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# Low temperature synthesis of calcium cobaltites in a solid state reaction

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**Abstract** This paper presents synthesis of calcium cobaltites of the nominal composition of $Ca_3Co_4O_9$ prepared by the solid state reaction. The reaction between $CaCO_3$ and $Co_3O_4$ was investigated at 700–900 °C during 20 h and at 800 °C during 2–30 h. Mass changes, phase composition and $Co^{+3}$, $Co^{+4}$ content were examined. Stability of the calcined specimens was tested by DTA/TG. It was found that two phases: $Ca_3Co_4O_9$ and $Ca_3Co_2O_6$ were present as a result of calcinations above 800 °C. On the other hand, the temperature of 750 °C was too low for calcium cobaltites to be synthesized. Mono-phase material with $Ca_3Co_4O_9$ phase was obtained after calcinations at 800 °C but non-stoichiometry of the compound and its relation to the calcinations time were found. Once synthesized, the compound was stable up to 900 °C.

**Keywords** Calcination · Powders—solid state reaction · Calcium cobaltites · DTA/TG

## 1 Introduction

Cobalt based oxides have attracted much attention as potential thermoelectric materials since the discovery of their thermoelectric properties by Terasaki et al. [1] Since that time the compounds of $[Ca_2CoO_3]_{0,62}CoO_2$, $Na_{0,75}CoO_2$ or $Ca_3Co_2O_6$ were reported to exhibit large thermopower S and simultaneously low electrical resistivity ρ and low thermal conductivity [2–12]. It is proposed that the thermopower in the transition metal oxides is strongly enhanced by the spin and orbital degrees of freedom [13]. On the other hand, the good electronic conduction is expected for the mixed valency of cobalt in the compound [14]. Both conditions are met in $Na_{0,75}CoO_2$ and $[Ca_2CoO_3]_{0,62}CoO_2$ cobaltites with the misfit-layered structures and presence of $CoO_2$ conduction sheets [15]. However, in the real structure, displacive modulation of the atomic sites occurs, interactions between the subsystems are possible and vacancies in the cationic and anionic subnetworks are present.

The previous study showed that the electrical resistivity of cobaltites was depended on the $Co^{+4}$ content while the kind of the relevant cations entering that layered compound (Na or Ca) did not influence the electrical resistivity if the amount of $Co^{+4}$ was similar [16]. In order to be able to produce and to apply thermoelectric cobaltite ceramics the basic studies on the synthesis and thermal stability of the cobaltite compounds are necessary. Up to date the measurement of thermoelectric properties of cobaltites were mostly performed on the single crystals [1, 2, 5], while the polycrystalline ceramics for thermoelectric measurements were characterized mainly by XRD and/or microscopic studies [10–12].

Calcium cobaltites were chosen as the subject of that study as they are more prospectus material for the practical thermoelectric application than sodium cobaltites because of the high sodium volatility at elevated temperature. The previous study showed that the calcium cobaltite compound was synthesized at temperature range of 880–1100 °C and the resultant product was characterized by XRD as the monophase product of $Ca_3Co_4O_9$ [3], $Ca_3Co_4O_{9+\delta}$ [4], $[Ca_2CoO_{3.34}]_{0.614}[CoO_2]$ [5], or $[Ca_2CoO_3]_{0,62}CoO_2$ [6].

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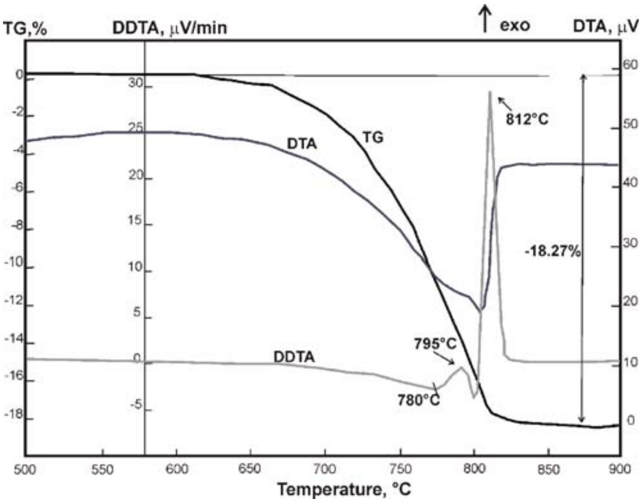


**Fig. 1** DTA/TG and DDTA of the starting cobalt oxide-calcium carbonate mixture

However, according to the CaO–CoO system, the $Ca_3Co_4O_9$ (Ca349) phase is stable up to 926 °C and then decomposes to $Ca_3Co_2O_6$ (Ca326) and to cobalt oxide over that temperature [17]. On the other hand, it was shown that the resulted phase assemblage of the synthesized cobaltites depended on the reaction parameters i.e. temperature of the calcination, the oxygen partial pressure as well as the grain size of the starting powders [18]. Thus the study of calcium cobaltite formation and its stability are necessary because the Ca:Co ratio in the starting mixture could influence the final composition of the non-stoichiometric Ca349 compound. Besides, the side products (the relevant oxides) would be present in the resultant product and they could influence on the thermoelectric efficiency. In this paper the synthesis process of the $Ca_3Co_4O_{9+\delta}$ compound below decomposition temperature was studied by the solid state reaction and the kinetics of the reaction at 800 °C was examined. Monitoring of mass changes, DTA/TG techniques on heating and cooling as well as the measurement of $Co^{4+}$ and $Co^{3+}$ weight fractions were applied for studies of the compound formation and its stability.

## 2 Experimental procedure

Calcium cobaltites were prepared by the solid state reaction of $CaCO_3$ (POCH, Gliwice) and $Co_3O_4$ (POCH-Lublin, the total cobalt content over 69.96 wt.%; $D_{50}=19.78$ µm). Preparation was carried out according to the following reaction:

$$9\ CaCO_3 + 4\ Co_3O_4 + O_2 \rightarrow 3\ Ca_3Co_4O_9 + 9\ CO_2 \qquad (1)$$

Cobalt (II, III) oxide and calcium carbonate were mixed in a molar ratio corresponding to the nominal composition of $Ca_3Co_4O_9$. Mixing was performed at the roller bench for 24 h with the zirconia balls and isopropyl alcohol. Subsequently, the mixture was dried, the powder was uniaxially pressed and the tablets with 10 mm diameter and 5–6 mm height were produced. Calcination was performed in an open horizontal tube furnace (Carbolite STF 16/50/450) with a diameter of 50 mm and length of 900 mm at the temperature range of 700–900 °C for 20 h. Kinetic studies were applied for the calcination at 800 °C during 2–30 h. Three tablets were placed in an alumina boat of 80 mm length, each tablet was weighed out before and after calcination. The boat was placed in the middle of the furnace hot zone . The hot zone of the furnace is 450 mm, while the uniform length (±5 °C) approaches 350 mm. The specimens were heated up and cooled down together with the furnace. The resultant tablets were aged at room temperature and weighted again after 30 days.

XRD measurements (XPERT-Pro, Philips; CuK$\alpha$ monochromatic radiation, $\lambda$=1.5406 Å, 5–90° 2$\theta$ range) were applied to the powdered specimens at room temperature. Some specimens were observed in a scanning electron microscope (HITACHI S-420 with VOYAGER EDS spectrometer).

DTA/TG study was applied to the starting mixtures as well as to the calcined material. The study was performed in the flowing air at temperature range of 20–1000 °C (SETARAM). The relevant curves were recorded during heating and cooling down.

Analysis of the total cobalt content, Co(IV), Co(III) and Co(II) content were applied to the calcined tablets. The chemical methods could have been employed because the specific properties of the reagents gave possibility for determination of the Co(III) amount in the presence of Co (IV) in such materials. Determination of Co(III) content was made using spectrophotometric determination of Co (III) complexes with EDTA. Co(IV) was clarified after the indirect measurement by the redox reaction with jodie. Franky reagent was used for the measurement of Co(II) and Ca content in the form of oxide or hydroxide. The amount of Ca in cobaltites and oxygen content were not determined. The results are expressed as wt.% of the relevant cation in the tested powder. The methods were described elsewhere [16].

**Table 1** Phase composition of the tablets after calcinations for 20 h at given temperature.

| Phase composition of tablets after 20 h calcinations | | | |
|---|---|---|---|
| 800 °C | 850 °C | 900 °C | 950 °C |
| Ca349 xxxx | Ca349 xxx | Ca349 xxxx | Ca349xx |
| Ca326- | Ca326 x | Ca326 x | Ca326 xx |

The number of “x” is proportional to the most intense peak of the relevant phase.

**Table 2** Mass losses after calcinations for 20 h at given temperature (1 and 3—tablets in the enter position, 2—midposition in an alumina boat).

| | Position of the tablets[a] | Temperature, °C | | | | | |
|---|---|---|---|---|---|---|---|
| | | 700 | 750 | 800 | 850 | 900 | 950 |
| Mass losses, wt.% | 1 | 18.85 | 19.05 | 19.10 | 19.59 | 20.02 | 19.90 |
| | 2 | 18.91 | 19.06 | 19.28 | 19.65 | 20.04 | 19.99 |
| | 3 | 18.93 | 19.06 | 19.26 | 19.63 | 20.02 | 19.97 |
| | Average | 18.89 | 19.06 | 19.21 | 19.62 | 20.03 | 19.97 |

[a] Numbers indicate the position of the tablets in an alumina boat. Nos. 1 and 3 stands for the tablets in the external position, while No. 2 stands for the midposition.

## 3 Results and discussion

The DTA/TG data of the relevant mixture of calcium carbonate and cobalt oxide are presented in Fig. 1. The main endothermic reaction accompanied by mass losses was attributed to the decomposition of $CaCO_3$ to CaO and to the simultaneous formation of $Ca_3Co_4O_9$ calcium cobaltite. Formation of that phase occurred between 795–812 °C and was preceded by other reaction in the range of 680–780 °C as indicated by DDTA. It is supposed that decomposition of calcium carbonate could start at that low temperature because of the cobalt ions action. The resultant calcia reacted with cobalt oxide and formed initially $Ca_3Co_4O_9$ as only the latter was present in the material after calcination at 800 °C as detected by XRD (Table 1).

The total mass losses registered on a TG curve during heating up to 900 °C are 18.3 wt.%. The mass losses of the samples after isothermal calcination at elevated temperature are presented in Table 2. Calculated mass change, equivalent to the formation of $Ca_3Co_4O_9$ according to the reaction 1, is 19.5 wt.%. Mass losses in the reaction 1 originate from the carbon dioxide evolution but they are reduced by the oxidation of cobalt. Cobalt is present as $Co^{+2}$ and $Co^{+3}$ in the starting cobalt oxide. Mass losses of the specimens calcined at 700–800 °C were lower than those from the reaction 1. One could expect that lower mass losses resulted from the non-completed decomposition of $CaCO_3$. If this is a case, then the increase of mass losses would be observed after the longer calcination time or after calcination at higher temperature. However, the value of 19.5 wt.% was not attained even after 20 h of calcination at 800 °C. Moreover, prolongation of the calcinations time up to 30 h resulted in the lower mass losses (Fig. 2). Calcination at 850–900 °C led to the higher mass losses over the expected value of 19.5 wt.% but the mass losses were again lower after calcinations at 950 °C.

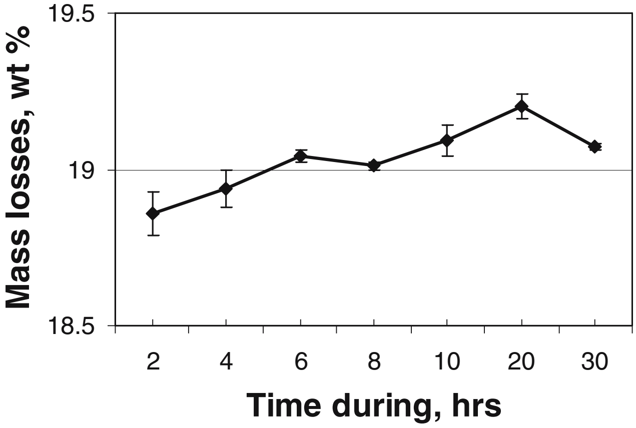


**Fig. 2** Mass losses of the tablets after isothermal calcination at 800 °C for a given time

This results suggest that oxidation of the initial cobalt in $Co_3O_4$ occurred to the higher extend during formation of calcium cobaltite and $Co^{+4}$ cations are present in the sample besides $Co^{+3}$ ones if calcined at 800 °C. The reaction 1 should be rewritten into the following form:

$$9\ CaCO_3 + 4\ Co_3O_4 + \delta O_2 \rightarrow 3\ Ca_3Co_4O_{9+\delta} + 9\ CO_2 \qquad (2)$$

Moreover, the largest mass losses after the isothermal calcination were observed in the mid-position samples if the calcination was conducted over 750 °C (Table 2). The effect was related probably to the oxygen partial pressure, because the reaction 2 involves oxygen from the ambient

**Table 3** Results of the chemical analysis of the tablets after calcinations for 20 h at given temperature.

| Cation content [%wt.] | Calcination temperature [°C] | | | | |
|---|---|---|---|---|---|
| | 750 | 800 | 850 | 900 | 950 |
| $Co^{+2}$ in the form of CoO, $Co(OH)_2$ | 0.9<br>±0.3 | 1.0<br>±0.3 | – | 2.6<br>±0.4 | 1.6<br>±0.4 |
| $Co^{+3}$ | 18.8<br>±0.5 | 14.9<br>±0.4 | 18.8<br>±0.4 | 17.7<br>±0.5 | 21.6<br>±0.4 |
| $Co^{+4}$ | 17.7<br>±0.4 | 19.0<br>±0.4 | 16.6<br>±0.5 | 18.2<br>±0.5 | 15.8<br>±0.4 |
| Ca in the form of CaO or $Ca(OH)_2$ | 0.0 | 0.0 | – | 0.5<br>±0.3 | 2<br>±0.3 |

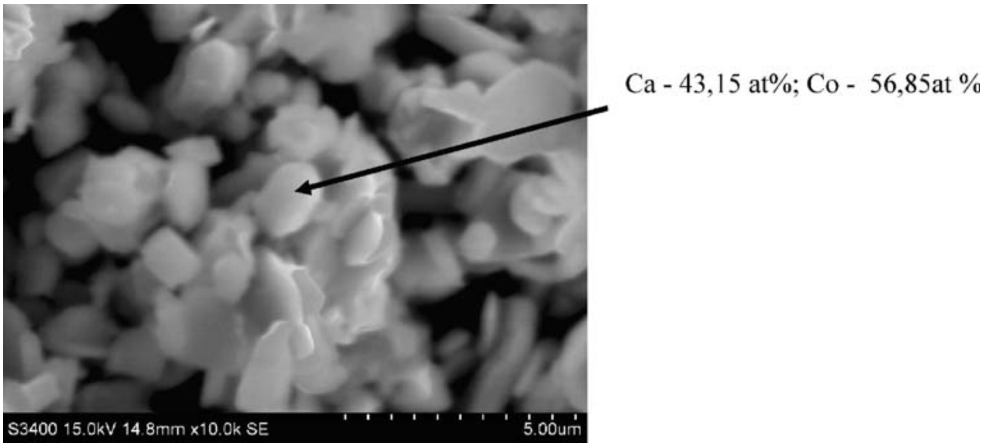


**Fig. 3** The microstructure of the sample cross section after calcinations at 800 °C for 20 h. EDS was performed on the indicated place

atmosphere and evolution of $CO_2$. We could expect that the oxygen partial pressure in the mid-position was always lower because of the $CO_2$ evolution and a gas flow disturbance. Thus the higher mass losses of the tablets at the mid-position could result from the lower cobalt oxidation degree. It is interesting to note that the effect was observed even after calcinations at 950 °C.

The results of the chemical analysis after isothermal calcination for 20 h at various temperature are presented in Table 3. The largest content of $Co^{+4}$ was observed in the specimens after calcination at 800 °C and it was accompanied by the least content of $Co^{+3}$. Calcination over that temperature led to the lower amount of $Co^{+4}$. No calcium ions were observed in the specimens after calcination at 850 °C or lower. We could assume that after decomposition of calcium carbonate for 20 h at 750–800 °C the all calcium ions entered the Ca349 structure. On the other hand, the results show presence of the non-reacted cobalt oxide after calcinations at 800 °C or lower.

The simultaneous cobalt oxide presence and the lack of calcia in the specimens (calcinations at 800 °C for 20 h) with the only Ca349 phase detected by XRD, indicate the non-stochiometry in the cobalt sublattice of Ca349 at room temperature. That effect was confirmed by the results from EDS (Energy Dispersive Spectroscopy) study; Ca/Co= 3.00:3.95 was found inside the crystals (Fig. 3).The lower cobalt amount than in stoichiometric formula of Ca349 phase was reported elsewhere [18] and is consistent with Y. Miyazaki findings [14].

Mass gain observed after aging (Fig. 4) indirectly shows the amount of cobalt outside the Ca349 compound. That amount falls if the calcination time is longer than 8 h (Fig. 3). Thus the non-stoichiometric formula of Ca349 compound should be written as: $Ca_3Co_{4-x}O_{9+\delta}$. Formation of that compound from the stoichiometric mixture of CaO and $Co_3O_4$ at 800 °C could be clarified by studying the mass losses after calcinations for the period of 2–30 h (Fig. 2) and check of their mass after aging for 30 days at room temperature (Fig. 4). Mass gain observed after aging indirectly shows the amount of the free oxides: CaO and/or CoO because of hydroxides or carbonates formation at room temperature.

One could expect that both curves: mass losses after calcinations (Fig. 2) and mass gain (Fig. 4) of the same tablets are coherent, but they are not. The slight increase of mass losses after calcinations for 2–8 h could be related to the completion of $CaCO_3$ decomposition but is accompanied by the increase of the amount of free oxides (Fig. 4). It means that the longer calcination time results in the slightly higher quantity of the non-reacted oxides. If the calcination time is longer than 8 h then the subsequent decrease of the non-reacted oxides is observed (Fig. 4) and after 20 h time no CaO was detected in the calcined specimens (Table 3). Prolongation of the calcination time over 20 h led to the increase of the cobalt oxidation state (decrease of mass losses in Fig. 2) and was accompanied by the less amount of free CoO (Fig. 4). Thus, the non-stoichiometry of cobalt and oxygen in the Ca349 compound are closely related.

Calcination at 850 °C and above that temperature led to the bi-phase composition: XRD results showed the Ca326 phase presence despite the Ca349 phase (Table 1). Moreover, the traces of the by-products were detected by the chemical analysis: CaO and CoO were found in the

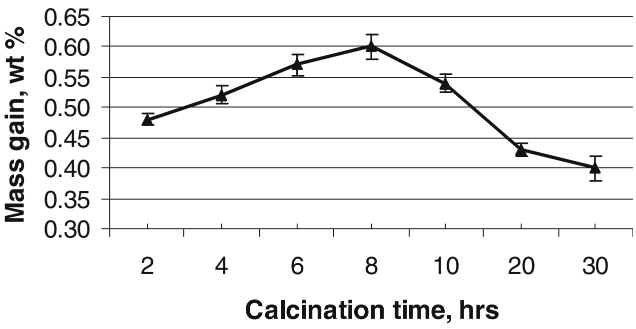
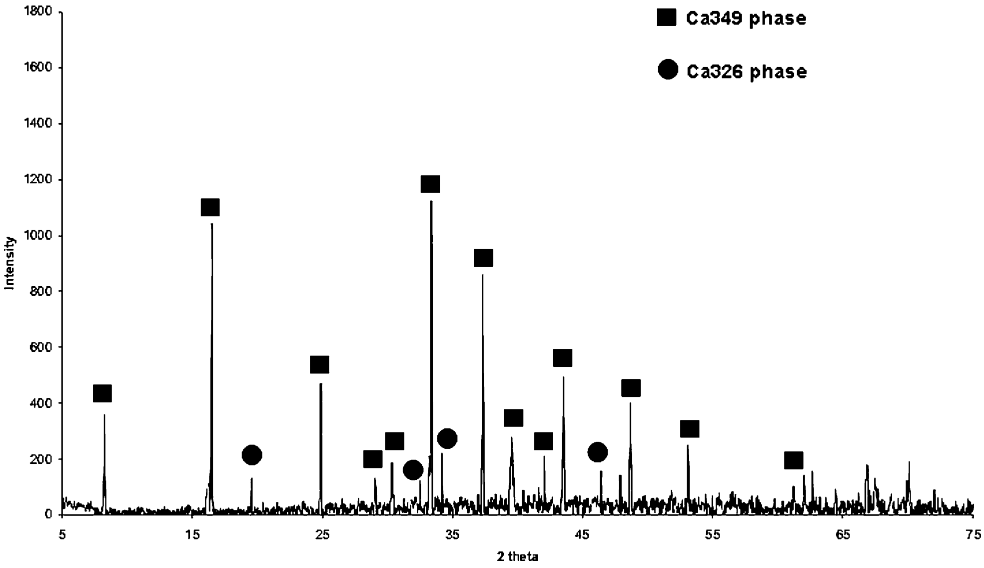


**Fig. 4** Mass gain after 30 days of aging. Mass gain refers to the tablets after calcination at 800 °C for a given time

**Fig. 5** XRD pattern of the sample after calcinations at 850 for 20 h



specimens calcined at 900 and 950 °C (Table 3). According to the CaO-CoO equilibrium system decomposition of the Ca349 compound occurs above 926 °C and CoO is present apart from the Ca326 compound. The present study shows that Ca326 phase could develop from calcium carbonate and cobalt oxide mixture at temperature as low as 850 °C (Fig. 5). The small amount of Ca326 phase must stabilize the Ca349 compound because no oxides were detected by the chemical analysis (Table 3). However, that stability was accompanied by the lower amount of $Co^{+4}$.

Stability of the Ca349 phase was studied by DTA/TG means. Summary results of DTA/TG and DDTA performed on the sample calcined previously at 800 °C are shown in Fig. 6 during heating and in Fig. 7 during cooling. Endothermic peak at 978 °C with accompanied mass losses of 4.48% wt.% were found (Fig. 6). DDTA shows the start of the reaction at 906 °C and that value is close to the equilibrium temperature of Ca349 decomposition. Thus the reaction corresponds to the decomposition of Ca349 and Ca326 formation. Because the cation ratio in the starting materials is different than that of the Ca326 phase, the residual must form cobalt oxide. Cobalt oxide is stable in the form of CoO over 950 °C. Thus, the reaction involves reduction of cobalt oxidation state and mass losses because of the oxygen evolution:

$$Ca_3Co_4O_{9+\delta} \rightarrow Ca_3Co_2O_6 + 2CoO + \delta O_2 \tag{3}$$

The reaction is reversible, starts below 900 °C and the exothermic peak during cooling is accompanied by the mass gain of 3.42 wt.% (Fig. 7). The latter involves the oxygen

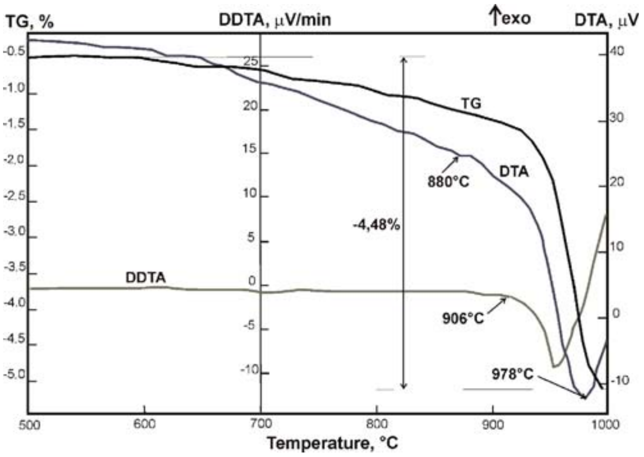


**Fig. 6** DTA/TG/DDTA of the sample with the nominal composition of $Ca_3Co_4O_9$. Measurement was performed on the sample previously calcined at 800 °C for 20 h. The *curves* were registered during heating up to 1000 °C

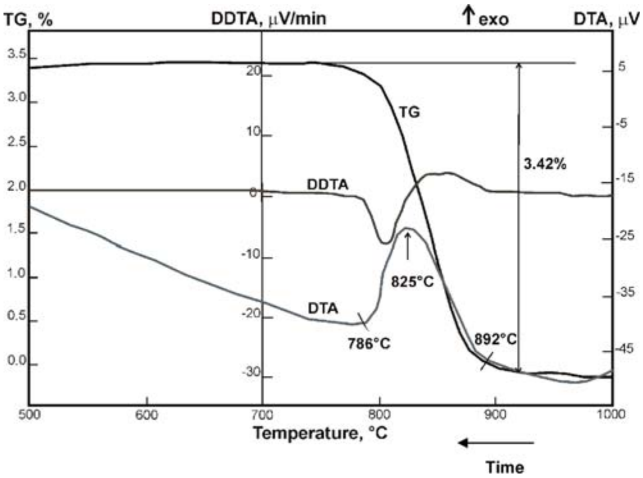


**Fig. 7** DTA/TG/DDTA of the sample with the nominal composition of $Ca_3Co_4O_9$. Measurement was performed on the sample previously calcined at 800 °C for 20 h. The *curves* were registered during cooling from 1000 °C

uptake from the ambient atmosphere thus one could expect that the powder/tablet microstructure would influence the reaction. The lower mass gain (3.42 wt.%) than mass loss (4.48 wt.%) during the reversible reaction shows the possibility of the side product formation during cooling if Ca349 compound was heated over its decomposition temperature. On the other hand, the non-isothermal studies show that the Ca349 compound once synthesized, is stable up to 900 °C. However, it is interesting to note that mass losses from 600 °C were observed for the Ca349 specimen with 1 wt.% of $Co^{+2}$ (Fig. 6). They could come from the cobalt carbonate decomposition.

## 4 Summary

The solid state reaction of calcium carbonate and cobalt oxide at 700–950 °C is influenced by the reaction time and temperature. The most stable composition of Ca349 was obtained after calcination at 800 °C for 20–30 h but traces of cobalt oxide were present because of the Ca349 non-stoichiometry at room temperature. Once synthesized, it was stable up to 900 °C. Calcination of the starting mixture with the Ca:Co=3:4 cation ratio at 850 °C or higher led to formation of $Ca_3Co_2O_6$ compound besides the Ca349 phase. Mass gain after aging the specimens after calcination at 800 °C was related to the presence of CoO, the latter being correlated to the time of calcination. Moreover, the smaller $Co^{+4}$ content after high temperature calcinations was related to the parallel formation of the Ca349 and Ca326 phases.

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