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Effect of lithium oxide doping on zinc ferrite formation

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Abstract

A DTA and XRD study of the effect of Li_2O doping on the solid–solid interaction between Fe_2O_3 and ZnO showed that Fe_2O_3 and ZnO interacted above 600°C to produce $ZnFe_2O_4$. The extent of ferrite formation increases with temperature, but not completely when pure mixed solids are pre-heated at 900°C. These results are attributed to the initially formed zinc ferrite layer inhibiting diffusion of Fe_2O_3 and ZnO and thus acting as an energy barrier. Li_2O doping (1.5 and 3 mol%) stimulated the formation of zinc ferrite to a degree that increased with the amount present. The mechanism of the promotion effect is discussed.

Keywords: Crystallization; Diffusion; Doping; Ferrite; Solid–solid interactions

1. Introduction

Ferrites, which are usually prepared by solid-state reactions [1–4], are important materials that can be used as catalysts and in microwave devices [5]. Transition metal ferrites, having a cubic spinel structure, have remarkable magnetic and semiconducting properties [1, 6–9].

Solid–solid interactions between ferric oxide and lithium carbonate, sodium nitrate and nickel carbonate, respectively, already been investigated, as has the effect of Li_2O and Al_2O_3-doping on nickel ferrite formation [4]; although both promoted the reaction, the effect of Li_2O was more pronounced.

In zinc ferrite formation [10–14], the reactions of ferric oxide, sharply decreases if the temperature of its preparation exceeds 675°C because of its sintering. The mechanism

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of the solid–solid interaction between ZnO and Fe_2O_3 [11–13] is reported to be diffusion of Fe_2O_3 and ZnO into the initially formed ferrite layer. Activation energies were between 301 and 460 kJ mol^{-1} [12,13], but Kolta et al. [11] found that the reaction obeyed a random nucleation equation with an activation energy of 123 kJ mol^{-1}. In this connection, Furuichi et al. [14] reported that the rate of the solid state reaction depends mainly on the contact area of the reacting particles.

Because, to our knowledge, the effect of doping with certain foreign oxide on zinc ferrite formation has not been investigated, the present work reports on the effects of addition of small amounts of Li_2O at different temperatures.

2. Experimental

2.1. Materials

Equimolar proportions of $Zn(NO_3)_2.3H_2O$ and basic ferric carbonate were mixed, homogenized, and subjected to thermal treatment in air at 500–900°C for six hours. Two doped mixed solid samples were obtained by treating known amounts of zinc/ferric salts with calculated amounts of lithium nitrate dissolved in the minimum amount of distilled water, dried then calcined in air at 500–900°C. The amounts of lithium, expressed as Li_2O, were 1.5 and 3 mol%. All the employed chemicals were of analytical grade and supplied by Prolabo company.

2.2. Techniques

DTA and XRD techniques were employed. Thermal analysis of uncalcined, pure and doped mixed solids was performed using the Perkin-Elmer, 7 series thermal analysis system. The rate of heating was fixed at 10°C min^{-1} and the mass of the solid specimens was about 40 mg. The measurements were carried out in a flow of nitrogen gas (50 ml min^{-1}).

X-ray investigation of pure and doped mixed solids pre-heated in air at 500, 600, 700, 800 and 900°C was carried out using a Philips diffractometer (type PW 1390). The patterns were recorded with iron-filtered cobalt radiation ($\lambda = 1.7889$ Å) at 30 kV and 10 mA with a scanning speed of 2° in 2θ min^{-1}.

3. Results

3.1. Thermal behaviour of pure and doped zinc nitrate and ferric carbonate mixed solids

Fig. 1 shows DTA curves of pure and lithium-doped specimens. The amount of lithium nitrate was 6 mol% (3 mol% Li_2O). Fig. 1, curve A, shows that the DTA curve of the pure mixed solids consists of three endothermic and two exothermic peaks. The maxima of the endothermic peaks are located at 135.5, 236.4 and 298.9°C. The first

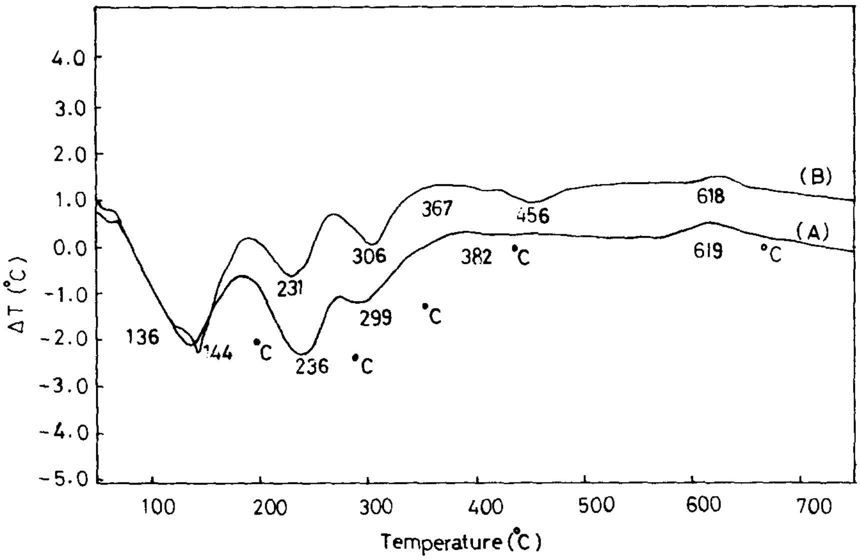

Fig. 1. DTA curves of pure and doped mixed solids: A, pure solids; B, doped solids.

peak corresponds to dehydration of trihydrated zinc nitrate, producing anhydrous zinc nitrate. The other two endothermic peaks indicate the thermal decomposition of anhydrous zinc nitrate and basic ferric carbonate, respectively, to produce ZnO and Fe_2O_3. The first exothermic peak, whose maximum was located at 381.8°C, might characterize a phase transformation and/or a solid–solid interaction between ZnO and Fe_2O_3. However, the solid–solid interaction between zinc oxide and ferric oxide requires relatively high temperatures [10–14]. The peak at 381.8°C more probably corresponds to the crystallization of anhydrous Fe_2O_3 into α-Fe_2O_3 phase [15–17]. This will be confirmed later by XRD measurements.

The last exothermic peak with its maximum at 618.7°C characterizes Fe_2O_3–ZnO interaction to produce zinc/iron compound (s).

Fig. 1 curve B, consists of four endothermic and two exothermic peaks. The maxima of the endothermic peaks are found at 143.5, 231.3, 305.5 and 455.9°C. The two exothermic peaks have their maxima at 366.5 and 617.8°C. The first three endothermic peaks correspond to dehydration of trihydrated zinc nitrate, and the thermal decomposition of anhydrous zinc nitrate and basic ferric carbonate to produce free ZnO and Fe_2O_3, respectively. The last endothermic peak characterizes the thermal decomposition of lithium nitrate producing Li_2O. Similar to the case of the pure mixed solids, the exothermic peaks are indicative of the crystallization of α-Fe_2O_3 and the formation of a new Zn/Fe compound, respectively. The identification of the produced compound(s) can be made by XRD measurements, seen below.

The comparison between the DTA curves of pure and doped mixed solids revealed that lithium doping enhances the crystallization of α-ferric oxide. This conclusion is in agreement with the results published recently by one of the authors [17].

3.2. XRD investigation of pure and doped mixed solids pre-calcined at different temperatures

X-ray diffractograms of pure and doped mixed solids pre-calcined at various temperatures were determined. The results obtained showed that pure and doped mixed solids pre-heated in air at 500°C consist entirely of α-Fe_2O_3 and ZnO (hexagonal) with a high degree of crystallinity. This indicates the absence of any appreciable solid–solid interaction between ZnO and Fe_2O_3.

Figs. 2–5 represent X-ray diffractograms of pure and doped mixed solids pre-heated in air at 600, 700 and 900°C. It is seen from Fig. 2 that pure and doped mixed solids heated at 600°C consist of very highly crystalline ZnO (hexagonal) and α-Fe_2O_3 phases; also present are the diffraction lines of $ZnFe_2O_4$ (franklinite), having a reasonable crystallinity [18]. However, the relative intensity of the diffraction lines relative to

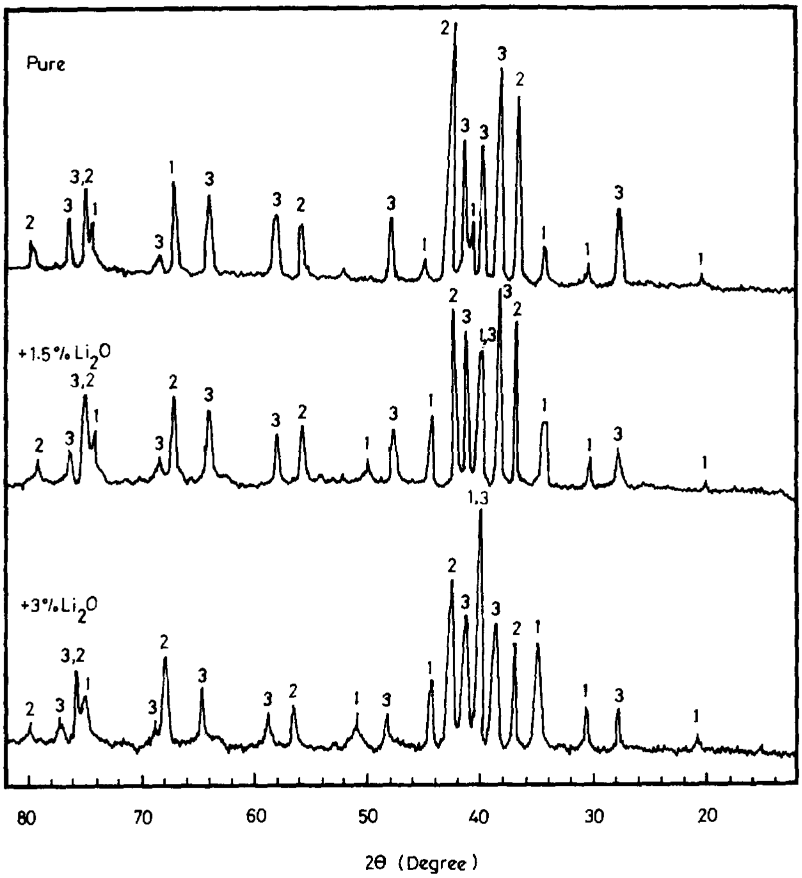

Fig. 2. XRD patterns of pure and doped mixed solids pre-heated in air at 600°C. Lines 1 refer to $ZnFe_2O_4$; lines 2 refer to ZnO (hexagonal) and lines 3 refer to α-Fe_2O_3.

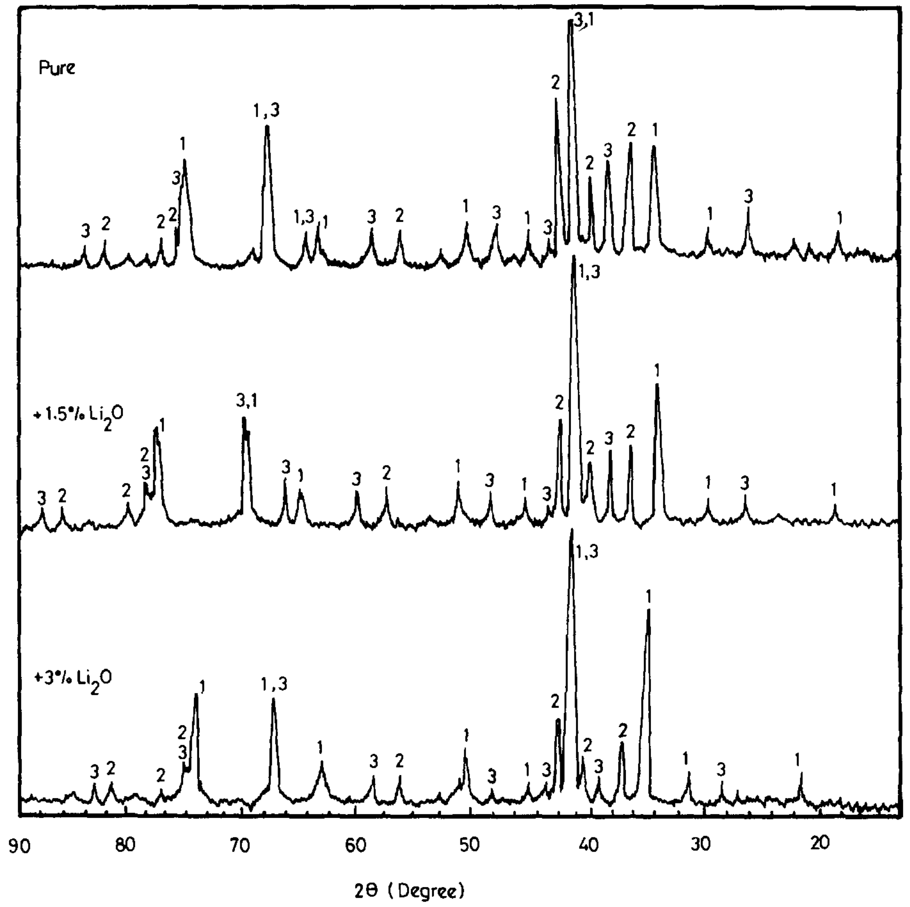

Fig. 3. XRD patterns of pure and doped mixed solid pre-heated in air at 700°C. Lines 1 refer to $ZnFe_2O_4$; lines 2 refer to ZnO and lines 3 refer to α-Fe_2O_3.

$ZnFe_2O_4$ phase increases on increasing the amount of lithium oxide present. The intensities of the diffraction lines of untreated α-Fe_2O_3 and ZnO solids decrease progressively on increasing the amount of lithium oxide added. These results clearly indicate that lithium oxide doping enhances the solid–solid interaction between α-Fe_2O_3 and ZnO to produce $ZnFe_2O_4$ to an extent proportional to the amount of dopant added.

Figs. 3 and 4 include XRD results of pure and doped mixed solids pre-heated at 700 and 800°C. These figures show that pure and doped solids heated at 700 and 800°C consist of α-Fe_2O_3, ZnO (hexagonal) and $ZnFe_2O_4$ phases. Inspection of these figures shows that the relative intensity of $ZnFe_2O_4$ phase increases on increasing the calcination temperature from 600 to 800°C and also on increasing the amount of lithium oxide present, and that the relative intensities of the diffraction lines of unreacted Fe_2O_3 and ZnO decrease on increasing the calcining temperature and also

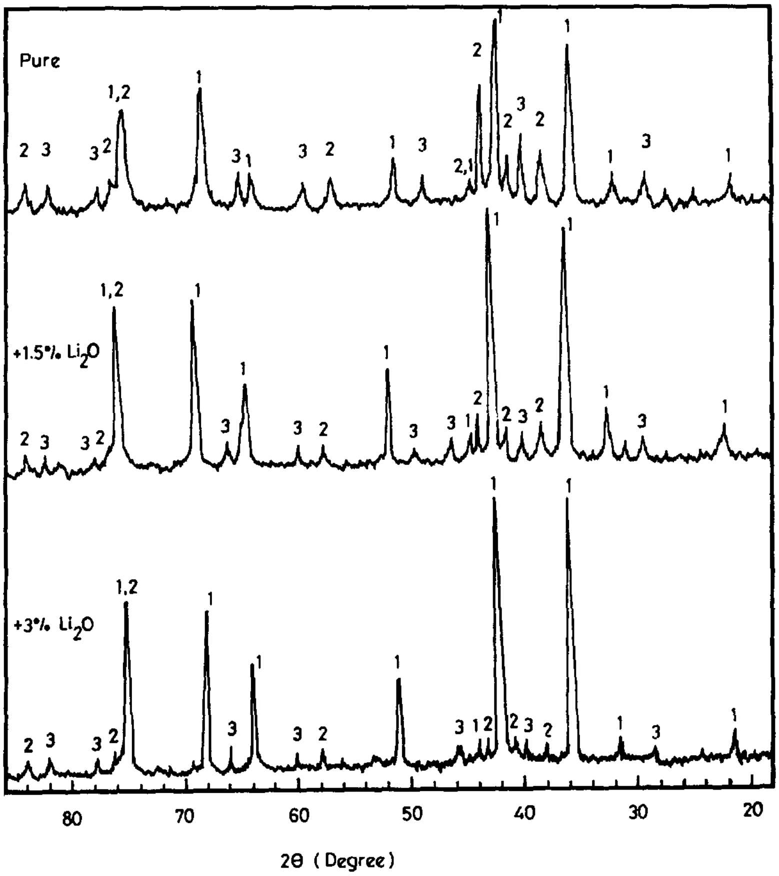

Fig. 4. XRD patterns of pure and doped mixed solids pre-heated in air at 800°C. Lines 1 refer to $ZnFe_2O_4$; lines 2 refer to ZnO (hexagonal) and lines 3 refer to α-Fe_2O_3.

on increasing the amount of lithium oxide present. These results clearly indicate that solid–solid interaction readily occurs at temperatures starting from 600°C, yielding $ZnFe_2O_4$ and that the amount of reacted oxides involved in the ferrite formation increases on increasing the reaction temperatures in the range 600–800°C and treating with Li_2O.

The pure mixed solid specimen pre-heated in air at 900°C still contains small portions of untreated iron and zinc oxides, as indicated from the intensity of their diffraction lines. So the complete conversion of these oxides into $ZnFe_2O_4$ requires a prolonged heating at 900°C or heatingg at temperatures above this limit. It seems that $ZnFe_2O_4$ produced at 600°C covers the surfaces of particles of the reacting oxides, hindering their diffusion through the ferrite layer, i.e the ferrite film acted as an energy barrier opposing the formation of further amounts of $ZnFe_2O_4$ compound [11–13].

It is seen from Fig. 5 that the mixed oxide specimen doped with 1.5 mol% Li_2O and pre-heated at 900°C consists entirely of $ZnFe_2O_4$. This indicates that 1.5 mol% Li_2O

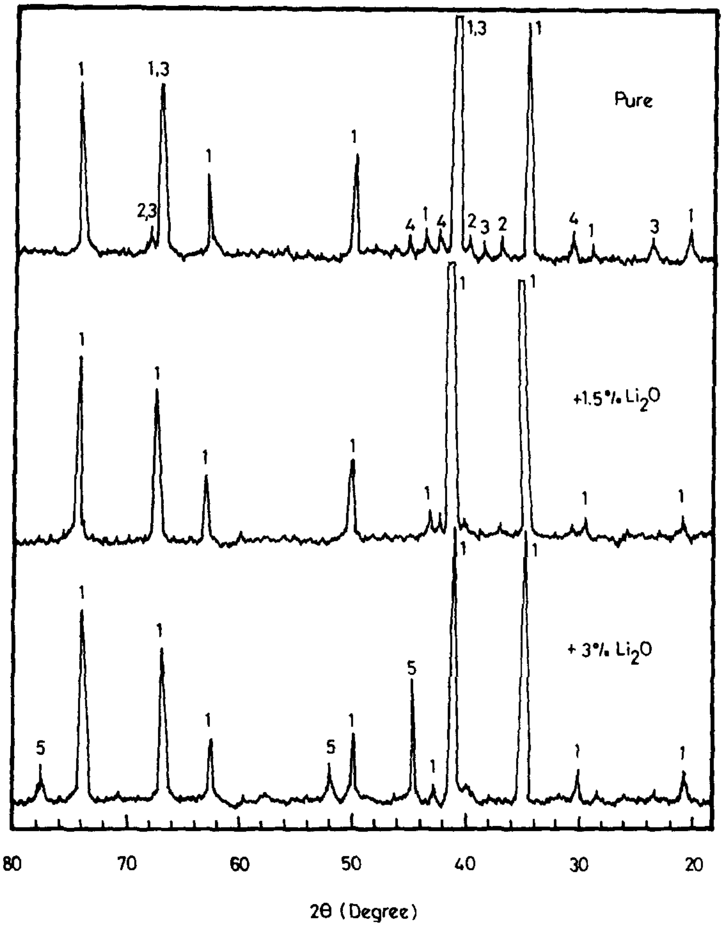

Fig. 5. XRD patterns of pure and doped mixed solids pre-heated in air at 900°C. Lines 1 refer to $ZnFe_2O_4$; lines 2 refer to ZnO; lines 3 refer to α-Fe_2O_3; lines 4 refer to ε-Fe_2O_3; and lines 5 refer to β-$LiFeO_2$.

was sufficient to stimulate the reaction $ZnO + Fe_2O_3 \rightarrow ZnFe_2O_4$, leading to complete conversion of Zn/Fe oxides into ferrite phase. The presence of 3 mol% Li_2O in the mixed solids pre-heated at 900°C also resulted in complete conversion of ferric and zinc oxides to zinc ferrite as well as the formation of a new compound with diffraction lines at 2.34, 2.02 and 1.48 Å. These lines characterize β-$LiFeO_2$ [17,18]. Although the amount of Li_2O added was relatively small (3 mol%), the intensity of the diffraction lines of the β-$LiFeO_2$ phase produced was high, indicating its presence in a well-crystallized state in the outermost surface layers of the Fe_2O_3 particles. The formation of lithium ferrite takes place according to

$$Fe_2O_3 + Li_2O \xrightarrow{900^{\circ}C} 2\beta\text{-}LiFeO_2$$

The formation of lithium ferrite in the doped mixed solids pre-heated at 900°C might indicate a limited solubility of Li_2O in Fe_2O_3 mixture. Therefore, Li_2O was preferientially dissolved in ZnO lattice [19].

4. Discussion

The results obtained in the present work revealed that solid–solid interaction between Fe_2O_3 and ZnO to produce $ZnFe_2O_4$ took place at temperatures starting from 600°C. However, the completion of this interaction requires prolonged heating at $\geqslant$ 900°C or via doping with a small amount of Li_2O (1.5–3 mol%). The formation of a limited amount of $ZnFe_2O_4$ at temperatures below 900°C might, as mentioned before, be due to the growth of an energy barrier as a result of the surfaces of the reacting oxide particles being a film of covered by ferrite, hindering diffusion.

It has also been shown from the XRD results that lithium doping of mixed oxide solids enhances the formation of $ZnFe_2O_4$ phase. This effect is better investigated by comparing the peak heights of some of the diffraction lines of α-Fe_2O_3 (2.69 Å), ZnO (2.81 Å) and $ZnFe_2O_4$ (2.97 Å) observed in the XRD diffractograms of pure and doped mixed solids pre-heated at 600–800°C. The choice of these diffraction lines was based on the fact that they are not common among the diffraction lines of Fe_2O_3, ZnO and $ZnFe_2O_4$. It can be shown from Figs. 2–4 that the peak height of the diffraction lines of $ZnFe_2O_4$ phase produced at 600–800°C increases regularly on increasing the amount of dopant present. However, the increase was more pronounced at a calcination temperature of 600°C. These results clearly indicate that lithium doping of mixed solids enhances ferrite formation to an extent proportional to its amount present. This conclusion finds its support from the regular decrease in the values of the peak heights of diffraction lines for untreated Fe_2O_3 and ZnO solids.

It can also be observed from Figs. 2–4 that the peak height of the diffraction lines of $ZnFe_2O_4$ also increases on increasing the temperature of heating the pure and doped mixed solids in the range 600–800°C. The increase was, however, more pronounced by increasing the heating temperature from 600 to 700°C. These results suggest that the enhancement of $ZnFe_2O_4$ formation by lithium doping takes place mainly via increasing the mobility of Zn species through the whole mass of Fe_2O_3 particles. The enhanced formation of ferrite phase due to treating with lithium could also result from an induced increase in the concentration of zinc species (Zn^{2+} ions) contributing to ferrite formation.

The XRD investigation showed that the heating of Li_2O-doped mixed solids (3 mol%) at 900°C also led to the formation of β-$LiFeO_2$. This suggests that the solubility of Li_2O in Fe_2O_3 lattice is limited, while Li_2O could be easily dissolved in ZnO solid [19–21]. The dissolution of Li_2O in ZnO lattice is the object of several investigations.

Heating pure zinc/iron mixed oxides at temperatures in the range 600–800°C might result in the formation of non-stoichiometric zinc oxide that contains Zn^+ ions [22–24]. The presence of Li_2O in the mixed oxides [22–24] hinders the formation of monovalent zinc ions due to

$$n\mathrm{Li_2O} + 2n\mathrm{Zn}^+ + 1/2\mathrm{O_2} \rightarrow 2n\mathrm{Li}^+(\mathrm{Zn}^{2+})$$

Where, adopting the Kröger notation [25], $Li^+(Zn^{2+})$ are monovalent lithium ions located in the position of the host cation, Zn^{2+}, of the ZnO lattice, and Zn^+ is monovalent ion present in pure ZnO heated at temperatures ≥ 500°C. This reaction is followed by the uptake of some atmospheric oxygen, with subsequent transformation of an equivalent amount of Zn^+ into Zn^{2+} ions.

It has previously been shown that Li_2O doping of NiO, V_2O_5 and MoO_3 results in an increase in the mobilities of their cations [4,17,26]. It seems logical to suppose that Li_2O doping of ZnO also increases the mobility of its cations in addition to converting some Zn^+ into Zn^{2+}. As Zn^+ does not contribute directly to ferrite formation, its conversion into Zn^{2+} must favour zinc ferrite formation.

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