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Thermochimica Acta 408 (2003) 75–84

thermochimica acta

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Solid–solid interactions in Fe_2O_3/MgO system doped with aluminium and zinc oxides

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Received 29 October 2002; received in revised form 21 May 2003; accepted 29 May 2003

Abstract

The solid–solid interactions between MgO and Fe_2O_3 in the presence and absence of small amounts of Al_2O_3 and ZnO (2 and 6 mol%) have been investigated using DTA and XRD techniques. Equimolar proportions of magnesium basic carbonate and α-Fe_2O_3 were employed and aluminium and zinc were added as aluminium and zinc nitrates. Pure and doped mixed solids were subjected to heat treatment at 500–1100 °C.

The results obtained revealed that the addition of small amounts of dopant nitrates to the reacting mixed solids much enhanced the thermal decomposition of magnesium carbonate to an extent proportional to their amounts added. The decomposition temperature of magnesium carbonate decreased from 520.6 to 382.8 and 375.7 °C in the presence of 12 mol% aluminium nitrate and 6 mol% zinc nitrate, respectively. MgO underwent solid–solid interaction with Fe_2O_3 at temperatures starting from 700 °C producing $MgFe_2O_4$. The degree of propagation of this reaction increases progressively by increasing the precalcination temperature and the amounts of dopant added. The heating of pure and doped mixed solids at 1100 °C for 6 h was not sufficient to effect the complete conversion of the reacting solids into $MgFe_2O_4$. However, the amounts of unreacted oxides much decreased as a function of the amount of ZnO or Al_2O_3 added. The stimulation effect of ZnO, and Al_2O_3 towards the thermal decomposition of magnesium carbonate and the ferrite formation was attributed to an effective increase in the mobility of the various reacting cations. The activation energy of formation (ΔE_a) of magnesium ferrite was determined for pure and different doped solids and the values obtained were 114, 78, 62, 91 and 76 kJ mol^{-1} for pure mixed solids and those doped with 2 and 6 mol% ZnO and 2 and 6 mol% Al_2O_3, respectively.

Keywords: ZnO; Al_2O_3 doping; $MgFe_2O_4$; Solid–solid interactions

1. Introduction

Most of the divalent metal oxides (MOs) interact with Fe_2O_3 yielding the corresponding ferrite with the formula MFe_2O_4 [1]. These ferrites are classified according to their structure and properties into two categories: (1) ferrites having cubic spinel structure, MFe_2O_4 (M = Mg, Co, Ni, Cu and Zn) and (2) ferrites with other different structures, e.g. the ferrites of alkaline earth elements [2–4]. Based on the distribution of cations, among the tetrahedral (T) and octahedral (O) sites of the coordinated oxygen, spinels can be either normal spinel $M_{tet.}^{2+}[Fe^{3+}Fe^{3+}]_{oct.}O_4$ or inverse spinel with half of trivalent ions in the T position and the other half together with divalent ions in the O-sites [5]. Transition metal ferrites find several applications as catalysts, microwave resistors,

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0040-6031/$ – see front matter © 2003 Published by Elsevier B.V.
doi:10.1016/S0040-6031(03)00323-X

ultrasonic vibrators, electrophotographic toners and electromagnetic absorbers [6–10]. Most ferrite powders are prepared as ceramic materials by heat treatment of mixed oxides, hydroxides or carbonates at temperatures within 600–1100 °C [11,12]. The calcinations step is of vital importance in determining the properties of the produced ferrites [9].

The kinetic description of solid–solid interactions in the ferrite formation is a complex issue and the literature provides several models that may describe the rate at which these types of reactions proceed [9,13,14]. Most of these models imply that a thin film of MFe_2O_4 may be formed at relatively low temperatures and covers the surfaces of reacting Fe_2O_3 grains, hindering the thermal diffusion of divalent cations through it yielding their ferrites. The produced ferrite film acts as an energy barrier against the further formation of MFe_2O_4 phase. Several successful attempts have been done to stimulate the ferrite formation via doping with certain foreign oxides [15–24]. In fact, it has been reported that Li_2O-doping enhanced the formation of Zn, Ni, Co, Mn and Cu ferrites [15–24]. Al_2O_3 and ZnO being added as dopants stimulated the formation of nickel and cobalt ferrites [16,21,24]. The enhancement of MFe_2O_4 formation due to doping had been attributed to an effective increase in the mobility of reacting cations taking part in the ferrite formation.

The present work reports the results of a study on the effect of addition of small amounts of ZnO and Al_2O_3 on $MgFe_2O_4$ formation, at different temperatures using DTA and XRD techniques.

2. Experimental

2.1. Materials

Equimolar proportions of α-Fe_2O_3 and magnesium basic carbonate were well mixed to ensure the homogeneity of the powdered solids. The obtained sample was heated in air at temperatures between 500 and 1100 °C for 6 h. Four doped mixed solid samples were obtained by treating a known mass of mixed solids with calculated amounts of aluminium or zinc nitrates dissolved in the minimum amount of distilled water, dried at 100 °C, and then calcined in air at 500–1100 °C. The concentration of aluminium and zinc expressed as mol% Al_2O_3 and ZnO were 2 and 6. The chemicals employed in the present work were of analytical grade supplied by Merck company.

2.2. Techniques

DTA curves of pure and variously doped uncalcined mixed solid samples were determined using a Shimadzu DTA-50. The rate of heating was kept at $10\,°C\,min^{-1}$ and the mass of solid specimen was 30 mg. The measurements were carried out in a current of nitrogen flowing at a rate of $30\,cm^3/min$.

An X-ray investigation of pure and variously doped solids preheated in air at 500, 700, 800, 900, 1000 and 1100 °C, was conducted using a Philips diffractometer (type PW1390). The patterns were run with iron–filtered-cobalt radiation ($\lambda = 1.7889$ Å) at 30 kV and 10 mA with a scanning speed of $2°\,min^{-1}$ in 2θ. The particle size of MgO phase in the investigated solids was calculated from X-ray line broadening analysis of some diffraction lines of MgO phase using Scherrer equation [25]: $d = k\lambda/B(1/2)\cos\theta$, where d is the mean crystallite diameter, λ the X-ray wavelength, K the Scherrer constant (0.89) and $B(1/2)$ the full width half maximum (FWHM) of the main diffraction line of MgO phase ($d = 2.11$ Å) and θ the diffraction angle. In line, broadening analysis the scanning rate was fixed at $0.2°\,min^{-1}$ in 2θ.

3. Results and discussion

3.1. Thermal behaviour of pure and doped mixed solids

TG and DTG investigation of the employed basic magnesium carbonate showed that its molecular formula could be given as follows: $MgCO_3Mg(OH)_2\cdot 1.5H_2O$.

Fig. 1 depicts the DTA curves of pure and $Al(NO_3)_3$ or $Zn(NO_3)_2$ treated uncalcined mixed solids (Fe_2O_3 and basic magnesium carbonate). The DTA curve of pure mixed solids consists of four endothermic peaks, the first and last one are sharp and strong and their maxima found at 285, 487.4, 498.9 and 520.6 °C. The first peak corresponds to dehydroxylation of basic magnesium carbonate yielding a mixture of MgO and $MgCO_3$. The second, third and fourth peaks are indicative for the thermal decomposition of magnesium

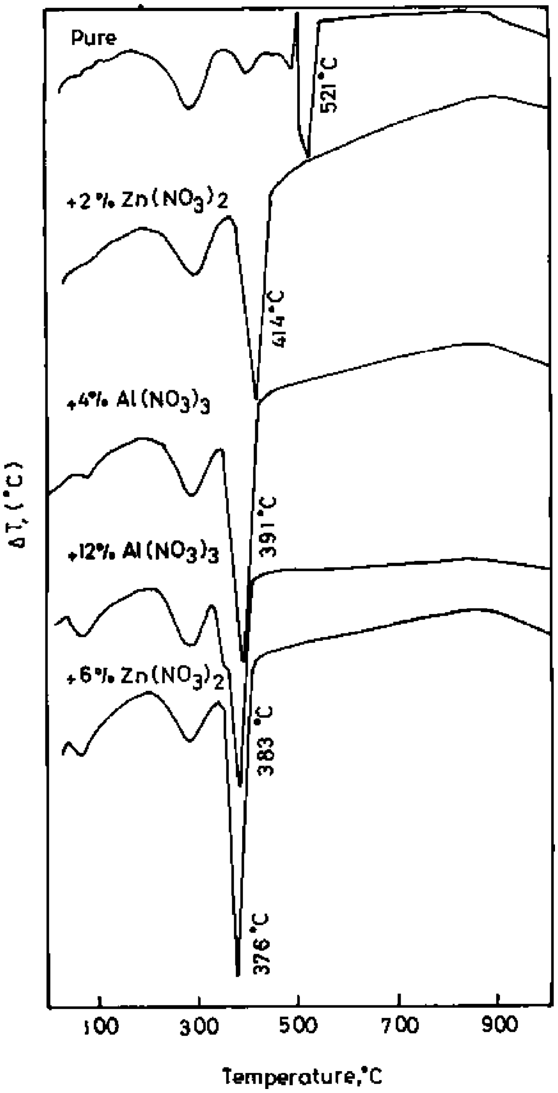

Fig. 1. DTA curves of uncalcined pure and doped mixed solids.

carbonate into magnesium oxide [23]. The DTA curves of pure and doped mixed solids did not include any thermal peak in the temperature range 600–1000 °C. However, a solid–solid interaction might take place between Fe_2O_3 and the produced MgO by heating at temperatures within 600 and 1000 °C with a very small rate that could be detected by the employed DTA technique. The DTA curves of variously doped mixed solids consist of two endothermic peaks besides an additional endothermic peak located at 67 °C. The area of this peak increases by increasing the amount of dopant added and corresponds to departure of water of crystallization of aluminium nitrate nona hydrate and zinc nitrate trihydrate. The second peaks are sharp and strong and having their maxima at 414.3, 375.7, 390.5 and 382.8 °C for the mixed solid samples doped with 2, 6, 4 and 12 mol% zinc nitrate and aluminium nitrate, respectively. The area and sharpness of this set of peaks increases as a function of the amount of dopant nitrate added. The first set of peaks have their maxima located at 284.2–290.5 °C, i.e. the doping process did not affect the position of the endothermic peak characteristic for dehydroxylation of magnesium basic carbonate yielding a mixture of MgO and $MgCO_3$. On the other hand, treatment of the employed magnesium basic carbonate with small amounts of zinc or aluminium nitrate much enhanced the thermal decomposition of $MgCO_3$ yield MgO. The addition of 6 mol% zinc nitrate decreased the decomposition temperature of magnesium carbonate from 520.6 to 375.7 °C. Similar results have been reported in the case of $LiNO_3$-doing of magnesium basic carbonate, and the addition of 6 mol% $LiNO_3$ decreased the decomposition temperature of magnesium carbonate to 381 °C [23]. The DTA results illustrated in Fig. 1 clearly indicate that doping of magnesium basic carbonate either with aluminium nitrate or zinc nitrate stimulated the decomposition of $MgCO_3$ into MgO to an extent proportional to the amount of dopant nitrate added. The stimulation effect may extend to enhance the possible solid–solid interaction between the produced magnesium oxide and ferric oxide present. In fact, it has been reported that $LiNO_3$-doping of Fe_2O_3/magnesium basic carbonate mixed solids which enhanced the thermal decomposition of $MgCO_3$ into MgO enhanced, also, the solid–solid interaction between MgO and Fe_2O_3 yielding magnesium ferrite [23].

3.2. X-ray investigation of pure and doped mixed solids precalcined at 500–1100 °C

The X-ray diffractograms of pure and variously doped ferric oxide and magnesium basic carbonate mixtures precalcined at 500, 700, 800, 900, 1000 and 1100 °C were determined. Fig. 2 depicts the diffractograms of pure and variously doped mixed solid samples precalcined at 500 °C. Inspection of Fig. 2

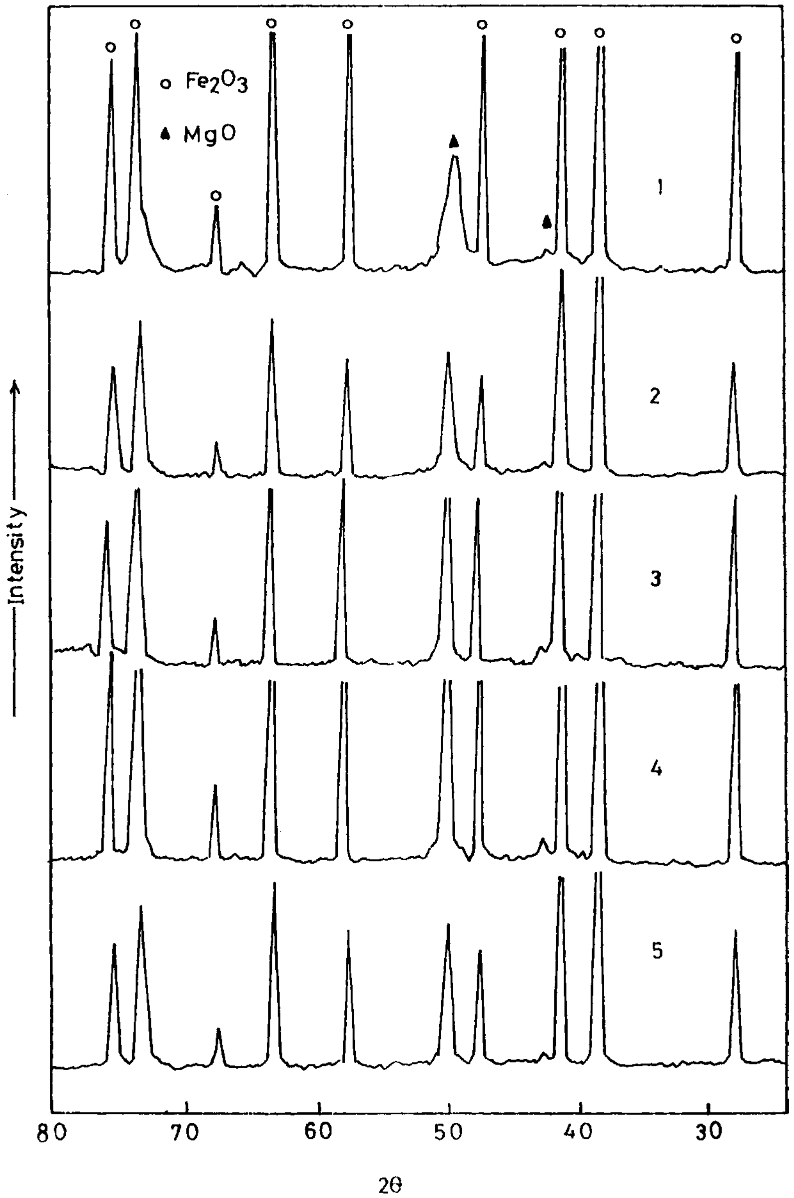

Fig. 2. X-ray diffractograms of pure and doped mixed solids precalcined at 500 °C: 1, 2, 3, 4 and 5 refer to pure mixed oxides and those doped with 2 and 6 mol% ZnO, and 2 and 6 mol% Al_2O_3, respectively.

revealed the following: (i) Pure mixed solids sample consisted of well crystallized α-Fe_2O_3 phase and moderately crystalline MgO phase. (ii) The doping process conducted at 500 °C resulted in a progressive increase in the degree of crystallinity and particle size of MgO phase as evidenced from the significant increase in the peak height of its diffraction lines and from a progressive narrowing of these peaks. (iii) The computed values of average particle size of MgO phase were 67, 134, 202, 185 and 226 Å in pure mixed solids sample and those doped with 2 and 6 mol% ZnO, and 2 and 6 mol% Al_2O_3. The decomposition temperature of $MgCO_3$ into MgO which was far below 500 °C (414–375 °C, cf. Fig. 1) in the case of variously doped mixed solid samples can account for the observed significant increase in both degree of crystallinity and particle size of the produced MgO phase. (iv) The diffractograms of pure and doped solids precalcined at 500 °C did not include any diffraction peak relative to magnesium ferrite. These results clearly indicate the absence of any solid–solid interaction between Fe_2O_3 and MgO being precalcined at 500 °C. However, the rise in precalcination temperature of pure and variously doped mixed solids to 700 °C led to the appearance of the diffraction peaks of $MgFe_2O_4$ phase. The obtained diffractograms not given, showed the detection of new peak at $d = 2.96$ Å whose relative intensity increases by increasing the amount of dopant added. This particular peak which corresponds to one of the main diffraction peaks of $MgFe_2O_4$ phase and having $I/I_0 = 100\%$ was taken as a reference line for magnesium ferrite phase. The other lines of this phase are common with unreacted MgO and α-Fe_2O_3 [26]. The further increase in precalcination temperature of pure and doped mixed solids to 800 °C resulted in a measurable increase in the peak height of the reference diffraction line of $MgFe_2O_4$ proportional to the amount of dopant added. In a recently published work by one of the authors [23] on the effect of Li_2O-doping on solid–solid interactions between α-Fe_2O_3 and MgO (employing chemicals of analytical grade supplied by Fluka), the diffraction lines of $MgFe_2O_4$ have not been detected in the diffractograms of pure and doped Fe_2O_3 and magnesium basic carbonate mixture being precalcined at 700 °C.

Fig. 3 depicts the X-ray diffractograms of pure and variously doped mixed solids precalcined at 900 °C. It is shown from Fig. 3 that the diffractograms of pure and doped solids consist of all diffraction peaks of MgO, α-Fe_2O_3 and $MgFe_2O_4$ phases. It can also be seen that the relative intensity of the reference diffraction peak of magnesium ferrite increases by increasing the amount of dopant added, while the intensity of the diffraction peak of unreacted α-Fe_2O_3 phase decreases by doping either with Al_2O_3 or ZnO. In fact, the height of diffraction peak at $d = 3.66$ Å, corresponding to α-Fe_2O_3 ($I/I_0 = 100\%$) in the diffractograms of pure and doped mixed solids precalcined at 900 °C measured 132, 130, 120, 118 and 95 a.u. for pure sample and those doped with 2 and 6 mol% ZnO, and 2 and 6 mol% Al_2O_3, respectively. These values were 142, 108, 50, 87 and 60 a.u. for the undoped sample and those heated at 1000 °C and being treated with 2 and 6 mol% ZnO, and 2 and 6 mol% Al_2O_3, respectively. These results indicate that the doping of the investigated system with zinc or aluminium oxide followed by calcination at 900 °C enhanced the solid–solid interaction between MgO and Fe_2O_3 yielding $MgFe_2O_4$. However, the heat treatment of pure and doped mixed solids at 900 °C did not effect the complete conversion of reacting oxides into $MgFe_2O_4$. So, the X-ray diffractograms of pure and variously doped mixed solids subjected to heat treatment at 1000 and 1100 °C were determined. The obtained diffractograms not given, showed that the peak height of the reference diffraction line of $MgFe_2O_4$ increases by increasing the precalcination temperature of the investigated solid samples and also by increasing the amounts of dopant oxides added. However, the diffraction lines of unreacted α-Fe_2O_3 phase were found in the diffractograms of pure and variously doped solids even those precalcined at 1100 °C for 5 h. But, the peak height of unreacted ferric oxide phase decreases by doping. In fact, the peak height of the main diffraction line of α-Fe_2O_3 ($d = 2.69$ Å; 100% for this phase) was 82, 55, 42, 56 and 20 a.u. for pure mixed solids sample and those doped with 2 and 6 mol% Al_2O_3, and 2 and 6 mol% ZnO, respectively. These results may suggest that the doping of the investigated system either with Al_2O_3 or ZnO enhanced the ferrite formation to an extent proportional to the amount of dopant oxide added. The promotion effect was, however, more pronounced for ZnO-doping. Indeed, the heat treatment of different investigated mixed solids at 1100 °C did not lead to the complete conversion of Fe_2O_3 and MgO to $MgFe_2O_4$.

The effects of precalcination temperature and doping of the system investigated on $MgFe_2O_4$ formation were investigated via measuring the peak height of the reference diffraction peak of $MgFe_2O_4$ ($d = 2.97$ Å) as a measure for the amount of the ferrite produced in a given mixed solids sample at a given precalcination temperature. The computed values of peak height of the line at $d = 2.97$ Å for pure and doped solids precalcined at 700–1000 °C are given in Table 1. The peak height of this particular diffraction line was considered as a measure for the amount of

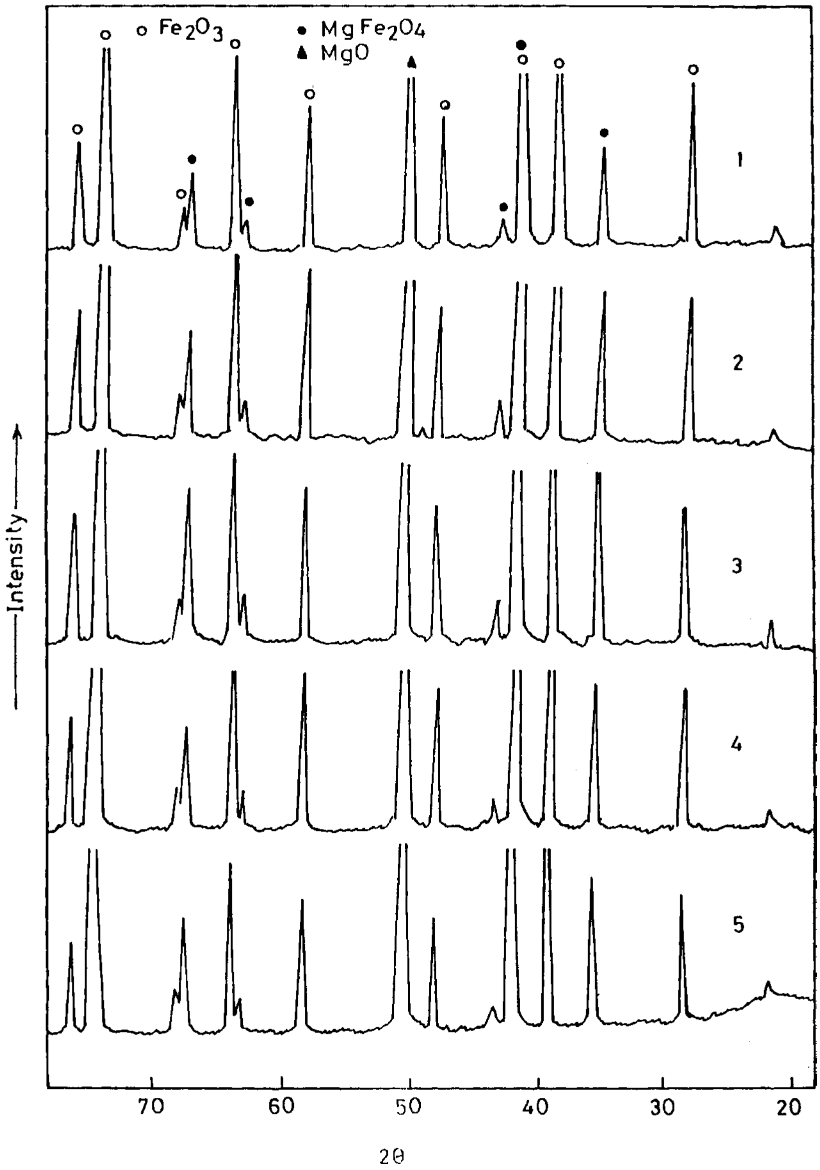

Fig. 3. X-ray diffractograms of pure and doped mixed solids precalcined at 900 °C: 1, 2, 3, 4 and 5 refer to pure mixed oxides and those doped with 2 and 6 mol% ZnO, and 2 and 6 mol% Al_2O_3, respectively.

$MgFe_2O_4$ produced simply because this peak is sharp for all investigated solids, indicating the formation of well crystallized $MgFe_2O_4$ phase in all cases. So, the observed increase in the peak height of the peak at $d = 2.97$ Å due to doping and/or increasing the precalcination temperature of the investigated solids did not correspond to a possible increase in the degree of crystallinity of $MgFe_2O_4$ produced. The observed increase in the peak height of this diffraction peak might be taken as a measure of the amount of produced ferrite phase. The stimulation effects of Li_2O, ZnO and Al_2O_3 towards the formation of $NiFe_2O_4$, $CoFe_2O_4$, $ZnFe_2O_4$ and $MnFe_2O_4$ have been reported [15–24]. Also, the effect of Li_2O-doping in the formation of

Table 1
The effects of Zn and Al_2O_3 doping on the height of selected diffraction line at *d* spacing of 2.97 Å for different mixed solids precalcined at different temperatures

Solids	Precalcination temperature (°C)	Peak height (a.u), 2.97 Å (40% $MgFe_2O_4$)
Pure $MgO + Fe_2O_3$	700	8
Pure $MgO + Fe_2O_3 + 2$ mol% ZnO	700	22
Pure $MgO + Fe_2O_3 + 6$ mol% ZnO	700	37
Pure $MgO + Fe_2O_3 + 2$ mol% Al_2O_3	700	11
Pure $MgO + Fe_2O_3 + 6$ mol% Al_2O_3	700	20
Pure $MgO + Fe_2O_3$	800	23
Pure $MgO + Fe_2O_3 + 2$ mol% ZnO	800	45
Pure $MgO + Fe_2O_3 + 6$ mol% ZnO	800	69
Pure $MgO + Fe_2O_3 + 2$ mol% Al_2O_3	800	32
Pure $MgO + Fe_2O_3 + 6$ mol% Al_2O_3	800	49
Pure $MgO + Fe_2O_3$	900	80
Pure $MgO + Fe_2O_3 + 2$ mol% ZnO	900	117
Pure $MgO + Fe_2O_3 + 6$ mol% ZnO	900	169
Pure $MgO + Fe_2O_3 + 2$ mol% Al_2O_3	900	92
Pure $MgO + Fe_2O_3 + 6$ mol% Al_2O_3	900	118
Pure $MgO + Fe_2O_3$	1000	150
Pure $MgO + Fe_2O_3 + 2$ mol% ZnO	1000	160
Pure $MgO + Fe_2O_3 + 6$ mol% ZnO	1000	205
Pure $MgO + Fe_2O_3 + 2$ mol% Al_2O_3	1000	168
Pure $MgO + Fe_2O_3 + 6$ mol% Al_2O_3	1000	190

$MgFe_2O_4$ had been investigated. These dopant oxides showed different stimulation effects depending on the nature of transition metal ferrite.

Fe_2O_3 undergoes solid–solid interactions with transition MO to produce the corresponding ferrite that covers the grains of each reacting oxide [27,28]. The propagation of these reactions is controlled by the thermal diffusion of reacting cations through the ferrite film, which acts as an energy barrier. It has been reported that Li_2O-doping of NiO/Fe_2O_3 and MgO/Fe_2O_3 systems followed heat treatment at 1100 °C for 24 h did not result in complete conversion of reacting oxides into the corresponding ferrites [15,23]. These findings give an indication of the height of the energy barrier, which has to be overcome. The enhancement of ferrites formation due to doping with certain foreign oxides had been discussed by El-Shobaky et al. [15–24]. Such enhancement had been attributed to an effective increase in the mobility of the reacting cations through the ferrite film via creation of cationic vacancies [16,23]. The observed enhancement of $MgFe_2O_4$ formation due to doping with ZnO or Al_2O_3 may be a consequence of an effective increase in the mobility of Mg^{2+} and Fe^{3+} cations. The dopant oxides added to MgO/Fe_2O_3 may dissolve in the lattices of MgO and Fe_2O_3 solids forming solid solutions. The dissolution process can be simplified by the use of Kroger's mechanism [29] in the following manner:

$$Al_2O_3 + 2Fe^{3+} \rightarrow 2Al(Fe^{3+}) \quad (1)$$

$$Al_2O_3 + 2Mg^{2+} \rightarrow 2Al(Mg^{2+}) + 2Mg^{2+} + \text{C.V.} \quad (2)$$

$$2ZnO + 2Fe^{3+} \rightarrow 2Zn(Fe^{3+}) + 2Fe^{3+} + \text{A.V.} \quad (3)$$

$$ZnO + Mg^{2+} \rightarrow Zn(Mg^{2+}) \quad (4)$$

$$Al_2O_3 + 2Fe^{3+} \rightarrow 2Al_{\triangle} + 2Fe^{3+} + 2\text{C.V.} \quad (5)$$

$$ZnO + Mg^{2+} \rightarrow Zn_{\triangle} + Mg^{2+} + \text{C.V.} \quad (6)$$

$Al(Fe^{3+})$ and $Al(Mg^{2+})$ are trivalent aluminium ions located in the positions of Fe^{3+} and Mg^{2+} of Fe_2O_3 and MgO lattices, respectively; C.V. and A.C. the created cationic and anionic vacancies, respectively; $Al_{\triangle}$ and $Zn_{\triangle}$ the trivalent aluminium ions and divalent zinc ions retained in interstitial positions in Fe_2O_3 and

MgO lattices (Eqs. (5) and (6)). Reactions (1)–(4) indicate the dissolution of Al^{3+} and Zn^{2+} cations in the lattices of Fe_2O_3 and MgO via substitution mechanism. All reactions followed by creation of cationic and anionic vacancies (reactions (2), (3), (5) and (6)) are expected to enhance the solid–solid interaction between the free oxides yielding $MgFe_2O_4$. The stimulation effect of the ferrite formation results mainly from an effective increase in the mobility of Fe^{3+} and Mg^{2+} cations through the produced ferrite film. However, most of the ZnO and Al_2O_3 dopants might dissolve in the lattices of Fe_2O_3 and MgO solids via substitution mechanism (Eqs. (1)–(4)). This speculation is based on geometric and structural characteristics of Fe_2O_3 and MgO solids [30]. The fact that ZnO and Al_2O_3 doping followed by precalcination at 700–1100 °C enhanced the formation of magnesium ferrite to an extent proportional to their amounts added suggested that most of the dopants added dissolved in the lattice of Fe_2O_3 and MgO with subsequent creation of cationic and anionic vacancies.

The speculated induced increase in the mobility of the reacted cations due to doping either with ZnO or Al_2O_3 as a result of creation of anionic and cationic vacancies could be investigated by the determination of the activation energy of formation of $MgFe_2O_4$ phase (ΔE_a) at temperatures between 700 and 1000 °C for pure and doped mixed solids. This has been tentatively achieved from the results given in Table 1, assuming that the height of the characterized diffraction line at 2.97 Å provides a measure of the amount of $MgFe_2O_4$ present in a given solid sample at a definite temperature (T). By plotting $\ln h$ of this line versus $1/T$, a straight line is obtained whose slope

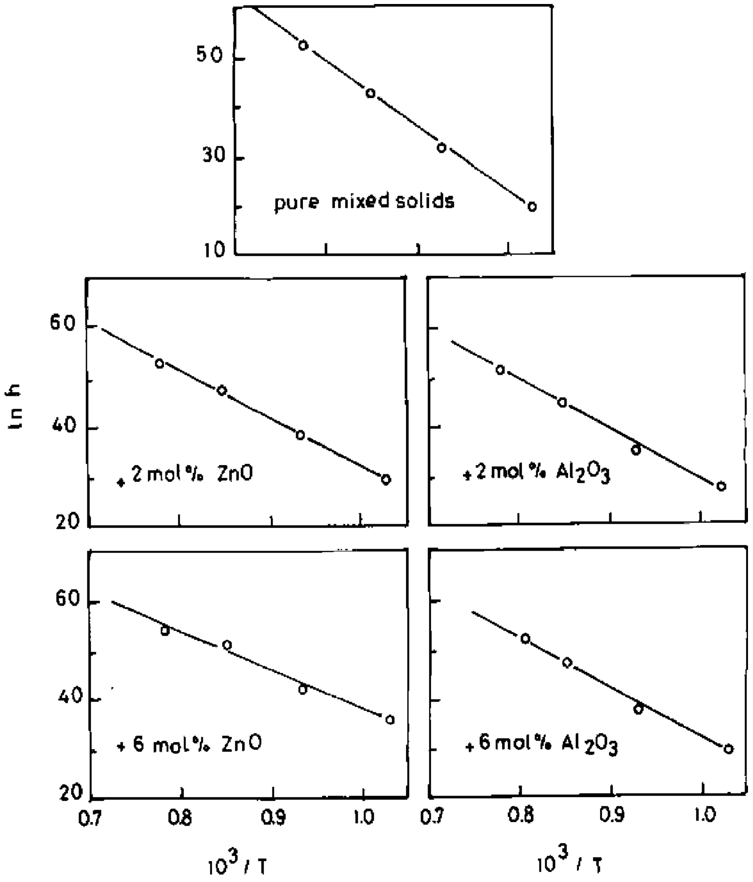

Fig. 4. Changes of ln peak height of diffraction line of $MgFe_2O_4$ (2.97 Å) as a function of $1/T$ for pure and doped mixed solids.

determines ΔE_a value by direct application of the Arrhenius equation. This test has been successfully done at 700, 800, 900 and 1000 °C and the obtained plots are given in Fig. 4 for pure and doped mixed solids. The computed ΔE_a values are 114, 78 and 62 kJ mol^{-1} for pure mixed solids and those doped with 2 and 6 mol% ZnO. The ΔE_a values for the samples doped with 2 and 6 mol% Al_2O_3 are 91 and 76 kJ mol^{-1}, respectively. This significant decrease in ΔE_a value due to the doping process showed clearly the role of ZnO and Al_2O_3 dopants in increasing effectively the mobility of the reacting cations. The computed ΔE_a values might suggest that ZnO-doping exhibited more enhancement effect towards the formation of $MgFe_2O_4$ than did Al_2O_3 dopant. This finding might show that ZnO dissolved in the lattices of MgO and Fe_2O_3 solids is more easier than Al_2O_3-dopant. This conclusion might find an evidence from a limited solubility of Al_2O_3 in the lattice of MgO due to a possible formation of $MgAl_2O_4$. This phase which has not been detected by XRD might exist in amorphous state and/or its amount was very small beyond the detection limit of X-ray diffractometer.

It has been reported in a recently published work by El-Shobaky et al. [23] that ΔE_a of $MgFe_2O_4$ formation was 203 kJ mol^{-1} instead of 113 kJ mol^{-1}, in the present work. This significant difference could point out to role of the nature of the employed chemicals influencing the ferrite formation. The employed magnesium basic carbonate and α-Fe_2O_3 in the published work were supplied by Fluka, while those used in the present study were supplied by Merck. It has been reported recently [23] that Li_2O-doping of MgO/Fe_2O_3 system much enhanced the $MgFe_2O_4$ formation to an extent proportional to the amount of dopant added. The addition of 6 mol% Li_2O decreased the activation energy of formation of $MgFe_2O_4$ from 203 to 61 kJ mol^{-1}. This considerable decrease in the value of ΔE_a had been attributed to an effective increase in the mobility of the reacting Mg^{2+} and Fe^{3+} cations. Li_2O-doping enhanced the thermal decomposition of $MgCO_3$ from 520 to 362 °C upon doping with 6 mol% lithia It has been also reported that doping of NiO/Fe_2O_3 system either with ZnO or Al_2O_3 enhanced the formation of $NiFe_2O_4$ [16,24]. The stimulation effect was, however, more pronounced in the case of ZnO-doping.

4. Conclusions

The main conclusions that may be derived from the obtained results are:

1. Treatment of equimolar proportion of magnesium basic carbonate and ferric oxide with small amounts of $Zn(NO_3)_2$ (2 and 6 mol%) or $Al(NO_3)_3$ (4 and 12 mol%) much enhanced the thermal decomposition of $MgCO_3$ into MgO which decreased from 520.6 to 382.8 and 375.7 °C in the case of pure mixed solids sample and those treated with 12 mol% aluminium nitrate and 6 mol% zinc nitrate, respectively. This finding, which showed that Al_2O_3 and ZnO dopants acted as reflux substrates, could be attributed to an effective increase in the mobility of Mg^{2+} cations in magnesium basic carbonate that undergoing a thermal decomposition.
2. MgO interacted readily with Fe_2O_3 at temperatures starting from 700 °C yielding $MgFe_2O_4$. The degree of propagation of $MgFe_2O_4$ formation increased as a function of precalcination temperature of the mixed solids investigated and also by increasing the amount of dopant oxides added.
3. Doping of MgO/Fe_2O_3 system either with ZnO or Al_2O_3 stimulated $MgFe_2O_4$ formation, the stimulation was, however, more pronounced in the case of zinc oxide treatment.
4. The addition of 6 mol% ZnO or 6 mol% Al_2O_3 to the system investigated followed by calcinations at 1100 °C for 5 h did not bring about the complete conversion of the reacted oxides into $MgFe_2O_4$. However, the portion of unreacted oxides decreased much by the doping process.
5. The computed values of activation energy of formation of magnesium ferrite were 114, 78 and 62 kJ mol^{-1} for pure mixed solids and those doped with 2 and 6 mol% ZnO, respectively, and were 91 and 76 kJ mol^{-1} for the mixed solids doped with 2 and 6 mol% Al_2O_3, respectively.
6. The promotion of ZnO and Al_2O_3 dopants towards the formation of magnesium ferrite might reflect an effective increase in the mobility of reacting Mg^{2+} and Fe^{3+} cations through the reacting oxides and produced ferrite due to creation of cationic and anionic vacancies in the lattices of doped MgO and Fe_2O_3.

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