ELSEVIER

Thermochimica Acta 380 (2001) 27–35

thermochimica acta

www.elsevier.com/locate/tca

Investigation of solid–solid interactions between pure and Li_2O-doped magnesium and ferric oxides

G.A. El-Shobaky[a,*], N.R.E. Radwan[b], F.M. Radwan[c]

[a]*Department of Physical Chemistry, National Research Centre, Dokki, Cairo, Egypt*
[b]*Department of Chemistry, Faculty of Education, Suez Canal University, Suez, Egypt*
[c]*Department of Chemistry, Faculty of Science, Suez Canal University, Ismailia, Egypt*

Received 20 February 2001; accepted 11 June 2001

Abstract

The solid–solid interactions between pure and lithium-doped magnesium and ferric oxides have been investigated using DTA and X-ray diffractograms (XRD) techniques. Equimolar proportions of basic magnesium carbonate and α-Fe_2O_3 were employed and lithium was added as lithium nitrate. The amounts of dopant were 0.75, 1.5, 3 and 6 mol% Li_2O.

The results obtained showed that the addition of small amounts of lithium nitrate to the reacting mixed solids much enhanced the thermal decomposition of magnesium carbonate to an extent proportional to its amount added. The addition of 12 mol% $LiNO_3$ decreased the decomposition temperature of $MgCO_3$ from 525.5 to 362°C. MgO underwent solid–solid interaction with Fe_2O_3 at temperatures starting from 800°C yielding $MgFe_2O_4$. The amount of ferrite produced increased when the precalcination temperature of the mixed solids was increased. However, the completion of this reaction required prolonged heating at elevated temperature >1100°C owing to the formation of $MgFe_2O_4$ phase which covered the surfaces of the grains of each solid, thus, hindering the diffusion of Mg^{2+} and Fe^{3+} ions. Doping with Li_2O much enhanced the solid–solid interaction between the mixed oxides to an extent proportional to the amount of Li_2O added leading to the formation of $MgFe_2O_4$ phase at temperatures starting from 700°C. The addition of 6 mol% Li_2O to the mixed solids followed by precalcination at 1050°C for 4 h resulted in complete conversion of the reacting oxides into magnesium ferrite. The promotion effect of Li_2O towards the ferrite formation was attributed to an effective increase in the mobility of the various reacting cations. The activation energy of formation (ΔE) of magnesium ferrite was determined for pure and variously doped solids and the values obtained were 203, 126, 95 and 61 kJ mol^{-1} for pure mixed solids and those treated with 1.5, 3 and 6 mol% Li_2O, respectively.

Keywords: $MgFe_2O_4$; Li_2O-doping; MgO; Fe_2O_3; Solid–solid interactions

1. Introduction

Ferrites, which are usually prepared by solid-state reactions [1–14], are important materials that can be used as catalysts and in microwave devices [15–20]. Transition metal ferrites, having a cubic structure have remarkable magnetic and semiconducting properties [7,21–25]. Magnesium, cobalt, nickel, copper zinc and manganese ferrites were normally employed as active catalysts in a big variety of catalytic reactions [26–38]. These reactions include oxidation, oxydehydrogenation, decomposition of alcohols and peroxide and decarboxylation of some organic acids [34–38].

---

[*] Corresponding author. Fax: +202-33700931.
E-mail address: elshobaky@yahoo.com (G.A. El-Shobaky).

PII: S0040-6031(01)00632-3

Solid–solid interactions between ferric oxide and transition metal oxides or carbonates to produce the corresponding ferrites are much influenced by the prehistory of parent solids, their ratio and also by addition of small amounts of certain foreign oxides [1–14]. In zinc ferrite formation [1–5], the reaction of ferric oxide sharply decreased if the temperature of its preparation exceeds 675°C because of sintering. The addition of small amounts of Li_2O or Al_2O_3 enhanced solid–solid interactions between Fe_2O_3 and NiO, Co_3O_4 and ZnO to yield the corresponding ferrites [9–12]. The mechanism of ferrite formation made the object of several investigations [1–14]. The solid–solid interactions between Fe_2O_3 and transition metal oxides were reported to be the diffusion of Fe_2O_3 and metal oxide through the initially formed ferrite layer acting as an energy barrier, thus, hindering their further diffusion. So, the completion of these solid-state reactions required prolonged heating at relatively elevated temperatures [9–14]. However, this energy barrier could be overcome by doping the reacting mixed solids with certain foreign oxide [9–12]. It has been reported that Li_2O doping (5 mol%) of Fe_2O_3/NiO system effected a decrease in the activation energy of formation (ΔE) of $NiFe_2O_4$ form 117 to 75 kJ mol^{-1}, Li_2O-treatment (3 mol%) of Fe_2O_3/Co_3O_4 led to a decrease in ΔE value of $CoFe_2O_4$ from 57 to 29 kJ mol^{-1} [9,10,13]. Similarly, Al_2O_3-doping (5 mol%) of Fe_2O_3/NiO decreased ΔE of $NiFe_2O_4$ from 117 to 82 kJ mol^{-1} [10] and doping of Fe_2O_3/ZnO with 6 mol% Al_2O_3 [14] effected a decrease in the ΔE of $ZnFe_2O_4$ formation from 73 to 57 kJ mol^{-1}.

The present work reports the results of a study on the effect of addition of small amounts of Li_2O on magnesium ferrite formation, at different temperatures. The techniques employed were DTA and X-ray diffractograms (XRD).

2. Experimental

2.1. Materials

Equimolar proportions of α-Fe_2O_3 and basic magnesium carbonate were well mixed to ensure the homogeneity of the powdered solids. The obtained sample was heated in air at temperatures between 700 and 1050°C for 4 h. Four doped mixed solid samples were obtained by treating a known mass of mixed solids the calculated amounts of lithium nitrate dissolved in the minimum amount of distilled water, dried at 100°C, then calcined in air at 700–1050°C. The concentration of lithium expressed as mol% Li_2O were 0.75, 1.5, 3 and 6. The chemicals employed in the present work were of analytical grade supplied by Fluka Company.

2.2. Techniques

DTA curves of pure and doped uncalcined mixed solid samples were determined using a PerkinElmer, seven series thermal analysis system. The rate of heating was kept at 10°C min^{-1} and the mass of solid specimen was 40 mg. The measurements were carried out in a current of nitrogen flowing at a rate of 50 cm^3 min^{-1}.

An X-ray investigation of pure and variously doped mixed solids, preheated in air at 700, 800, 900, 950, 1000 and 1050°C, was conducted using a Philips diffractometer (type PW 1390). 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° in 2θ per min.

3. Results and discussion

3.1. Thermal behavior of pure and doped mixed solids

TG and DTG investigation of the basic magnesium carbonate showed that its molecular formula could be given as follows:

$$MgCO_3Mg(OH)_2 \cdot 2.5H_2O$$

Fig. 1 depicts the DTA curves of pure and $LiNO_3$-doped uncalcined mixed solids (Fe_2O_3 and basic magnesium carbonate). The DTA curve of pure mixed solids consists of three endothermic peaks, the first and last one are sharp and strong and their maxima located at 285.4, 417.8 and 525.5°C. The first peak corresponds to dehydroxylation of basic magnesium carbonate yielding $MgCO_3$. The second and third peaks are indicative for the thermal decomposition of magnesium carbonate into magnesium oxide. The DTA curve of pure mixed solids did not include any

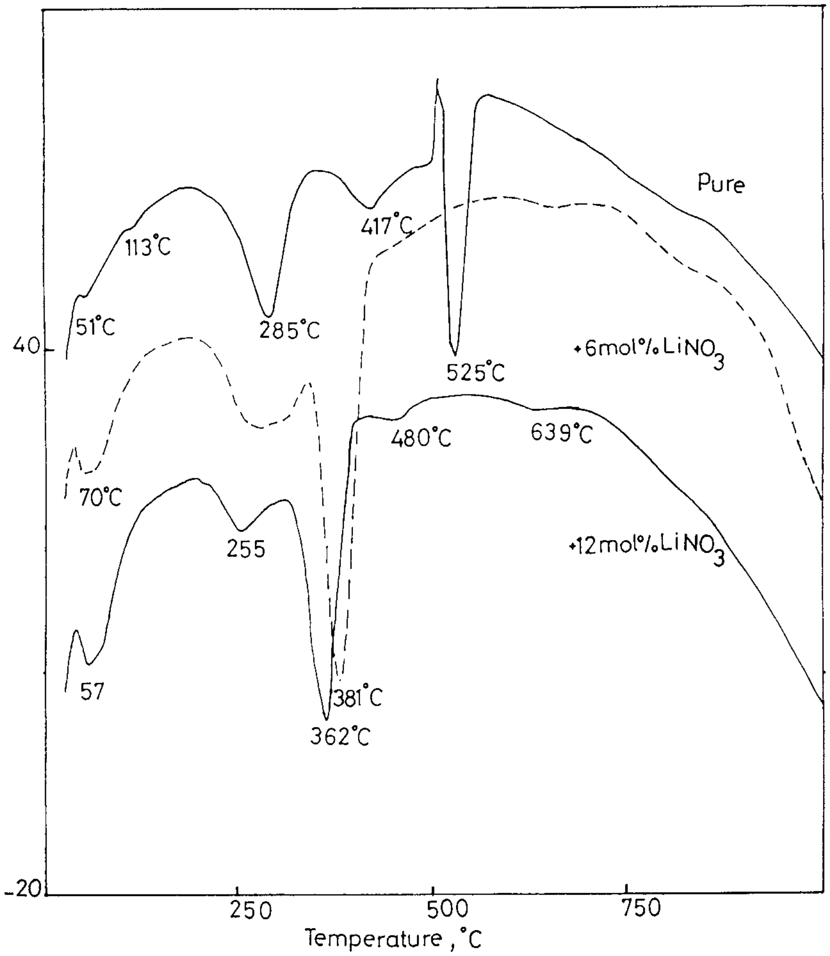

Fig. 1. DTA curves of pure and doped uncalcined mixed solids.

thermal peak in the temperature range 600–1000°C. However, a possible solid–solid interaction might take place between the produced MgO and the ferric oxide by heating at temperatures ranged between 600 and 1000°C with a very small rate that could not be easily detected by the employed DTA technique. The DTA curves of the two doped mixed solid samples consist of five endothermic peaks, the last two peaks are weak and broad. The maxima of these peaks were found at 57, 255–278, 362–380, 480 and 632–639°C. The first three peaks correspond to the thermal decomposition of basic magnesium carbonate into MgO. The comparison of DTA curves of pure and doped mixed solids revealed that lithium doping much enhanced the thermal decomposition of basic magnesium carbonate into magnesium oxide. The endothermic peak relative to thermal decomposition of magnesium carbonate was shifted from 525.5 to 382 and 362°C for the 6 and 12 mol% $LiNO_3$-treated mixed solids, respectively. These results which agree with those of weight loss measurements previously given in present work showed that lithium nitrate enhanced the thermal decomposition of basic magnesium carbonate to an extent proportional to its amount added. The endothermic peak at 480°C found in the DTA curve of the 6 mol% lithium nitrate-doped mixed solids sample might correspond to thermal decomposition of lithium nitrate yielding Li_2O [6]. The last endothermic peak in the DTA curves of doped mixed solids found at 632–638°C might characterize a solid–solid interaction between MgO and Fe_2O_3 producing magnesium–iron mixed solids. The identification of this or these compounds could be achieved by XRD analysis of the calcination products of pure and variously doped mixed solids.

3.2. X-ray investigation of pure and doped solids precalcined at 700–1050°C

The XRD were determined for pure and doped ferric oxide and magnesium carbonate mixtures precalcined at 700, 800, 900, 950, 1000 and 1050°C. The diffractograms of Fe_2O_3 and magnesium carbonate mixture preheated at 700°C not given, correspond to very well crystallized α-Fe_2O_3 and MgO phases. The diffractograms of pure and variously doped mixed solids precalcined at 700°C, not given, consisted of all the diffraction lines of well crystallized α-Fe_2O_3 phase and some lines of MgO and γ-Fe_2O_3 phases.

These results might indicate the absence of any appreciable solid–solid interaction between pure Fe_2O_3 and MgO being precalcined at 700°C. However, the addition of increasing amounts of Li_2O followed by precalcination at 700°C resulted in a progressive decrease in the intensity of the diffraction lines of unreacted α-Fe_2O_3. In fact, the peak height of the line

Table 1
The effects of precalcination temperature and doping on the height of some diffraction lines at '*d*' spacing of 2.69 Å (100% α-Fe_2O_3), 2.51 Å (100% $MgFe_2O_4$ and 50% α-Fe_2O_3)

Solids	Precalcination temperature (°C)	Peak height (a.u.)		Ratio between (*b*/*a*)
		2.69 Å (*a*)	2.51 Å (*b*)	
Pure MgO + Fe_2O_3	700	101	56	0.55
Pure MgO + Fe_2O_3 + 0.75 mol% Li_2O	700	82	60	0.73
Pure MgO + Fe_2O_3 + 1.5 mol% Li_2O	700	72	53	0.73
Pure MgO + Fe_2O_3 + 3 mol% Li_2O	700	72	53	0.73
Pure MgO + Fe_2O_3 + 6 mol% Li_2O	700	63	46	0.73
Pure MgO + Fe_2O_3	800	84	63	0.75
Pure MgO + Fe_2O_3 + 0.75 mol% Li_2O	800	77	60	0.78
Pure MgO + Fe_2O_3 + 1.5 mol% Li_2O	800	68	58	0.86
Pure MgO + Fe_2O_3 + 3 mol% Li_2O	800	68	62	0.91
Pure MgO + Fe_2O_3 + 6 mol% Li_2O	800	60	68	1.13
Pure MgO + Fe_2O_3	900	84	70	0.83
Pure MgO + Fe_2O_3 + 0.75 mol% Li_2O	900	75	78	1.04
Pure MgO + Fe_2O_3 + 1.5 mol% Li_2O	900	52	68	1.31
Pure MgO + Fe_2O_3 + 3 mol% Li_2O	900	50	90	1.80
Pure MgO + Fe_2O_3 + 6 mol% Li_2O	900	38	110	2.90
Pure MgO + Fe_2O_3	950	100	85	0.85
Pure MgO + Fe_2O_3 + 0.75 mol% Li_2O	950	78	123	1.58
Pure MgO + Fe_2O_3 + 1.5 mol% Li_2O	950	65	96	1.48
Pure MgO + Fe_2O_3 + 3 mol% Li_2O	950	60	120	2.00
Pure MgO + Fe_2O_3 + 6 mol% Li_2O	950	28	101	3.62
Pure MgO + Fe_2O_3	1000	55	100	1.82
Pure MgO + Fe_2O_3 + 0.75 mol% Li_2O	1000	37	130	3.51
Pure MgO + Fe_2O_3 + 1.5 mol% Li_2O	1000	32	128	4.00
Pure MgO + Fe_2O_3 + 3 mol% Li_2O	1000	24	139	5.80
Pure MgO + Fe_2O_3 + 6 mol% Li_2O	1000	5	158	31.6
Pure MgO + Fe_2O_3	1050	75	117	1.56
Pure MgO + Fe_2O_3 + 0.75 mol% Li_2O	1050	32	164	5.12
Pure MgO + Fe_2O_3 + 1.5 mol% Li_2O	1050	39	179	4.60
Pure MgO + Fe_2O_3 + 3 mol% Li_2O	1050	20	145	7.25
Pure MgO + Fe_2O_3 + 6 mol% Li_2O	1050	0	157	∞

at 2.69 Å (100% α-Fe_2O_3 phase) decreased from 101 to 63 a.u. upon the addition of 6 mol% Li_2O (cf. Table 1). Furthermore, the ratio between the relative intensity of the diffraction lines at 2.51 Å (common line for α-Fe_2O_3 50%, and low-temperature $MgFe_2O_4$ 100%) and 2.69 Å (100% α-Fe_2O_3 [39]) increased from 55 to 73% due to the addition of the least amount of Li_2O (0.75 mol%). These findings might suggest that Li_2O-treatment of MgO and Fe_2O_3 followed by precalcination at 700°C resulted in the formation of a small amount of the $MgFe_2O_4$ phase.

Figs. 2 and 3 depict the diffractograms of pure and variously doped mixed solids precalcined at 800 and 1000°C. It is seen from Fig. 2 that the diffractograms of pure mixed solids sample and those treated with 0.75 mol% Li_2O followed by precalcination at 800°C consisted of α-Fe_2O_3, γ-Fe_2O_3 and MgO phase, similar to all investigated mixed solids precalcined at 700°C. On the other hand, a new diffraction line at 2.96 Å appeared in the patterns of the other doped (0.75–6% Li_2O) mixed solids preheated at 800°C. This line at 2.96 Å characterizes $MgFe_2O_4$ (40%) [39]. The area of the diffraction peak at '*d*' spacing of 2.96 Å increased by increasing the amount of Li_2O added (cf. Fig. 2). It is clear from Tables 1 and 2 that the increase in both the precalcination temperature of various investigated mixed solids in the range of 900–1050°C and the amount of lithia added much enhanced the solid–solid interaction between MgO and Fe_2O_3 yielding $MgFe_2O_4$ as indicated form the progressive increase in the intensity of the diffraction lines of $MgFe_2O_4$ with subsequent decrease in the intensity of the lines of free oxides. The addition of 6 mol% Li_2O to magnesium oxides and ferric oxide mixed solids followed by precalcination at 1050°C for 4 h resulted in their complete conversion into $MgFe_2O_4$. Preliminary experiments showed that the prolonged heating of pure mixed oxide solids at 1050°C for 24 h brought about a partial conversion of the mixed solids into magnesium ferrite. The XRD analysis of such mixed solids sample revealed the presence of significant portion of unreacted α-Fe_2O_3 phase.

The role of precalcination temperature and treatment with small amounts of Li_2O in the solid–solid

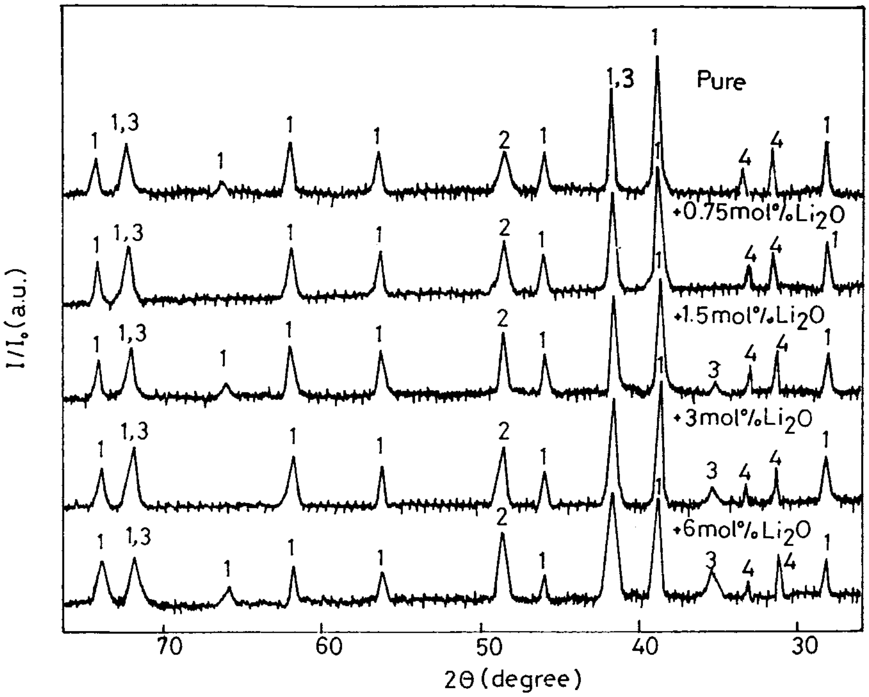

Fig. 2. XRD diffractograms of pure and variously doped mixed solids precalcined at 800°C, lines 1–4 refer to α-Fe_2O_3, MgO, $MgFe_2O_4$ and γ-Fe_2O_3, respectively.

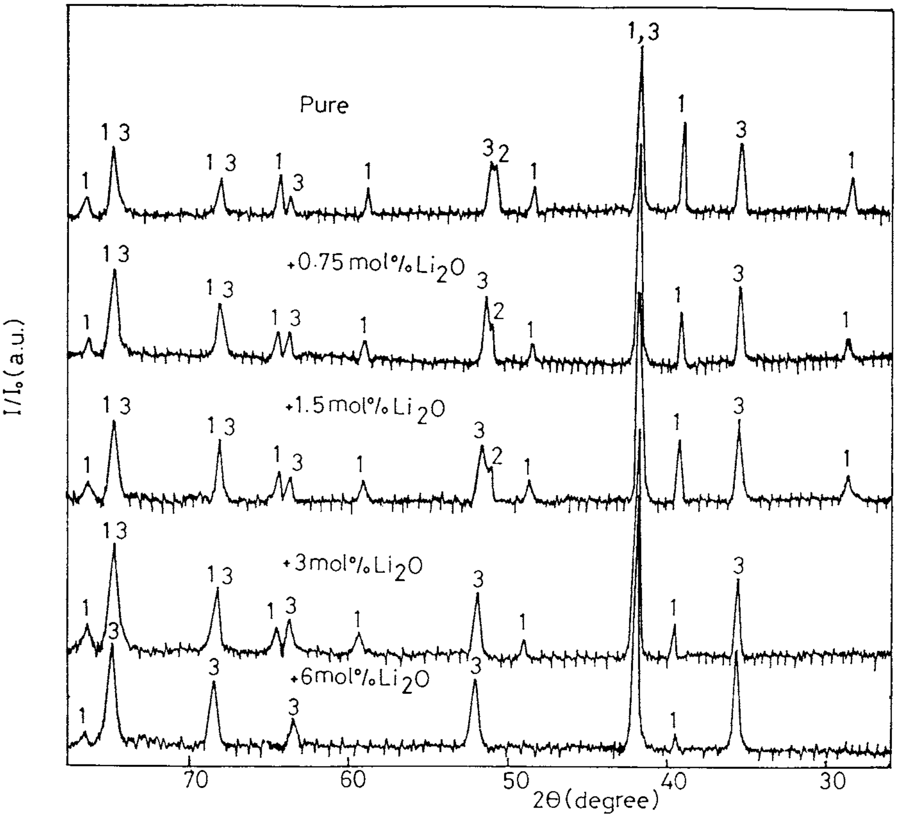

Fig. 3. XRD diffractograms of pure and variously doped mixed solids precalcined at 1000°C, lines 1–4 refer to α-Fe_2O_3, MgO, $MgFe_2O_4$ and γ-Fe_2O_3, respectively.

interaction between Fe_2O_3 and MgO producing magnesium ferrite is better investigated by measuring the height of certain diffraction lines characteristic for α-Fe_2O_3 and one of the common lines relative to both $MgFe_2O_4$ and α-Fe_2O_3 phases. This was done and the results obtained are given in Table 1. Inspection of this Table revealed that: (i) the ratio (*R*) between the peak height of the lines at '*d*' spacing of 2.51 and 2.69 Å for pure mixed oxides precalcined at 700°C is 0.55 which is very close to that of pure α-Fe_2O_3 (0.50). This indicates absence of the $MgFe_2O_4$ phase. (ii) The addition of small amounts of Li_2O followed by precalcination at 700°C led to a measurable increase in the value of *R* with subsequent decrease in peak height of line at 2.69 Å relative to the unreacted α-Fe_2O_3 phase. This finding suggests the enhancement of $MgFe_2O_4$ formation due to Li_2O treatment at 700°C. (iii) The increase in the temperature of heat treatment of various solids investigated in the range of 700–1050°C resulted in progressive increase in the value of *R* indicating a progressive increase in the extent of produced $MgFe_2O_4$ phase. (iv) The increase in the amount of Li_2O added to mixed solids precalcined at various temperatures between 800 and 1050°C brought about a progressive increase in the value of *R* with subsequent progressive decrease in the height of the line at '*d*' spacing of 2.69 Å. (v) The addition of 6 mol% Li_2O to mixed solids precalcined at 1050°C for 4 h resulted in the complete disappearance of all diffraction lines of unreacted α-Fe_2O_3 phase and its complete conversion into $MgFe_2O_4$ phase.

The stimulation effects of Li_2O towards the formation of Ni, Co, Zn and copper ferrites have been reported [9–14]. The treatment NiO/Fe_2O_3, Co_3O_4/Fe_2O_3 and ZnO/Fe_2O_3 solids with small amounts of

Table 2
The effects of Li_2O-doping and precalcination temperature on the height of selected diffraction line at '*d*' spacing of 2.96 Å

Solids	Precalcination temperature (°C)	Peak height (a.u.) 2.96 Å (40% $MgFe_2O_4$)
Pure $MgO + Fe_2O_3$	900	8
Pure $MgO + Fe_2O_3 + 0.75$ mol% Li_2O	900	16
Pure $MgO + Fe_2O_3 + 1.5$ mol% Li_2O	900	24
Pure $MgO + Fe_2O_3 + 3$ mol% Li_2O	900	28
Pure $MgO + Fe_2O_3 + 6$ mol% Li_2O	900	38
Pure $MgO + Fe_2O_3$	950	20
Pure $MgO + Fe_2O_3 + 0.75$ mol% Li_2O	950	30
Pure $MgO + Fe_2O_3 + 1.5$ mol% Li_2O	950	37
Pure $MgO + Fe_2O_3 + 3$ mol% Li_2O	950	40
Pure $MgO + Fe_2O_3 + 6$ mol% Li_2O	950	50
Pure $MgO + Fe_2O_3$	1000	44
Pure $MgO + Fe_2O_3 + 0.75$ mol% Li_2O	1000	48
Pure $MgO + Fe_2O_3 + 1.5$ mol% Li_2O	1000	50
Pure $MgO + Fe_2O_3 + 3$ mol% Li_2O	1000	53
Pure $MgO + Fe_2O_3 + 6$ mol% Li_2O	1000	59
Pure $MgO + Fe_2O_3$	1050	40
Pure $MgO + Fe_2O_3 + 0.75$ mol% Li_2O	1050	50
Pure $MgO + Fe_2O_3 + 1.5$ mol% Li_2O	1050	63
Pure $MgO + Fe_2O_3 + 3$ mol% Li_2O	1050	68
Pure $MgO + Fe_2O_3 + 6$ mol% Li_2O	1050	75

Li_2O enhanced the formation of nickel, cobalt, and zinc ferrites and led, also, to the formation of β-lithium ferrite β-$LiFeO_2$ [6,10].

Fe_2O_3 and MgO undergo a solid–solid interaction to produce $MgFe_2O_4$ that covers the grains of each reacting oxide [9–12]. The propagation of this reaction is controlled by the thermal diffusion of magnesium and iron cations through the ferrite film, which acts as an energy barrier. The fact that free Fe_2O_3 and MgO phase were detected in pure mixed solids precalcined at 1050°C for 4 and 24 h, gives an indication of the height of the energy barrier which has to be overcome. Similar results have been reported in the case of NiO/Fe_2O_3 system doped with Li_2O [9,10]. Although lithia stimulated $NiFe_2O_4$ formation was incapable of effecting a complete conversion of the reacting oxides into nickel ferrite even by precalcination at 1100°C [6,9–12], this is considered as a special case for Li_2O dopant because of the big solubility of lithia in NiO lattice, which dissolves more than 16 mol% Li_2O. This process increased much the mobility of nickel cations, facilitating, thus, the $NiFe_2O_4$ formation, but effected the conversion of some of Ni^{2+} into Ni^{3+} ions which did not contribute to the ferrite formation. The observed enhancement of $MgFe_2O_4$ formation due to doping with lithium oxide may be a consequence of an effective increase in the mobility of Mg^{2+} and Fe^{3+} cations. In contrast with the case of NiO/Fe_2O_3, Co_3O_4/Fe_2O_3, ZnO/Fe_2O_3 systems [6,9–12], Li_2O-doping of MgO/Fe_2O_3 solids did not effect in the formation of lithium ferrite. In other words, all the lithia added dissolved completely 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 [40] in the following manner:

$$Li_2O \rightarrow 2Li(Mg^{2+}) + AV \tag{1}$$

$$Li_2O + 2Mg^{2+} \rightarrow 2Li^+ + CV \tag{2}$$

$$\tfrac{1}{2}Li_2O \rightarrow Li(Fe^{3+}) + AV \tag{3}$$

$$Li_2O + 2Fe^{3+} \rightarrow 2Li^+ + 2Fe^{2+} + \tfrac{1}{2}O_{2(g)} \tag{4}$$

$Li(Mg^{2+})$, $Li(Fe^{3+})$ are monovalent lithium ions located in the positions of host cations Mg^{2+} and Fe^{3+} of MgO and Fe_2O_3 lattices, AV and CV are created anionic and cationic vacancies, Li^+ is monovalent lithium ion retained in interstitial positions in

MgO and Fe_2O_3 lattices. Reactions 1 and 3 indicate that the dissolution of $2Li^+$ ions in the lattice of MgO and Li^+ ion in the lattice of Fe_2O_3 is followed by creation of one anionic vacancy in each doped solid.

The location of Li^+ ions in interstitial positions of MgO lattice is accompanied by creation of cationic vacancies, one vacancy per each $2Li^+$ dissolved in MgO according to reaction 2. Dissolution of Li^+ ions in Fe_2O_3 according to reaction 4 is followed by transformation of some of Fe^{3+} into Fe^{2+} ions. The dissolution of lithium oxide in the lattices of MgO and Fe_2O_3 according to reactions 1–3 is expected to be accompanied by an increase in the mobility of Mg^{2+} and Fe^{3+} cations due to creation of anionic and cationic vacancies. On the other hand, incorporation of Li_2O in the lattice of Fe_2O_3 according to reaction 4 did not favor the formation of magnesium ferrite because of transformation of some of Fe^{3+} into Fe^{2+} cations, which did not contribute in $MgFe_2O_4$ formation. The fact that Li_2O-doping followed by precalcination at 700–1050°C enhanced the formation of magnesium ferrite formation to an extent proportional to its amount added suggested that most of the dopant added is dissolved in MgO and Fe_2O_3 according to reactions 1–3. The speculated induced increase in the mobility of the reacted cations due to treatment with Li_2O 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) at temperatures between 900 and 1000°C for pure and doped mixed solids. This has been tentatively achieved from the results given in Table 2, assuming that the height of the characterized diffraction line at 2.96 Å provides a measure of the amount of $MgFe_2O_4$ present in a given solid sample at a definite temperature (T). By plotting the peak height of this line versus $1/T$, a straight line is obtained whose slope determines ΔE value by direct application of the Arrhenius equation. This test has been successfully done at 900, 950 and 1000°C and the obtained plots are given in Fig. 4 for pure and variously doped mixed solids. The computed ΔE values are 203, 126, 95 and 61 kJ mol^{-1} for pure mixed solids sample and those doped with 0.75, 1.5 and 6 mol% Li_2O, respectively. This considerable decrease in ΔE value due to the doping process reflects clearly the role of Li_2O-treatment in increasing effectively the mobility of the reacting cations.

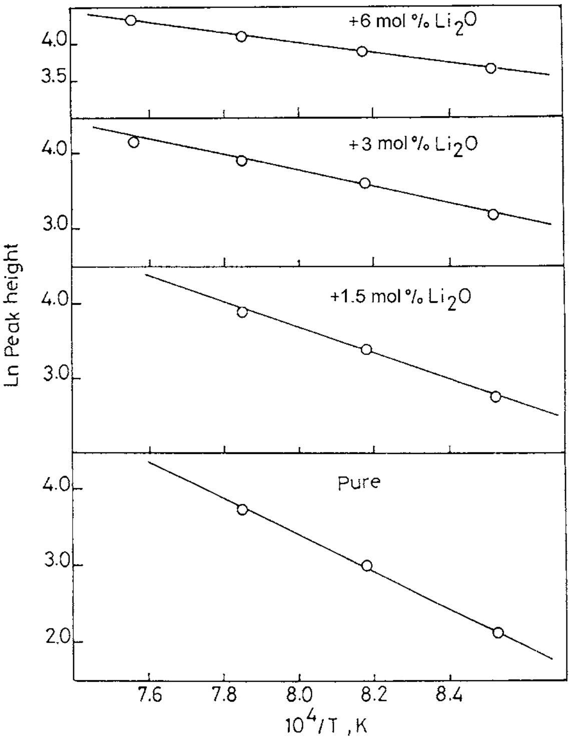

Fig. 4. Change of ln peak height of the diffraction line of $MgFe_2O_4$ (2.96 Å) as a function of precalcination temperature for pure and Li_2O-doped mixed solids.

4. Conclusions

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

1. Treatment of equimolar proportion of basic magnesium carbonate and ferric oxide with small amounts of $LiNO_3$ (1.5–12.0 mol%) much enhanced the thermal decomposition of $MgCO_3$ to an extent proportional to its amount added. The addition of 6 mol% lithium nitrate decreased the decomposition-temperature of $MgCO_3$ from 525.5 to 362°C.
2. MgO interacted with Fe_2O_3 at temperatures starting from 800°C yielding $MgFe_2O_4$. The prolonged heating of pure mixed solids at 1050°C for 24 h effected the partial conversion of the reacting oxides into the ferrite phase.
3. Li_2O-doping of MgO and Fe_2O_3 mixed solids followed by precalcination at temperatures starting

from 700°C resulted in an enhanced formation of $MgFe_2O_4$ phase. The stimulation effect of $MgFe_2O_4$ formation due to treatment with small amounts of Li_2O was increased by increasing its amount added.

4. The addition of a very small amount of Li_2O (0.75 mol%) followed by precalcination at 1050°C for 4 h brought about the conversion of most of reacting oxides into $MgFe_2O_4$ phase.
5. The computed values of activation energy of formation of magnesium ferrite were 203, 126, 95 and 61 kJ mol^{-1} for pure mixed solid samples and those doped with 0.75, 1.5 and 6 mol% Li_2O, respectively.

References

[1] D.W. Hopkins, J. Electrochem. Soc. 96 (1949) 195.

[2] G.A. Kolta, S.Z. El-Tawil, A.A. Ibrahim, N.S. Felix, Thermochim. Acta 39 (1980) 359.

[3] A. Feltz, M. Martin, Mater. Sci. Non-Org. React. Solids 28A (1985) 137

[4] R.K. Tami, K.K. Kamada, T. Ishci, React. Solids 1 (1986) 309.

[5] F.J.C. Toolenaar, J. Mater. Sci. 24 (1989) 1089.

[6] G.A. El Shobaky, F.H.A. Abdalla, A.A. Fouad Zikry, Thermochim. Acta 289 (1996) 81.

[7] M. Crisan, D. Crisan, Mater. Sci. Monogr. (Ceram. Powder) (1983) 429.

[8] G.A. El-Shobaky, A.A. Ibrahim, S. El-Defrawy, Thermochim. Acta 131 (1988) 115.

[9] G.A. El-Shobaky, A.A. Ibrahim, Thermochim. Acta 132 (1988) 117.

[10] G.A. El-Shobaky, A.A. Ibrahim, Bull. Soc. Chim. France (1989) 34.

[11] G.A. El-Shobaky, A.N. Al-Noaimi, A. Abd El-Aal, A.M. Ghozza, Mater. Lett. 2 (1995) 39.

[12] G.A. El-Shobaky, G.A. Fagal, A. Abd El-Aal, A.M. Ghozza, Thermochim. Acta 256 (1995) 429.

[13] G.A. El-Shobaky, F.H.A. Abdalla, A.M. Ghozza, Thermochim. Acta 292 (1997) 123.

[14] H.G. El-Shobaky, Thermochim. Acta 343 (2000) 145.

[15] A.A. Said, E.A. Hassan, A.M. El-Awad, K.M. Salaam, M.M. El-Wahad, J. De Phys. IV IP (1997) 687.

[16] L. Jianjun, L. Gongxuan, H. Hongliang, T.J. Tao, X. Kang, Electrochim. Acta 41 (17) (1996) 1049.

[17] H. Armendariz, G. Aguilar, P. Sales, M. Valenzuela, I. Schifter, H. Arriola, H. Nava, Appl. Catal. 92 (1) (1992) 29.

[18] T. Mimani, P. Rauindranathan, K.C. Patil, Chem. Sci. 99 (4) (1987) 209.

[19] T. Masahiron, A. Kazuhiri, N. Ken, M. Keisuke, Y. Takashi, T. Masamichi, T. Yutka, J. Mater. Sci. 28 (24) (1993) 6753.

[20] X. Peiuo, G. Xiongyi, D. Yingchum, J. East Chin. Inst. Chem. Technol. 16 (6) (1996) 706.

[21] P. Pascal, Nouveau Triate de Chimie Minerale, Tome II, Masson, Paris, 1996, p. 702.

[22] V.V. Valkov, A. Deneva, D. Stavrakeva, in: Proceedings of the Seventh International Congress on Chemical Ceramics, Vol. 3, Paris, France, 1980, pp. V/98–V/101.

[23] L.M. Letyuk, M.N. Shipko, V.S. Tikhonov, M.V. Dimetriev, Izv. Akad. Nauk SSSR; Neorg. Mater. 18 (1980) 1751.

[24] T. Mitev, T. Dimova, G. Khristova, Bulg. Sklar. Keram. 32 (8) (1982) 207.

[25] M.S. Selim, G. Turky, M. Shouman, G.A. El-Shobaky, Solid-State Ionics 120 (1999) 173.

[26] G. Busca, E. Finocchio, V. Lorenzelli, M. Trombetta, S.A. Rossini, J. Chem. Soc., Faraday Trans. 92 (23) (1996) 4687.

[27] M. Zhang, R. Lan, J. Liu, X. Chen, W. Zhou, J. Chem. Soc., Faraday Trans. 88 (4) (1992) 637.

[28] J. Johan, A.J. Van Dillen, J.W. Geus, J. Chem. Soc., Faraday Trans. 87 (10) (1991) 1623.

[29] B.S. Randhawa, S. Kaur, P.S. Bassi, Indian J. Chem. A 28 (6) (1989) 463.

[30] L. Dong, Z. Liu, Y. Hu, B. Xu, Y. Chen, J. Chem. Soc., Faraday Trans. 94 (19) (1998) 3033.

[31] N.J. Jebarathinam, M. Eswaramoorthy, V. Krishnasamy, Bull. Chem. Soc. Jpn. 67 (12) (1994) 3334.

[32] P. Lahiri, S. Sengupta, Can. J. Chem. 69 (1) (1991) 33.

[33] P. Lahiri, S. Sengupta, J. Chem. Soc., Faraday Trans. 91 (19) (1995) 3489.

[34] N.K. Singh, S.K. Tiwari, K.L. Anitha, R.N. Singh, J. Chem. Soc., Faraday Trans. 92 (13) (1996).

[35] J. Miki, M. Asanuma, Y. Tachibana, T. Shikada, J. Catal. 151 (2) (1995) 323.

[36] K.P. Tikhomolova, I.B. Dmitrieva, M.V. Ivanova, Russ. J. Appl. Chem. 71 (4) (1998) 550.

[37] G.R. Dube, V.S. Darshane, Bull. Chem. Soc. Jpn. 64 (8) (1991) 2449.

[38] S. Rajadurai, J.C. Kuriacose, Indian J. Chem. A 26 (7) (1987) 384.

[39] Powder Diffraction File (JCPDS), International Centre for Diffraction Data, Swarthmore, PA, 1979.

[40] F.A. Kroger, Chemistry of Imperfect Crystals, North-Holland, Amsterdam, 1964.