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# Solid–solid interactions between ferric and cobalt oxides as influenced by $Al_2O_3$-doping

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## Abstract

The solid–solid interactions between pure and alumina-doped cobalt and ferric oxides have been investigated using DTA, IR and XRD techniques. Equimolar proportions of basic cobalt carbonate and ferric oxide and different amounts of aluminum nitrate were added as dopant substrate. The amounts of dopant were 0.75, 1.5, 3.0 and 4.5 mol% $Al_2O_3$.

The results obtained revealed that solid–solid interaction between $Fe_2O_3$ and $Co_3O_4$ takes place at temperatures starting from 700°C to produce cobalt ferrite. The degree of propagation of this reaction increases progressively as a function of precalcination temperature and $Al_2O_3$-doping of the reacting solids. However, the heating of pure mixed solids at 1000°C for 6 h. was not sufficient to effect the complete conversion of the reacting solids into $CoFe_2O_4$, while the addition of a small amount of $Al_2O_3$ (1.5 mol%) to ferric/cobalt mixed solids followed by precalcination at 1000°C for 6 h conducted the complete conversion of the reacting solids into cobalt ferrite. The heat treatment of pure and the 0.75 mol%-doped solids at 900 and 1000°C effected the disappearance of most of IR transmission bands of the free oxides with subsequent appearance of new bands characteristic for the $CoFe_2O_4$ structure. An increase in the amount of $Al_2O_3$ added from 1.5–4.5 mol% to the mixed solids precalcined at 1000°C led to the disappearance of all bands of free oxides and appearance of all bands of cobalt ferrite. The promotion effect of $Al_2O_3$ in cobalt ferrite formation was attributed to an effective increase in the mobility of the various reacting cations. The activation energy of formation ($\Delta E$) of $CoFe_2O_4$ phase was determined for pure and doped solids. The computed values of $\Delta E$ were, respectively, 99.6, 87.8, 71.9, 64.7 and 48.7 kJ mol$^{-1}$ for the pure solid and those treated with 0.75, 1.5, 3 and 4.5 mol% $Al_2O_3$.

*Keywords:* $CoFe_2O_4$; Doping; Mobility; Activation energy of formation

## 1. Introduction

Cobalt ferrite has several applications, such as catalyst microwave resistor, ultrasonic vibrator and electrophotographic toner [1–3]. Cobalt ferrite can be obtained by a variety of methods [1,4–10]. One of these methods is by heating a mixture of ferric oxide and cobalt carbonate or oxide at temperatures starting from 700°C [4,11].

Solid–solid interaction 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 the addition of small amounts of certain foreign oxides [11–23].The mechanism of ferrite formation has been the object of several investigations [11–23]. The solid–solid interaction between $Fe_2O_3$ and transition

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metal oxides to produce the corresponding ferrite is normally controlled by the thermal diffusion of the reaction cations through the whole mass of each solid as well as the initially formed film covering the surface of the grains of each oxide [11,17,20,22,23] which act as energy barriers, thus hindering their diffusion. So, the completion of these solid-state reactions required a prolonged heating at relatively elevated temperatures [8,11,20–23]. The effects of $Li_2O$ and $Al_2O_3$ doping on the formation of $NiFe_2O_4$ and $ZnFe_2O_4$ [17,20,22,23] and $Li_2O$ doping on $CoFe_2O_4$ formation [11] were previously studied. It was found that both $Li_2O$ and $Al_2O_3$ enhanced the ferrite formation with different degrees via increasing the mobility of thermal diffusion of reacting cations through the earlier formed ferrite film.

The present work reports the results of a study on the effect of addition of small amounts of $Al_2O_3$ on cobalt ferrite formation at different temperatures. The techniques employed were DTA, IR and XRD.

## 2. Experimental

### 2.1. Materials

Equimolar mixtures of ferric oxide and basic cobalt carbonate were well mixed to ensure the homogeneity of the powdered solids. The obtained sample was heated in air temperatures between 700 and 1000°C for 6 h. Four doped, mixed solid samples were obtained by treating a known mass of mixed solids with calculated amount of aluminum nitrate dissolved in the least amount of distilled water, dried at 100°C, then calcined at 700–1000°C for 6 h. The concentrations of aluminum expressed as mol% $Al_2O_3$ were 0.75, 1.5, 3.0 and 4.5. The chemicals employed in the present work, $Fe_2O_3$, $CoCO_3$, $Co(OH)_2{\cdot}2H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$, were of analytical grade supplied by the BDH company.

### 2.2. Techniques

DTA curves of pure and doped uncalcined solid samples were determined using Shimadzu DTA-50H system. The rate of heating was maintained 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 and 1000°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 $2\theta\ min^{-1}$.

Infrared transmission spectra were determined using Perkin–Elmer spectrophotometer (type 1430). The IR spectra were determined from 400 to $4000\ cm^{-1}$, but the portions between 1500–$400\ cm^{-1}$ were only considered in this investigation. Two milligrams of each solid sample were mixed with 200 mg of vacuum-dried IR-grade KBr. The mixture was dispersed by grinding for 3 min in a vibratory ball mill and placed in a steel die 13 mm in diameter and subjected to a pressure of 12 t. The sample disks were placed in the holder of a double-grating IR spectrometer.

## 3. Results

### 3.1. Thermal behaviour of pure and doped uncalcined solids

Fig. 1 shows the DTA curves of pure basic cobalt carbonate, basic carbonate mixed with $Fe_2O_3$ (equimolar proportions), basic carbonate: $Fe_2O_3$ treated with 6 and 9 mol% $Al(NO_3)_3{\cdot}9H_2O$. The comparison of DTA curves of pure and variously doped mixed solids revealed that: (i) the maximum endothermic peaks relative to thermal decomposition of basic cobalt carbonate decreases on increasing the amounts of dopant added; and (ii) the area of the endothermic peak relative to thermal decomposition of cobalt oxide according to [24–26]

$$Co_3O_4 \rightarrow 3CoO + \tfrac{1}{2}O_2$$

located at about 890°C, decreases considerably on increasing the amount of aluminum nitrate added. These findings clearly indicate the role of aluminum nitrate treatment in enhancing the thermal decomposition of basic cobalt carbonate and also in stimulating the solid–solid interactions between $Co_3O_4$ and $Fe_2O_3$ to produce cobalt–ferric compound.

The identification of the produced cobalt-ferric oxides compound could be identified by IR and XRD techniques.

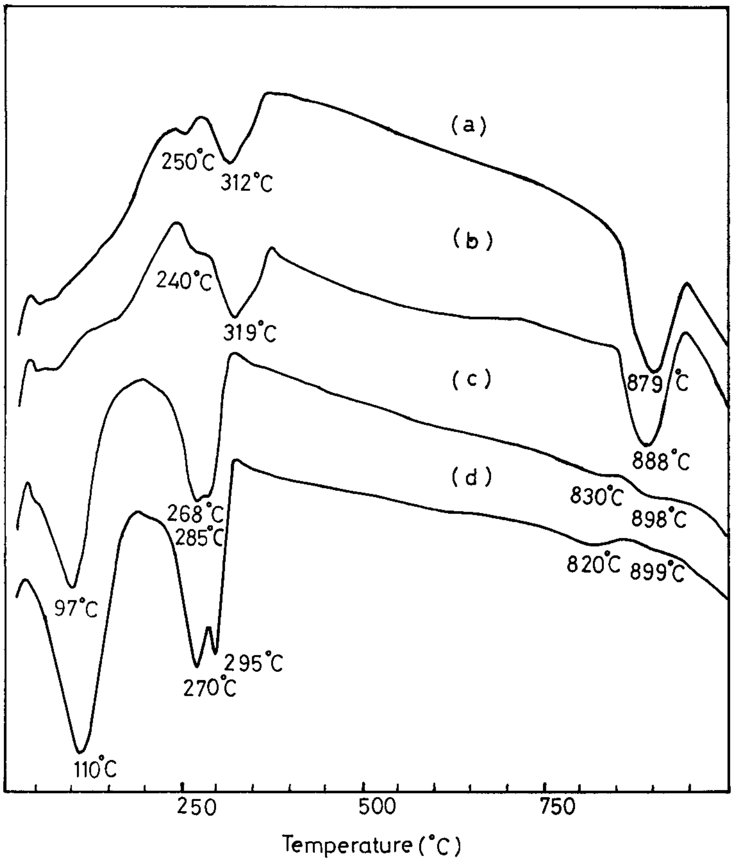

Fig. 1. DTA curves of uncalcined samples of basic cobalt carbonat (a), basic cobalt carbonate and $Fe_2O_3$ (b), and basic cobalt carbonate and $Fe_2O_3$ treated with 6 and 9 mol% $Al(NO_3)_3\ 9H_2O$ (c,d).

### *3.2. IR spectrophotometric investigation of various solids*

The IR transmission spectra were measured for ferric oxide, cobalt oxide precalcined at 700°C and pure, and variously doped, mixed solids preheated in air at 900 and 1000°C. Figs. 2 and 3 show the transmission spectra of individual oxides precalcined at 700°C and pure and variously doped mixed solids precalcined at 900 and 1000°C. It is observed from Fig. 2 that the spectrum of ferric oxide consists of very strong bands at 453, 534, and 1050 $cm^{-1}$ besides sharp and relatively weak bands at 363 and 775 $cm^{-1}$. The spectrum of cobalt oxide precalcined at 700°C consists of very strong and sharp bands at 538 and 665 $cm^{-1}$. Inspection of Fig. 2 revealed that: (i) the spectra of pure and doped mixed solids precalcined at 900°C include the transition bands of free oxides, $Co_3O_4$ and $Fe_2O_3$ besides new bands (shoulders) at 870 and 974 $cm^{-1}$ and relatively strong band at 1058 $cm^{-1}$; (ii) the intensity of the transmission bands of free or unreacted oxides decreases by increasing the amount of $Al_2O_3$ dopant added; and (iii) the intensity of the newly detected band at 1058 $cm^{-1}$ increases by increasing the amount of dopant added. These results suggest that the thermal treatment of mixed solids at 900°C resulted in disappearance of some of the free oxides with subsequent appearance of a new compound. The addition of increasing amounts of $Al_2O_3$ (0.75–4.5 mol%) enhanced the formation of the new compound with its IR bands at 870, 974 and 1058 $cm^{-1}$. Examination of the detected spectra of pure and variously doped mixed solids precalcined at 1000°C showed that the intensity of the transmission

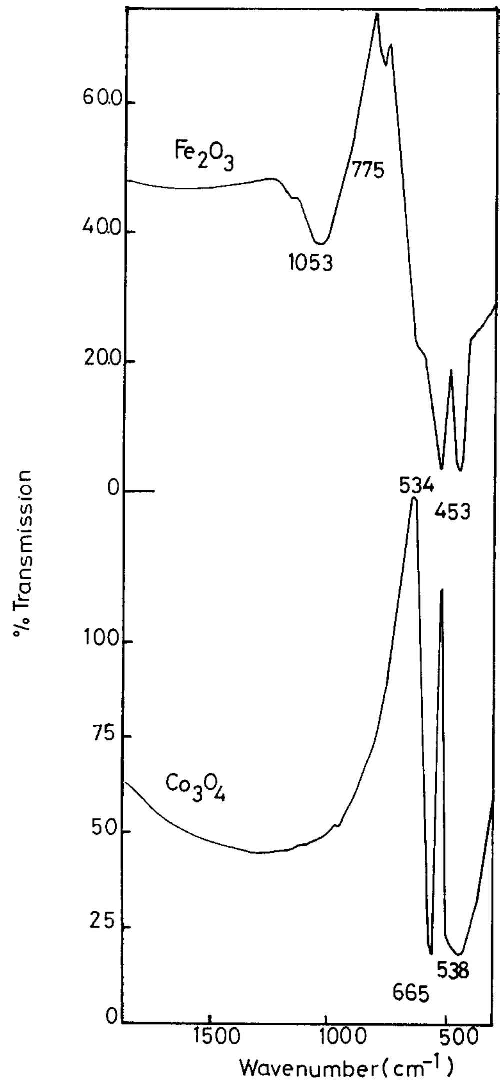

Fig. 2. IR-transmission bands of $Fe_2O_3$ and $Co_3O_4$ precalcined at 700°C.

IR bands at 870, 970 and 1058 cm$^{-1}$ increases progressively as a function of the amount of aluminum oxide added. These bands should characterize the newly formed compound. These results clearly show the role of $Al_2O_3$ in stimulating the solid–solid interaction between cobalt and ferric oxides yielding cobalt oxide–ferric oxide compound. The stimulating effect of the dopant employed ran parallel to its amount added to the reacting solids. The identification of the newly formed compound whose IR bands are found at 870, 970 and 1058 cm$^{-1}$ has been achieved by XRD analysis of pure and variously doped mixed solids precalcined at different temperatures.

### *3.3. X-ray investigation of pure and a doped solids precalcined at different temperatures*

X-ray diffractograms of pure and doped, mixed oxide solids, precalcined at 700, 800, 900, 950 and 1000°C, were determined. The patterns of pure mixed oxide solids and those doped with 0.75–4.5 mol% $Al_2O_3$ and calcined at 700°C are similar to each other. Only the patterns of pure and heavily doped samples are given in Fig. 4. These patterns consist entirely of the characteristic lines of $\alpha$-$Fe_2O_3$, $\gamma$-$Fe_2O_3$ and $Co_3O_4$ phases. The absence of any diffraction lines characteristic to $CoFe_2O_4$ did not exclude the possibility of solid–solid interaction between $\alpha$-$Fe_2O_3$ and $Co_3O_4$ yielding the formation of minute amounts of poorly crystalline $CoFe_2O_4$ phase. This assumption arises from examining the intensity of the diffraction line at '*d*' spacing of 2.51 Å which is a common line between $\alpha$-$Fe_2O_3$ (50%) and $CoFe_2O_4$ (100%). Preliminary experiments showed that the ratio (*R*) between the peak height of the diffraction line at '*d*' spacing of 2.51 Å to that of the line at 2.69 Å, in the diffraction pattern of pure cobalt and ferric oxide mixed solids precalcined at 600°C was 0.55. This value is very close to that characteristic for $\alpha$-$Fe_2O_3$ phase. The values of $R > 0.50$ might suggest the presence of $CoFe_2O_4$ phase. So, the calculation of the ratio *R* between the peak heights of both lines at '*d*' spacing of 2.51 and 2.69 Å can give a measure for the probability of existence of $CoFe_2O_4$. This has been done and the results obtained are given in Table 1. This Table also includes the different values of the peak height of characteristic diffraction lines of $\alpha$-$Fe_2O_3$ and $Co_3O_4$ at 2.69 and (100%) and 2.43 Å (100%), respectively. The computed *R* value for pure mixed oxide solids calcined at 700°C is 0.69 and not 0.55 like the sample calcined at 600°C. Since the line at 2.51 Å is common between $\alpha$-$Fe_2O_3$ and cobalt ferrite, so the difference between the two *R* values for pure samples calcined at 700 and 600°C may be attributed to the presence of $CoFe_2O_4$ phase resulting from solid–solid interaction between $\alpha$-$Fe_2O_3$ and $Co_3O_4$ taking place at 700°C. Table 1 shows that the doping of mixed

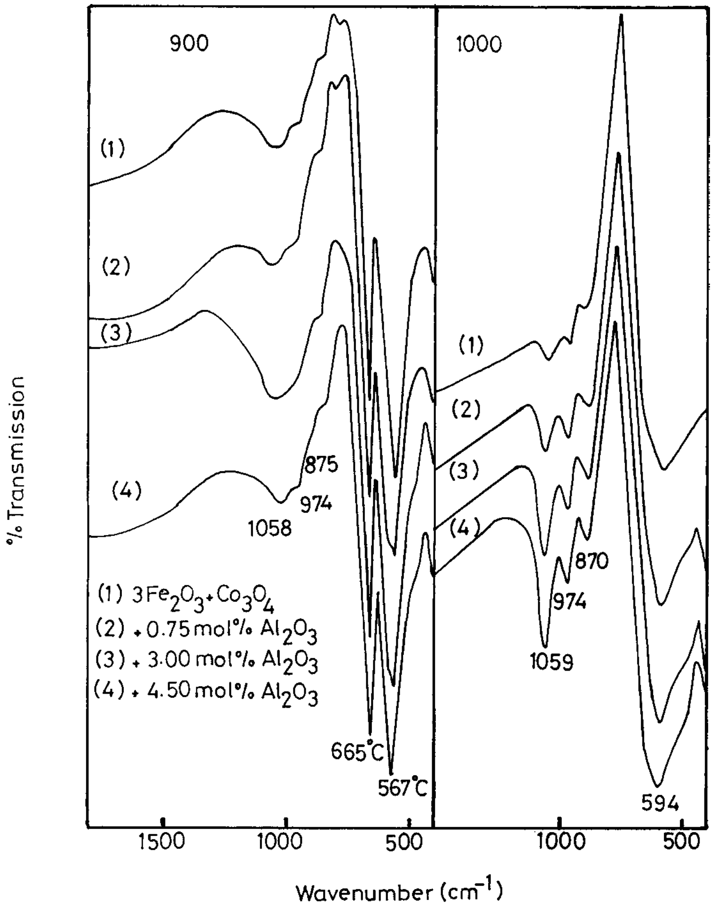

Fig. 3. IR-transmission bands of pure and doped solids calcined at 900 and 1000°C.

oxide solids with increasing amounts of alumina followed by calcination at 700°C was accompanied by a progressive decrease in peak heights of the free oxides with subsequent increase in the R value from 0.69 reaching to 0.83.

The X-ray diffraction patterns of pure and doped mixed solids calcined at 800°C are similar to each other and include the diffraction lines of α-$Fe_2O_3$, γ-$Fe_2O_3$, $Co_3O_4$ and $CoFe_2O_4$ phases. Fig. 4 represents the patterns of pure mixed oxide solids and that doped with 4.5 mol% $Al_2O_3$. Comparing the patterns given in Fig. 4 for samples calcined at 700°C with those calcined at 800°C, it can be shown that calcination of pure and doped mixed solids at 800°C resulted in the appearance of new diffraction lines at '*d*' spacing of 2.96 Å and 2.08 Å which characterize $CoFe_2O_4$ phase (40%). The area under these peaks increased by doping with $Al_2O_3$.

The X-ray diffractograms of pure and doped mixed solids calcined at 900°C (Fig. 5) and 950°C (not given here) consisted of the characteristic lines of α-$Fe_2O_3$, γ-$Fe_2O_3$, $Co_3O_4$ and $CoFe_2O_4$ phases. The heights of the lines corresponding to $CoFe_2O_4$ phase increase on increasing the dopant concentration and temperature. On the other hand, the *R* value given in Table 1 increases from 0.69 to 1.59 on increasing the precalcination temperature of pure mixed solids from 700 to 950°C. Also this value increases as a function of dopant concentration with subsequent decrease in the peak height of the free oxides. So, it can be concluded that both temperature and doping with $Al_2O_3$(0.75–4.5 mol%) enhanced the solid–solid

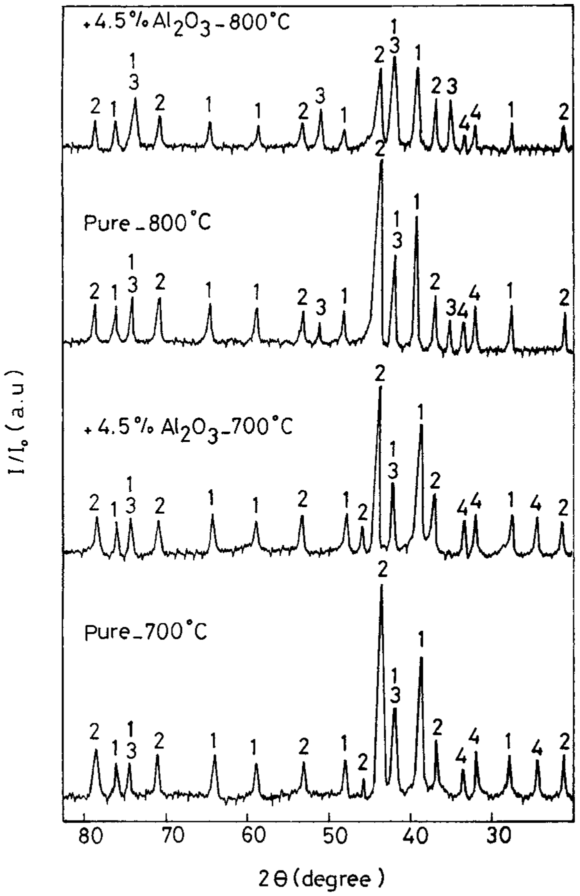

Fig. 4. XRD patterns of pure and heavily doped mixed oxide solids precalcined at 700 and 800°C, line (1) refer to $\alpha$-$Fe_2O_3$, lines (2) refer to $Co_3O_4$, lines (3) refer to $CoFe_2O_4$, and lines (4) refer to $\gamma$-$Fe_2O_3$ phases.

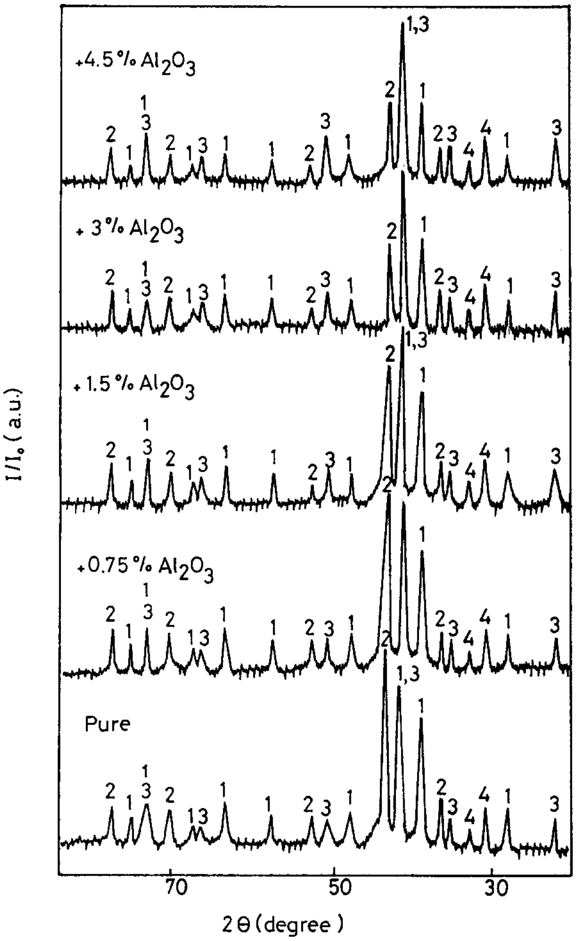

Fig. 5. XRD patterns of pure and doped mixed solids precalcined at 900°C, line (1) refer to $\alpha$-$Fe_2O_3$, lines (2) refer to $Co_3O_4$, lines (3) refer to $CoFe_2O_4$, and lines (4) refer to $\gamma$-$Fe_2O_3$ phases.

interactions between $\alpha$-$Fe_2O_3$ and $Co_3O_4$ yielding $CoFe_2O_4$ to an extent proportional to the amount of dopant added.

Fig. 6 depicts the X-ray diffractograms of pure and doped mixed oxide solids calcined at 1000°C. This figure shows that the patterns of pure and the 0.75 mol% $Al_2O_3$-doped solids consisted of the characteristic lines of $\alpha$-$Fe_2O_3$, $\gamma$-$Fe_2O_3$, $Co_3O_4$ and $CoFe_2O_4$ phases. It is regarded that there is a jump in the intensity of cobalt ferrite peaks for the solids calcined at 1000°C rather than those calcined at lower temperatures (700–950°C). This jump was evidenced from the jump in the *R* value given in Table 1 which reached up to 3.7 and 5.67 for pure and the 0.75 mol% $Al_2O_3$ -doped samples, respectively. It can be seen from Table 1 that the increase in the precalcination temperature and the amount of dopant added of the various investigated solids brought about an important increase in the amount of $CoFe_2O_4$ produced with subsequent decrease in the extent of the unreacted portions of $\alpha$-$Fe_2O_3$ and $Co_3O_4$. This conclusion is reached from the fact that all diffraction lines of different phases are sharp and only I/I0 of their values change on changing the precalcination temperature and amount of dopant added. So, the peak height relative to $CoFe_2O_4$ phase can be considered as a measure of the amount of $CoFe_2O_4$ phase present in given solid samples at a definite temperature *T*.

Table 1
Effects of precalcination temperature and amount of dopant on the height of some diffraction lines of α-$Fe_2O_3$, $Co_3O_4$ and $CoFe_2O_4$ phases

| Solids | Calcination temperature (°C) | Peak height (arbitrary units) | | 2.08 Å (40%) $CoFe_2O_4$ | $R$ (2.51/2.69) |
|---|---|---|---|---|---|
| | | 2.69 Å (100%) α-$Fe_2O_3$ | 2.43 Å (100%) $Co_3O_4$ | | |
| $Co_3O_4$+$Fe_2O_3$ | 700 | 90 | 130 | – | 0.69 |
| +0.75% $Al_2O_3$ | | 82 | 118 | – | 0.72 |
| +1.5% $Al_2O_3$ | | 79 | 108 | – | 0.75 |
| +3% $Al_2O_3$ | | 75 | 96 | – | 0.79 |
| +4.5% $Al_2O_3$ | | 70 | 67 | – | 0.83 |
| $Co_3O_4$+$Fe_2O_3$ | 800 | 83 | 125 | – | 0.75 |
| +0.75% $Al_2O_3$ | | 75 | 115 | 7 | 0.86 |
| +1.5% $Al_2O_3$ | | 68 | 105 | 9 | 0.99 |
| +3% $Al_2O_3$ | | 53 | 85 | 10 | 1.04 |
| +4.5% $Al_2O_3$ | | 47 | 55 | 12 | 1.17 |
| $Co_3O_4$+$Fe_2O_3$ | 900 | 80 | 120 | 15 | 1.22 |
| +0.75% $Al_2O_3$ | | 75 | 108 | 16 | 1.39 |
| +1.5% $Al_2O_3$ | | 66 | 90 | 17 | 1.45 |
| +3% $Al_2O_3$ | | 50 | 55 | 18 | 1.75 |
| +4.5% $Al_2O_3$ | | 44 | 50 | 19 | 1.82 |
| $Co_3O_4$+$Fe_2O_3$ | 950 | 69 | 56 | 18 | 1.59 |
| +0.75% $Al_2O_3$ | | 59 | 60 | 21 | 1.87 |
| +1.5% $Al_2O_3$ | | 48 | 43 | 22 | 2.04 |
| +3% $Al_2O_3$ | | 41 | 35 | 23 | 2.35 |
| +4.5% $Al_2O_3$ | | 32 | 30 | 24 | 2.59 |
| $Co_3O_4$+$Fe_2O_3$ | 1000 | 45 | 26 | 31 | 3.70 |
| +0.75% $Al_2O_3$ | | 30 | 19 | 36 | 5.67 |
| +1.5% $Al_2O_3$ | | – | – | 37 | $\propto$ |
| +3% $Al_2O_3$ | | – | – | 39 | $\propto$ |
| +4.5% $Al_2O_3$ | | – | – | 45 | $\propto$ |

It can be concluded that heating of $Co_3O_4$/$Fe_2O_3$ system at 1000°C much enhanced the solid–solid interactions of the free oxides producing $CoFe_2O_4$. On the other hand, doping of the mixed oxides under investigation with 1.5–4.5 mol% $Al_2O_3$ followed by calcination at 1000°C resulted in a complete conversion of reacting oxides into cobalt ferrite as given in Fig. 6 which shows that doping of the free oxides with 1.5–4.5 mol% $Al_2O_3$ and heating at 1000°C led to disappearance of the characteristic diffraction lines of $Fe_2O_3$ and $Co_3O_4$ phases.

## 4. Discussion

$Fe_2O_3$ and $Co_3O_4$ undergo solid–solid interaction to produce $CoFe_2O_4$ which is formed either between crystals of the two reacting oxides or around one of them. The rate of ferrite formation is then controlled by diffusion across the ferrite film acting as a barrier against the diffusion process [11]. The propagation of this reaction is controlled by the thermal diffusion of cobalt and iron cations through the ferrite film which acts as an energy barrier, thus hindering the diffusion of $Co^{2+}$ and $Fe^{3+}$ ions and the completion of the reaction requires prolonged heating at elevated temperature >1100°C. $Al_2O_3$-doping facilitates the diffusion of the reacting cations up to a limit that the reaction is completely finished at 1000°C upon doping with 1.5 mol% $Al_2O_3$, due to dissolution of $Al_2O_3$ in both oxide lattices and formation of solid solutions. Similar results have been reported in case of $Co_3O_4$/$Fe_2O_3$ system [11] doped with $Li_2O$. Doping of the above system with 1.5 mol% $Li_2O$ not only stimulated the reaction propagation of ferrite formation, but also led to completion of the reaction between $Co_3O_4$ and

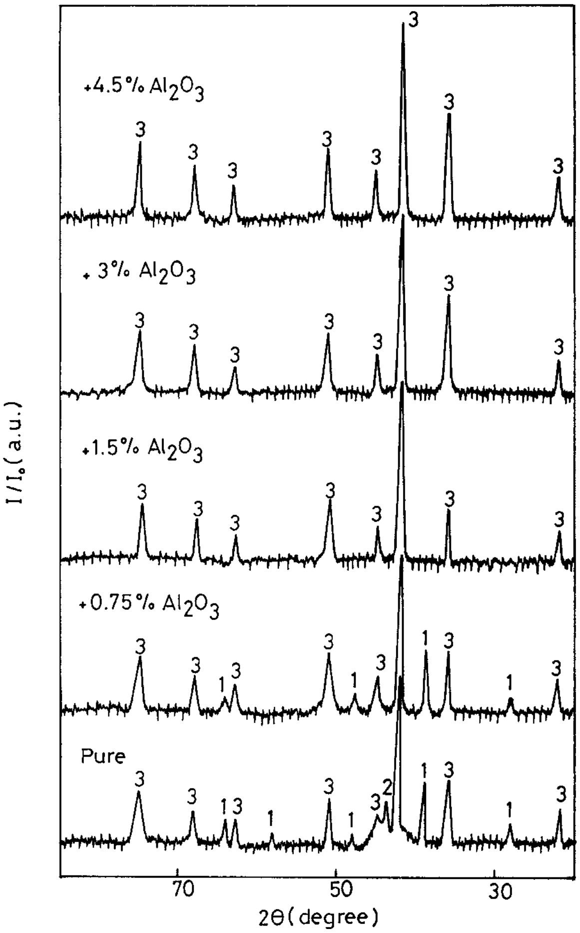

Fig. 6. XRD patterns of pure and doped mixed oxide solids precalcined at 1000°C, lines (1) refer to $\alpha$-$Fe_2O_3$, lines (2) refer to $Co_3O_4$, and lines (3) refer to $CoFe_2O_4$ phases.

$Fe_2O_3$ on heating at 1000°C. The effect of $Al_2O_3$ doping on NiO/$Fe_2O_3$ has been studied before [20]. $Al_2O_3$ was found to enhance the solid–solid interaction between NiO and $Fe_2O_3$, producing $NiFe_2O_4$. Although the degree of reaction propagation increased in parallel to the amount of $Al_2O_3$ added, the reaction was not completed by doping with 10 mol% $Al_2O_3$ and subsequent calcination at 1000°C. Comparison of these results with the results under investigation reflects the high degree of solubility of alumina in $Co_3O_4$ lattice rather than in NiO lattice.

The dissolution process of $Al_2O_3$ in both oxide lattices can be simplified by the use of Kröger's mechanism [27] in the following manner:

$$Al_2O_3 + 2Co^{3+} \rightarrow 2AlCo^{2+} + 2Co^{2+} + \tfrac{1}{2}O_2 \quad (1)$$

$$Al_2O_3 + 6Co^{3+} \rightarrow 2Al_\Delta + 6Co^{2+} + \tfrac{3}{2}O_2 \quad (2)$$

$$\tfrac{3}{2}Al_2O_3 \rightarrow 3AlFe^{3+} + \text{C.V.} \quad (3)$$

$$Al_2O_3 + 6Fe^{3+} \rightarrow 2Al_\Delta + 6Fe^{2+} + \tfrac{3}{2}O_2 \quad (4)$$

Here, $AlCo^{2+}$ and $AlFe^{3+}$ are trivalent aluminum ions located in the positions of host cations $Co^{2+}$ and $Fe^{3+}$ of $Co_3O_4$ and $Fe_2O_3$ lattice, C.V. a created cationic vacancy. $Al_\Delta$ is trivalent aluminum ion retained in interstitial position in $Co_3O_4$ and $Fe_2O_3$ lattices (reactions (2) and (4)). Reactions 1 and 3 indicate the dissolution of $2Al^{3+}$ ions in $Co_3O_4$ and $Fe_2O_3$ lattices via substitution mechanism.

The dissolution of aluminum oxide in $Co_3O_4$ and $Fe_2O_3$ according to reaction (3) is expected to be accompanied by increase in the mobility of $Fe^{3+}$ cations due to the creation of cationic vacancies. The dissolution of $Al_2O_3$ in $Co_3O_4$ via location in interstitial position (Eq. (2)) is accompanied by an increase in the concentration of the divalent cobalt cations, which is required in the ferrite formation. While the dissolution of alumina in ferric oxide lattice according to reaction (4) is followed by reduction in the concentration of trivalent ions. Reactions 1, 2 and 3 enhance the solid–solid interactions between $Fe_2O_3$ and $Co_3O_4$ yielding $CoFe_2O_4$, while reaction (4) suppresses the propagation of this reaction.

The speculated induced increase in the mobility of the reacted cations due to treatment with $Al_2O_3$ as a result of creation of cationic vacancies could be investigated by the determination of the activation energy of formation of $CoFe_2O_4$ phase $\Delta E$ at temperatures between 800 and 1000°C for pure and doped mixed solids, respectively. This has been tentatively achieved by assuming the height of the characteristic diffraction line at 2.08 Å as a measure of the amount of $CoFe_2O_4$ 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 $\Delta E$ value by direct application of the Arrhenius equation (Fig. 7). The computed $\Delta E$ values are 99.6, 87.8, 71.9, 64.7 and 48.7 kJ mol$^{-1}$ for pure mixed solids sample and those doped with 0.75, 1.5, 3 and 4.5 mol% $Al_2O_3$, respectively. This indicates that alumina-doping enhances the ferric formation via

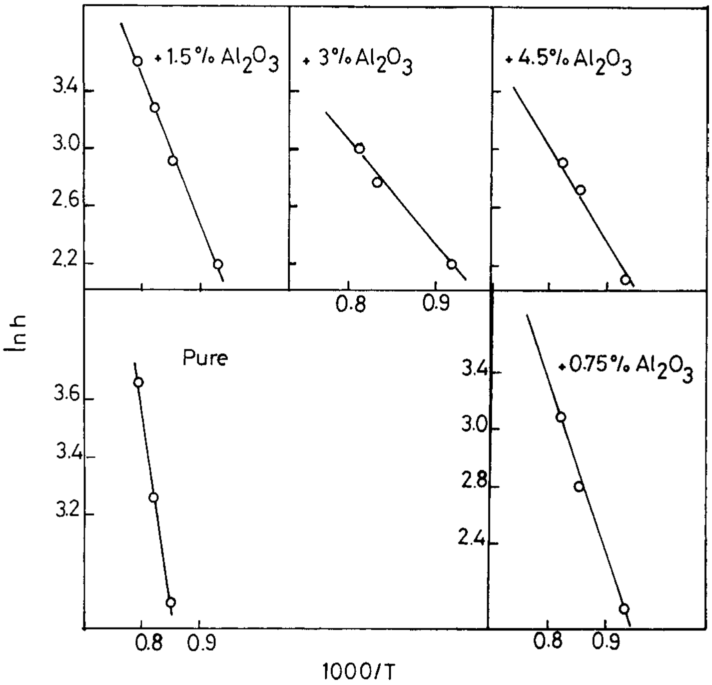

Fig. 7. Change of ln (peak height of diffraction line of $CoFe_2O_4$ (2.08 Å) as a function of 1/*T* for pure and $Al_2O_3$-doped mixed solids.

facilitating diffusion. The activation energy of cobalt ferrite formation of pure mixed oxide solids was previously computed [11] at 57.3 kJ mol$^{-1}$, while in our investigation it is 99.6 kJ mol$^{-1}$. The large difference between the two values arises from the prehistory of the ferric oxide used. In the previous investigation, $Fe_2O_3$ was prepared by precipitation of ferric hydroxide from $Fe_2(SO_4)_3$ using 1 mol $NH_4OH$ at 70°C. $Fe(OH)_3$ was directly mixed with $Co_3O_4$ and calcined at variable temperatures. So, $Fe_2O_3$ was nacently formed via decomposition of ferric hydroxide. The ferric oxide exerted much high reactivity toward the ferrite formation.

## 5. Conclusions

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

1. $Al_2O_3$-doping hindered the thermal decomposition of $Co_3O_4$ to CoO at $\simeq$850°C.
2. Solid–solid interaction between $\alpha$-$Fe_2O_3$ and $Co_3O_4$ occurred at temperatures starting from 700°C to produce a cobalt ferrite phase. The extent of this reaction increased on increasing the heating temperature in the 700–1000°C range. The reaction was not finished up to 1000°C.
3. Alumina-doping promoted the cobalt ferrite formation to an extent proportional to its amount added.
4. Doping of the investigated system with 1.5 mol% $Al_2O_3$ was found sufficient to effect the complete conversion of cobalt and ferric oxides into $CoFe_2O_4$ by heating at 1000°C.
5. The activation energy of formation of $CoFe_2O_4$ was determined for pure and $Al_2O_3$-doped solids and found to be 99.6, 87.8, 71.9, 64.7 and 48.7 kJ mol$^{-1}$, respectively. These values suggest that aluminum oxide-doping enhanced the ferrite formation process through an increase in the concentration and mobility of thermal diffusion of the reacting cations.

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