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Solid–solid interaction between ferric oxide and manganese carbonate as influenced by lithium oxide doping

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Abstract

The solid–solid interaction between pure and lithia-doped manganese and ferric oxides have been investigated using DTA and XRD techniques. Equimolar proportions of manganese carbonate and ferric oxide were employed, while the dopant substrate was added as lithium nitrate. The amounts of dopant were 0.89, 1.68 and 3.36 mol% Li_2O.

The results obtained revealed that the thermal treatment of manganese carbonate and ferric oxide at 800°C resulted in the formation of Mn_2O_3 (Partridgeite) and α-Fe_2O_3 phases having an excellent degree of crystallinity. Solid–solid interaction took place between the produced oxides at temperatures starting from 900°C yielding $MnFe_2O_4$ (Jacobsite). The degree of propagation of this reaction was found to increase by increasing both the precalcination temperature and the amount of Li_2O added. The progressive increase in the height of the diffraction line of $MnFe_2O_4$ at "d" spacing of 2.56 Å (100%) as a function of precalcination temperature for pure and variously doped mixed solids was utilized in the determination of activation energy of formation of manganese ferrite (ΔE). The computed ΔE values were 174, 153, 134 and 117 kJ mol^{-1} for pure mixed solids and those doped with 0.84, 1.68 and 3.36 mol% Li_2O. These results were discussed in terms of dissolution of lithium cations in the lattices of Fe_2O_3 and Mn_2O_3 solids with subsequent increase in the mobility of the reacting ferric and manganese cations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $MnFe_2O_4$; Li_2O-doping; Mobility

1. Introduction

Ferrospinels, which form an important class of compounds having the general formula $M^{II}[Fe^{III}Fe^{III}]O_4$, find with application in both the technological and the catalytic fields [1–5]. Based on the distributions of cations, among the tetrahedral (T) and octahedral (O) sites of the coordinated oxygen, spinels can be either normal M_{tet}^{2+} $[Fe^{3+}Fe^{3+}]_{oct.}O_4$ or inverse with half of the trivalent ions in the T-position and the other half together with divalent ions in the O-sites.

Fe/Mn mixed oxides have attracted much interest and have been studied in detail by number of workers [6–10]. The manganese ferrite is nearly normal spinel about 80% manganese ions occupy T-sites, these ions are Mn^{2+} ions [11]. However, in the octahedral sites (O-sites) Mn^{3+} ions occur which are connected by the presence of Fe^{2+} ions on these sites [12], so the cation distribution can be represented by $[Mn_{0.8}{}^{2+}Fe_{0.2}{}^{3+}]_{tet.}$ $[Mn_{0.2}{}^{3+}Fe_{0.2}{}^{2+}Fe_{1.6}{}^{3+}]_{oct.}O_4$ and the carriers are created by the following reaction of electron exchange on octahedral sites: $Mn^{2+} + Fe^{3+} = Mn^{3+} + Fe^{2+}$. Even if reduction of Fe^{3+} to Fe^{2+} occurs, the lattice

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configuration remains unaltered, and upon reoxidation, the original state can be regained. Several authors have reported that the major influence in the activity comes from the O-ions, probably due to the exposure of these ions on the surface, as revealed by Jacobs et al. [13] using LEIS measurements (low energy ion scattering, a technique which is sensitive to the outermost atomic layer).

Mixed ferrites are usually employed due to their remarkable magnetic and semiconducting properties [14–17]. These properties depend, mainly, on the chemical composition, calcination temperature, structure and surface properties of the Fe_2O_3 used and the addition of small amount of certain foreign oxides [18]. The solid–solid interaction between Fe_2O_3 and various transition metal oxides as influenced by doping with a certain foreign cations such as Li^{2+}, Zn^{2+} and Al^{3+} [19–24]. It has been shown that Li-, Zn- or Al-doping enhanced the ferrites formation by increasing the mobility of thermal diffusion of reacting cations through the early formed ferrite film.

The present work reports a study of the effect of addition of small amounts of Li_2O on solid–solid interaction between ferric oxide and manganese carbonate at different temperatures. The techniques employed were DTA and X-ray diffraction.

2. Experimental

2.1. Materials

Pure mixed solids were obtained by mixing equimolar proportions of finely powdered α-Fe_2O_3 and manganese carbonate. The specimens of doped mixed solids were prepared by treating a given mass of the prepared mixed solids with solutions containing different proportions of lithium nitrate. The extent of the dopant agent, expressed in mol% Li_2O, was 0.84, 1.68 and 3.36. The obtained solids, pure and doped, were dried at 100°C, then fired in air at 800, 900, 1000 and 1100°C for 6 h. All the chemicals used were of analytical grade supplied by Fluka company.

2.2. Techniques

Differential thermal analysis (DTA) of the different samples was carried out using Perkin-Elmer thermal analysis apparatus. A 40 mg solid specimen was taken in each experiment, the rate of heating was kept at $10°C\ min^{-1}$.

An X-ray investigation of the thermal products of the various solids was carried out a Philips diffractometer (type PW 1390). The patterns were run with iron without filter radiation ($\lambda = 1.9373$ Å) at 36 kV and 16 mA with scanning speed in 2θ of $2°\ min^{-1}$.

3. Results

3.1. Thermal behavior of pure and lithia-doped manganese carbonate and ferric oxide

Fig. 1 represents DTA curves of $MnCO_3$, pure and doped $MnCO_3/Fe_2O_3$ mixed solids. The amounts of lithium nitrate were 3.68 and 6.72 mol% (1.84 and 3.36 mol% Li_2O). This figure shows that DTA curves consist of five sets of endothermic peaks located at 60, 280, 450, 530 and 850°C. The first sets of peaks correspond to desorption of physisorbed water. The second sets of peaks indicate dehydroxylation of structural water from manganese carbonate. The third and fourth sets of peaks are indicative for thermal decomposition of $MnCO_3$ to MnO_2 and transformation of MnO_2 to Mn_2O_3, respectively. The fifth peak in case of pure $MnCO_3$ corresponds to the conversion of Mn_2O_3 to Mn_3O_4. However, the fifth sets of peaks for pure and doped mixed solids might characterize solid–solid interactions between the thermal products of manganese/iron mixed solids and/or phase transformation process of one of the produced product. This will be confirmed later by XRD measurements.

Since the weight of pure and doped mixed solids was constant in each run, the area of each endothermic peak for each solid could be regarded as a measure of the amount of solid undergoing a chemical change. Comparison of the thermal curves of the various investigated mixed solids given in Fig. 1 reveals that: (i) The presence of α-Fe_2O_3 together with $MnCO_3$ does not modify the thermal stability of $MnCO_3$ simply because all endothermic peaks of pure $MnCO_3$ and $MnCO_3/Fe_2O_3$ mixed solids are similar to each other except the last one which is relatively weak and broad. (ii) The presence of α-Fe_2O_3 in case of mixed solids led to partial transformation of Mn_2O_3 to Mn_3O_4 simply because the area of peak at 850°C

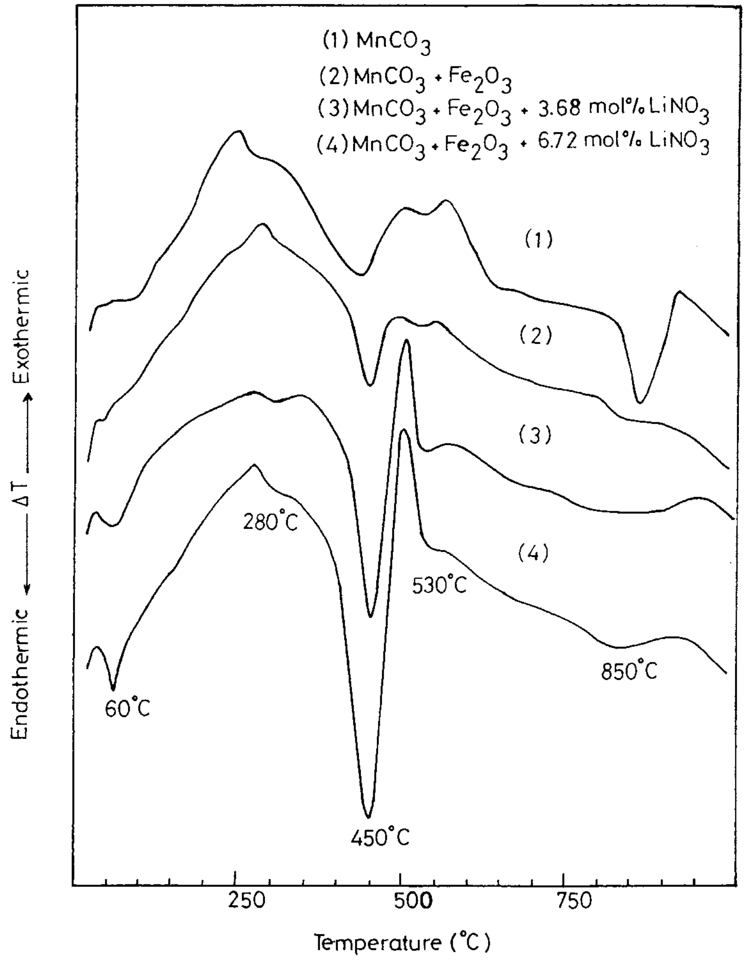

Fig. 1. DTA curves of $MnCO_3$, pure and $LiNO_3$-doped $MnCO_3/Fe_2O_3$ mixed solids.

for pure mixed solids decreased in presence of α-Fe_2O_3 indicating solid–solid interaction between the thermal products of manganese/iron mixed solids. This will be confirmed later by XRD investigation. (iii) The presence of lithium nitrate resulted in an increase in the amount of physisorbed water and a decrease in the thermal stability of $MnCO_3$ depending on the increase in areas of the first and third sets of peaks. The identification of the phases produced will be confirmed later in this work by X-ray investigation.

3.2. XRD investigation of various solids

X-ray diffractograms of pure and doped mixed solids precalcined at various temperatures were determined. The results obtained showed that pure mixed solids preheated at 800°C consist entirely of Mn_2O_3 (Partridgeite) and α-Fe_2O_3 phases that have an excellent degree of crystallinity. This indicates the absence of any appreciable solid–solid interaction between Mn_2O_3 and Fe_2O_3. Raising the calcination temperature to 900°C resulted in the appearance of new diffraction lines characterizing of $MnFe_2O_4$ (Jacobsite) phase together with all diffraction lines of free Mn_2O_3 (Partridgeite) and α-Fe_2O_3. However, the rise in calcination temperature ranged between 900–1100°C brought about a progressive increase in the peak height of the lines relative to $MnFe_2O_4$ phase with subsequent decrease in the peak height of unreacted Mn_2O_3 and Fe_2O_3.

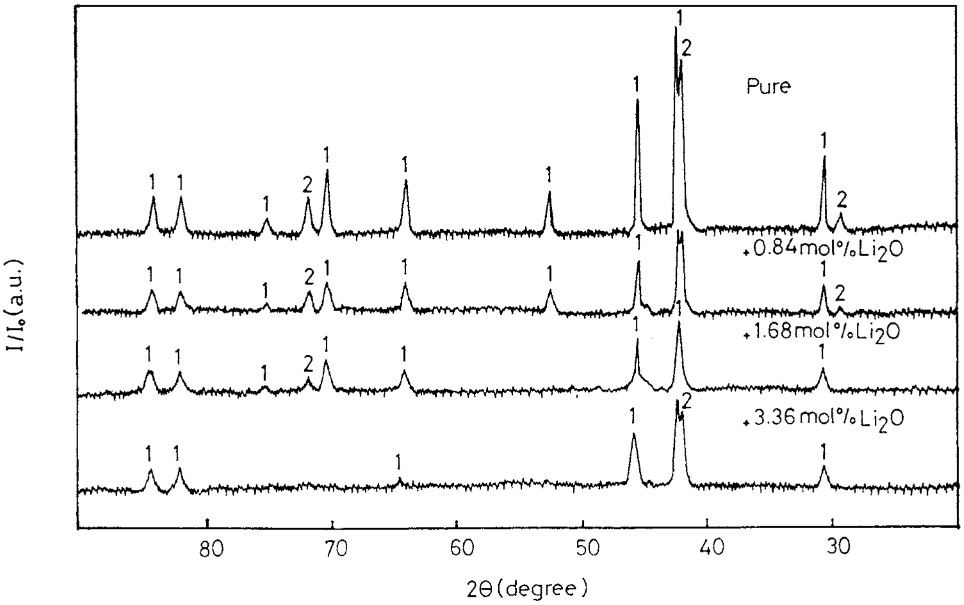

Fig. 2. X-ray diffractograms of Mn/Fe mixed oxide solids precalcined at 800°C. Lines (1) α-Fe_2O_3 and (2) Mn_2O_3 (Partridgeite).

Figs. 2–5 represent X-ray diffractograms of pure and doped mixed solids preheated at 800, 900, 1000 and 1100°C. It is seen from Fig. 2 that pure and doped mixed solids heated at 800°C consist of Mn_2O_3 (Partidgeite) and α-Fe_2O_3 phases. However, the relative intensity of the diffraction lines relative to these phases decreases on increasing the amount of lithium oxide present.

Figs. 3–5 include XRD results of pure and doped mixed solids precalcined at 900, 1000 and 1100°C. These figures show that pure and doped solids heated at 900, 1000 and 1100°C consist of α-Fe_2O_3, Mn_2O_3 and $MnFe_2O_4$. Inspection of these figures shows that the presence of Li_2O enhances the ferrite formation to an extent proportional to its amount present. This conclusion comes from the fact that Li_2O-doping brought about a progressive increase in the peak height of diffraction lines relative to $MnFe_2O_4$ phase with subsequent decrease in peak height of the free Mn_2O_3 and Fe_2O_3 solids.

The promotion effect of lithium-doping in manganese ferrite formation is better investigated by comparing the peak height of some diffraction lines characteristics for α-Fe_2O_3, Mn_2O_3 (Partridgeite) and $MnFe_2O_4$ phases. These lines are located at "d" spacing of 2.69, 2.72 and 2.56 Å for the earlier mentioned compounds, respectively. The choice of these lines is based on the fact that they are not common among the diffraction lines of α-Fe_2O_3, Mn_2O_3 and $MnFe_2O_4$ phases.

The peak height of some diffraction lines of α-Fe_2O_3 (2.69 Å), Mn_2O_3 (2.72 Å) and $MnFe_2O_4$ (2.56 Å) phases were determined for pure and variously doped mixed solids precalcined at 900, 1000 and 1100°C, the data obtained are given in Table 1. Inspection of Table 1 reveals that the peak height of free oxides decreases progressively by increasing the calcination temperature in the rang of 900–1100°C. On the other hand, this treatment led to a progressive increase in the peak height of the produced ferrite phase. This indicates enhancing the ferrite formation by increasing the calcination temperature to 1100°C. However, the appearance of diffraction lines of free oxides, in case of pure and doped mixed solids heated at 1100°C for 6 h, showed that the complete conversion of these oxides into $MnFe_2O_4$ requires a prolonged heating at temperature >1100°C.

It can also be seen from Table 1 that the presence of Li_2O brought about a progressive decrease in the peak height of the diffraction lines at 2.69 and 2.72 Å with

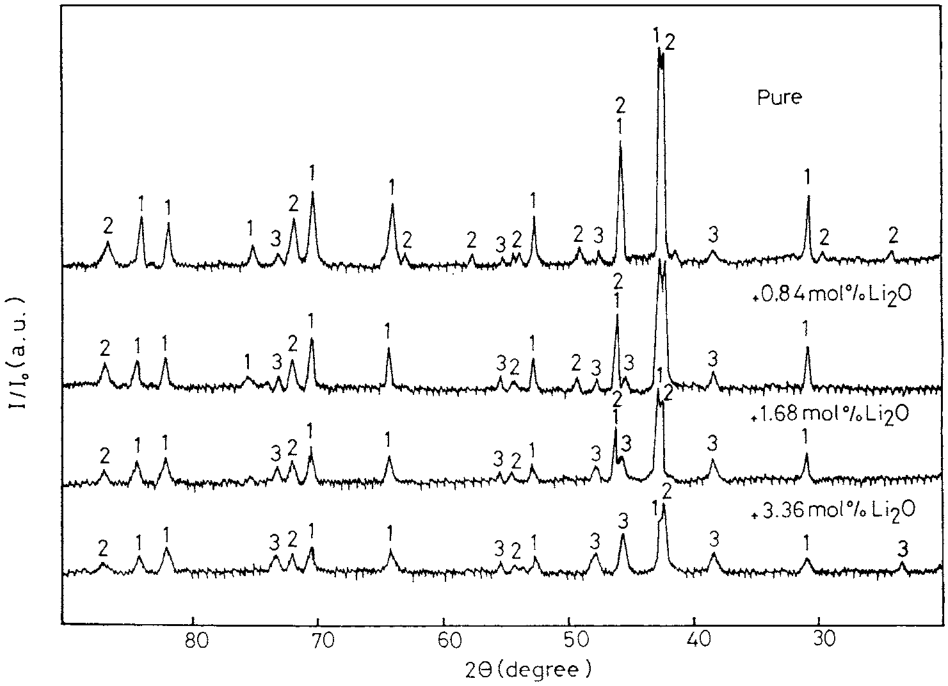

Fig. 3. X-ray diffractograms of Mn/Fe mixed oxide solids precalcined at 900°C. Lines (1) α-Fe_2O_3, (2) Mn_2O_3 (Partridgeite) and (3) $MnFe_2O_4$.

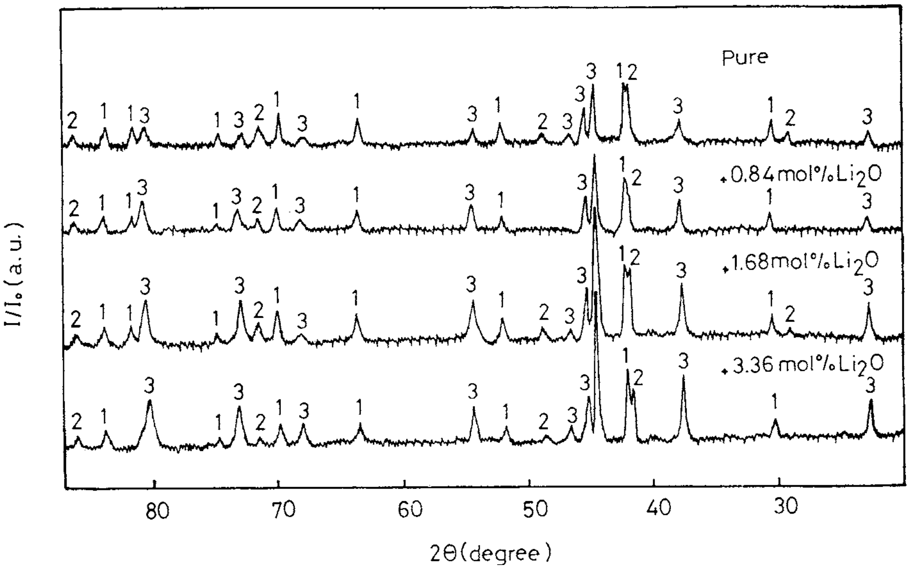

Fig. 4. X-ray diffractograms of Mn/Fe mixed oxide solids precalcined at 1000°C. Lines (1) α-Fe_2O_3, (2) Mn_2O_3 (Partridgeite) and (3) $MnFe_2O_4$.

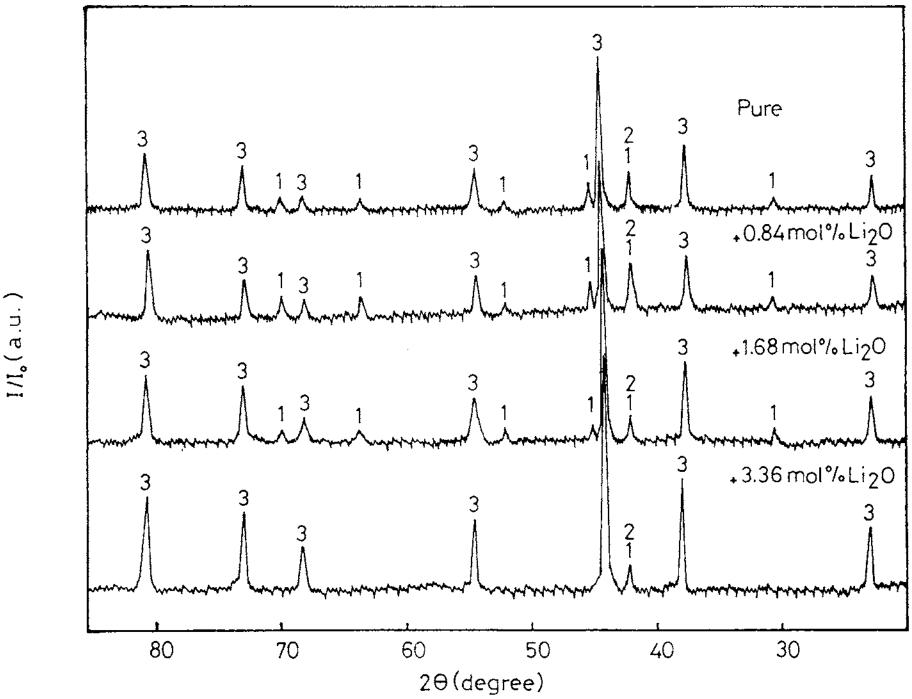

Fig. 5. X-ray diffractograms of Mn/Fe mixed oxide solids precalcined at 1100°C. Lines (1) α-Fe_2O_3, (2) Mn_2O_3 (Partridgeite) and (3) $MnFe_2O_4$.

Table 1

Effect of lithium-doping on the heights of some diffraction lines of α-Fe_2O_3, Mn_2O_3 and $MnFe_2O_4$ for pure and doped mixed solids precalcined at different temperatures

Solids	Reaction temperature (°C)	Peak height (a.u.)		
		α-Fe_2O_3 (2.69 Å) (100%)	Mn_2O_3 (2.72 Å) (100%)	$MnFe_2O_4$ (2.56 Å) (100%)
Mn_2O_3/Fe_2O_3	900	170	169	10
Mn_2O_3/Fe_2O_3 + 0.84 mol% Li_2O	900	105	105	15
Mn_2O_3/Fe_2O_3 + 1.68 mol% Li_2O	900	75	65	22
Mn_2O_3/Fe_2O_3 + 3.36 mol% Li_2O	900	55	55	31
Mn_2O_3/Fe_2O_3	1000	45	45	46
Mn_2O_3/Fe_2O_3 + 0.84 mol% Li_2O	1000	40	32	66
Mn_2O_3/Fe_2O_3 + 1.68 mol% Li_2O	1000	55	55	95
Mn_2O_3/Fe_2O_3 + 3.36 mol% Li_2O	1000	58	42	120
Mn_2O_3/Fe_2O_3	1100	35	35	120
Mn_2O_3/Fe_2O_3 + 0.84 mol% Li_2O	1100	30	20	125
Mn_2O_3/Fe_2O_3 + 1.68 mol% Li_2O	1100	22	20	155
Mn_2O_3/Fe_2O_3 + 3.36 mol% Li_2O	1100	15	15	192

subsequent increase in the peak height of the lines at 2.56 Å. These results showed clearly that the formation of manganese ferrite increases by increasing both the amount of Li_2O present and the calcination temperature of pure and doped mixed solids.

4. Discussion

Fe_2O_3 and Mn_2O_3 undergo solid–solid interaction to produce $MnFe_2O_4$ that appear to cover the grains of each reacting oxide [25–28]. The propagation of this reaction is controlled by thermal diffusion of manganese and iron cations through the ferrite film which acts as an energy barrier. It seems that the ferrite produced at 900°C covers the surfaces of grains of the free oxides hindering their further diffusion. So, the $MnFe_2O_4$ formed initially acts as an energy barrier against the completion of the solid–solid interaction between Fe_2O_3 and Mn_2O_3. Similar results have been obtained by heating NiO and Fe_2O_3 at temperatures as high as 1100°C which was sufficient to conduct partial conversion of the reacting oxides into $NiFe_2O_4$ [29,30]. The fact that minute amounts of free Fe_2O_3 and Mn_2O_3, were detected in the pure and doped mixed solids heat at 1100°C, gives an indication of the partial conversion of the reacting oxides into $MnFe_2O_4$. Indeed, Li_2O-treatment of Mn/Fe mixed solids at 800°C resulted in a decrease in the intensity of the diffraction lines of Mn_2O_3 and Fe_2O_3 phases. The decrease can be considered as the result of a progressive decrease in the particle size of Mn_2O_3 and Fe_2O_3 crystallites. This behavior might result from a possible coating some of manganese and ferric oxides with lithium oxide film. This film hindered or opposed the particle adhesion of Mn_2O_3 and Fe_2O_3 particles retarding their grain growth. However, Li_2O-doping at 900–1100°C showed an effective enhancement of manganese ferrite formation. Manganese oxide is known as n-type electronic semiconductor and dissolve Li_2O in its lattice [31–34]. In fact, the dissolution of monovalent ions in p-type semiconductors is known to increase the concentration of their charge carriers and to decrease the concentration of the charge carriers in n-type semiconductors [33]. The decrease in the concentration of charge carriers is followed by a decrease in the n-type semiconducting character and a subsequent decrease in the oxidation state of the treated oxide. These effects are expected when dissolution of the foreign ions takes place via substitution of some of the host cations of the doped oxides. In such case the incorporation of monovalent ions in the lattice of an n-type semiconductor might be accompanied by an increase and not a decrease in the state of the treated solid. This process can be simplified by the use of Kröger's notion [34] in the following manner:

$$Li_2O + O_2\ (g) \rightarrow 2Li(Mn^{3+}) + 4Mn^{4+}$$

where $Li(Mn^{3+})$ are the univalent ions located in the position of the host Mn^{3+} cations present in the Mn_2O_3 lattice and Mn^{4+} is the quadrivalent manganese ion created which exists as a lattice defect in Mn_2O_3. The question raised could be what is the possible effect of conversion of some manganese ions to tetravalent state in the ferrite formation? The solid–solid interaction between Fe_2O_3 and certain transition metal oxides to produce the corresponding ferrite requires that the reacting metal oxide is preferably existing in the divalent state, it is expected that Li_2O-doping might inhibit the ferrite formation.

Ferric oxide can dissolve a very small amount of Li_2O due to the ability of formation of lithium ferrite [29,30]. On this basis, most of the dopant (Li_2O) added was dissolved in the Mn_2O_3 lattice. The results obtained opposite to the predicted effect of Li_2O-doping, showed an effective enhancement of manganese ferrite formation. These results may point to the role of Li-doping in increasing the mobility of thermal diffusion of manganese ions facilitating their diffusion through the whole mass of the doped manganese oxide and also through the early-formed $MnFe_2O_4$ phase. It has been reported Li-doping increases the mobility of nickel, molybdenum and vanadium ions through the whole mass of their corresponding oxides [29,30,35,36]. The observed enhancement of manganese ferrite formation as a result of doping with Li_2O and the consequent increase in the mobility of the diffusion of manganese ions through the growing $MnFe_2O_4$ phase, can be investigated by determining the activation energy of manganese ferrite (ΔE) for pure and lithium-doped mixed solids. This has been tentatively achieved from the results given in Table 1 by assuming that heights of the characterized diffraction lines at 3.005, 2.56 and 2.12 Å are a measure of the amount of $MnFe_2O_4$ present in a given mixed

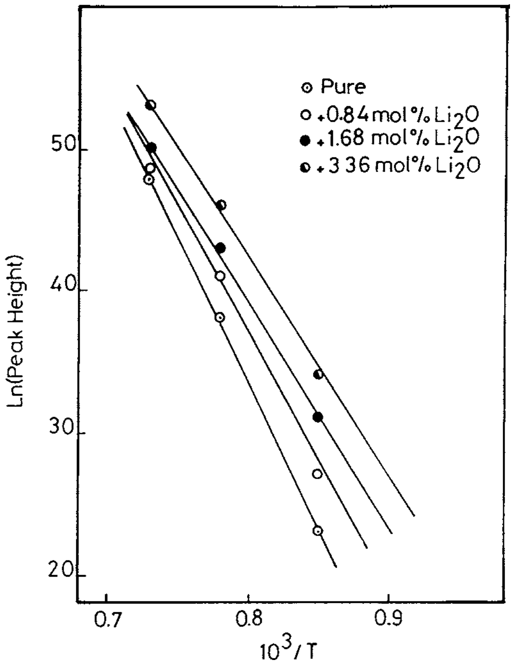

Fig. 6. Changes of ln peak height of the diffraction line of $MnFe_2O_4$ (2.56 Å) as a function of 1/*T* of pure and doped mixed oxide solids.

solids at definite temperature *T*. By plotting the peak height of one of these lines versus 1/*T*, a straight line is obtained whose its slope determines the ΔE value by direct application of the Arrhenius equation. This trial has been successfully carried out at temperatures between 900 and 1100°C, and the plots obtained are given in Fig. 6. The computed ΔE values obtained from the diffraction line at d spacing at 2.56 Å, are 174, 153, 134 and 117 kJ mol^{-1} for pure mixed solids and those doped with 0.84, 1.68 and 3.36 mol% Li_2O, respectively. Also, the activation energy of nickel ferrite formation has been determined adopting the same method used in the present work [37]. The ΔE values for $NiFe_2O_4$ were 112.9, 87.8 and 75.2 kJ mol^{-1} for pure solids and those doped with 3 and 5 mol% Li_2O, respectively. The decrease in ΔE values, due to lithium-doping to an extent proportional to the amount of Li_2O present, reflects an effective increase in the mobility of thermal diffusion of the reacting cations through the whole mass of the reacting oxides and through the early-produced $MnFe_2O_4$ film.

5. Conclusions

The main conclusions that can be derived from the obtained results are

1. Solid–solid interaction between α-Fe_2O_3 and Mn_2O_3 occurred at temperature starting from 900°C to produce manganese ferrite phase. The extent of this reaction increased on increasing the heating temperature in the range of 900–1100°C.
2. Lithium-doping was found to simulate the ferrite formation to an extent proportional to the amount of Li_2O present. The promotion effect of lithium doping has been evidenced from the observed reduced amounts of free oxides and the increased amount of $MnFe_2O_4$ present in the doped mixed solids preheated at temperatures between 900 and 1100°C. However, minute amounts of unreacted oxides were detected in pure and doped mixed solids heated at 1100°C which indicate the partial conversion of the reacting oxides into $MnFe_2O_4$.
3. The activation energy of formation of $MnFe_2O_4$ was determined for pure and Li-doped solids and found to be 174, 153, 134 and 117 kJ mol^{-1} for pure mixed solids and those treated with 0.84, 1.68 and 3.36 mol% Li_2O, respectively. These values suggest that lithium oxide-doping enhanced the ferrite formation process through an increase in the mobility of thermal diffusion of the reacting cations.

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