Thermochimica Acta, 64 (1983) 259–265
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SOME PHYSICO-CHEMICAL PROPERTIES OF PURE AND DOPED NICKEL OXIDE. THERMAL ANALYSES AND X-RAY DIFFRACTION STUDIES

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(Received 2 November 1982)

ABSTRACT

In this investigation pure and doped NiO with different concentrations of Al, Ga or In are thermally analysed. The results indicate the presence of two endothermic peaks at about 120 and 250°C which were attributed to the loss of adsorbed water and phase change, respectively.

X-Ray data indicated that all samples belong to the cubic system. In the case of samples doped with high concentrations of Ga or In, a new line is observed which may be due to the formation of a spinel form. There is no systematic change between the calculated values of lattice parameters, *a*, of doped samples and the type or concentration of dopant. This change has been related to the difference in the values of the ionic radii of Ni^{2+} and those of dopant elements.

INTRODUCTION

The electronic properties of semiconductors can be modified by introducing various additives into the parent lattice. Such modifications play a prominent role in the study of several properties. Nickel oxide doped with monovalent elements has been studied extensively. Very little work concerning the group IIIA elements was found in the literature. Three dopants were chosen, namely, Al, Ga or In in different concentrations.

The aim was to obtain some information concerning the influence of dopant type on the thermal properties and structure of NiO.

EXPERIMENTAL

The different samples of nickel oxide were prepared as described.

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Undoped samples

The method applied in the preparation of nickel oxide was devised by Francois [1] where nickel carbonate was heated at 400, 550 and 1000°C for 3 h to produce black, gray and green nickel oxide, respectively.

Doped samples

The method used by Deren et al. [2] in doping with gallium was adopted in the preparation of all samples containing the three dopant atoms Al, Ga or In. The concentrations of the additives were 0.1, 0.5 and 1.0 at.% of Al, Ga or In.

Three undoped samples and nine differently doped samples were obtained. In this investigation the samples were subjected to thermal analysis using a derivatograph in the temperature range 25– ~ 950°C. X-Ray diffraction studies were conducted using CuK_α radiation and a Ni filter. All samples were analysed under the same instrumental conditions.

RESULTS AND DISCUSSION

The results of thermal analysis of the three undoped and nine doped samples are shown in Fig. 1. The positions of the peaks are listed in Table 1. From Table 1 it is observed that the DTA curves of undoped samples prepared at 400 and 550°C contain an endothermic peak at about 120°C. This peak may be attributed to a loss of adsorped water. The other endothermic peak, which occurs at about 250°C in all samples, may be due to a phase transformation from a cubic structure with a slight rhombohedral deformation to a perfect cubic structure [3–6].

The X-ray diffraction patterns obtained show that all samples belong to the cubic system. There are no lines corresponding to a rhombohedral modification of NiO. This result indicates that the amount of this form in the prepared samples is not in the X-ray limit.

In the case of undoped samples, the breadth of diffracted lines decreases when the temperature of preparation increases. This decrease was attributed to a decrease in the lattice defects [7]. Therefore, the undoped samples prepared at 1000°C represent the most stoichiometric composition of nickel oxide, NiO.

For Al-doped samples, no new lines are observed in the charts up to 1.0 at.% Al. But in the case of Ga-doped samples, a new line appears at $d = 2.48$ Å for the sample doped with 1.0 at.% Ga. This value may be correlated with $d = 2.49$ Å for the line corresponding to 80 or 100% intensity in the A.S.T.M. cards of Ga_2O_3 or $NiGa_2O_4$ spinel, respectively. To detect which of these two compounds has contaminated this Ga-doped sample, the

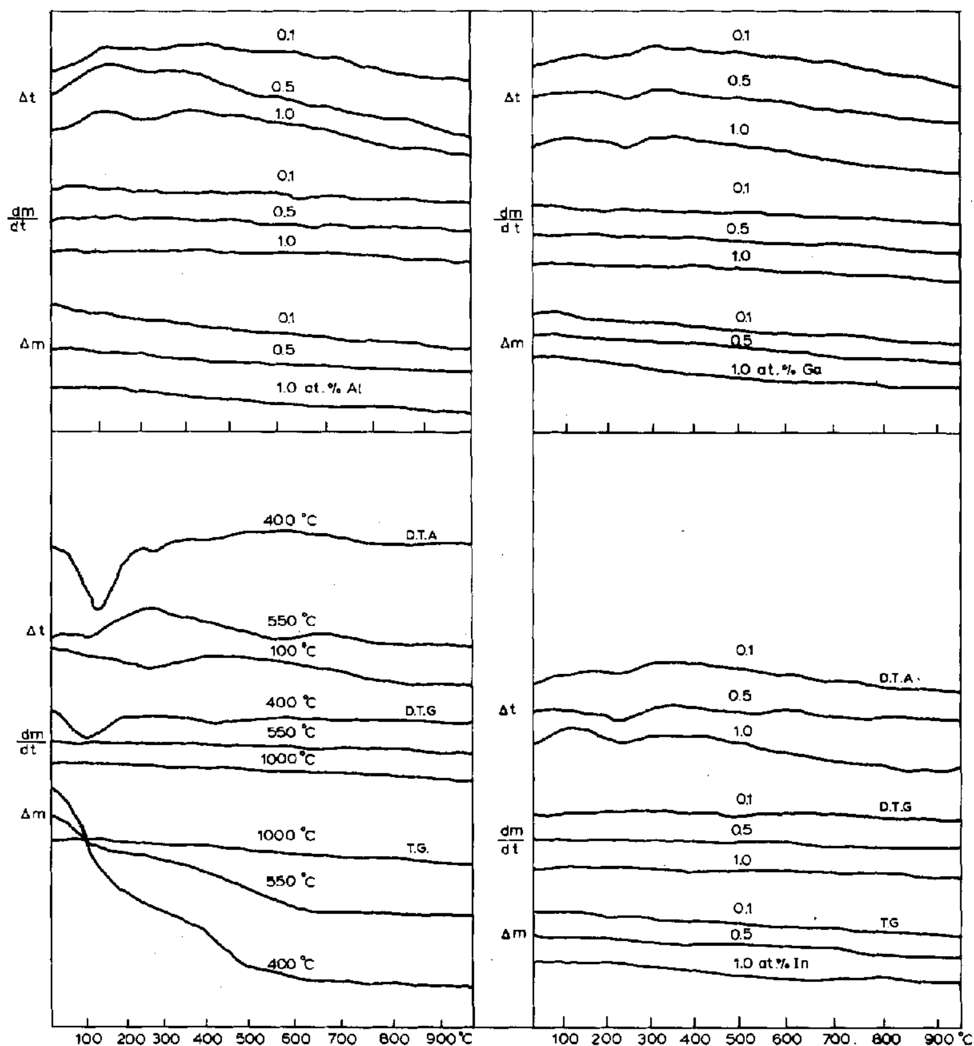

Fig. 1. TG, DTG and DTA curves of undoped and doped samples of NiO.

TABLE 1

Peak positions obtained from thermal analysis of doped and undoped NiO samples

Sample	Peak position (°C)
Undoped NiO	
NiO prepared at 400°C	120, 260
NiO prepared at 550°C	115, 250
NiO prepared at 1000°C	250
Doped NiO	
NiO doped with Al (0.1, 0.5 or 1.0 at.%)	250
NiO doped with Ga (0.1, 0.5 or 1.0 at.%)	255
NiO doped with In (0.1, 0.5 or 1.0 at.%)	250

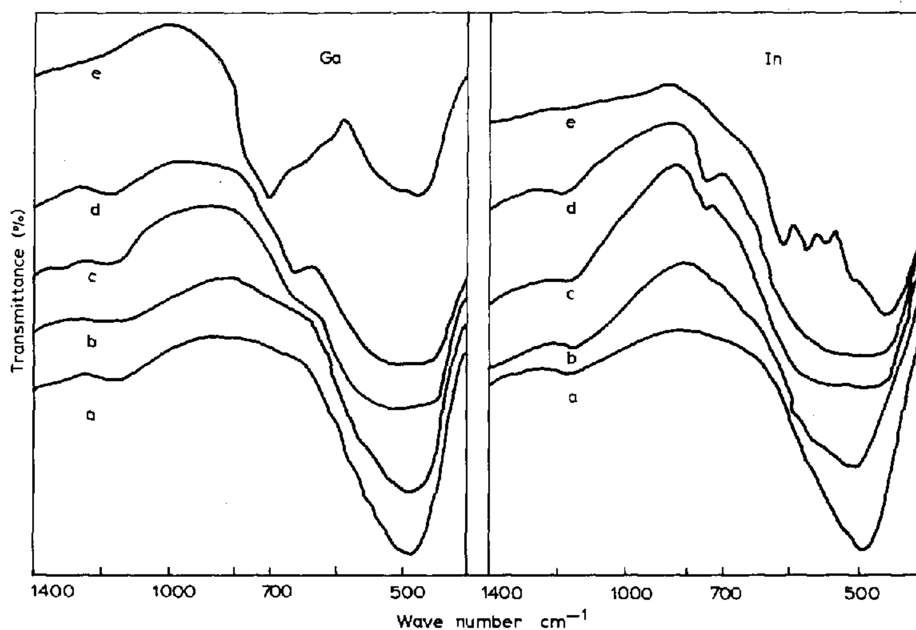

Fig. 2. IR absorption spectra. For Ga: (a) pure NiO (1000°C); (b) NiO + 0.1 at.% Ga; (c) NiO + 0.5 at.% Ga (d) NiO + 1.0 at.% Ga; (e) Ga_2O_3. For In: (a) pure NiO (1000°C); (b) NiO + 0.1 at.% In; (c) NiO + 0.5 at.% In; (d) NiO + 1.0 at.% In; (e) In_2O_3.

TABLE 2

Values of a calculated for doped and undoped NiO samples

Sample	a(Å)
Undoped NiO	
NiO prepared at 400°C	4.1790
NiO prepared at 550°C	4.1771
NiO prepared at 1000°C	4.1768
Doped NiO	
NiO doped with Al	
0.1 at.%	4.1740
0.5 at.%	4.1774
1.0 at.%	4.1699
NiO doped with Ga	
0.1 at.%	4.1755
0.5 at.%	4.1757
1.0 at.%	4.1759
NiO doped with In	
0.1 at.%	4.1745
0.5 at.%	4.1801
1.0 at.%	4.1735

infrared absorption spectra were investigated using a technique previously described [8]. Figure 2, curve 1, shows the IR absorption spectra of a Ga-doped sample (1.0 at.% Ga). A new band at 665 cm^{-1} can be observed. This band is not detected in the spectra of undoped samples (1000°C) or that of Ga_2O_3. Therefore, it may be due to the formation of $NiGa_2O_4$. Rooksby and Vernon [9] reported that when firing 3% Ga_2O_3 with NiO, a compound with the formula $NiGa_2O_4$ is formed.

Similarly, a new line appears for the 0.5 and 1.0 at.% In-doped samples at $d = 2.93$ Å. This line also represents the formation of In_2O_3 or $NiIn_2O_4$ spinel. This new line is more intense for the sample doped with 1.0 at.% In. The IR spectra of these samples show a band around 700 cm^{-1}. This band is not observed in the spectra of pure NiO or In_2O_3. Thus the 1.0 at.% In-doped sample may be contaminated with $NiIn_2O_4$.

The *a* values of all samples were calculated from the experimental data [10] assuming that samples possess perfectly cubic structures. These values are listed in Table 2 and represented in Fig. 3. It is clear that the relation between the dopant concentration and *a* value is not a linear one, except in the case of undoped and Ga-doped samples. Values of the ionic radii of different ions are listed in Table 3.

The value of the ionic radius of Ga^{3+} is nearly the same as that of Ni^{2+}.

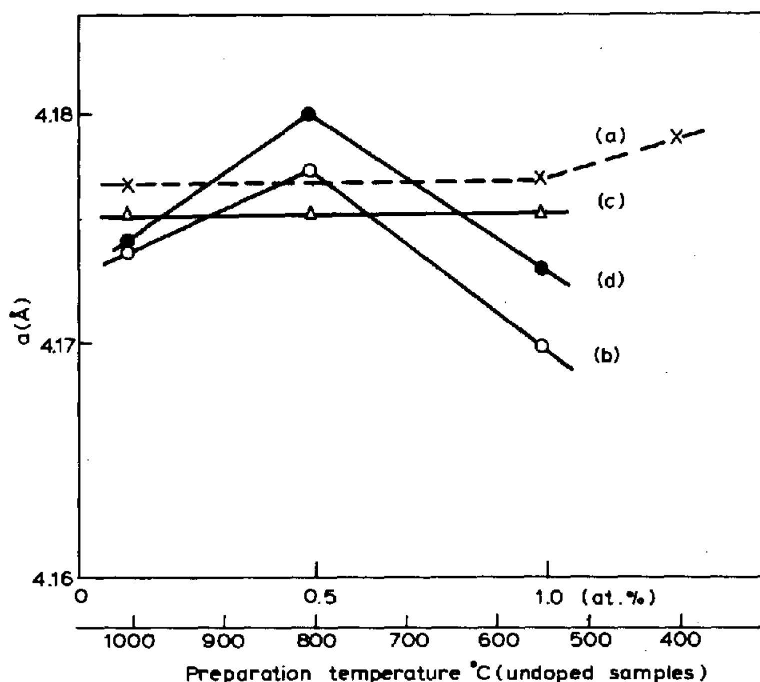

Fig. 3. Values of *a* for (a) undoped samples; (b) samples doped with Al; (e) samples doped with Ga; (d) samples doped with In.

TABLE 3

Ionic radii values

Ion	Ni^{2+}	Ni^{3+}	Al^{3+}	Ga^{3+}	In^{3+}
Ionic radius (Å)	0.69	0.62	0.50	0.62	0.81

This may lead one to assume that Ga^{3+} can replace Ni^{2+} in the NiO lattice with a very small change in the lattice parameter. In the case of Al and In-doped samples, the change in the lattice parameter may be due to the lattice deformation [10]. These results are in harmony with those obtained by Mehandjiev [11].

To see if the addition of Al, Ga or In has led to the formation of a solid solution, the change in the lattice parameter as a function of the at.% of these added elements is calculated according to Vegard's law [12] which is

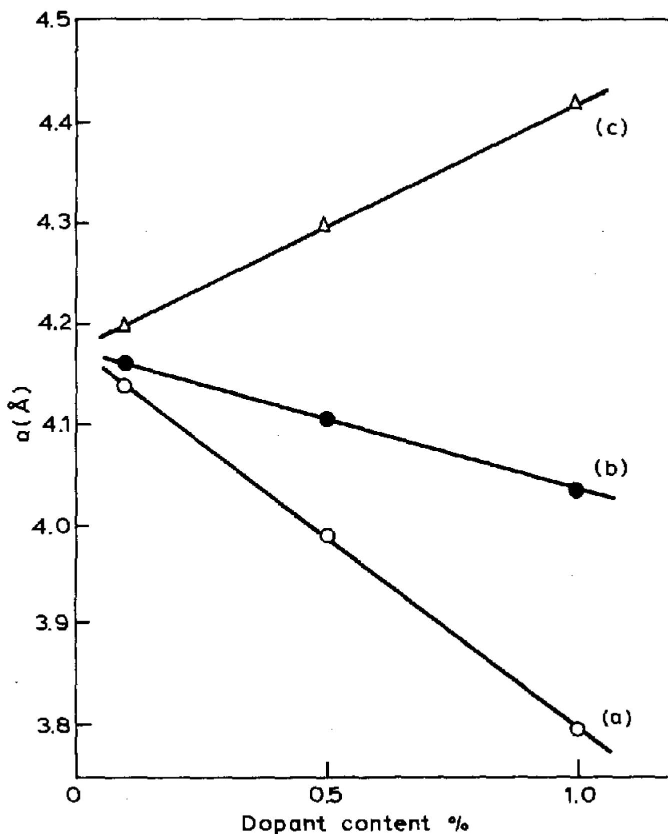

Fig. 4. Values of a as deduced from Vegard's law for samples doped with (a) Al; (b) Ga; (c) In.

given as

$a = 2rx$

where a is the change in the lattice parameter (sample prepared at 1000°C as standard), r is the difference in the ionic radii between Ni^{2+} and each of Al^{3+}, Ga^{3+} or In^{3+}, and x is the at.% of the oxide dissolved. The results are represented graphically in Fig. 4. It is observed that these values deviate considerably from the present experimental values, indicating that the preparation containing Al, Ga or In may be considered as a solid solution.

In conclusion, doping NiO with Al, Ga or In does not affect the thermal behaviour, but it changes the lattice parameters. This change depends greatly on the type and concentration of dopant and may be due to lattice defects.

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