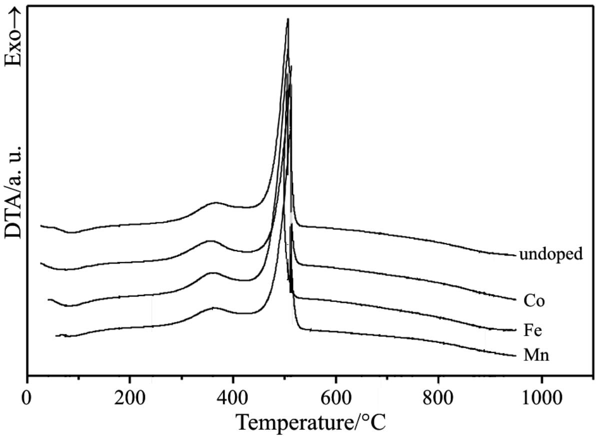

Fig. 3 DTA curves of the powder precursor of undoped and doped $\mathrm{Mg_2TiO_4}$

The results obtained by X-ray diffraction are presented in Fig. 4. The crystallization of spinel starts at 600ºC. However, above 800ºC, the presence of ilmenite, $\mathrm{MgTiO_3}$, can be observed. With the further increase of the temperature, the intensities of the ilmenite peaks decrease, concomitantly with the increase of the spinel concentration.

In order to determine if ilmenite crystallizes from the amorphous material, or from the own spinel, the DTA curve of the substance heat treated at 700ºC was recorded (Fig. 5). The DTA curve indicates a broad exotherm effect between 600 and 1400ºC. This is probably due to the decomposition spinel into ilmenite and magnesium oxide, which recombines at higher temperatures leading to the spinel formation (Eq. (2)).

$$\mathrm{Mg_2TiO_4} \rightarrow \mathrm{MgTiO_3} + \mathrm{MgO} \rightarrow \mathrm{Mg_2TiO_4} \qquad (2)$$

The decomposition reaction was not avoided by the dopant addition. However, according to Fig. 6, the amount of the formed ilmenite was decreased with the decrease of the temperature of the heat treatments.

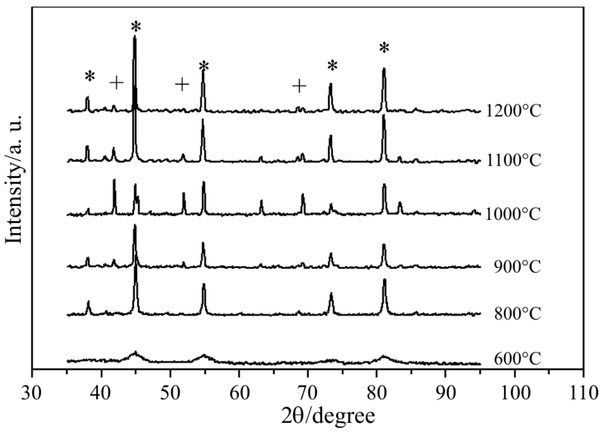

Fig. 4 X-ray diffraction patterns of the calcined samples: * – $\mathrm{Mg_2TiO_4}$ and + – $\mathrm{MgTiO_3}$

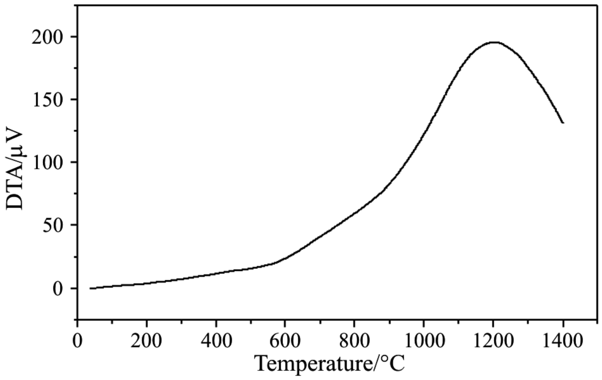

Fig. 5 DTA curve of spinel obtained after calcination at 700ºC

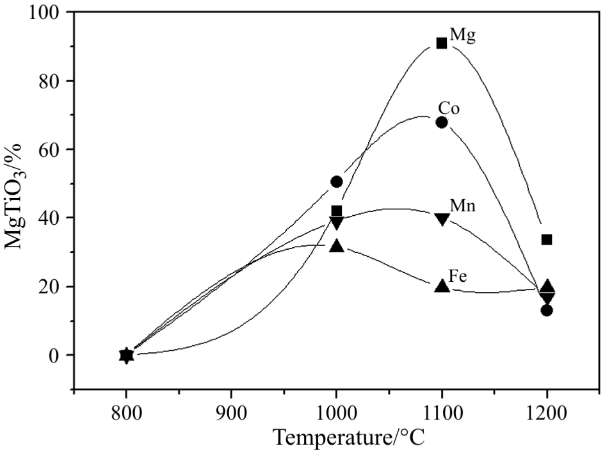

Fig. 6 Effect of the dopant addition on the ilmenite formation

As to the effect of dopants, the amount of the formed ilmenite varied in the following order: iron<manganese<cobalt. It can be attributed to the distortion of the unit cell, which is due to the formation of defects.

Evaluating the ionic radii of the dopants, it is observed that in an octahedral coordination, the ionic radius of Co^{2+} (r=0.075 nm) is similar to Mg^{2+} (r=0.072 nm), whereas the radius of Mn^{2+} (r=0.083 nm) is higher than Mg^{2+} one, leading to a higher distortion in the lattice. Fe^{2+} substitution can lead to even higher distortion, despite of the smaller difference between their ionic radii (r=0.078 nm), due to the oxidation of Fe^{2+} to $\mathrm{Fe}^{3+.}$ Defects such as metal vacancies may be formed to keep the neutral charging increase the lattice distortion. The possible mechanism is represented by Eq. (3), using the Kröger–Vink notation.

$$\mathrm{Fe_2O_3} \rightarrow 2\mathrm{Fe}^{\bullet}_{\mathrm{Mg}} + \mathrm{V}''_{\mathrm{Mg}} + 3\mathrm{O}^{x}_{0} \tag{3}$$

A better evaluation of the effect of dopant can be taken from crystallite sizes and the FWHM values of the diffraction peaks (Figs 7 and 8). The position of diffraction peak was also evaluated, but an arbitrary behavior was observed.

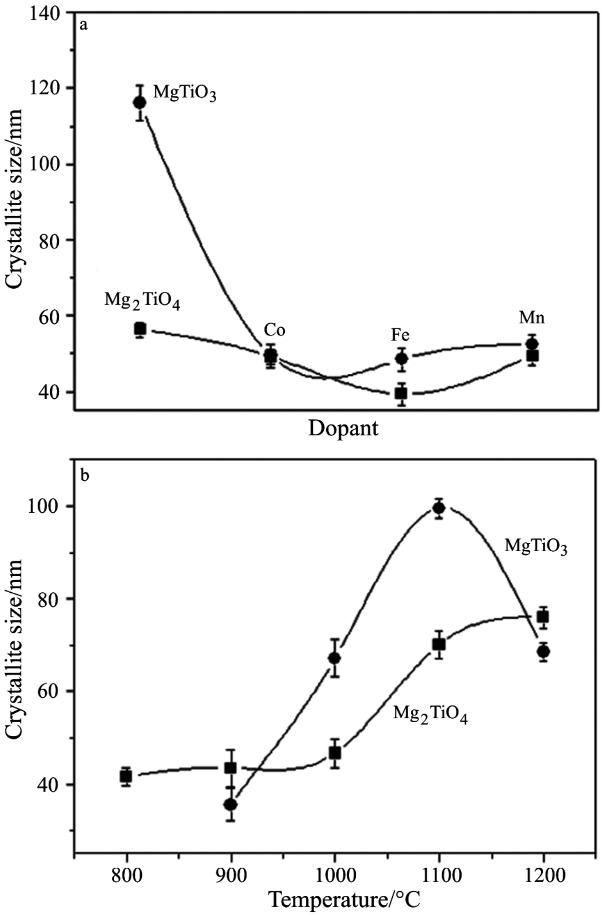

Fig. 7 Crystallite size of the formed phases after thermal treatment; a – effect of dopant, after calcination at 1000ºC, b – effect of temperature for the undoped sample

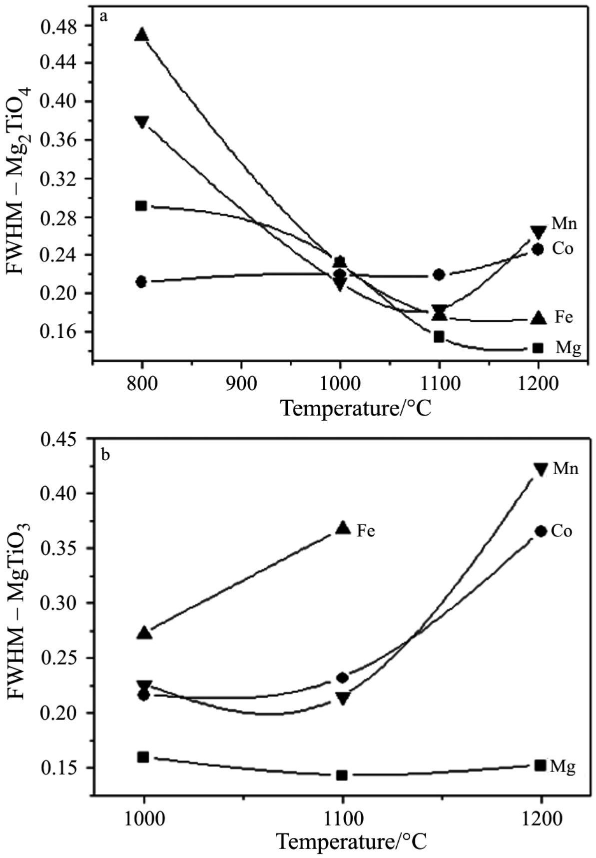

Fig. 8 FWHM values of the diffraction peaks of the formed phases after thermal treatment; a – peak (311) of Mg_2TiO_4, b – peak (104) of $MgTiO_3$

It can be observed that dopant addition leads to a decrease in the crystallite sizes of ilmenite and spinel (Fig. 7a). This may be attributed to the nucleation and the crystal growth process. Since XRD patterns do not indicate a change in crystallization, this decrease is probably related to a more difficult diffusion, changing the crystallite growth. This may be due to a distortion of the unit cell, as it was discussed before. Literature results indicate that nanometric crystallites may lead to a higher stability of some cubic phases [11, 12]. Thus, this decrease in crystallite size may be responsible for the lower amount of ilmenite phase, which is hexagonal, and a higher amount of spinel, which is cubic.

The increase of the temperature plays an important role in the increase of the crystallite size (Fig. 7b). The decrease in the crystallite size of ilmenite above 1100ºC is probably due to its decomposition.

With regard to the crystallite size, FWHM results (Fig. 8) show a different behavior. As FWHM is also related to microstrain, this result may related to the unit cell distortion. It is observed that the increase of temperature leads to a higher distortion of the ilmenite unit cell, accompanied by a higher organization of the spinel unit cell. Moreover, the addition of the dopant, especially of iron, leads to a higher distortion of ilmenite, what does not occur with the spinel. The authors believe that this is due to its own spinel structure, which exhibits several tetrahedral and octahedral available sites, allowing a better place for the substituting cations.

Conclusions

In the present work, the Mg_2TiO_4 phase was obtained at low temperatures, which decomposes into $MgTiO_3$ and MgO at 1000ºC. The recrystallization starts at 1100ºC. The addition of dopant did not alter the decomposition of Mg_2TiO_4 to $MgTiO_3$, but changed the amount of formed ilmenite. Fe^{2+} provided a smaller amount of $MgTiO_3$, probably due to a higher distortion in the unit cell, since the oxidation of Fe^{2+} to Fe^{3+} takes place easily, leading to the formation of cationic vacancies. Another possible reason for the higher stability of spinel in Fe-doped samples is the smallest crystallite size.

Acknowledgements

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References

1 M. J. Martinez-Lope, M. P. Baura-Pena and M. E. Garcia-Clavel, Thermochim. Acta, 194 (1992) 59.
2 G. Pfaff, Ceram. Int., 20 (1994) 111.
3 Y. M. Chiang, D. Birnie III and W. D. Kingery, Physical Ceramics, John Wiley and Sons, Inc., New York, USA 1997.
4 S. E. Hadigui, S. Vilminot and J. C. Bernier, Mater. Sci. Eng. A, 109 (1989) 221.
5 D. M. Flot and J. T. S. Irvine, Solid State Ionics, 135 (2000) 513.
6 I. Shindo, J. Cryst. Growth, 50 (1980) 839.
7 N. Pechini, U.S. Patent number 3,330,697, 1967.
8 C. S. Xavier, C. E. F. Costa, S. C. L. Crispim, M. I. B. Bernardi, M. A. M. A. Maurera, M. M. Conceição, E. Longo and A. G. Souza, J. Therm. Anal. Cal., 75 (2004) 461.
9 K. S. Mazdiyasni, Ceram. Int., 9 (1982) 42.
10 S. G. Cho, P. F. Johnson and R. A. Condrate, J. Mater. Sci., 25 (1990) 4738.
11 P. R. Arya, P. Jha and A. K. Ganguli, J. Mater. Chem., 13 (2003) 415.
12 C. Huang, Z. Tang, Z. Zhang and J. Gong, Mater. Res. Bull., 35 (2000) 1503.