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EFFECTS OF Li_2O DOPING ON THERMAL SOLID–SOLID INTERACTION BETWEEN FERRIC OXIDE AND NICKEL CARBONATE

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ABSTRACT

The effects of Li_2O doping on the interaction between α-Fe_2O_3 and basic nickel carbonate were investigated using DTA, TG, DTG and X-ray diffraction techniques.

The results obtained showed that ferric oxide underwent solid–solid interaction with pure NiO at temperatures starting from 800 °C, yielding well-crystallized $NiFe_2O_4$ (trevorite). The amount of ferrite produced increased when the roasting temperature of the mixed solids was increased. However, the completion of this reaction required prolonged heating at elevated temperatures, $\geqslant 1100\,°C$, owing to the formation of the $NiFe_2O_4$ phase which covered the surfaces of the grains of each oxide thus hindering the diffusion of Ni^{2+} and Fe^{3+} ions. Doping with Li_2O (although effecting the transformation of some Ni^{2+} ions into Ni^{3+} ions (not contributing in the ferrite formation)) enhanced the solid–solid interaction between the mixed oxides to an extent proportional to the amount of Li_2O added. The promotion effect of lithium oxide was attributed to an effective increase in the mobility of the various reacting ions. The activation energy of formation (ΔE) of nickel ferrite was determined for pure and lithium-doped mixed solids. This was achieved by following up the change in the height of some diffraction lines, or key lines of the $NiFe_2O_4$ phase (with d spacings at 2.95 and 1.605 Å) as a function of roasting temperature. The computed values of ΔE were 26, 19 and 16 kcal mol^{-1} for pure solids and those doped with 3 and 5 mol% Li_2O, respectively.

INTRODUCTION

Most divalent metal oxides (MO) 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 possessing a cubic spinel structure e.g. Mg, Co, Ni, Cu and Zn and (2) ferrites with other different structures e.g. the ferrites of the alkaline earth elements [2–4]. The spinel-type ferrites are commonly utilized in fine electronic devices owing to their remarkable magnetic and semiconducting properties [1,5–10]. Mixed ferrites are usually employed and their properties can be modified to give better performance [1,9,10]. The magnetic and semiconducting properties of ferrites depend mainly on their chemical

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composition, calcination conditions, structure and surface properties of the Fe_2O_3 employed and on the addition of small amounts of certain foreign oxides [7,9,10]. The mechanisms of ferrite formation have been studied by some investigators [9,10]. Fe_2O_3 interacts readily with MO with the subsequent formation of a thin layer of MFe_2O_4. This covers the surfaces of the grains of each oxide and thus hinders the diffusion of reacting cations [1].

The present work reports the results of a study on the effects of the addition of small amounts of Li_2O on nickel ferrite formation at different temperatures. The techniques employed were DTA, TG, DTG and X-ray diffraction.

EXPERIMENTAL

Materials

Pure mixed solids were prepared by mixing equimolar proportions of finely powdered α-Fe_2O_3 and basic nickel carbonate with the addition of a small amount of distilled water. Three specimens of doped mixed solids were obtained by treating a given mass of the prepared mixed solids with solutions containing different proportions of Li_2CO_3. The concentrations of the dopant agent were 3, 5 and 10 mol% lithium carbonate. Two additional specimens of lithium-doped mixed solids were prepared by mixing equimolar proportions of α-Fe_2O_3 and NiO doped with 3 or 5% Li_2CO_3 and were precalcined in air at 700 °C for 6 h. The solids obtained (pure and doped) were dried at 100 °C, then roasted in air at temperatures between 700 and 1100 °C; the time of heating was fixed at 6 h.

Techniques

DTA, TG and DTG analyses of the mixed solids were carried out using a thermal analyzer (Shimadzu, Koto, Japan). The rate of heating was 10 °C min^{-1} and the sensitivity was 0.5 °C min^{-1}. A 40 mg sample of each solid specimen was employed in each case and the heating process was conducted in the presence of a current of dry air flowing at a rate of 50 ml min^{-1}.

An X-ray investigation of the thermal products of the pure and doped mixed solids was performed with a Philips diffractometer (type PW 1390). The patterns were run with iron-filtered Co radiation ($\lambda = 1.7889$ Å) at 40 kV and 30 mA with a scanning speed of 1° in 2 θ min^{-1}.

RESULTS

Thermal behaviour of pure and doped Fe_2O_3:$NiCO_3 \cdot Ni(OH)_2$ mixed solids

Figures 1 and 2 show DTA, TG and DTG curves of pure and doped mixed solids. Two endothermic peaks were observed in the DTA curves of

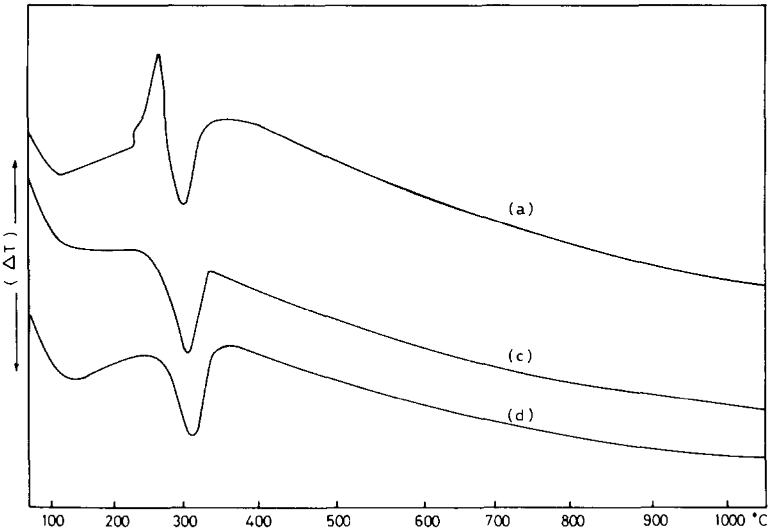

Fig. 1. DTA curves of ferric oxide mixed with equimolar proportions of pure and doped basic nickel carbonate: (a) Fe_2O_3:$NiCO_3$; (c) Fe_2O_3:$NiCO_3$ + 5 mol% Li_2CO_3; (d) Fe_2O_3:$NiCO_3$ + 10 mol% Li_2CO_3.

the various mixed solids. The first peak was weak and broad and extended between 50 and 150 °C. The second peak was strong and sharp and had its maximum at 300 °C. The weak endothermic peak indicated desorption of

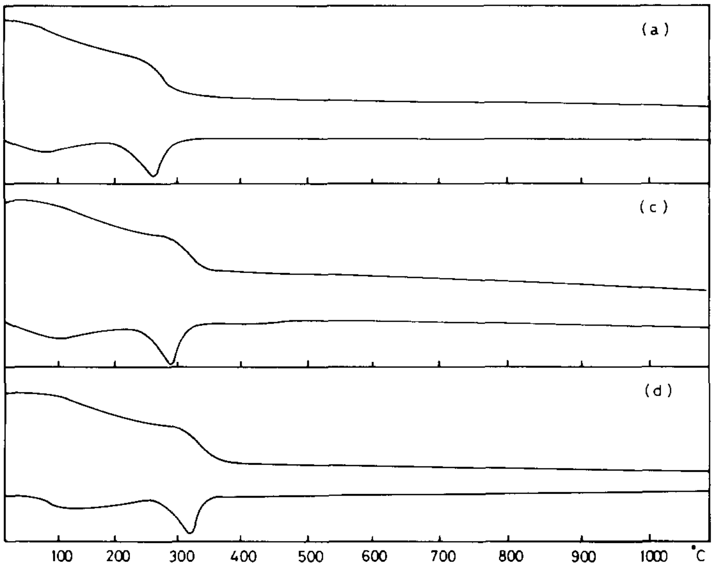

Fig. 2. TG and DTG curves of ferric oxide mixed with equimolar proportions of pure and doped basic nickel carbonate; (a) Fe_2O_3:$NiCO_3$; (c) Fe_2O_3:$NiCO_3$ + 5 mol% Li_2CO_3; (d) Fe_2O_3:$NiCO_3$ + 10 mol% Li_2CO_3.

physisorbed water. No other peaks were detected in the DTA curves of the investigated solids heated up to 1000 °C and no detectable loss in weight was recorded at temperatures between 400 and 1000 °C. The total losses in weight were 14, 12 and 13% for pure mixed solids and those doped with 5 and 10 mol% Li_2CO_3, respectively. The theoretical loss in weight accompanying the complete transformation of the various mixed solids investigated into mixed oxides is about 12%. The strong endothermic peak in the DTA curves of the solids must, therefore, indicate the complete thermal decomposition of basic nickel carbonate into NiO. The absence of any endothermic or exothermic peaks in the DTA curves of the investigated solids at temperatures between 400 and 1000 °C may indicate the absence of any phase transformation or solid–solid interaction between α-Fe_2O_3 and the

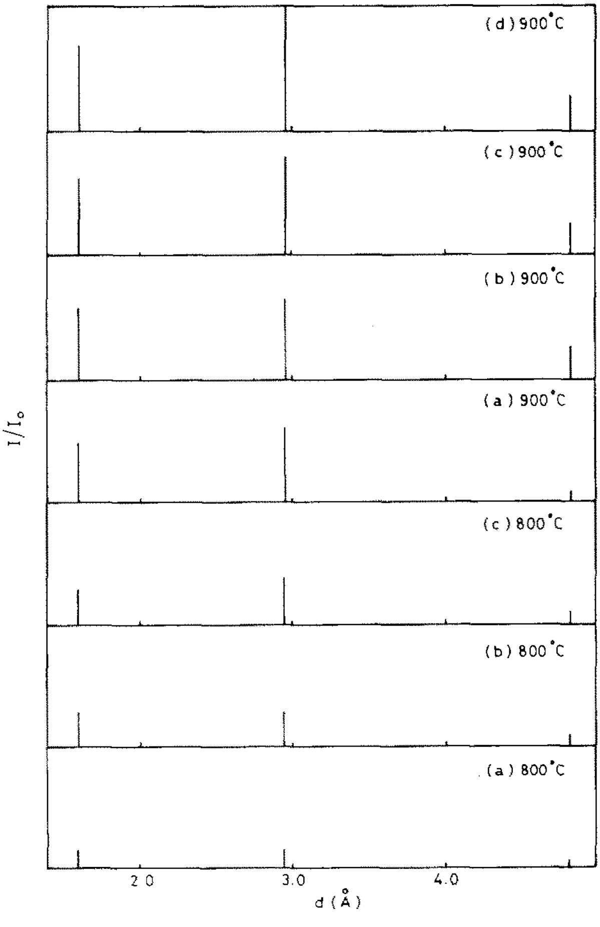

Fig. 3. X-ray diffraction patterns (the characterized diffraction lines or key lines of $NiFe_2O_4$ are present) of pure and doped mixed solids roasted at 800 and 900 °C: (a) Fe_2O_3:$NiCO_3$; (b) Fe_2O_3:$NiCO_3$ + 3% Li_2CO_3; (c) Fe_2O_3:$NiCO_3$ + 5% Li_2CO_3; (d) Fe_2O_3:$NiCO_3$ + 10% Li_2CO_3.

NiO produced or, more probably, such interactions may occur at an extremely slow rate so that they cannot be easily detected by a simple DTA analysis. These expectations can be clarified via an X-ray investigation of the various mixed solids precalcined in air for 6 h at different temperatures.

X-ray investigation of the thermal products of pure and doped mixed solids

XRD revealed that the ferric oxide employed consisted entirely of the well-crystallized α-Fe_2O_3 phase. All the diffraction lines of α-Fe_2O_3 and NiO were detected in the diffraction patterns of the various mixed solids precalcined at 700 °C. This indicates the complete transformation of basic nickel carbonate into well-crystallized NiO phase and also shows the absence of any solid–solid interaction between Fe_2O_3 and NiO at 700 °C. In contrast, other diffraction lines, besides those of NiO and Fe_2O_3, were detected in the patterns of pure and Li_2CO_3-doped mixed solids precalcined at 800 °C. The newly detected lines characterize $NiFe_2O_4$ (trevorite). Figures

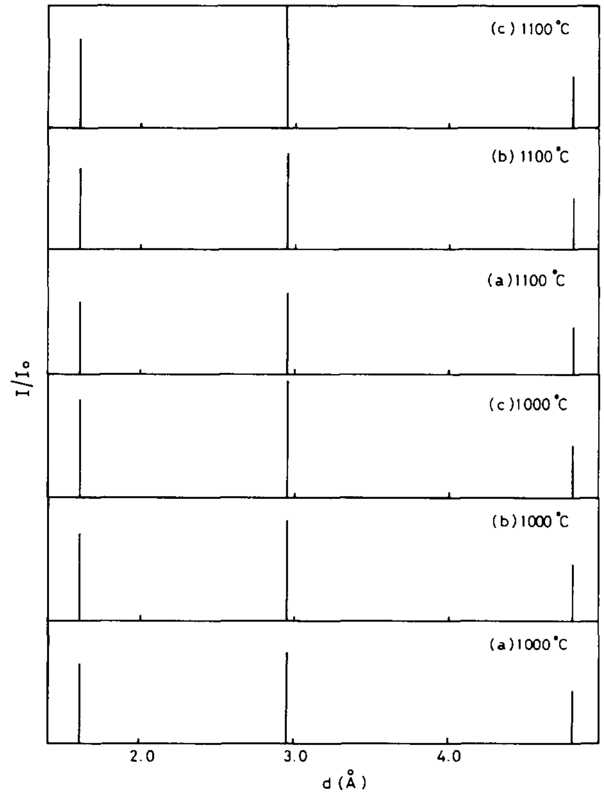

Fig. 4. X-ray diffraction patterns (the key lines of $NiFe_2O_4$) for pure and doped mixed solids roasted at 1000 and 1100 °C: (a) Fe_2O_3:$NiCO_3$; (b) Fe_2O_3:$NiCO_3$ + 3% Li_2CO_3; (c) Fe_2O_3:$NiCO_3$ + 5% Li_2CO_3.

3 and 4 show the X-ray diffraction patterns of the solids roasted in air at 800, 900, 1000 and 1100 ° C. The diffraction lines of the unreacted portions of α-Fe_2O_3 and NiO, which were detected in the patterns of all investigated solids roasted at temperatures up to 1100 ° C, are not given in Fig. 3 and 4. The relative intensities of the different lines of the free oxides were significantly high indicating the existence of important portions of unreacted NiO and α-Fe_2O_3. Some of the characteristic lines of the nickel ferrite phase are common with those of NiO and α-Fe_2O_3 [11,12]; the lines at 2.41, 2.09 and 1.48 Å exist in both nickel oxide and nickel ferrite phases and the lines at 2.51, 1.70 and 1.48 Å are common to both α-Fe_2O_3 and $NiFe_2O_4$. However, the lines at 4.82, 2.95 and 1.605 Å are among the characteristic diffraction lines of $NiFe_2O_4$ that are not common with either NiO or α-Fe_2O_3 phases and have reasonable intensities (20, 30 and 30%, respectively). These three lines were thus considered to be characterizing lines or key lines for the $NiFe_2O_4$ phase and only these lines are given in Figs. 3 and 4. The figures show clearly that the intensities of these lines increase with an increase in the calcination temperature from 800 to 1000 ° C. However, it is worth noting that the key lines of the $NiFe_2O_4$ phase are sharp for all the solids investigated even those preheated at the lowest temperature (800 ° C). This indicates that the ferrite produced at temperatures between 800 and 1100 ° C

TABLE 1

The effects of roasting temperature and doping on the height of some characteristic diffraction lines of the $NiFe_2O_4$ phase

Solid	Calcination temp. (° C)	Height of some diffraction lines (arbitrary units)		
		4.82Å	2.95 Å	1.605 Å
Fe_2O_3:$NiCO_3$	800	10	25	20
+ 3% Li_2CO_3	800	12	38	35
+ 5% Li_2CO_3	800	15	55	38
Fe_2O_3 + 3%-doped NiO	800	10	32	30
Fe_2O_3 + 5%-doped NiO	800	12	47	30
Fe_2O_3:$NiCO_3$	900	32	80	65
+ 3% Li_2CO_3	900	35	87	77
+ 5% Li_2CO_3	900	35	110	82
+ 10% Li_2CO_3	900	35	130	90
Fe_2O_3:$NiCO_3$	1000	85	150	130
+ 3% Li_2CO_3	1000	85	170	140
+ 5% Li_2CO_3	1000	90	195	150
Fe_2O_3:$NiCO_3$	1100	75	135	120
+ 3% Li_2CO_3	1100	80	165	135
+ 5% Li_2CO_3	1100	80	200	140

is well crystallized $NiFe_2O_4$ (trevorite) [12] and its amount increases as a function of the precalcination temperature of the mixed oxide solids. The height of the characterizing lines of the nickel ferrite can thus be taken as a measure of its abundance. Table 1 includes the actual height, given in arbitrary units, of the diffraction lines (4.82_{20}, 2.95_{30} and 1.605_{30} Å) of the various mixed solids investigated. Table 1 shows that the amount of $NiFe_2O_4$ produced increased suddenly when the roasting temperature of the pure mixed solids was increased from 800 to 900 ° C, and increased progressively by heating to 1000 ° C. It can also be seen from this table that the amounts of nickel ferrite produced in the lithium-doped solids are much greater than those formed in the pure mixed solids. Indeed, the amount of ferrite formed was directly proportional to the amount of lithium carbonate added. It can thus be concluded that lithium oxide doping of mixed NiO and Fe_2O_3 solids enhances the formation of $NiFe_2O_4$ to an extent proportional to the amount of dopant agent added. It can also be concluded, from the results given in Table 1, that the stimulating effect of lithium doping at 800 ° C is slightly less pronounced if the ferric oxide employed is mixed with NiO, doped with lithium and preheated at 700 ° C.

DISCUSSION

Fe_2O_3 and NiO undergo solid–solid interaction to produce $NiFe_2O_4$ that covers the grains of each reacting oxide [1]. The propagation of this reaction is controlled by the thermal diffusion of nickel and iron cations through the ferrite film which acts as an energy barrier. The fact that free NiO and Fe_2O_3 were detected in all investigated solids roasted at temperatures up to 1100 ° C, gives an indication of the height of the energy barrier which has to be overcome. The solid–solid interactions between Fe_2O_3 and Li_2CO_3 or Li_2O, which yield lithium ferrites, have been reported to take place at a temperature starting from 400 ° C with completion at about 800 ° C [13,14]. The comparison of the formation of lithium ferrites with that of $NiFe_2O_4$ reveals that the early-formed lithium ferrite phases are much more easily passed by lithium ions as they move towards the Fe_2O_3 lattice. This leads to the progressive formation of lithium ferrites until all the Li^+ ions interact with Fe_2O_3 giving a homogeneous lithium ferrite. The formation of homogeneous compact $NiFe_2O_4$ requires prolonged heating at much higher temperatures, > 1100 ° C [12]. The stimulating effect of Li_2CO_3 or Li_2O doping may be a consequence of the increased mobility of Ni^{2+} ions [15,16]. In fact, NiO is known to dissolve Li_2O forming a solid solution with a maximum concentration of 33 atm% Li^+ [17]. The dissolution process takes place according to different mechanisms depending mainly on the atmosphere in contact with the investigated solids and the calcination temperature. Lithium ions can be easily incorporated in the NiO lattice at temperatures starting from 300 °C via substitution of some of the host nickel ions according to [18,19]

$Li_2O + 0.5O_2(g) \rightarrow 2Li^+(Ni^{2+}) + 2Ni^{3+}$

$Li^+(Ni^{2+})$ is monovalent lithium ion located in the position of the host cation, Ni^{2+}; Ni^{3+} is a trivalent nickel cation (charge carrier). Dissolution of Li_2O in solid NiO, according to the mechanism expressed by the equation above, is accompanied by transformation of some of the host cations, Ni^{2+}, to Ni^{3+}, followed by fixation of O_2 in the oxide lattice. It has been reported that dissolution of lithium ions in the NiO lattice, besides the creation of trivalent nickel ions, greatly increases the mobility of the lattice cations of NiO [16,20]. The Ni^{3+} ions created cannot participate directly in the nickel ferrite formation. The creation of these ions may thus be followed by a decrease in the amount of $NiFe_2O_4$ formed in the mixed solids doped with

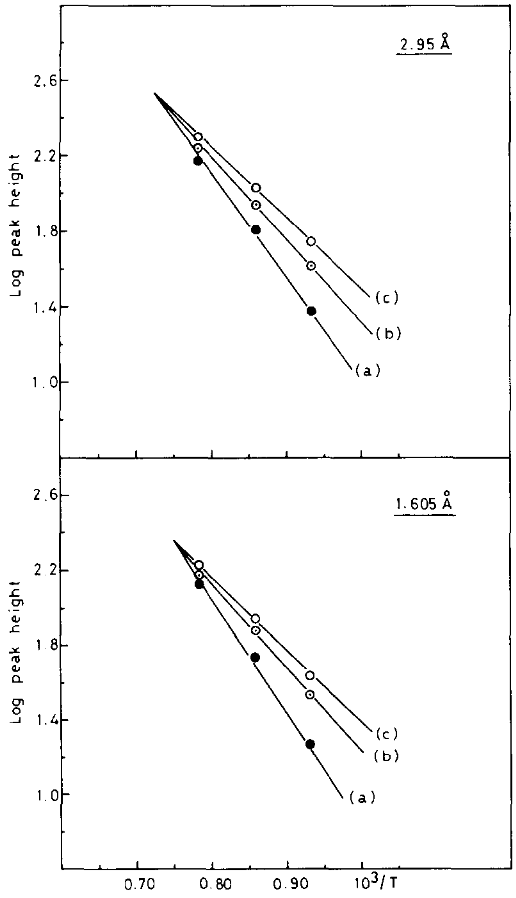

Fig. 5. Variation in log peak height of the diffraction lines of $NiFe_2O_4$ at *d* spacings of 2.95 Å and 1.605 Å for pure and Li-doped mixed solids, as a function of roasting temperature. (a) Fe_2O_3:$NiCO_3$; (b) Fe_2O_2:$NiCO_3$ + 3% Li_2CO_3; (c) Fe_2O_3:$NiCO_3$ + 5% Li_2CO_3.

lithium. However, the opposite effect has been clearly verified in our case. These results may point to the role of Li doping in increasing the mobility of nickel ions of NiO facilitating their thermal diffusion through the whole mass of the doped nickel oxide and also through the early-formed $NiFe_2O_4$ phase. The enhancement of nickel ferrite formation, as a result of doping with Li_2CO_3 or Li_2O and the consequent increase in the mobility of the diffusion of nickel ions through the growing $NiFe_2O_4$ phase, can be investigated by determining the activation energy of formation of spinel nickel ferrite (ΔE) for pure and lithium-doped mixed solids. This has been tentatively achieved from the results given in Table 1, by assuming that the height of the characterized diffraction lines or the key lines at 4.82, 2.95 and 1.605 Å are a measure of the amount of $NiFe_2O_4$ present in a given mixed solid at a definite temperature T. By plotting the peak height of these lines versus $1/T$, a straight line is obtained, whose slope determines the ΔE value by direct application of the Arrhenius equation. This trial has been successfully carried out at temperatures between 800 and 1000 °C, and the plots obtained are given in Fig. 5 for two diffraction lines at d spacings of 2.95 and 1.605 Å for pure mixed solids and those doped with 3 and 5 mol% Li_2CO_3. The computed ΔE values, obtained from the first diffraction line, are 26, 19 and 16 kcal mol^{-1} for pure solids and those doped with 3 and 5 mol% Li_2CO_3, respectively. The calculated ΔE data, obtained from the second line, are 27, 21 and 18 kcal mol^{-1}. These two sets of values which are in close agreement clearly indicate that lithium doping decreases the activation energy of diffusion of the various reacting species through the early-formed nickel ferrite phase to an extent proportional to the amount of lithium carbonate added. The decrease in ΔE values reflects an effective increase in the mobility of thermal diffusion of the reacting cations owing to lithium doping of nickel–ferric mixed oxide solids.

CONCLUSIONS

The following conclusions can be derived from the results obtained.

(1) Alpha-Fe_2O_3 underwent solid–solid interaction with pure or Li-doped NiO to yield well-crystallized spinel nickel ferrite, $NiFe_2O_4$ (trevorite), at temperatures starting from 800 °C. The diffraction lines with d spacings of 4.82, 2.95 and 1.605 Å were considered to be characterizing or key lines for the recognition of the ferrite phase in the presence of free α-Fe_2O_3 and NiO solids.

(2) The completion of the solid–solid interactions yielding $NiFe_2O_4$ required prolonged heating of pure or doped mixed oxide solids at elevated temperatures > 1100 °C.

(3) Li_2O doping enhanced the formation of nickel ferrite to an extent proportional to the amount added to the reacting ferric and nickel oxides.

(4) The activation energy of formation of $NiFe_2O_4$ was determined for pure and Li-doped solids and found to be 26, 19 and 16 kcal mol^{-1} for pure mixed solids and those doped with 3 and 5 mol% Li_2O, respectively. These values suggest that lithium oxide doping stimulated the ferrite formation process through an increase in the mobility of the reacting cations.

REFERENCES

1 P. Pascal, Nouveau Traité de Chimie Minérale, Tome II, Masson, Paris, 1966, p. 702.
2 V.V. Valkov, A. Deneva and D. Stavrakeva, Proc. 7th Int. Congr. Chem. Cem., Paris, France, 1980, 3, V/98-V/101.
3 L.M. Letyuk, M.N. Shipko, V.S. Tikhonov and M.V. Dimetriev, Izv. Akad. Nauk SSSR, Neorg. Mater., 18 (10) (1980) 1751.
4 K. Tae Ok and K.E. Dong, Yo-op Hoe Chi (Korea), 20 (4) (1983) 340.
5 M.W. Shafer, J. App. Phys., 33 (1962) 1210.
6 N. Yoji and M. Kimio, Patent, Japan, Kokai, Tokkyo Koho, 79, 159, 696 (Cl. H01F1/34), 17 December 1979, Appl. 78/68, 682.
7 V.V. Pan'Kov, L.A. Bashkiro and Yu. G. Saksonov, Izv. Akad. Nauk SSSR, Neorg. Mater., 15 (5) (1978) 922.
8 T. Mitev, T. Dimova and G. Khristova, Bulg. Sklar Keram. 32 (8) (1982) 207.
9 M. Crisan and D. Crisan, Mater. Sci. Monogr. 16 (Ceram. Powders) (1983) 429.
10 Fuji Electrochem. Co., Ltd. Patent, Japan, Kokai, Tokkyo Koho, 59, 213, 627 (84,213,627) Cl. Clog 53/00, 3 December 1984, Appl. 83/87, 046, 8 May 1983.
11 Powder Diffraction File (JCPDS), International Centre for Diffraction Data, Swarthmore, PA, 1979.
12 Nat. Bur. Stand. (U.S) Circ., 539 (10) (1960) 44.
13 L.L. Shoria and S.S. Lisnyak, in V.V. Klimov (Ed.), Mater Mezhotrasl. Soveshch. Method. Poluch. Anal. Ferritovykh, Segento-Pezoelectricheskikh Mater. Syr'ya Nikh., 3rd. Issled. Inst. Donetsk U.S.S.R., 1969 (published 1971), Vol. 3, p. 162.
14 G.A. El-Shobaky and A.A. Ibrahim, Thermochim. Acta, 118 (1987) 151.
15 G.A. El-Shobaky, Ph.D. Thesis, Lyon, 1966.
16 G.A. El-Shobaky, P.C. Gravelle and S.J. Teichner, in K. Hauffe and Th. Volkenstein (Eds.), Symposium on Electronic Phenomena in Chemisorption and Catalysis on Semiconductors, Moscow, 1968, Walter de Gruyter, Berlin, 1969.
17 N. Perakis and F. Kern, C.R. Acad. Sci., Ser. B, 269 (1969) 281.
18 E.J.W. Verwey, P.W. Haaijam, F.C. Romeijn and O. Van, Philips Res. Rep., 5 (1950) 173.
19 F.A. Kroger, Chemistry of Imperfect Crystals, North-Holland, Amsterdam, 1964.
20 S.H. Koide, J. Phys. Soc. Jpn., 1 (1965) 123.