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EFFECTS OF BeO-DOPING ON THE THERMAL BEHAVIOUR OF COBALT OXIDES

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ABSTRACT

The effects of beryllium oxide (1.5 to 12 mol%) on the thermal stability of Co_3O_4 and reactivity of CoO towards reoxidation, by O_2 yielding Co_3O_4, were investigated. The techniques employed were DTA with controlled rate of heating and cooling, X-ray, and IR spectrometry.

The addition of 1.5 mol% BeO was found to induce a decrease of about 7% in the thermal stability of Co_3O_4 and no detectable change in the reactivity of CoO towards reoxidation. This decrease was attributed to the location of Be^{2+} ions in interstitial positions and/or in cationic vacancies in the Co_3O_4 lattice. Increasing the amount of BeO above this limit was followed by a progressive increase in both the thermal stability of Co_3O_4 and the reactivity of CoO. A marked increase in the thermal stability of cobaltic oxide (20%) was found on the addition of 12 mol% BeO. This behaviour was explained in terms of dissolution of Be^{2+} ions in the Co_3O_4 lattice via substitution of some of its Co^{4+} ions. Such a substitution led to an increase in the oxidation character of the doped solid. Beside the dissolution of BeO in cobaltic oxide, modifying its thermal behaviour, a portion of the doping oxide added underwent a solid–solid interaction with both Co_3O_4 and CoO producing new compound(s) having specified *d*-spacings and IR absorption bands.

INTRODUCTION

Cobalt oxides are commonly employed in different industries. Various grades of blue colouration in glass and ceramic technology are currently obtained by treating with different amounts of pure CoO or CoO mixed with other oxides [1,2]. Cobaltic oxide, Co_3O_4, is commonly employed as an active catalyst for oxidation–reduction reactions [3–7]. It undergoes thermal decomposition yielding CoO on heating in air at temperatures around 850°C [8]. However, the cobaltous oxide produced reacts readily with atmospheric O_2 giving Co_3O_4 [9]. Such a behaviour might have an undesirable effect upon its use as a colouring agent. It seems important to investigate the different parameters effecting its transformation to CoO and the reactivity of the cobaltous oxide produced for reoxidation by oxygen to give Co_3O_4.

It has been found in our previous studies [8–12] that the addition of small amounts of different oxides, namely, Li_2O, Na_2O, MgO, ZrO_2, ThO_2, V_2O_5

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and MoO_3, exerted different effects on the thermal behaviour of cobalt oxides. These effects depended mainly on the valence state and ionic radii of the dissolved foreign cations [8–12]. The cations of the previously employed oxides exhibit ionic radii near those of the host cobalt cations (Co^{2+} and Co^{4+}). It seems important to investigate the role of foreign cations, having very small radius, in the thermal behaviour of cobalt oxides. Beryllium has been selected in the present investigation for the very small ionic radius of its Be^{2+} ions (0.30 Å) [13].

EXPERIMENTAL

Materials

Pure and doped cobalt oxides were prepared by thermal decomposition of pure basic cobalt carbonate [10,14] and basic cobalt carbonate mixed with different proportions of beryllium sulphate ($BeSO_4 \cdot 4H_2O$) solution. The amounts of the foreign cations added were varied between 1.5 and 12 atom% per mole of Co_3O_4. Pure and treated cobalt carbonate samples were subjected to heating in air at 1000°C for 4 h followed by both rapid and slow cooling to room temperature.

Techniques

Differential thermal analysis (DTA) of pure and doped basic cobalt carbonate was carried out using a DuPont 990 thermal analyser with a differential scanning calorimeter cell. The rate of heating and cooling was kept constant at 20°C min^{-1}, and the sensitivity was 0.4 mV cm^{-1}. A 30 mg-sample of each solid specimen was employed in each case.

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

An IR absorption spectrum was determined for each solid using a Beckman IR 4250 spectrometer. The IR spectra were determined from 4000 to 300 cm^{-1}, but only the portion between 1500 and 300 cm^{-1} was considered in the present work. A 2-mg sample of each solid was dispersed by grinding for 3 min in a vibratory ball mill, placed in a steel die 30 mm in diameter, and subjected to a pressure of 12 tonnes.

RESULTS

Thermal behaviour of pure and treated cobalt oxides

Figure 1 represents the DTA (heating and cooling) of pure basic cobalt carbonate and cobalt carbonate treated with different proportions of beryl-

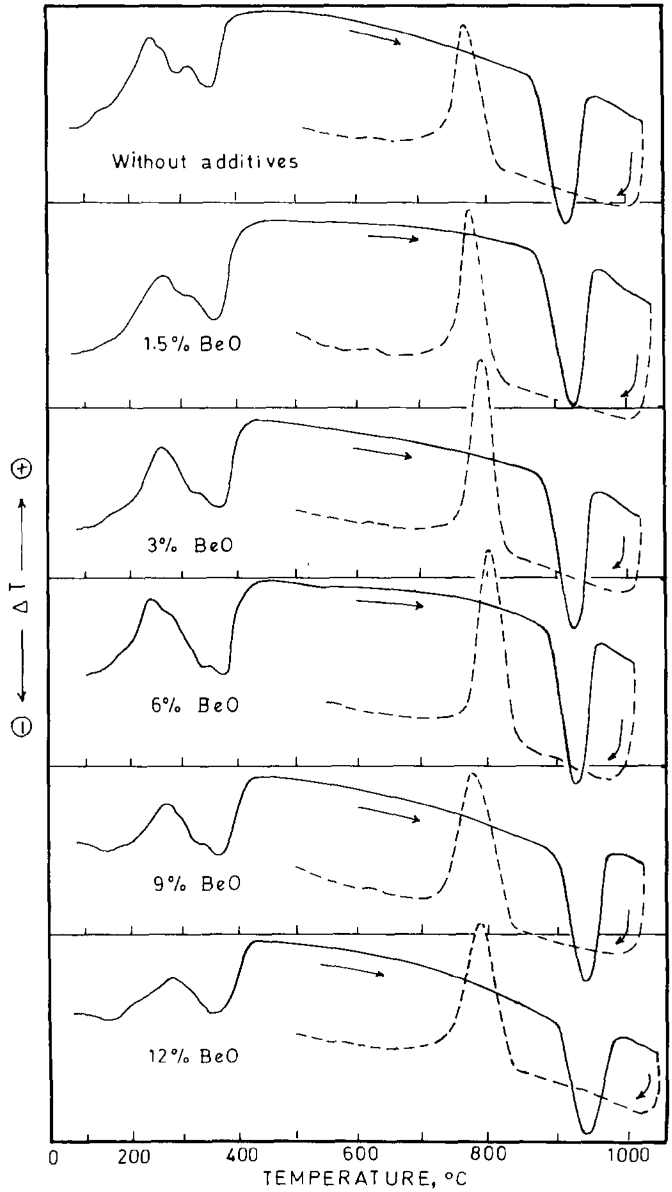

Fig. 1. DTA heating and cooling curves of pure and beryllium sulphate-treated specimens of basic cobalt carbonate.

lium sulphate. A strong endothermic peak with its maximum at about 915°C was observed in all cases. This peak indicates the decomposition of Co_3O_4 to CoO [8]. The presence of BeO resulted in a slight shift of this maximum to higher temperatures. A strong exothermic peak was observed during the cooling of pure and treated solids. This peak corresponds to the oxidation of CoO to Co_3O_4 [9]. The maximum of this peak was found at 770, 790 and

805°C for pure solid and those treated with 3 and 6 mol% BeO, respectively.

Once a fixed mass (30 mg) of pure and treated cobalt carbonate was taken in each DTA run, the area of the endothermic and exothermic peaks could be considered as a measure of the extent of the solid that undergoes change (decomposition of Co_3O_4 to CoO, and oxidation of CoO to Co_3O_4). The data of endothermic and exothermic peaks corresponding to the decomposition and oxidation of cobalt oxides are given in Table 1. This table also includes the percentage change in the area of the endothermic peak due to doping with BeO, and the ratio between the areas of the endothermic and exothermic peaks. Table 1 shows that the treatment of Co_3O_4 with a small amount of BeO (1.5 mol%) enhanced the decomposition of cobaltic oxide. Increasing the amount of BeO added in the range 3–12 mol% exerted an opposite effect on the decomposition of Co_3O_4 via retarding its thermal decomposition. In other words, the first addition of BeO (up to 1.5 mol%) decreased the thermal stability of cobaltic oxide while the other additions of the doping oxide (3–12 mol%) increased this thermal stability. These results might indicate that BeO was dissolved in the Co_3O_4 lattice according to two different mechanisms. It can also be seen from Table 1 that BeO-doping of cobalt oxide enhances the reactivity of the product CoO towards reoxidation by O_2 yielding Co_3O_4 to an extent proportional to the amount of the foreign oxide added.

TABLE 1

The effect of BeO-doping on the peak area of the DTA curves of the thermal decomposition of Co_3O_4 and oxidation of CoO

Solid	Peak area (arbitrary units)		% Change in the area of endothermic peak [a]	Ratio between the areas of exothermic and endothermic peaks
	Endothermic peak	Exothermic peak		
Pure basic cobalt carbonate	25.60	20.51	0.0	0.80
Basic carbonate +				
1.5% BeO	27.30	23.64	−6.64	0.87
3.0% BeO	24.68	27.04	+3.60	1.10
6.0% BeO	23.54	28.68	+8.05	1.22
9.0% BeO	23.58	33.06	+7.90	1.40
12% BeO	20.38	28.06	+20.39	1.37

[a] These data were obtained by subtracting the area of the endothermic peak for each solid from 25.60 (that of the pure solid). The negative and positive signs indicate a decrease or increase in the thermal stability of Co_3O_4, respectively.

X-ray investigation of pure and doped cobalt oxides

X-ray diffraction patterns were made for the pure and treated solids heated in air at 1000°C and subjected to both slow and rapid cooling to room temperature. All the diffraction lines of the Co_3O_4 phase were only detected in the X-ray diffraction patterns of the pure solid subjected to slow cooling. In contrast, in the case of the rapidly cooled pure oxide the characteristic diffraction lines of both CoO and Co_3O_4 phases were observed, indicating an incomplete oxidation of cobaltous to cobaltic oxide.

Figure 2 represents the diffraction lines of BeO-treated solids subjected to rapid cooling. It can be observed from this figure that the cobalt oxide

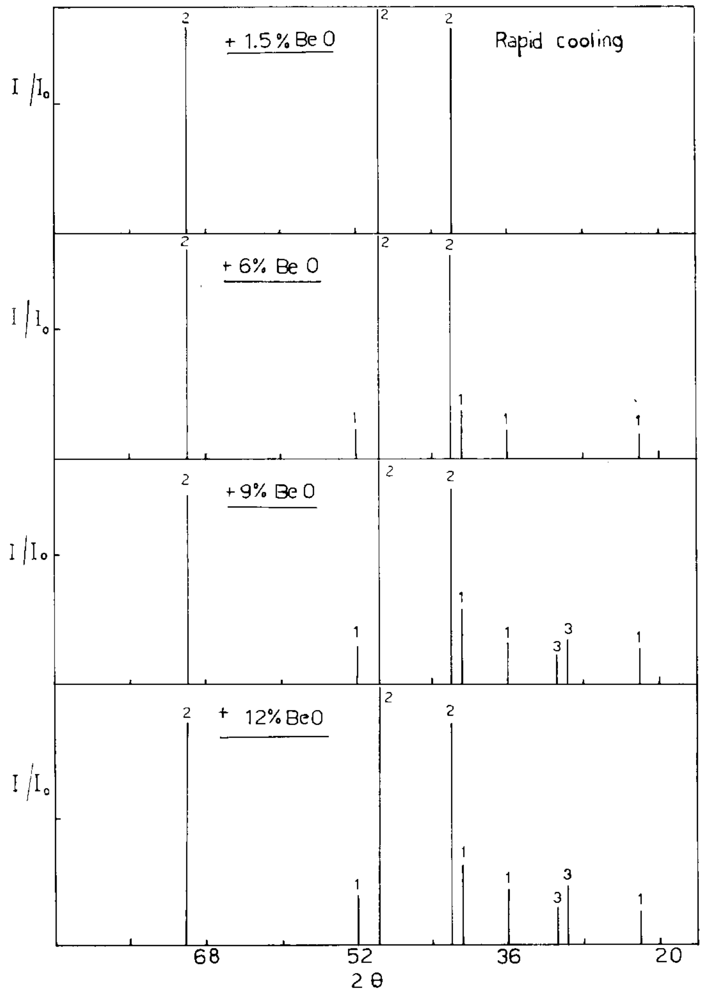

Fig. 2. X-ray diffraction patterns of BeO-doped cobalt oxides heated in air at 1000°C and subjected to rapid cooling. (1) Co_3O_4 phase; (2) CoO phase; (3) a new compound.

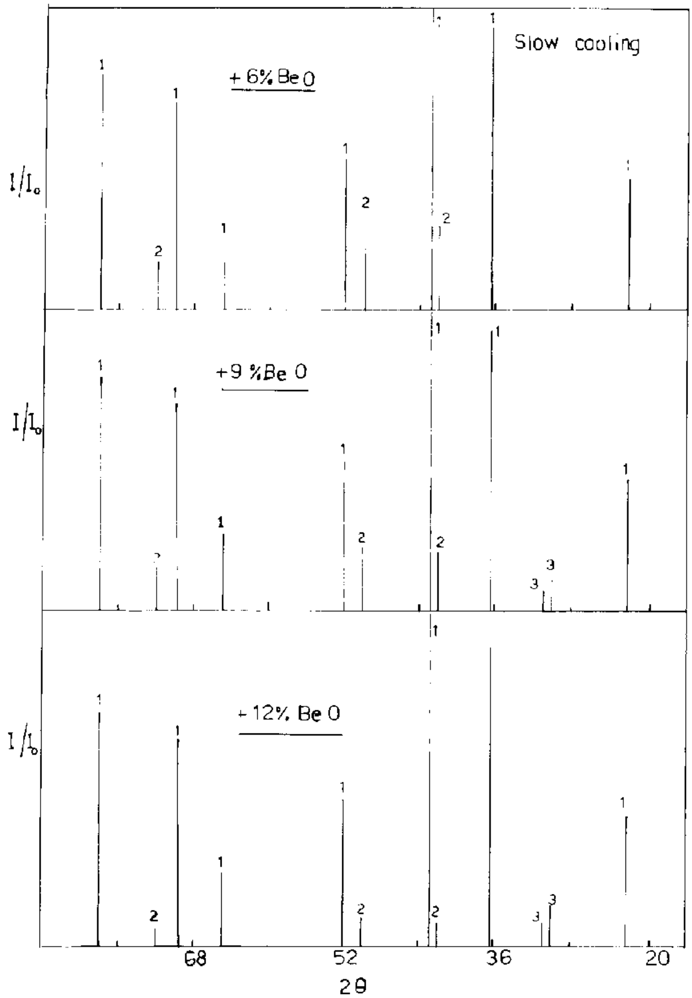

Fig. 3. X-ray diffraction patterns of BeO-doped cobalt oxides heated at 1000°C and subjected to slow cooling. (1) Co_3O_4 phase; (2) CoO phase; (3) a new compound.

specimen treated with 1.5 mol% BeO heated at 1000°C and rapidly cooled to room temperature was entirely composed of a well-crystalline CoO phase indicating a complete decomposition of Co_3O_4 to CoO. These results, which agree well with those of the DTA previously given in this investigation (cf. Table 1), show that the addition of a small amount of BeO (1.5 mol%) enhances the decomposition of cobaltic oxide to cobaltous oxide. Figure 3 also shows that the increase in the amount of BeO added in the range 3–12 mol% led to the appearance of Co_3O_4 together with CoO phases. The height of the main diffraction line of the Co_3O_4 phase was considered as a measure of the extent of this phase in the rapidly cooled solids and the height of the main diffraction line of the CoO phase as a measure of the amount of this phase in the slowly cooled solids. The amount of Co_3O_4 in the rapidly cooled solids could be taken as an indication of the thermal stability of cobaltic oxide, and the amount to the unoxidised CoO in the slowly cooled oxides indicates the reactivity of this phase towards reoxidation by O_2 giving Co_3O_4. The greater the reactivity of CoO the smaller the amount of unoxidised CoO. The amounts of Co_3O_4 and CoO in various solids were, thus, calculated and the data obtained are given in Table 2. It can be seen from Fig. 2 and Table 2 that increasing the amount of BeO from 3 to 12 mol% was followed by a progressive increase in the intensity of the characteristic lines of the cobaltic oxide phase. These results, which are in good agreement with those of the DTA investigation (cf. Table 1), clearly indicate that the addition of BeO above 1.5 mol% to cobaltic oxide effected an increase in its thermal stability proportional to the concentration of the foreign oxide added.

Figure 3 represents the diffraction lines of BeO-treated solids (6–12 mol%) heated at 1000°C and subjected to slow cooling. It can be observed from this figure that the diffraction lines of both Co_3O_4 and CoO phases are present. However, the intensity of the cobaltic oxide's lines is more pronounced than that of CoO diffraction lines indicating an incomplete oxidation of cobaltous to cobaltic oxide. Furthermore, the intensity of the characteristic lines of the unoxidised CoO phase is inversely proportional to the concentration of the doping oxide added. This may indicate that the

TABLE 2

The effect of BeO-doping on the appearance of different cobalt oxides, free dopant oxide and a new compound

Solid	Phase present	Extent of Co_3O_4 (arbitrary units) [a]
Rapid cooling from 1000°C		
Cobalt oxide +		
1.5% BeO	CoO only	0.0
3% BeO	CoO + Co_3O_4	22
6% BeO	CoO + Co_3O_4	35
9% BeO	CoO + Co_3O_4 + new compound	38
12% BeO	CoO + Co_3O_4 + new compound	42
Slow cooling from 1000°C		Extent of CoO (arbitrary units) [a]
Cobalt oxide +		
6% BeO	Co_3O_4 + CoO	60
9% BeO	Co_3O_4 + CoO + new compound	40
12% BeO	Co_3O_4 + CoO + new compound	20

[a] These data were obtained in terms of the height of the main diffraction lines of Co_3O_4 and CoO phases in the solids subjected to both rapid and slow cooling from 1000°C to room temperature, respectively.

reactivity of the CoO formed towards reoxidation by O_2 yielding Co_3O_4 increases on increasing the amount of beryllium oxide employed.

Figures 2 and 3 also show that the cobaltic oxide samples treated with 9 and 12 mol% dopant and heated in air at 1000°C then subjected to both rapid and slow cooling contained, besides the CoO and Co_3O_4 phases, a new compound. The 2θ values and the *d*-spacings of this compound were calculated and found to be

2θ	29.7	30.3
d-spacing (Å)	3.61	3.54

These lines, which did not belong to free BeO [15], may characterize a new beryllium–cobalt oxide solid resulting from an interaction between BeO and cobalt oxides (Co_3O_4 and/or CoO). The absence of free beryllium oxide in all treated cobalt oxide samples indicates that a portion of the foreign oxide added was effectively dissolved in cobalt oxides modifying the thermal stability of Co_3O_4 and the reactivity of CoO towards reoxidation and the other portion underwent a solid–solid interaction with cobalt oxides yielding a new compound. However, it was not an easy task to determine the size of the portions contributing to each process.

IR investigation of BeO-doped cobalt oxides

The IR absorption spectra were measured for pure and doped cobalt oxide solids heated in air at 1000°C for 4 h and subjected to both rapid and slow cooling to room temperature. All the characteristic absorption bands of Co_3O_4 [9,11] were only detected in the case of the pure solid subjected to slow cooling.

Figure 4 shows the absorption spectra of cobalt oxide treated with different proportions of BeO at 1000°C and subjected to slow cooling. It is observed from Fig. 4 that all the characteristic bands of the Co_3O_4 structure were only detected in the solids treated with 1.5 and 3.0 mol% dopant. However, other bands located at 1195, 1150, 1125 and 1100 cm^{-1} were also found for the samples containing 6, 9 and 12 mol% dopant. The percentage transmission of these new bands increases greatly on increasing the extent of the foreign oxide added. Preliminary experiments have shown that pure BeO heated at 1000°C exhibits a very strong broad band extending between 640 and 1050 cm^{-1} together with another strong band at 1400 cm^{-1} with a shoulder at 1390 cm^{-1}. It can, thus, be concluded that the newly observed bands in the case of doped solids did not correspond to free BeO, but characterize a newly formed beryllium–cobalt oxide compound. The 2θ values and *d*-spacings of this new compound have been determined and are given above. The amount of the newly formed compound in the case of 6 mol% BeO-treated solid was too small to be detected in the X-ray diffraction patterns.

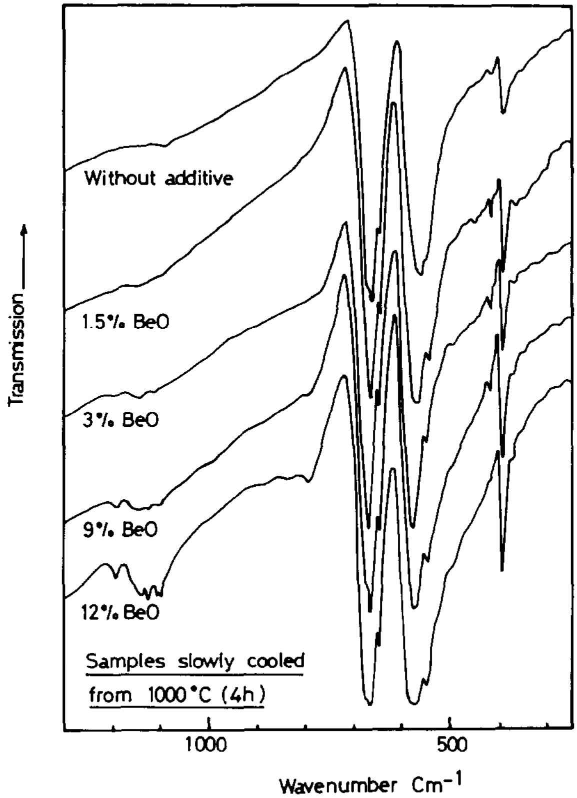

Fig. 4. IR absorption spectra of pure and beryllium sulphate-treated specimens of basic cobalt carbonate heated at 1000°C and subjected to slow cooling in air.

Figure 5 represents the absorption spectra of cobalt oxide treated with different amounts of beryllium oxide heated at 1000°C and subjected to sudden cooling. Figure 5 shows that all the treated solids exhibited a very strong band corresponding to the CoO structure together with two bands at 560 and 660 cm^{-1} characterizing a Co_3O_4 structure. The percentage transmission of Co_3O_4 bands increases on increasing the amount of BeO added between 3 and 12 mol%. This indicates that beryllium oxide being added to cobalt oxide (3–12 mol%) effected an increase in the thermal stability of Co_3O_4. It can also be observed from Fig. 5 that all beryllium oxide-treated solids exhibited other new bands located at 1195, 1150, 1125 and 1100 cm^{-1} which are the same bands as those detected in the case of slowly cooled solids. However, the percentage transmission of these bands, which increases on increasing the amount of BeO added, is much more pronounced in the case of the rapidly cooled solids. In the case of the sample treated with 12 mol% BeO an additional strong absorption band at 1380 cm^{-1} was also observed (cf. Fig. 5). It has been found in our previous investigation [9] that the treatment of cobalt oxide with different proportions of MgO and Al_2O_3

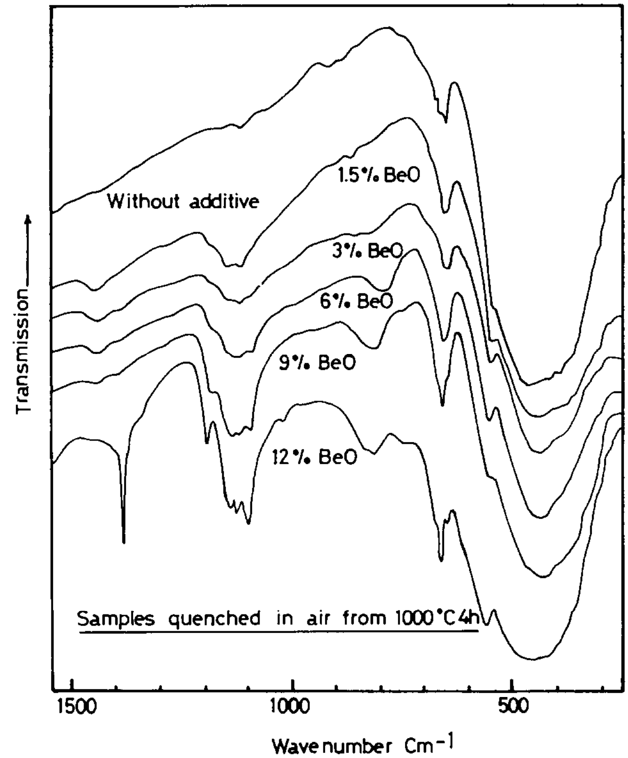

Fig. 5. IR absorption spectra of pure and beryllium sulphate-treated specimens of basic cobalt carbonate heated at 1000°C and subjected to rapid cooling in air.

(1.5–6 mol%) at 1000°C led to the appearance of a strong IR band also located at 1380 cm^{-1}. This band might characterize a cobalt oxide structure different from those of Co_3O_4 and CoO. It seems plausible to suggest that the addition of a relatively large amount of BeO (12 mol%) stabilized such a cobalt oxide structure. The decrease in the percentage transmission of the new bands, corresponding to a new beryllium–cobalt oxide compound, by subjecting the solids to slow cooling might indicate that the interaction between CoO and O_2 yielding Co_3O_4 was energetically more favourable than the interaction between CoO and BeO to give the new compound.

DISCUSSION

The DTA, X-ray diffraction and IR spectrometric investigations of pure and doped cobalt oxides clearly indicated that the addition of a small amount of divalent Be^{2+} ions (1.5%) resulted in a decrease in the thermal stability of Co_3O_4. This decrease could be attributed to a corresponding decrease in the oxidation character of the doped solid. The Be^{2+} ions could be dissolved in the Co_3O_4 lattice via location in interstitial positions and/or in cationic vacancies, and also by substituting some of divalent and tetravalnet cobalt ions of the cobaltic oxide lattice. These processes can be simplified, adopting Kröger's notions [16] as follows

$$BeO + 2Co^{3+} \rightarrow Be\boxed{\triangle} + 2Co^{2+} + 1/2O_2(g) \qquad (1)$$

$$BeO + 1/2O_2(g) \rightarrow Be(Co^{4+}) + 2Co^{3+} \qquad (2)$$

$$BeO \rightarrow Be(Co^{2+}) \qquad (3)$$

$Be\boxed{\triangle}$ represents a beryllium ion located in a cationic vacancy or in an interstitial position, Co^{3+} ions are the charge carriers in the non-stoichiometric, p-type semiconductor Co_3O_4 solid [8,17]. The ionic radius of Be^{2+} being very small (0.3 Å) [18] made its location in the interstitial position geometrically and energetically quite possible. The dissolution of divalent Be^{2+} ions in the cobaltic oxide lattice according to such a mechanism is accompanied by degassing of some excess oxygen of Co_3O_4 followed by subsequent transformation of some of Co^{3+} into Co^{2+} ions. In other words, the oxidation character of cobaltic oxide decreases by doping with Be^{2+} ions and its reduction to CoO becomes energetically easier. Such a mechanism accounts for the results obtained in this investigation in the case of the cobalt oxide sample treated with a small amount of BeO (1.5 mol%). The dissolution of Be^{2+} ions in the Co_3O_4 lattice according to the mechanism expressed by eqn. (3) is not accompanied by any change in the oxidation character of cobaltic oxide and consequently exerted no effect on its thermal stability. By contrast, the dissolution of divalent berylium ions in the Co_3O_4 lattice according to mechanism (2) is followed by an increase in the oxidation character of Co_3O_4 leading to a consequent increase in its thermal stability. The observed increase in the thermal stability of cobaltic oxide due to doping with BeO (3–12 mol%) could thus be attributed to an effective substitution of some of Co^{4+} ions by Be^{2+} ions. One cannot exclude the possibility of substitution of some of the cobalt ions of Co_3O_4 by Be^{2+} ions according to both mechanisms (1) and (2). On this basis, mechanism (1) dominates in the case of the cobalt oxide doped with small amounts of BeO up to 1.5 mol% and mechanism (2) dominates for the solids treated with BeO in the range 3–12 mol%. The marked increase in the thermal stability of Co_3O_4 from 8 to 20% induced by increasing the amount of BeO added from 9 to 12 mol% might indicate the absence of any possible location of the foreign ions in interstitial positions in the doped cobaltic oxide lattice.

It has also been observed that BeO being added to cobalt oxide was followed by an increase in the reactivity of CoO towards reoxidation by O_2 yielding Co_3O_4. It seems that some of the added Be^{2+} ions could be dissolved in the CoO lattice leading to an increase in the concentration of the anionic vacancies [19,20] which acted as active centres for chemisorption of oxygen which might lead to its oxidation to Co_3O_4.

The existence of a newly formed beryllium–cobalt oxide compound in most of the BeO-treated cobalt oxides pointed to a possible solid–solid interaction between a portion of the foreign oxide added and both Co_3O_4 and CoO. This conclusion was also reached at by a preliminary experiment showing the appearance of all characteristic IR bands of the new beryllium–cobalt oxide compound in the case of the cobalt oxide sample treated with BeO (12 mol%) and heated at 800°C. At such a temperature cobalt oxide existed in the form of Co_3O_4. This indicates that some of the added BeO interacted with a corresponding portion of Co_3O_4 at 800°C leading to the formation of a new compound which remained stable by heating in air at 1000°C.

REFERENCES

1 W.D. Kingery, Introduction to Ceramics, Wiley, New York, 1960.
2 F. Singer and S.S. Singer, Industrial Ceramics, Chapman and Hall, London, 1963.
3 G.A. El-Shobaky, M.M. Selim and I.F. Hewaidy, Surf. Technol., 10 (1980) 57.
4 G.A. El-Shobaky, I.F. Hewaidy and Th. El-Nabarawy, Surf. Technol., 10 (1980) 225.
5 G.A. El-Shobaky and I.F. Hewaidy, Surf. Technol., 10 (1980) 311.
6 G.A. El-Shobaky and Th. El-Nabarawy, Surf. Technol., 10 (1980) 401.
7 G.A. El-Shobaky, N. Petro and T. Ghazy, Surf. Technol., 15 (1982) 33.
8 G.A. El-Shobaky, I.F. Hewaidy and N.M. Ghoneim, Thermochim. Acta, 53 (1982) 105.
9 G.A. El-Shobaky, N. Ghoneim, I.F. Hewaidy and I. Morsi, Thermochim. Acta, 61 (1983) 107.
10 G.A. El-Shobaky, N. Ghoneim and I. Morsi, Thermochim. Acta, 67 (1983) 293.
11 G.A. El-Shobaky, N. Ghoneim and I. Morsi, Thermochim. Acta, 70 (1983) 325.
12 N.M. Ghoneim and G.A. El-Shobaky, Thermochim. Acta, 80 (1984) 165.
13 N.N. Greenwood, Ionic Crystals, Lattice Defects and Non-stoichiometry, Butterworth, London, 1968.
14 G.A. El-Shobaky, I.F. Hewaidy and Th. El-Nabarawy, Surf. Technol., 12 (1981) 301
15 Powder Diffraction File (JCPDS), International Centre for Diffraction Data, Swarthmore, PA, 1979.
16 F.A. Kröger, Chemistry of Imperfect Crystals, North-Holland, Amesterdam, 1964.
17 P. Kostad, Non-Stoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides, Wiley-Interscience, New York, 1972, p. 426.
18 N.N. Greenwood, Ionic Crystals, Lattice Defects and Non-stoichiometry, Butterworth, London, 1968, pp. 40, 41.
19 P.C. Gravelle, G.A. El-Shobaky and S.J. Teichner, J. Chim. Phys., 66 (1969) 1953.
20 P.C. Gravelle, G.A. El-Shobaky and S.J. Teichner, in K. Hauffe and Th. Volkenstein (Ed.), Int. Symp. Electrical Phenomena in Chemisorption and Catalysis, Walter de Gruter, Berlin, 1969, p. 124.