Available online at www.sciencedirect.com

Journal of the European Ceramic Society 25 (2005) 1997–2001

www.elsevier.com/locate/jeurceramsoc

Preparation and characterization of calcium cobaltite for thermoelectric application

Małgorzata Sopicka-Lizer[a,*], Paweł Smaczyński[a], Karolina Kozłowska[b], Ewa Bobrowska-Grzesik[c], Julian Plewa[b], Horst Altenburg[b]

[a] *Katedra Nauki o Materiałach, Politechnika Śląska, 40-019 Katowice, ul Krasińskiego 8, Poland*
[b] *University of Applied Sciences, D-48565 Steinfurt, Germany*
[c] *Katedra Chemii Analitycznej i Ogólnej, Politechnika Śląska, 44-100 Gliwice, ul Strzody 9, Poland*

Abstract

Starting powders of $CaCO_3$ with different Ca:Co ratio and three different sources of cobalt (II,III) oxide were mixed and calcined at 700–1100 °C. DTA/TG, mass changes, density, grain size distribution, phase composition were examined. It has been found that phase composition of the resulted product was dependent on calcination temperature and properties of starting cobalt oxide. Three stages of cobaltite formation were established: simultaneous decomposition of $CaCO_3$ with $Ca_3Co_4O_9$ formation (800–900 °C), decomposition of $Ca_3Co_4O_9$ and formation of $Ca_3Co_2O_6$ (about 950 °C) and the last stage at 1050 °C was dependent on starting cation ratio and source of cobalt (II,III) oxide. It has been found that total decomposition of the previous phases was observed after calcinations at 1050 °C in the batches with Ca:Co = 1:1 ratio if very pure Co_3O_4 was used for preparation. Replacement of pure Co_3O_4 by cobalt oxide contaminated by cobalt hydroxide lead to re-formation of $Ca_3Co_4O_9$ phase at 1050 °C in 1:1 batches. Residual Co_3O_4 and CaO were always present in calcined specimens. It seems that prolonged heat treatment did not lead to better reaction degree.

Keywords: Calcination; Powders-solid state reaction; Transition metal oxides; Functional applications; Substrates

1. Introduction

The layered cobaltites as $Ca_3Co_4O_9$ (denoted as $[Ca_2CoO_{3.34}]_{0.614}[CoO_2]$ or Ca349)[1,2] and as $[Ca_2CoO_3]_{0.62}[CoO_2]$ (denoted as CCCO)[3] and as (Bi, Ca)Co_4O_9[4] were lately reported as promising thermoelectric materials. They exhibit surprising thermoelectric properties due to a large thermopower S at room temperature with simultaneously small resistivity ρ. Their small thermal conductivity κ and good thermal stability up to 700 °C makes them a good example of the “electron crystal and phonon glass”,[5] an ideal material for thermoelectric application. According to the CaO-CoO system,[6] $Ca_3Co_4O_9$ phase (Ca349) is stable up to 926 °C and then decomposes to $Ca_3Co_2O_6$ (Ca326) and cobalt oxide. On the other hand, Ca349 based ceramics were sintered at 1100 °C[4] or at 920 °C[1] but Ca326 phase was reported to exhibit higher electrical resistivity than Ca349 at temperature up to 700 °C.[7] Thus a final phase assemblage could influence thermoelectric performance of the ceramic. The aim of this paper is to study influence of temperature and source of cobalt oxide on calcium cobaltite formation.

2. Experimental procedure

Three different commercially available cobalt (II,III) oxide sources were tested: oxide (1) POCH reagent grade (min. of Co-71 wt.% and max. of 0.02 Mn, 0.001 Cu, 0.1Ni, 002Na, 0.02 Ca, 0.01 Fe wt.%:); oxide (2) Przedsiebiorstwo Odczynniki Chemiczne Lublin standard oxide (min. Co, 68 wt.%) and oxide (3) ChemPur (min. of Co-73.0 wt.%), extra pure. A small amount of Co_3O_4 was prepared in laboratory by sol–gel method: cobalt acetate was added to solution of 10 mol citric

---

[*] Corresponding author. Tel.: +48 32 6034476; fax: +48 32 6034400.
E-mail address: lizer@mail.polsl.katowicre.pl (M. Sopicka-Lizer).

0955-2219/$ – see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2005.03.222

Table 1
Properties of cobalt (II,III) oxides

	Total cobalt content (wt.%)	Oxygen content (wt.%)	Co^{2+} content (wt.%)	Temperature of decomposition (°C)	Oxygen loss of Co_3O_4 decomposition* (wt.%)	Mass loss below decomposition (wt.%)	Density (g/cm^3)	Average grain size d_{50} (μm)
(1) POCH	71.71	26.02	0.3	916	6.09	0.37	6.132	0.92
(2) Lublin	69.96	26.27	1.7	876	6.31	2.27**	5.876	19.78
(3) ChemPur	72.6	26.39	0.1	916	6.64	0.0	6.114	4.36
(4) Sol–gel				911	6.11	0.75		–
Stoichio-metric	73.42	26.58	0.0	about 900	6.64	0.0	6.110	–

* According to reaction: $Co_3O_4 = 3CoO + \frac{1}{2}O_2$.
** Decomposition at 116 °C.

acid and 5 mol ethyleneglicol, boiled and calcined at 500 °C. Properties of the oxides are shown in Table 1. Density of the powders was determined by helium pycnometer. Oxygen content was examined by TG study in hydrogen. Decomposition of the cobalt oxides was tested by DTA/TG study in air during heating and cooling. Co^{2+} content was determined after reaction with Franky's reagent. Infrared spectroscopy was applied to all the oxides. Total cobalt content was examined by spectrophotometric determination of cobalt thiocyanate complexes and spectrophotometric analysis of cobalt complexes with EDTA.

Calcium cobaltites were prepared by solid state reaction of $CaCO_3$ (POCH, Poland) and two different commercially available Co_3O_4 sources: reagent grade oxide (1) and standard oxide (2). Two composition with Ca:Co cation ratio of 1:1 and 3:4 were chosen for synthesis; the latter reflects cation ratio in Ca349 compound while the former gives average composition for the mixture of Ca349 and Ca326. The stoichiometric amount of $CaCO_3$ and Co_3O_4 were mixed with Si_3N_4 balls in isopropyl alcohol for 24 h. After drying the powder was uni-axially pressed (tablets with 10 mm diameter and 5–6 mm height) and calcined in an open horizontal tube furnace at temperature range 800–1050 °C for 20 h and cooled together with the furnace. Three tablets were placed in an alumina crucible, each tablet was weighed out before and after calcinations. XRD study (X'PERT PAN, Philips; Cu Kα radiation) was performed on the powdered specimens at room temperature. Other tablets were aged at room temperature and weighed after 10 and 20 days after calcinations.

DTA/TG study was applied to all the batches in flowing air at temperature range 20–1350 °C (NETZSCH STA 409). The relevant curves were recorded during heating and cooling down. Some specimens were observed in scanning electron microscope and EDS was done.

3. Results and discussion

Analysis of cobalt (II,III) oxide powder properties shows small differences of physical properties and thermal behavior (Table 1). EDS study of powders did not show any concentration of contaminants on the surface of studied powder specimens. According to the producers, cation contaminants in all the examined powders are below 0.17 wt.% level and can not change significantly such properties as density or oxygen content. It is supposed that observed differences of densities resulted from various cobalt oxidation state and relevant oxygen content. Oxide (2) contains small amount of cobalt hydroxide or hydrate, as confirmed by DTG and IR-study. However, the reason of lower decomposition temperature is not clear: presence of OH group or cations (Na, K, Al). Surface area of the tested powders does not affect decomposition of Co_3O_4 (thermally activated process) but does influence reoxidation of CoO during cooling (heterogeneous reaction). Fig. 1 shows mass gain of three oxides during cooling and it can be noticed that mass gain of oxide (2) with remarkable higher grain size is the lowest among the other oxides.

Summary results of DTA/TG study of 1:1 and 3:4 compositions are shown in Table 2 and on Fig. 2. Four endothermic reactions are found for each composition but only three first reactions are solid phase reactions and the last one must be related to liquid formation (the last reaction is not shown on Fig. 2). It could be seen that the first reaction (I) of calcium carbonate decomposition and calcium cobaltite formation is the most influenced by cobalt oxide source and starting cation ratio. Cobalt oxide (2) exhibits lower temperature of the new compound formation in comparison to the oxide (1) and it corresponds to the behaviour of cobalt oxide. Creation of the Ca349 compound happens simultaneously with $CaCO_3$ decomposition in the 3:4 batches. In the case of 1:1 batches the relevant peak is splitted (oxide no. 2) or separated into the

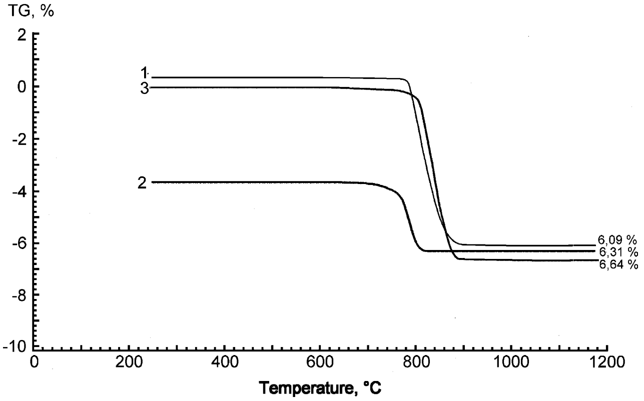

Fig. 1. TG of cobalt oxides during cooling. Numbers on the left side refers to the number of the relevant oxide. Values on the right side indicates mass loss as a result of heating up to 1200 °C.

Table 2
DTA/TG results of 1:1 and 3:4 batches prepared from pure (1) and standard (2) cobalt (II,III) oxide

Cation ratio	1st reaction calcium cobaltites formation		2nd reaction Ca326 formation		3rd reaction decomposition of Ca326		4th reaction liquid formation
	Temp$_{max.}$ (°C)	Mass loss (wt.%)	Temp$_{max.}$ (°C)	Mass loss (wt.%)	Temp$_{max.}$ (°C)	Mass loss (wt.%)	Temp. (°C)
Pure (1)							
1:1	874 920	22.6	960	1.2	1059	2.4	1285
Standard (2)							
3:4	819	18.5	955	3.1	1039	2.3	1304
1:1	818 848	22.4	948	2.5	1041	2.5	1309

two peaks (oxide no. 1). The one at higher temperature (Ia on Fig. 2) corresponds to decomposition of Co_3O_4 and it means that non-reacted cobalt oxide is present after Ca349 formation. It is unexpected because in the case of cobalt deficiency in 1:1 batches one could rather wait for Ca326 formation, an equilibrium phase besides Ca349, at that temperature. Moreover, 3:4 compositions did not yield pure Ca349 because of the first peak splitting.

Reactions at higher temperature cause further mass losses; they are reversible and are influenced by the powder surface area. The second reaction happens at 948–960 °C and corresponds to decomposition of Ca349 and Ca326 formation. Because cation ratio in starting materials is different from that of Ca326 phase, the residual must form CoO. Thus the second reaction involves decrease of average cobalt oxidation state and its re-oxidation during cooling. Exothermic peak during cooling of cobaltites happens at the same temperature as CoO oxidation and is accompanied by mass gain and could be treated as indication of the presence and amount of the non-reacted oxide. It must be stressed that $CoO \rightarrow Co_3O_4$ oxidation occurred in the all examined batches during cooling.

The third reaction at 1039–1059 could be ascribed to Ca326 decomposition to CaO and CoO. Ca326 decomposition involves Co^{3+} reduction to Co^{2+} and relevant mass losses were observed on a TG curve. The results of DTA/TG study are consistent with the CaO-CoO system,[6] however temperatures of the relevant reactions are higher, which is obvious in the case of dynamic studies. The source of cobalt oxide influences only formation of Ca349 phase: the reaction happens at lower temperature ($\Delta T = 56$ °C) if oxide (2) was applied.

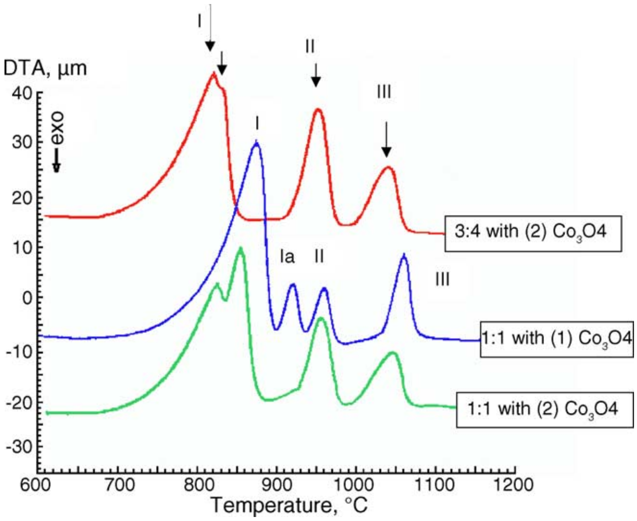

Fig. 2. DTA study of 1:1 and 3:4 batches prepared from pure (1) and standard (2) cobalt (II,III) oxide.

The fourth reaction at 1285–1309 °C occurs at lower temperature than eutectic temperature for liquid formation, 1350 °C. It could be assumed that contaminants in the both oxides resulted in lower temperature of eutectic liquid formation.

Isothermal calcinations results (Table 3, Fig. 3) show that Ca349 phase was formed as a main phase at 850 °C (oxide 1) or at 800 °C (oxide 2). That temperature is much lower than reported calcination/sintering temperature for Ca349 based thermoelectric ceramics: 920 °C[1] or 1100 °C.[4] Calcination at higher temperature led to increase of Ca326 phase. Total or significant decomposition of Ca349 was observed after calcinations at 950 °C. Low-temperature formation of Ca349 at 800 °C was not completed after 20 h calcinations and traces of residual reagents ($CaCO_3$ and Co_3O_4) were detected by XRD if 1:1 cation ratio was applied. Increase of calcination temperature up to 850 °C caused formation of a small amount of Ca326 and no traces of $CaCO_3$ were detected by XRD. On the other hand, presence of Co_3O_4 was detected by DTA/TG, if performed on the specimens after calcinations. Study of

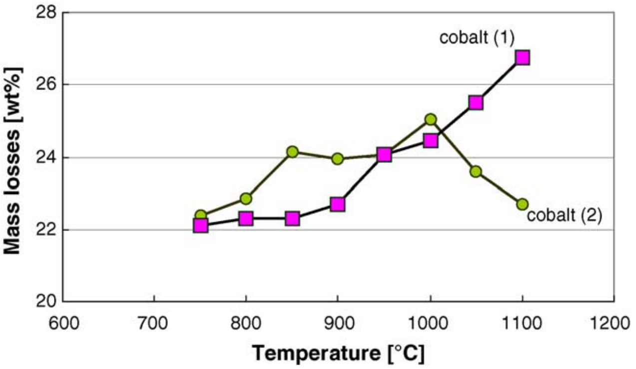

Fig. 3. Mass losses of 1:1 composition after calcinations for 20 h vs. temperature; specimens of cobalt oxide (1) were significantly sintered after calcinations at 1050–1100 °C.

Table 3
Phase composition of the tablets of 1:1 and 3:4 composition after calcinations for 20 h at given temperature

Cation ratio	Calcination temperature				
	800 °C	850 °C	900 °C	950 °C	1050 °C
Pure (1)					
1:1		Ca349 xxx Ca326 x	Ca 349 xxxx Ca326 xx	Ca349 x Ca326 xxxx $Ca(OH)_2$ x	Ca326 xx Co_3O_4 x $Ca(OH)_2$ xx CoO x
Standard (2)					
1:1	Ca349 xx Ca326 x CoO tr. Co_3O_4 tr. $CaCO_3$ tr.	Ca349 xx Ca326 xx	Ca349 xxxx Ca326 xxx	Ca349 x Ca326 xx	Ca349 xxx Ca326 x Co_3O_4 tr.
3:4		Ca349 xxx Ca326 x	Ca349 xxxxx Ca326 tr.	Ca349 xx Ca326 x	

Number of "x" is proportional to the highest peak of the relevant phase. XRD measurements were applied to the powders at the room temperature.

two various cation ratio compositions show that at the same temperature Ca326 phase forms more easily than Ca349 if 1:1 ratio is predominant in the tablets. It is supposed that local inhomogenity inside 3:4 tablets could lead rather to formation of Ca326 phase than to the full completion of Ca349.

Mass loss after isothermal calcinations (Fig. 3) confirms various behavior of the batches prepared with different cation ratio and various Co_3O_4 sources. Higher mass losses for batches composed from oxide (2) indicate higher reaction degree in specimens calcined up to 950 °C. Indeed, stoichiometric mass loss in the case of 1:1 tablets was achieved after 20 h calcination at 800 °C for oxide (2) in comparison to 900 °C for composition with oxide (1).

Calcination above 950 °C shows two different reaction paths, if composition of the two various cobalt oxide sources are compared. Isothermal annealing of tablets from oxide (1) above 950 °C led to increasing mass loss (oxygen depletion), while oxide (2) derived product exhibits lower mass loss. XRD study of product calcined at 1050 °C showed surprising results: presence of Ca349 phase in tablets from oxide (2) or cobaltite decomposition to starting oxides in tablets from oxide (1). According to equilibrium system of CaO-CoO[6] decomposition of both cobaltites above 1026 °C is unavoidable. That was the case for composition from oxide (1) but after 20 h calcination only Ca349 disappeared while Ca326 was still present. Decomposition of Ca349 led to formation of CoO at 1050 or 1100 °C, its re-oxidation to Co_3O_4 during cooling was retarded as a result of sintering and higher mass losses were observed (Fig. 3). Calcium hydroxide found in some calcined specimens must have formed from CaO during specimens aging at room temperature.

On the other hand behaviour of cobaltites prepared from oxide (2) was different: however amount of Ca349 decreased slightly after calcinations at 1050 °C, only traces of Ca326 were visible even in specimens with 1:1 cation ratio. It could be concluded that Ca349 from oxide (2) was stabilized but the reason is unknown (contaminants?). The effect of stabilization of Ca349 at 900 °C by Bi_2O_3 was reported earlier by S. Lambert et al.[8] but such contaminant was not found in tested material.

Low temperature formation of Ca349 studied by DTA and isothermal calcinations shows excess of cobalt after cobaltite formation. It is present in the form of Co_3O_4/CoO or forms Ca326 after prolonged calcinations. It proves that proper formula for Ca349 should be written as $Ca_3Co_{4-x}O_{9+\delta}$.

4. Summary

Source of cobalt (II,III) oxide could have decisive influence on the final phase composition of the calcinations product. The most significant effect was observed for low temperature formation of Ca349 and/or Ca326. Presence of residual OH group in starting cobalt oxide could decrease temperature of the relevant cobaltite formation. Ca349 phase with claimed thermoelectric properties could be obtained at such a low temperature as 800 or 850 °C, however high-temperature stabilization of Ca349 phase was observed if oxide (2) was applied. Presence of residual starting oxides after calcinations could be diminished by homogeneity improving rather than by higher temperature or prolonged calcinations.

References

1. Miyazaki, Y., Kudo, K., Akoshima, M., Ono, Y., Koike, Y. and Kajitani, T., Low-temperature thermoelectric properties of the composite crystal $[Ca_2CoO_{3..34}]_{0.614}[CoO_2]$. *Jpn. J. Appl. Phys.*, 2000, **39**, L531–L533.
2. Horii, S., Matsubara, I., Fujie, K., Shin, W., Murayama, N., Shimoyama, J. *et al.*, Thermoelectric properties of grain-aligned Ca-based cobaltites by a magneto-scientific method. *Proc. 22 Int. Conf. Thermoelectr.*, 2003, 239–242.
3. Itahara, H., Xia, C., Seno, Y., Sugiyama, J., Tani, T. and Koumoto, K., Synthesis of textured thermoelectric layered cobaltites by reactive templated grain growth. *Proc. 22 Int. Conf. Thermoelectr.*, 2003, 188–191.

4. Li, S., Funahashi, R., Matsubara, I., Ueno, K., Sodeoka, S. and Yamada, H., Synthesis and thermoelectric properties of the new oxide materials $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ $(0.0 < x < 0.75)$. *Chem. Mater.*, 2000, **12**, 2424–2427.
5. Hebert, S., Flahaut, D., Pelloquin, D., Martin, C., Maignan, A. and Hejtmanek, J., Cobalt oxides as potential thermoelectric elements: the influence of the dimensionality. *Proc. 22 Int. Conf. Thermoelectr.*, 2003, 161–163.
6. Woermann, E. and Muan, A., Phase equilibria in the system CaO-cobalt oxide in air. *J. Inorg. Nucl. Chem.*, 1970, **32**, 1455–1459.
7. Mikami, M. and Funahashi, R., High-temperature thermoelectric properties of single-crystal $Ca_3Co_2O_6$. *Proc. 22 Int. Conf. Thermoelectr.*, 2003, 200–202.
8. Lambert, S., Leligny, H. and Grebille, D., Three forms of the misfit layered cobaltite $[Ca_2CoO_3]$ $[CoO_2]_{1.62}$. A 4D structural investigation. *J. Sol. State Chem.*, 2001, **160**, 322–331.