

THERMAL BEHAVIOUR OF COBALT OXIDES DOPED WITH ZrO_2 AND ThO_2 AND THE POSSIBLE CUBIC PHASE STABILIZATION OF ZIRCONIA

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ABSTRACT

The effects of doping cobalt oxides with different amounts of ZrO_2 and ThO_2 (1.5–9 mol%) on the thermal stability of Co_3O_4 and the re-oxidation of CoO by O_2 to Co_3O_4 were investigated. The techniques employed were DTA, with a controlled rate of heating and cooling, X-ray diffraction, and IR spectrometry.

The results obtained by DTA revealed that the addition of both Th^{4+} and Zr^{4+} (up to 6 mol%) exerted no appreciable effect on the thermal stability of Co_3O_4 . Increasing the amount of the dopant ions to 9% resulted in no further change in the thermal stability of Co_3O_4 in the case of Th^{4+} , and an increase of 16% in case of Zr^{4+} -doping. However, ThO_2 -doping of cobalt oxide was accompanied by an enhancement in the reactivity of CoO towards re-oxidation by O_2 to Co_3O_4 to an extent proportional to the amount of dopant oxide.

The X-ray investigation of ZrO_2 -doped cobalt oxides calcined in air at $1000^\circ C$ revealed the presence of highly crystalline and stable zirconia in the cubic form. Such a stable phase could not be obtained at temperatures below $2370^\circ C$ in the absence of stabilizing agents.

X-ray and IR investigations of different solids showed the presence of free thoria and zirconia together with new thorium–cobalt and zirconium–cobalt compounds. However, the slow cooling of Zr-treated cobalt oxides from $1000^\circ C$ to room temperature led to the decomposition of the newly formed compound. The d -spacings and absorption bands of the newly formed compounds were determined.

INTRODUCTION

Cobalt oxides, beside their reactivity as adsorbents and catalysts [1–6], are commonly used in the glass industry as colouring agents [7]. Cobalt oxide (CoO) reacts with Fe_2O_3 to form a cobalt ferrite spinel which has wide applications in the electronic ceramic industry [8].

Cobalt oxide, in the form of Co_3O_4 , has a spinel structure, however, it decomposes by heating in air at temperatures in the region of $850^\circ C$ giving the CoO phase. Treating Co_3O_4 with small amounts of different dopant oxides, such as Li_2O , Na_2O [9,10], Al_2O_3 [11], V_2O_5 and MoO_3 , greatly increases its thermal stability. In a recent work [13], the γ -radiation of

cobaltic oxide greatly decreased its thermal stability. The mechanisms of the thermal stabilization of Co_3O_4 by doping or γ -irradiation has been discussed in previous investigations [8–12].

The role of doping with tetravalent ions in the thermal stability of Co_3O_4 has not been studied before.

The present work studies the effect of doping with zirconium oxide and thorium oxide on the thermal stability of cobaltic oxide and on the reactivity of the cobaltous oxide produced for oxidation by O_2 to Co_3O_4 . The techniques employed were DTA, X-ray diffraction, and IR spectrometry.

EXPERIMENTAL

Materials

Pure and doped cobalt oxides were obtained by the thermal dissociation of pure basic cobalt carbonate [5,11] and basic cobalt carbonate treated with different proportions of thorium nitrate ($\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$) and zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$). The calcination of pure and doped solids was carried out at 1000°C for 4 h. Pure and doped oxide solids were subjected to both rapid and slow cooling from 1000°C to room temperature. Four zirconium oxide and thorium oxide doped Co_3O_4 solids were prepared which contained 1.5, 3.0, 6.0 and 9.0 mol%.

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 $20^\circ\text{C min}^{-1}$, and the sensitivity was 1 mV in^{-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 doped basic cobalt carbonate was performed with a Philips diffractometer (type PW 1050). The patterns were run with iron-filtered cobalt radiation, $\lambda = 1.7889 \text{ \AA}$, at 30 KV and 10 mA with a scanning speed of 2° in $2\theta \text{ min}^{-1}$.

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 1400 and 300 cm^{-1} was considered in the present work. A 2-mg sample of each solid was mixed with 200 mg of vacuum-dried IR-grade KBr. The mixture 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 ton.

RESULTS

Thermal behaviour of pure and doped cobalt oxides

Figures 1 and 2 represent the DTA (heating and cooling) of pure basic cobalt carbonate and cobalt carbonate doped with different amounts of $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ and $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$. Four endothermic peaks are observed in all cases. The first peak is broad, extending between 50 and 220 °C, while the other three peaks are sharp and strong, especially the last one. The second and third peaks, having their maxima at 300 and 370 °C, indicate the loss of water of crystallization and the decomposition of CoCO_3 to Co_3O_4 , respectively [9]. The last peak, with its maximum at 915 °C in the case of

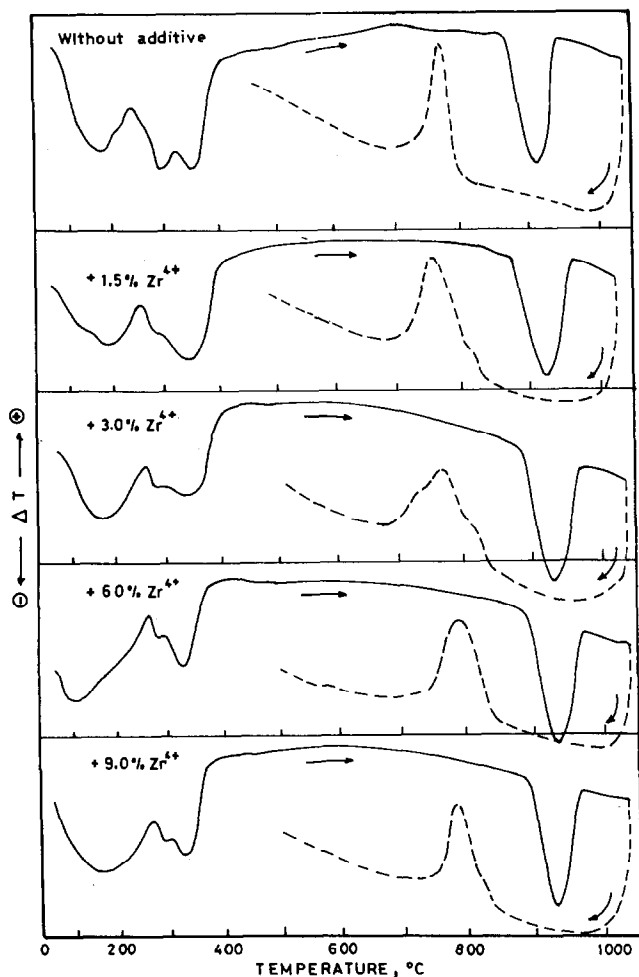


Fig. 1. DTA heating and cooling curves of pure and zirconium oxychloride-treated specimens of basic cobalt carbonate.

pure and Th-doped solids, and 930°C in the case of Zr-doped solids, corresponds to the decomposition of Co_3O_4 to CoO [9]. It can, therefore, be deduced that the presence of zirconium oxide, even in small amounts (1.5 mol%), slightly increases the temperature of the decomposition of Co_3O_4 to CoO . A strong exothermic peak was observed during the cooling of pure and doped solids. The maximum of this peak was found at 770°C for pure and Th-doped solids (up to 3 mol%), and at 745°C for 6.0 and 9.0 mol% Th-treated solids. The cooling curves of pure and Th-doped solids exhibit almost identical features. However, in the case of Zr-doped oxides (1.5–3.0 mol%) the exothermic peaks show some changes in their shape, duration temperature, and their maxima. The addition of 1.5 and 3.0 mol% resulted in

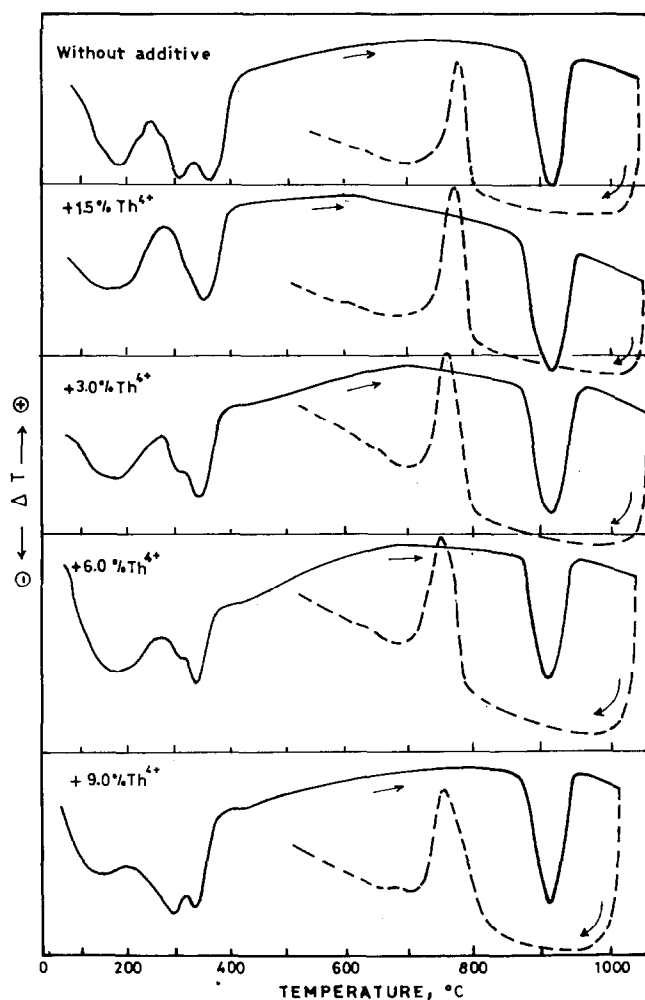


Fig. 2. DTA heating and cooling curves of pure and thorium nitrate treated specimens of basic cobalt carbonate.

splitting of the exothermic peak into two and three overlapping peaks, respectively. These results may point to some changes in the oxidation mechanism of Zr-doped cobaltous oxide by oxygen into cobaltic oxide. However, the addition of 6.0 and 9.0 mol% ZrO₂ brought about no appreciable changes in the features of the exothermic peak, except a slight increase in their maxima from 770 to 790 °C.

Once a fixed weight (30 mg) of pure and treated cobalt carbonate was taken in each DTA run, the areas of endothermic and exothermic peaks could be regarded as a measure of the extent of the solid that suffers a chemical change (decomposition of Co₃O₄ to CoO, and oxidation of CoO to Co₃O₄). The data of endothermic and exothermic peaks corresponding to the decomposition and oxidation of the cobalt oxides are given in Table 1. This table also includes the percentage decrease in the area of the endothermic peak due to doping with ZrO₂ and ThO₂, and the ratio between the area of the endothermic and exothermic peaks. It can be observed from Table 1 that the doping of Co₃O₄ with either ZrO₂ or ThO₂ produced no significant change on its thermal stability, except in the sample containing 9.0 mol% ZrO₂ which showed an increase in thermal stability of 16%.

The ratio between the area of exothermic and endothermic peaks (Table 1, last column) gives a measure of the reactivity of the produced CoO towards re-oxidation by O₂ during the cooling process. It can be deduced that doping cobalt oxide with ThO₂ increases the reactivity of the CoO produced for

TABLE 1

The effect of ZrO₂- and ThO₂-doping on the peak area of the DTA curves of the thermal decomposition of Co₃O₄ and oxidation of CoO

Solid	Peak area (arbitrary units)		% Decrease in the area of endothermic peak ^a	Ratio between the area of exothermic and endothermic peaks
	Endothermic peak	Exothermic peak		
Pure basic cobalt carbonate	22.52	16.02	0.0	0.745
Basic cobalt Carbonate +				
1.5% ZrO ₂	21.44	19.30	4.8	0.900
3.0% ZrO ₂	20.68	21.00	8.17	1.015
6.0% ZrO ₂	20.50	18.68	8.96	0.911
9.0% ZrO ₂	18.88	14.24	16.16	0.754
1.5% ThO ₂	22.56	18.84	0.0	0.935
3.0% ThO ₂	20.70	20.96	8.1	1.031
6.0% ThO ₂	20.84	20.72	7.5	0.996
9.0% ThO ₂	21.36	22.56	5.15	1.056

^a These data were obtained by subtracting the area of the endothermic peak for each solid from 22.52 (that for pure solid).

re-oxidation. The fact that this ratio is smaller than unity (0.745 in case of pure solid), and tends to unity for most of doped solids, indicates that the CoO produced was not completely oxidized to Co_3O_4 in case of pure, and was almost entirely oxidized to cobaltic oxide in case of doped solids. These results will be confirmed later in this work through an X-ray investigation of the different solids.

X-ray investigation of the thermal products of basic cobalt carbonate treated with $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ and $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$

X-ray diffraction patterns were produced for the pure and doped solids heated in air at 1000°C and subjected to both slow and rapid cooling from 1000°C to room temperature. All the diffraction lines of the Co_3O_4 phase were only detected in the X-ray diffraction patterns of pure solid subjected to slow cooling. In contrast, in the case of rapidly cooled pure oxide the characteristic diffraction lines of both Co_3O_4 and CoO were detected. However, the intensity of the CoO lines was much higher than that of Co_3O_4 , indicating an incomplete oxidation of CoO into Co_3O_4 . These results are in good agreement with those of DTA (Table 1, last column).

Figures 3 and 4 represent the diffraction lines of Th- and Zr-doped solids, respectively. Figure 3 shows that the 6.0 mol% Th-doped solid heated at 1000°C and subjected to slow cooling to room temperature is composed of Co_3O_4 , ThO_2 , and a new compound. The $2\theta^\circ$ values and d -spacings of the newly found compound are:

$2\theta^\circ$	37.20	88.20
d -spacing	2.804	1.285

Figure 3 also shows that the Th-doped solid heated at 1000°C and subjected to sudden cooling to room temperature was composed of CoO, Co_3O_4 , ThO_2 , and the same new compound. However, the intensity of the diffraction lines of the newly formed compound is higher in case of the rapidly cooled than the slowly cooled solids. The intensity of the ThO_2 lines, contrary to the new compound, showed a slight increase on slow cooling of the solid. The fact that the ThO_2 phase was detected in the doped cobalt oxide specimens indicates that most of the added solid remained as a separate phase while part of it may be dissolved in the cobalt oxide lattice, thus modifying its thermal behaviour and oxidizability with oxygen. The other part of thoria underwent a solid-solid interaction forming the newly found compound. The fact that the intensity of the newly formed compound decreases by slow cooling while that of free ThO_2 increases may indicate that the newly formed compound was preferably formed through the interaction between ThO_2 and CoO. The slow cooling of Th-doped solid effected a complete oxidation of cobaltous oxide into cobaltic oxide in agreement with the DTA results presented in the preceding section.

Figure 4 shows that the slowly cooled 9.0% ZrO_2 -doped cobalt oxide heated at $1000^\circ C$ consisted of a highly crystalline Co_3O_4 phase together with cubic phase zirconia and a minute amount of non-oxidized CoO phase. However, the quenched sample was composed of a highly crystalline CoO phase, cubic phase zirconia, and a newly formed compound. These results indicate that, similar to the ThO_2 -doping, most of the ZrO_2 added to cobalt oxide remained as a separate phase, while part of it might be dissolved in the cobalt oxide lattice effecting a modification in its thermal behaviour (Table 1) and another part of the ZrO_2 underwent a solid-solid interaction with cobalt oxide to produce a new compound. The $2\theta^\circ$ values and d -spacings of this compound were calculated and found to be:

$2\theta^\circ$	93.6	88.4	88.2
d -spacing	1.227	1.283	1.285

The appearance of the CoO phase in the slowly cooled zirconia-doped solid may indicate a possible mutual interaction between ZrO_2 and CoO leading

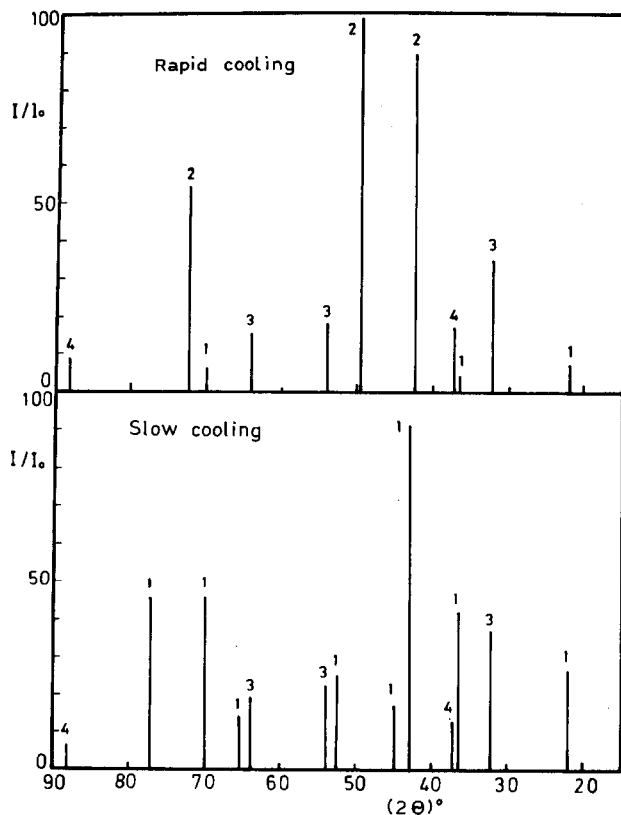


Fig. 3. X-ray diffraction patterns of 6 mol% thorium-doped cobalt oxide heated at $1000^\circ C$ and subjected to both slow and rapid cooling. (1) Co_3O_4 phase; (2) CaO phase; (3) ThO_2 phase; (4) a new compound.

to a kind of relative passivation of CoO towards re-oxidation by oxygen. Such an effect, which is in agreement with the DTA results (cf. Table 1, last column), was not observed in the case of ThO₂-doping. The disappearance of the Zr-Co new compound in the case of the slow cooling might indicate that the formation of such a new compound occurred via an interaction between zirconia and cobaltous oxide, and not with cobaltic oxide. It is worthy to mention here that the slow cooling process also led to an increase in the intensity of the diffraction lines of free ZrO₂, compared with that observed in the case of the rapidly cooled solid. This might show that the mode of cooling of the doped solid greatly affected the amount of the dopant oxide involved in solid solution and the formation of the new compound.

The X-ray investigation revealed that ZrO₂ present in both rapidly and slowly cooled doped solids is in the form of the cubic fluorite structure. At room temperature, pure zirconia is stable in the monoclinic form and it transforms into the tetragonal form at ~1000°C, accompanied with ~9% volume contraction [14-16]. Above 2370°C zirconia transforms into the

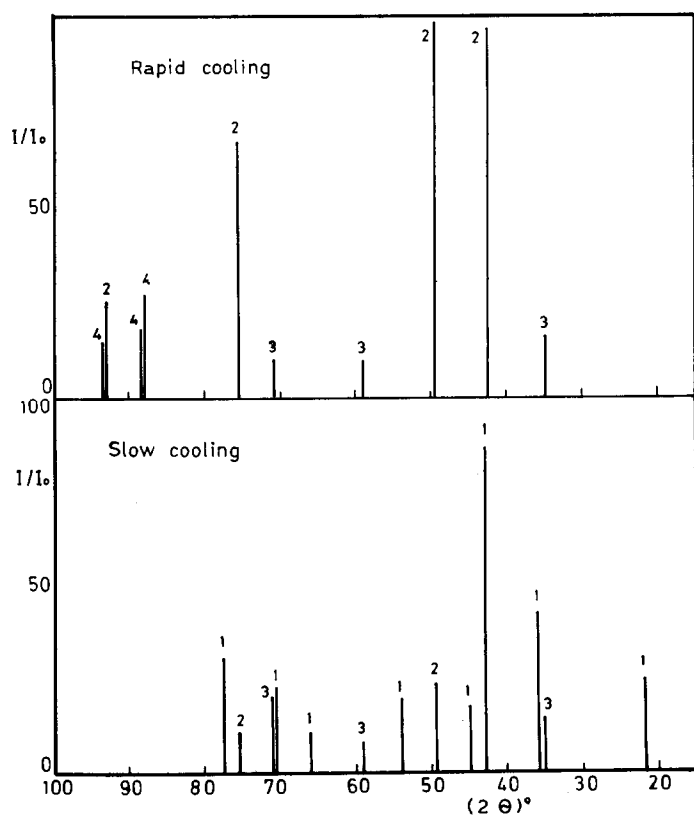


Fig. 4. X-ray diffraction patterns of 9 mol% zirconium-doped cobalt oxide heated at 1000°C and subjected to both slow and rapid cooling. (1) Co₃O₄ phase; (2) CoO phase; (3) ZrO₂ phase; (4) new compound.

cubic fluorite structure [17]. Because of this allotropic nature zirconia cannot be sintered into a coherent solid body. To overcome this difficulty zirconia is stabilized in the cubic fluorite structure by the addition of RO or R_2O_3 metal oxides, such as CaO, MgO, Y_2O_3 , and La_2O_3 [17]. Such additions lower the transformation temperatures to an extent dependent on the nature and amount of the oxide added [17–21]. Ytria, which is known as the most efficient stabilizing agent, must be added in a concentration of 15% to decrease the stabilization temperature to 1750 °C [18]. Cobalt oxide has not yet been employed, to our knowledge, as a cubic zirconia stabilizing agent. However, Donstov et al. [21], in a study on the CoO-CeO₂-ZrO₂ phase diagram, reported the absence of any appreciable solubility of CoO in ZrO₂ up to 1450 °C, and that the zirconia present was in the tetragonal form.

The results obtained in the present work clearly show an effective interaction between CoO and ZrO₂ leading to the formation of a new compound together with the stabilization of cubic zirconia at temperatures as low as 1000 °C.

IR spectrometric investigation of the thermal products of pure basic cobalt carbonate and cobalt carbonate doped with $ZrOCl_2 \cdot 8 H_2O$

The IR absorption spectra were measured for pure and doped solids heated at 1000 °C for 4 h and subjected to both rapid and slow cooling to room temperature. Figures 5 and 6 show the absorption spectra of pure and doped oxides containing 3, 6 and 9 mol% ZrO₂ for both slowly cooled and quenched solids. Figure 5 reveals the presence of all the characteristic bands of Co₃O₄ [10–12] in pure and doped oxides. These bands are located at 675, 665, 645, 580–550, 420 and 390 cm⁻¹. The IR spectra of quenched pure and doped solids (Fig. 6) are different from those measured for the slowly cooled solids. Most of the characteristic bands of Co₃O₄ disappeared, except those at 665 and 580 cm⁻¹. The intensity of these bands was found to increase with increasing ZrO₂ content. Together with these two bands, the broad characteristic band (600–300 cm⁻¹) of CoO was observed in all cases. Two additional bands at 1180 and 1120 cm⁻¹ were detected, only in the doped solids. These results indicate that pure cobalt oxide heated at 1000 °C and subjected to rapid cooling is mainly composed of CoO and a minute amount of Co₃O₄. The amount of the cobaltic oxide phase increase with increasing dopant oxide concentration. These findings are in good agreement with the DTA results given in Table 1. The fact that the X-ray technique could not detect the Co₃O₄ phase in the quenched solids might indicate that Co₃O₄ contents are too small to be detected by such a method. The bands at 1180 and 1120 cm⁻¹ (cf. Fig. 6) could not correspond to either free zirconia [20] or any cobalt oxide structure [10–12]. It could be argued that these bands correspond to the new compound resulting from the interaction between zirconium oxide and cobalt oxide. The disappearance of these two bands in

the slowly cooled solids, together with the previously mentioned X-ray results, are in favour of such an argument.

IR spectrometric investigation of the thermal products of cobalt carbonate doped with $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$

The IR absorption spectra of Th-doped solids heated at 1000°C for 4 h and subjected to quenching and slow cooling to room temperature were measured. The spectra of the samples containing 3 and 9 mol% ThO_2 are given in Figs. 7 and 8. It can be seen from Fig. 7 that all the characteristic bands of Co_3O_4 , located at 670 , 660 , 650 , 580 – 560 , 420 and 390 cm^{-1} , are

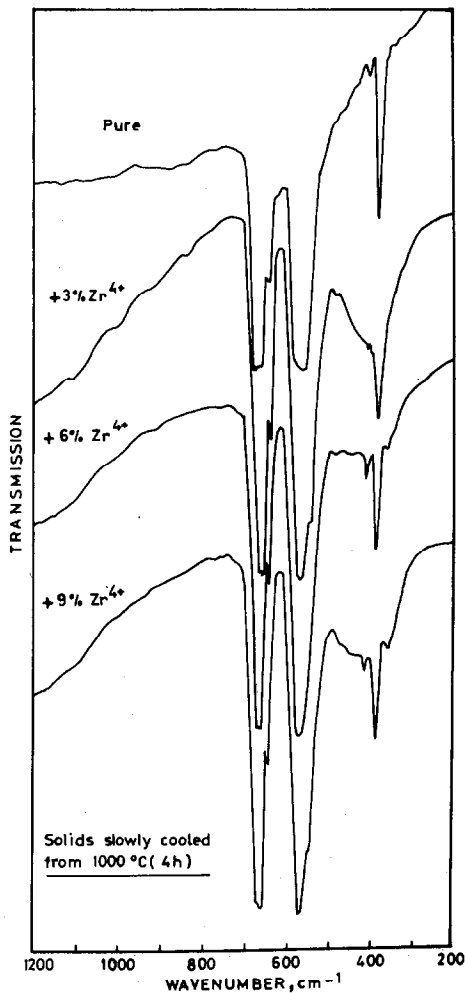


Fig. 5. IR absorption spectra of pure and zirconium oxychloride-treated specimens of basic cobalt carbonate heated at 1000°C and subjected to slow cooling in air.

observed. Very weak bands at 1160 and 1080 cm^{-1} appeared in the IR spectra of these solids.

The rapid cooling of Th-doped solids from 1000°C to room temperature resulted in the appearance of a broad band (600–300 cm^{-1}) corresponding to CoO and the disappearance of all Co_3O_4 bands except those at 660 and

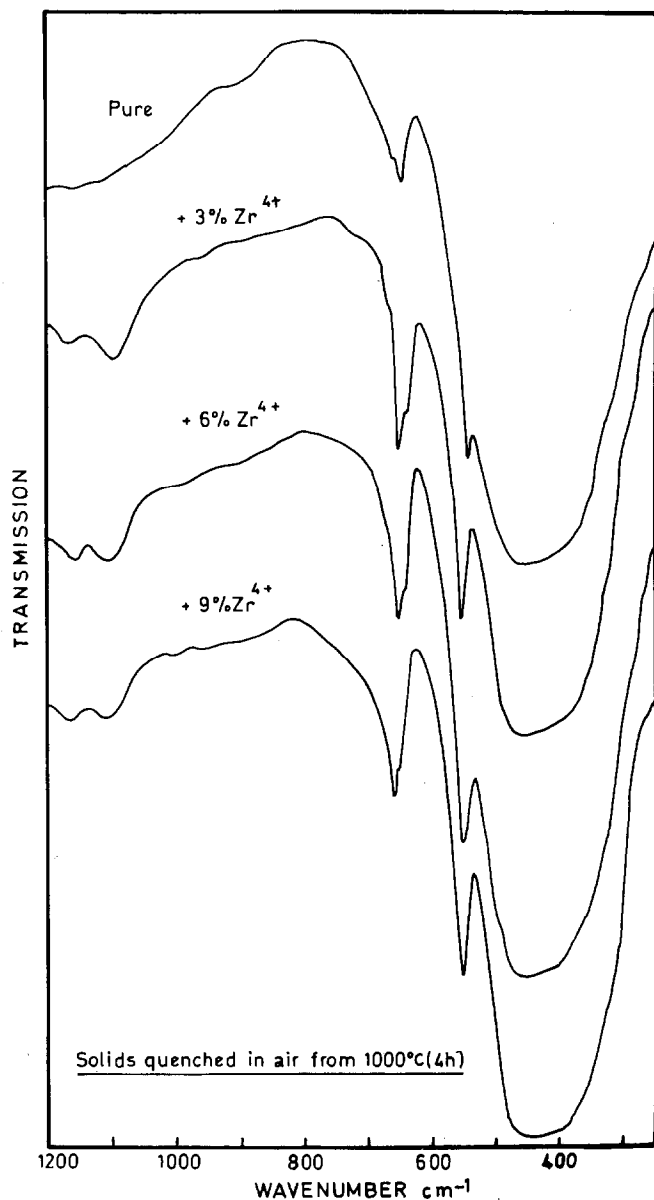


Fig. 6. IR absorption spectra of pure and zirconium oxychloride-treated specimens of basic cobalt carbonate heated at 1000°C and subjected to rapid cooling in air.

650 cm^{-1} . However, the band at 650 cm^{-1} may also belong to free ThO_2 , as confirmed experimentally in this work. The rapid cooling of Th-doped solids also led to an increase in the intensity of the bands at 1160 and 1080 cm^{-1} . These bands most probably characterize the newly formed Th-Co compound whose d -spacings were determined previously.

DISCUSSION AND CONCLUSIONS

The DTA, X-ray and IR spectrometric investigation of pure and doped cobalt oxides revealed that the addition of tetravalent Zr^{4+} (up to 6 mol%) and Th^{4+} (up to 9 mol%) resulted in no appreciable change in the thermal stability of cobaltic oxide. However, Th-doping of cobalt oxide enhances the reactivity of CoO towards re-oxidation by O_2 to produce Co_3O_4 . The addition of tetravalent dopant ions to Co_3O_4 may substitute some of the Co^{2+} or Co^{4+} of cobaltic oxide. The substitution could be simplified as follows [22]

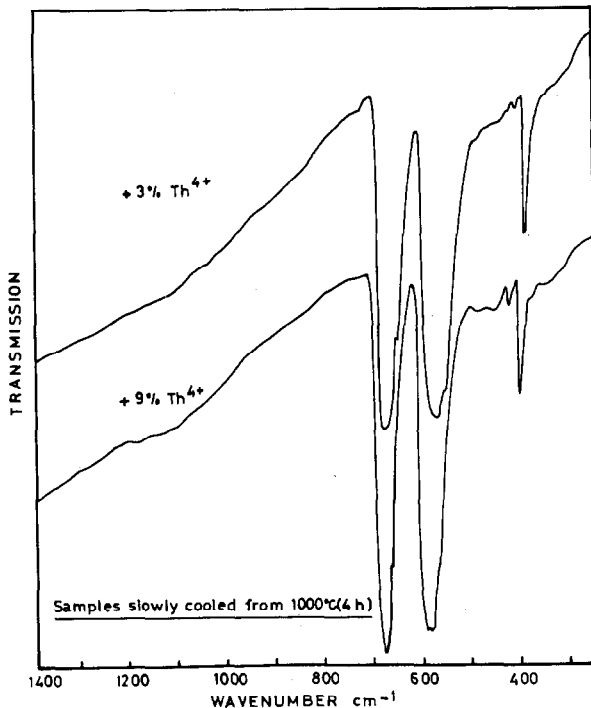
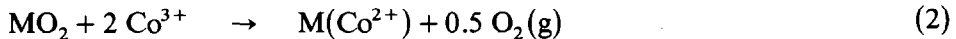
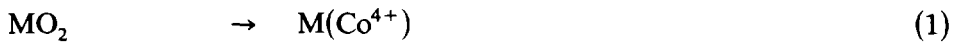


Fig. 7. IR absorption spectra of thorium nitrate-treated specimens of basic cobalt carbonate heated at 1000°C and subjected to slow cooling in air.

where MO_2 , $\text{M}(\text{Co}^{4+})$, $\text{M}(\text{Co}^{2+})$ are zirconium or thorium oxide, zirconium or thorium ions located in the positions of host cations Co^{4+} or Co^{2+} present in the cobaltic oxide lattice, respectively, and Co^{3+} is the charge carrier ion present in non-stoichiometric Co_3O_4 . Dissolution of tetravalent Zr^{4+} and Th^{4+} according to eqn. (1) is not accompanied by any change in the oxidation character of Co_3O_4 . By contrast, doping of cobaltic oxide according to eqn. (2) is accompanied by a decrease in the amount of Co^{3+} ions, i.e., a decrease in the oxidation character of the doped solid. The diminution in the oxidation character of Co_3O_4 might lead to a corresponding decrease in its thermal stability [9–13]. The substitution of some of the Co^{4+} by Th^{4+} or Zr^{4+} seems to be very difficult because of the large differences in their ionic radii (ionic radii of Co^{4+} , Zr^{4+} and Th^{4+} are 0.58, 0.80 and 0.95 Å, respectively). The ionic radius of Co^{2+} (0.78 Å) is very close to that of Zr^{4+} , which might lead to a possible substitution of some of the divalent cobalt ions by Zr^{4+} , and such process might lead to a decrease in the thermal stability of cobaltic oxide. The fact that no significant change in the thermal stability of Co_3O_4 was observed by doping with both ThO_2 (up to 9 mol%) and ZrO_2 (up to 6 mol%) might show an absence of the

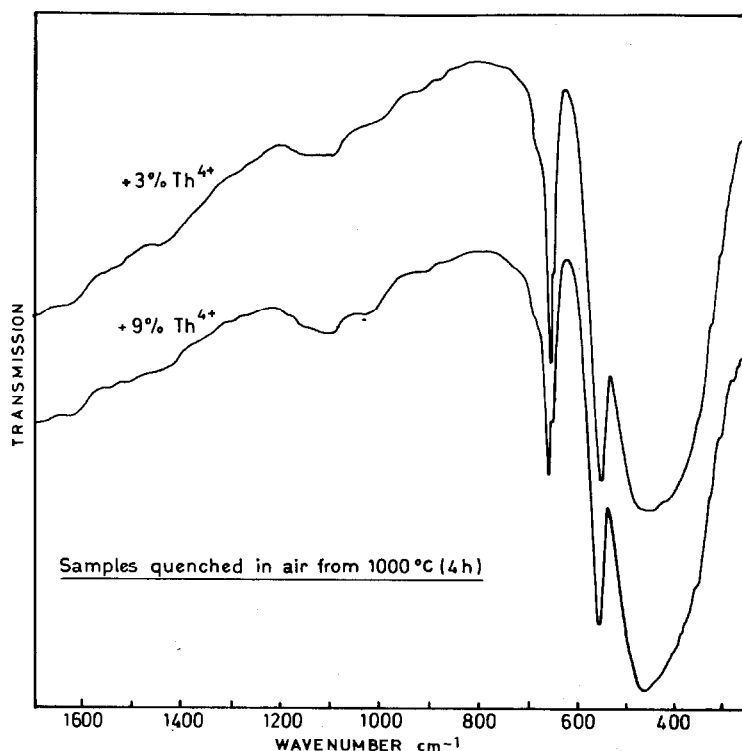


Fig. 8. IR absorption spectra of thorium nitrate-treated specimens of basic cobalt carbonate heated at 1000 °C and subjected to rapid cooling in air.

dissolution of appreciable amounts of dopant oxide in Co_3O_4 lattice.

The observed modifications in the reactivity of CoO, towards re-oxidation by O_2 to give Co_3O_4 , by doping with ThO_2 might indicate a possible dissolution of Th^{4+} in the cobaltous oxide lattice. The substitution of some of the divalent cobalt ions of CoO by tetravalent ions could result in an increase in the Fermi-level of CoO which behaves as a p-type semiconductor [23,24]. It is predicted from the electronic theory of chemisorption and catalysis on semiconductors [25,26] that the increase in the Fermi-level of a p-type semiconductor greatly enhances the chemisorption of electron acceptor gases, such as O_2 . The observed enhancement in the reactivity of Th-doped CoO towards re-oxidation by O_2 could thus be understood. The formation of a new compound via the interaction between ThO_2 and CoO, as shown by X-ray and IR spectrometric investigations of all ThO_2 -doped cobalt oxides, might indicate that the solubility of ThO_2 in CoO is limited. Concerning ZrO_2 -doping, the similarity between the ionic radii of Co^{2+} and Zr^{4+} might make the dissolution of Zr^{4+} in the CoO lattice easier than in the case of ThO_2 -doping. However, the addition of ZrO_2 to cobalt oxide (1.5–6 mol%) effected an increase in the reactivity of CoO towards re-oxidation by O_2 , then a decrease in this reactivity was observed on a further increase in the extent of dopant oxide. It seems that augmenting the amount of ZrO_2 added to cobalt oxide favoured the formation of a new CoO– ZrO_2 compound rather than the dissolution of Zr^{4+} in the CoO lattice.

The presence of zirconia in the cubic form could render CoO as one of the RO metal oxides capable of stabilizing zirconia in the fluorite structure. Further investigations are recommended to determine the least amount of CoO needed to stabilize cubic zirconia, without affecting its excellent refractory properties, since cobaltous oxide is much preferred to yttria or lanthana from the economic point of view. The stabilization of zirconia by cobalt oxide will be the subject of a forthcoming study.

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