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SOME PHYSICO-CHEMICAL PROPERTIES OF PURE AND DOPED NICKEL OXIDE. ELECTRICAL CONDUCTIVITY AND THERMOELECTRIC POWER MEASUREMENTS

Z.M. HANAFI, F.M. ISMAIL and S.M. ELOUI

Inorganic Chemistry Department, National Research Centre, Dokki, Cairo (Egypt)

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ABSTRACT

Relative values of a.c. conductivity for all the samples prepared, whether undoped or doped, are measured at temperatures in the range from room temperature to about 400°C. The activation energy obtained from the curve of $\log \sigma$ vs. $1/T$ indicates that nickel oxide prepared at 1000°C is the most stoichiometric form. The high temperature range in these measurements does not reach the intrinsic region. The change in activation energy as a function of dopant concentration is very slow in the case of gallium, but is marked in the case of alluminium.

For undoped samples, it is found that the starting values of thermoelectric power increase with increase in the preparation temperature, which is attributed to the different concentration of defects present.

The measurements on the different doped samples reveal that doped nickel oxide is still *p*-type, except in the case of In-doped samples in which the sign of conduction changes to *n*-type.

INTRODUCTION

Investigation of the electrical conductivity and thermoelectric power of several compounds of the group 3*d* transition metals showed that the nature of the electrical conductivity in such compounds remains semiconducting at impurity concentrations up to 0.1%.

A detailed study was carried out on NiO belonging to this group [1–26]. A lot of information was obtained for Li-doped NiO. Very little information is available on the electrical properties of NiO doped with Al [27,28], Ga [28,32] or In [32].

The aim of this investigation is to trace the electrical conductivity and thermoelectric power values of NiO prepared at different temperatures and NiO doped with Al, Ga or In with different concentrations. These measurements can provide considerable information about the concentration of lattice defects assumed to be present in NiO together with the type and concentration of dopant elements.

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EXPERIMENTAL

Three undoped samples of nickel oxide were prepared at 400, 550 and 1000°C according to the method devised by Francois et al. [33]. The method used by Deren et al [31] was applied to the preparation of the nine doped specimens studied. The nickel oxide samples obtained consisted of three sets, each doped with Al, Ga or In. Three concentrations of dopant were used in each case, namely, 0.1, 0.5 and 1.0 at.%.

In the present investigation the a.c. method [34] was applied for measuring the electrical conductivity of the different samples of NiO. The coefficient of thermoelectric power was determined separately by using the method described by Middleton and Scalon [35]. These measurements were carried out at temperatures from room temperature to about 400°C, using the same conditions for all samples.

RESULTS AND DISCUSSION

Figure 1, (1) (curves a, b and c) shows the plots of σ vs. $1/T$ for the undoped NiO samples initially prepared at 400, 550 and 1000°C, respectively. The room temperature values of conductivity decrease in the direction of the increase of temperature of preparation. This is in agreement with the well-known fact established by Nachman et al. [16], that the electrical conductivities of NiO samples prepared at lower temperature are higher than those of samples prepared at higher temperatures.

The different temperature portions vary exponentially according to the well-known relation

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{2KT}\right)$$

The activation energies for the different parts of the curves were calculated and are given in Table 1. The activation energy values obtained by different authors are listed in Table 2.

From Tables 1 and 2, it can be seen that the values of activation energy obtained here and by different authors differ from each other. This may be attributed to the effect of different methods or temperatures of preparation used.

The activation energy values for the lower temperature region, ΔE_1, deviated from one sample to another. This is most probably due to the variation in defect concentration [34]. This assumption is based on the fact that the activation energy due to grain boundaries is approximately the same since all samples have been subjected to the same pretreatment as regards their particle size and the pressure used for compression into pellets.

It is known that in p-type semiconductors the activation energy increases

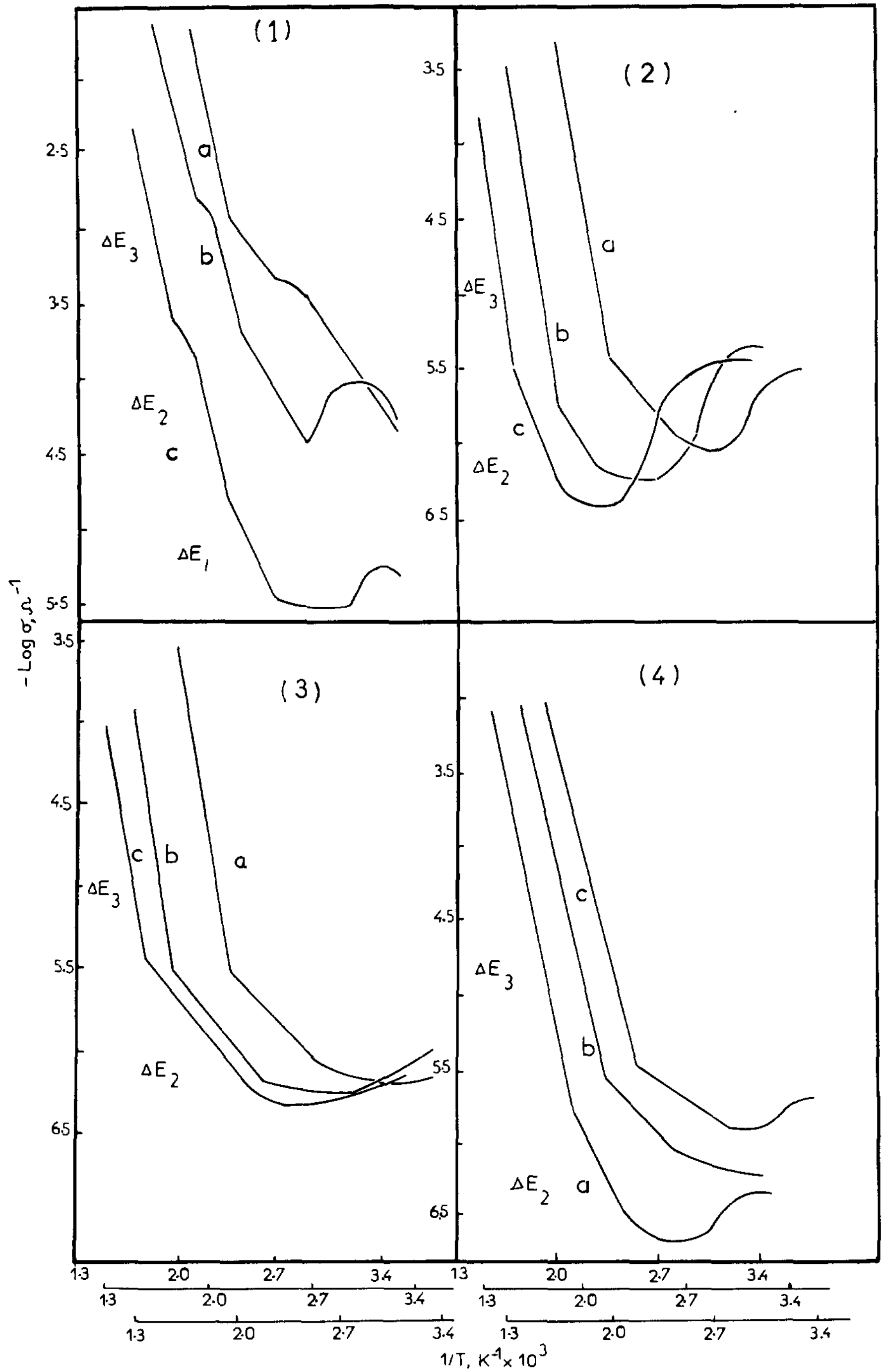

Fig. 1. Electrical conductivity as a function of temperature for (1) undoped NiO; (2) NiO doped with Al; (3) NiO doped with Ga; (4) NiO doped with In. Curves a, prepared at 400°C and doped with 0.1 at.% Al, Ga or In; curves b, prepared at 550°C and doped with 0.5 at.% Al, Ga or In; curves c, prepared at 1000°C and doped with 1.0 at.% Al, Ga or In.

TABLE 1

Values of ΔE for undoped and doped NiO samples

Sample	ΔE_1	ΔE_2	ΔE_3
NiO prepared at 400°C	0.55	0.55	1.73
NiO prepared at 550°C	0.69	1.73	1.73
NiO prepared at 1000°C	0.86	1.73	1.73
NiO with 0.1 at.% Al		0.46	2.06
NiO with 0.5 at.% Al		0.64	2.06
NiO with 1.0 at.% Al		0.94	2.06
NiO with 0.1 at.% Ga		0.40	2.27
NiO with 0.5 at.% Ga		0.42	2.27
NiO with 1.0 at.% Ga		0.48	2.27
NiO with 0.1 at.% In		0.69	1.88
NiO with 0.5 at.% In		0.41	1.73
NiO with 1.0 at.% In		0.28	1.49

with decrease of impurity content [36]. Thus the green sample prepared at 1000°C can be considered as the most stoichiometric one, as it has the highest energy. These results are in harmony with those obtained by other measurements [37].

The higher temperature regions have nearly the same value of ΔE_3 for the three samples, namely, 1.73 eV. From these identical values it is safe to conclude that both the concentration of charge carriers as well as the current transfer mechanisms are the same. Accordingly, conduction in this range may approach an intrinsic dominant region, and the value of the energy needed for transversing the forbidden band may be 1.73 eV. However, examining the values obtained by others, a value of 2.00 eV for ΔE_3 at higher temperatures is obtained by Foex [38]. While Pizzini and Morlotti [39]

TABLE 2

Values of ΔE obtained from the literature

Author	ΔE_1	ΔE_2
Wright and Andrews [4]	0.3–0.65	2.0
Takenchi and Igaki [5]		1.2
Hogarth [6]	0.55	0.93
Bransky and Tallan [21]		0.92
Margineanu et al. [22]	0.6	
Deren et al. [25]		0.86
Deren and Mrowec [26]		0.86

found that in the temperature range 1000–1400 K the value of ΔE is 1.80 eV for polycrystalline material. Feinleib and Adler [23] obtained a value of 1.90 eV for the temperature range 700–1770 K. These values are more or less in agreement with those obtained in the present study. The forbidden band width was found by Ksandzov and Drabkin [40] to be 3.70 eV. Furthermore, Powell and Spicer [41] obtained an intrinsic ΔE of 4.0 eV. Therefore, the ΔE_2 value obtained here, i.e. 1.73 eV cannot be considered as a gap-width value but rather as the activation energy.

Figure 1 (2)–(4) represent the electrical conductivity as a function of temperature for nickel oxide doped with Al, Ga and In, respectively. It is clear that the conductivity values of doped samples are less than those of pure NiO.

In the low temperature region, the values of activation energy, ΔE_1, increase with increase of the concentration of Al and very slightly in the case of Ga. Schwab and Schmid [32] stated that the rise in activation energy of NiO is due to trivalent dopant; it appeared that there is an energy distribution among the acceptor terms. In the case of In-doped samples, the values of ΔE_2 decrease with increase in the concentration of In. The study of Komatsu et al. [42] was the only one that was devoted to In-doped NiO. They reported that doping with In increases the positive charge in NiO. Parravano and Domenicali [7] reported that an increase in the concentration of some trivalent ions decreased the activation energy of NiO. This decrease may be due to the increase of lattice defects created by the introduction of In^{3+} into the NiO lattice. Schwab and Schmid [32] stated that the ionic radius of dopant element compared with that of NiO^{2+} affected the lattice defects. The ΔE_2 values increase in the higher temperature region, reaching a constant value in each case but the values differ from one dopant to another. This behaviour was also observed by Schwab and Schmid [32] and Parravano and Bomenicali [7] who stated that at higher temperatures the doped samples tend to a common value of ΔE_2, probably because of the approaching range of intrinsic behaviour. The fact that the ΔE_3 values obtained here are generally higher than that of pure NiO (1.73 eV) may be due to the creation of new impurity levels. The results did not depend on the systematic increase in the value of the ionic radius for the three dopants Al, Ga or In as might be expected.

In Fig. 2, (1), curves a, b and c show the variation of the thermoelectric power, α, in mV K^{-1} as a function of the absolute temperature for NiO prepared at 400, 550 and 1000°C, respectively. The three curves resulted from measurements carried out over the temperature range 373–673 K, and they indicate that NiO is a p-type semiconductor. This is in conformity with the findings of other authors [4,7,15,40,43]. All three curves are, to some extent, similar in shape. The values of α are found to decrease with rise in temperature until about 260°C. This is in agreement with the results obtained by Hogarth [6]. Above 260°C a sharp increase is observed with the

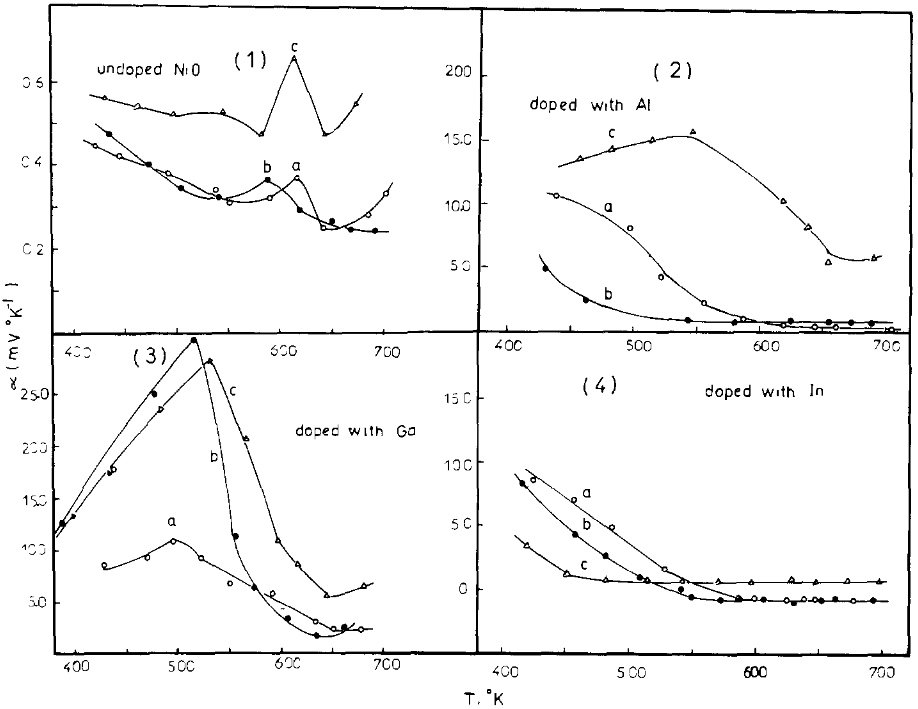

Fig. 2. Thermoelectric power as a function of temperature for (1) undoped NiO; (2) NiO doped with Al; (3) NiO doped with Ga; (4) NiO doped with In. Curves a, prepared at 400°C and doped with 0.1 at.% Al, Ga or In; curves b, prepared at 550°C and doped with 0.5 at.% Al, Ga or In; curves c, prepared at 1000°C and doped with 1.0 at.% Al, Ga or In.

formation of maxima and then the values return to approximately those observed before the maxima. These maxima may be due to the phase transformation observed for these oxides around this temperature.

The values of α plotted for the samples prepared at 400 and 550°C (curves a and b) approach each other, while that of the sample prepared at 1000°C (curve c) is in general higher than those of the other two. This may be due to the different positions of the impurity level present according to the different temperature of preparation.

In the case of Al, it is noticed that increasing the percentage of dopant leads to a decrease in the initial α value and then to an increase. At higher temperatures, the α value of 0.1 and 0.5 at.% Al-doped samples are nearly the same, while that of 1.0 at.% Al shows a greater increase than the other two. Also, at higher temperatures, it is seen that the α values of NiO doped with Al approach those of NiO prepared at 400 and 550°C. This may be due to the fact that the same concentration of carriers is present in these two groups of samples. This observation was attributed to the fact that the ionic radius of Al^{3+} is smaller than that of Ni^{2+} and can thus be easily incorporated into the NiO lattice. This is in conformity with the finding of Suntsov and Miloslavskii [44] who stated that the addition of Al leads to the substitution of Ni by Al. Deren et al. [31] stated that the addition of Ga to NiO does not alter the type of conduction unless there is spinel-type formation which leads to an *n*-type semiconductor. Schlosser [11] found that NiO doped with Ga at concentrations above 0.6 mole% is *n*-conducting.

Doping NiO with Ga shows that all values increase as the dopant concentration is increased. In the plot of α vs. T a maximum is observed at about 250°C which is found to be more distinct with increase in Ga concentration. This may be due to the phase transformation [45] observed for pure and doped NiO samples as detected by DTA around the same temperature.

Figure 2, represents the effect of In on the values of α at different temperatures. The sign of α changes at about 250°C. This may be due to the formation of $NiIn_2O_4$ spinel [45].

Measurement of the electrical properties of undoped NiO shows that undoped NiO prepared at 1000°C is the most stoichiometric. This NiO has the lowest value of activation energy. The addition of dopants markedly changes the ΔE and α values. Although the change depends greatly on the type and concentration of the dopants, it cannot be directly correlated with the systematic increase of the ionic radii from Al to In as might have been proposed.

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