

# Comparison of thermal oxidation behaviour of CoSb<sub>3</sub> and CoP<sub>3</sub>

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## Abstract

One of the most important aspects in fabrication of thermoelectric generators is the thermal stability of a thermoelectric material. Preliminary studies for skutterudites in temperature range 400-700°C show that depending on environment they can undergo decomposition and oxidation in an inert and oxidizing atmosphere respectively.

The goal of this work was to investigate thermal durability of CoSb<sub>3</sub> and CoP<sub>3</sub> in air atmosphere in temperature range of 20-850°C, and to compare their oxidation products, reaction kinetics and influence of degradation on electric properties. It was established that oxidation behaviour of CoSb<sub>3</sub> and CoP<sub>3</sub> exhibits significant differences in reaction products and kinetic. The oxidation rate of CoSb<sub>3</sub> is at least ten times greater than that for CoP<sub>3</sub>. Electrical measurements performed on initial and oxidized samples showed large influence of oxidation on electrical properties especially in case of CoSb<sub>3</sub> samples.

## Introduction

Recently CoSb<sub>3</sub> and related materials were recognized as candidate materials for thermoelectric generators. Numerous investigations showed that high values of thermoelectric figure of merit  $ZT$  exceeding 1 are achievable for CoSb<sub>3</sub> based compounds in temperature range of 400-700°C. Simultaneously some studies showed that CoSb<sub>3</sub> undergoes oxidation in temperatures above 400°C. This is an important information if we keep in mind potential skutterudite application in energy recuperation in terrestrial conditions. In our previous work [1] we have determined from TG and DTA data that cobalt triantimonide oxidation starts at around 380°C. This result is consistent with Savtchuk et al.[2] observations for Co<sub>1-x</sub>Fe<sub>x</sub>Sb<sub>3</sub> thin films, which revealed that for CoSb<sub>3</sub> oxidation starts at 380°C and for Fe-doped samples even at 300°C. We didn't observe so strong shift in the oxidation starting temperature for tellurium doped samples but we noticed much higher reaction rates for oxidation and for decomposition in helium. Oxidation of the cobalt triantimonide leads to formation of a complex layer of antimony oxides and antimony cobaltates. Hara et al.[3] studying changes in CoSb<sub>3</sub> during aging in air at 600°C established that two layers of oxidation products are formed on samples surface. They identified a mixture of antimony oxides  $\beta$ -Sb<sub>2</sub>O<sub>4</sub>, Sb<sub>2</sub>O<sub>4</sub>, and Sb<sub>2</sub>O<sub>3</sub> to be the outer layer and CoSb<sub>2</sub>O<sub>6</sub>, CoSb<sub>2</sub>O<sub>4</sub>, Sb<sub>2</sub>O<sub>3</sub> and  $\beta$ -Sb<sub>2</sub>O<sub>4</sub> as the inner layer. Savtchuk et al. for Co<sub>1-x</sub>Fe<sub>x</sub>Sb<sub>3</sub> thin films oxidation identified (Co,Fe)O<sub>x</sub>, FeSb<sub>2</sub>O<sub>4</sub> and Sb<sub>2</sub>O<sub>3</sub> as the degradation products. In our earlier results we have also observed that oxidation products form two layers consisting mainly of Sb<sub>2</sub>O<sub>4</sub> on the surface and CoSb<sub>2</sub>O<sub>6</sub> inside the scale. Hara et al. noticed for oxidized sample decrease of  $n$  Hall carrier concentration from 3.4 to 2.7  $10^{26} \cdot m^{-3}$  and subsequent

increase of resistivity resulting in decreasing overall thermoelectric performance.

As can be seen from the preliminary results CoSb<sub>3</sub> and allied compounds undergo oxidation in the full range of temperatures of their optimum thermoelectric properties. Therefore determination of their thermal durability in air and searching for other more stable compounds is a very important issue. In this study we have chosen CoP<sub>3</sub> for comparison with CoSb<sub>3</sub> as it was reported by Caillat[4] as more stable in high temperatures and has higher peritectic temperature.

## Experimental

Cobalt triantimonide powder was synthesised by direct solid state reaction of stoichiometric mixture of cobalt and antimony. Differences in chemical properties of phosphorous and antimony caused different approach in cobalt triphosphide synthesis. CoP<sub>3</sub> was synthesized by tin-flux method from an alloy with Co:P:Sn molar ratio 1:4:20. Chemical and phase composition of the synthesized compounds were studied by traditional wet chemical analysis methods, ICP-ESA and XRD. All these measurements validated that homogeneous cobalt triantimonide and cobalt triphosphide with skutterudite structure were synthesized. Prepared powders with average diameter 15  $\mu m$  for CoSb<sub>3</sub> and 2  $\mu m$  for CoP<sub>3</sub>, estimated from microscopic observations, were used for polycrystalline samples fabrication and for thermal analysis studies. Both CoSb<sub>3</sub> and CoP<sub>3</sub> bulk samples were prepared by hot pressing technique. More details about the synthesis and sintering of CoSb<sub>3</sub> and CoP<sub>3</sub> can be found elsewhere[5,6]. Chemical and phase composition were confirmed to be the same as in the starting powders.

Nonisothermal DTA and TG measurements of the powders oxidation as well as isothermal gravimetric measurements for reaction kinetics were carried out in an apparatus of the Paulik-Paulik-Erdey system equipped with Sartorius balance with accuracy  $10^{-4}g$  and computer data acquisition and control system. Measurements were conducted on pulverized samples having weight  $50 \pm 2$  mg, placed in quartz plates in dynamic air atmosphere (20 dm<sup>3</sup>/h). Thin layer of examined powder was applied to prevent influence of gaseous oxygen diffusion through the powder deposit. Chemical and phase composition as well as morphology of degradation products were determined using the same methods as in starting materials characterization.

## Results and discussion

Cobalt triantimonide TG and DTA oxidation curves are presented in Fig. 1. Oxidation starts at about 380°C and involves several stages. Exothermic peaks on DTA signal correspond to rapid increases of oxidation rate starting at about 580°C, 660°C, 740°C. A total oxidation weight gain

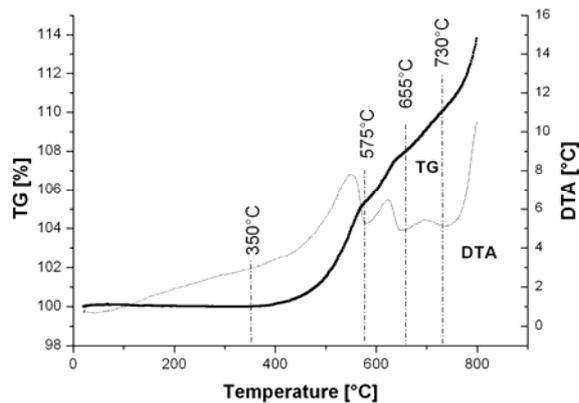


Fig. 1. TG and DTA curves for CoSb<sub>3</sub> oxidation in air (5°C/min)

was determined for different temperatures and compared with possible products. Up to 650°C the weight gain is 22.1 – 22.7% comparable with formation of CoSb<sub>2</sub>O<sub>4</sub> + Sb<sub>2</sub>O<sub>4</sub> and for higher temperatures 700°C and 750°C the weight gain raises up to 25.4% which means that formation of both cobalt antimonates CoSb<sub>2</sub>O<sub>4</sub> and CoSb<sub>2</sub>O<sub>6</sub> and antimony oxide Sb<sub>2</sub>O<sub>4</sub> could be expected. XRD measurements for completely oxidized CoSb<sub>3</sub> powders at 550°C and 700°C (Fig. 5) indicates that in each examined temperature the main oxidation products are Sb<sub>2</sub>O<sub>4</sub>, CoSb<sub>2</sub>O<sub>6</sub> and CoSb<sub>2</sub>O<sub>4</sub>. Morphology and microstructure of grown scales were examined by scanning electron microscopy SEM. EDS analysis of the surface indicates it contains almost only antimony and oxygen. Cross-section pictures for different oxidation times presented in Fig. 3 have revealed that scale morphology is complex. For thin layers (<7 μm) formed during short time oxidation the atomic ratios are uniform inside the scale in the precision of EDS method and no diversification into two layers is observed. In case of longer oxidation times a thick scale (>10 μm) splits up and two layers with different composition could be distinguished by EDS analysis. In order to determine a phase composition of the observed product layers X-ray diffraction depth profile was done on long-term oxidized sample. XRD profile results revealed that the scale consists of three main layers. The surface antimony oxide layer is built from α-Sb<sub>2</sub>O<sub>4</sub>. The internal layers consists mainly of cobalt antimonates

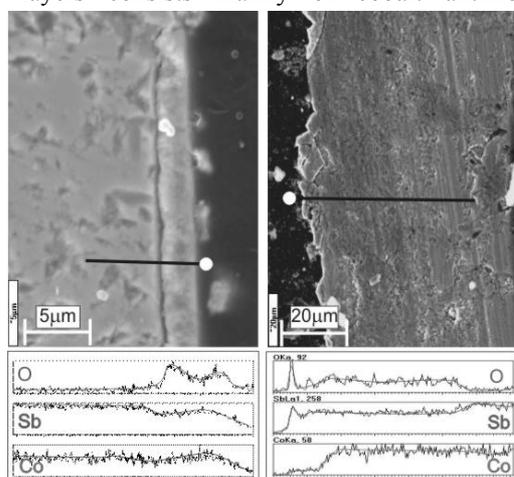


Fig. 3. Cross-section SEM image of oxidized CoSb<sub>3</sub>.

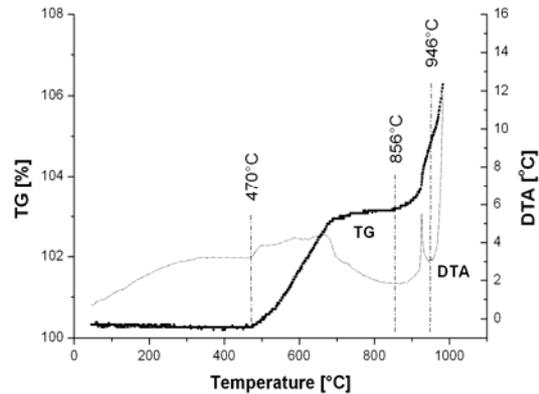


Fig. 2. TG and DTA curves for CoP<sub>3</sub> oxidation in air (5°C/min)

CoSb<sub>2</sub>O<sub>6</sub> and CoSb<sub>2</sub>O<sub>4</sub>.

Cobalt triphosphide TG and DTA oxidation curves are presented in Fig. 2. CoP<sub>3</sub> oxidation starts at about 470°C and involves two stages starting at about 860°C and 950°C. For temperatures below 800°C it wasn't possible to carry out complete oxidation of examined powders. Scanning electron microscope observations (Fig. 4) showed that very thin oxidation products layer is formed. For this reason it was also impossible to determine oxidation products from XRD measurements on this powders. In order to increase the extent of reaction several cycles of oxidation and grinding was applied to the CoP<sub>3</sub> powder. As a result XRD pattern of such treated powder revealed presence of reflexes which could be attributed both to cobalt metaphosphate Co<sub>2</sub>P<sub>4</sub>O<sub>12</sub> and cobalt polyphosphate Co(PO<sub>3</sub>)<sub>2</sub>. Performed wet chemical analysis of dissolved oxidation products pointed out Co:P ratio equal to 0.5-0.52 which is in agreement with the XRD but cannot distinguish meta- and polyphosphates. In order to distinguish potential CoP<sub>3</sub> oxidation products FTIR technique was applied. It was determined that absorption FTIR spectrum contains all characteristic bands for cobalt metaphosphate 1260-1315, 720, 740, 500 cm<sup>-1</sup>, and does not exhibit the presence of lines specific to chain polyphosphates. This indicates that probably the only solid state oxidation product of CoP<sub>3</sub> is the Co<sub>2</sub>P<sub>4</sub>O<sub>12</sub>. After that the scale thickness was estimated on the basis of weight gain, grain size and reaction product to be about 0.1 μm.

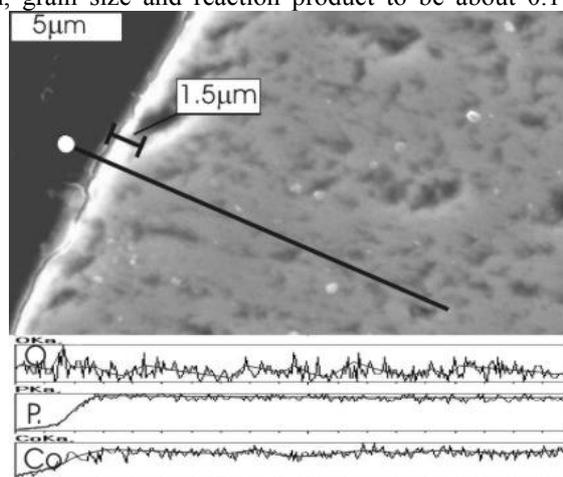


Fig. 4. Cross-section SEM image of oxidized CoP<sub>3</sub>.

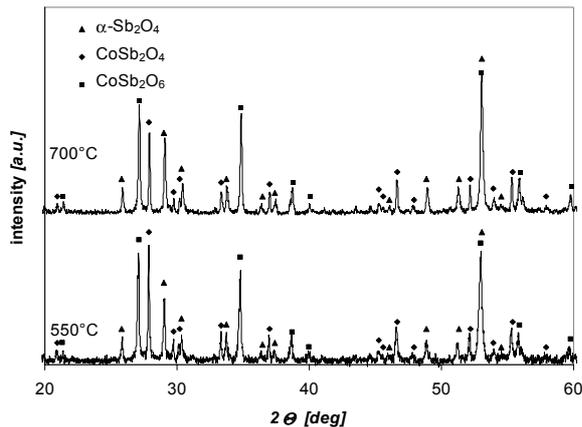
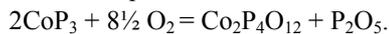


Fig. 5. XRD of completely oxidized  $\text{CoSb}_3$  powder for different temperatures.

Co:P ratio discovered in the oxidation products means that only 2/3 of P atoms from  $\text{CoP}_3$  form metaphosphate. This points out that the rest of P atoms during oxidation escapes in a volatile form. A special experiment was conducted in which hot gases flowing over oxidized  $\text{CoP}_3$  were cooled on quartz tube walls. Condensation of a liquid was observed and chemical analysis revealed it is orthophosphoric acid created from  $\text{P}_2\text{O}_5$  and water vapour. Therefore we can propose  $\text{CoP}_3$  oxidation equation:



#### Oxidation kinetic

Temperature range 410 – 550°C was chosen for  $\text{CoSb}_3$  kinetic oxidation studies. Typical isothermal oxidation curves are presented in Fig. 7. Oxidation involves two stages. In order to determine the most appropriate conversion function for stage I, weight gain was recalculated to degree of reaction  $\alpha$  assuming 0 for the beginning of the reaction and 1 for the weight gain corresponding to stage I end. Kinetic analysis fitting criterions were: correlation coefficient and standard deviation to oxidation reaction rate ratio. Several conversion functions for solid state reactions without initial stage were tested and the most appropriate function was found to be one dimensional diffusion equation

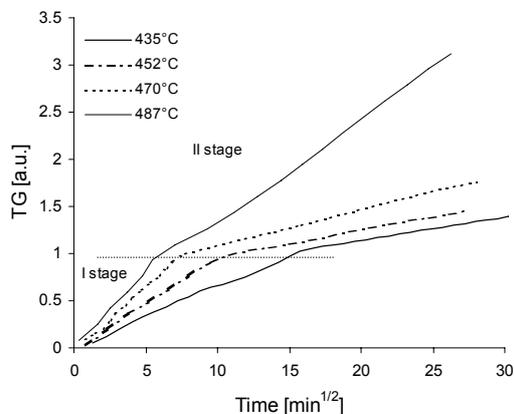


Fig. 7. TG curves for  $\text{CoSb}_3$  oxidation at different temperatures in a semi-square coordinate system.

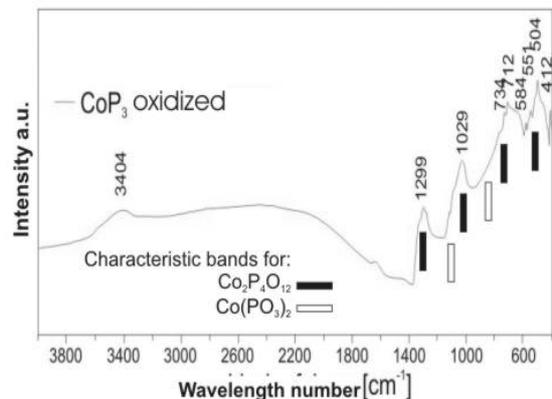


Fig. 6. FTIR spectrum for oxidized  $\text{CoP}_3$  powder (617°C, 24 hours)

described by the parabolic law  $\alpha = kt^2$ . Isothermal oxidation results presented in a linearized coordinate system for parabolic equation (Fig. 7) have revealed that for both stages this equation describes well oxidation kinetics. On the basis of oxidation kinetics data activation energy  $E_{act}$  and rate constant  $k_0$  were calculated for parabolic equation. For the stage I these values are  $E_{act, I} = 160 \pm 21$  kJ/mol,  $\ln k_I = 23.6$  and for the stage II:  $E_{act, II} = 106 \pm 9$  kJ/mol,  $\ln k_{II} = 11$ . Fulfilling of the one dimensional diffusion equation, if one keeps in mind composition and formation of the multilayer scale, suggests that diffusion of reactants through the growing products layer is the rate limiting step of both  $\text{CoSb}_3$  oxidation stages. Different kinetic parameters denote a change in the diffusion path controlling the reaction rate in stage I and II. Stage I can be assigned to the formation of mixed antimony oxide and cobalt antimonite layer, and the stage II can be assigned to the formation of three layer scale.

Temperature range 530 – 650°C was chosen for  $\text{CoP}_3$  kinetic oxidation studies. Oxidation of this compound involves one stage (Fig. 8). Kinetic analysis fitting criterions were same as for  $\text{CoSb}_3$ . The most appropriate kinetic equation was determined to be the area contraction equation:  $1 - (1 - \alpha)^{1/2} = kt$ . On the basis of oxidation kinetics data activation energy  $E_{act}$  and rate constant  $k_0$  were calculated

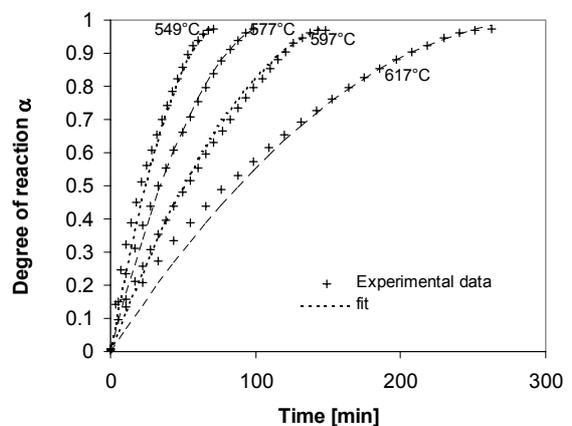


Fig. 8. Isothermal oxidation curves for  $\text{CoP}_3$ .

for area contraction model and they are:  $E_{act.}=117 \pm 13$  kJ/mol,  $\ln k=11.4$ . Experimental data and data estimated on

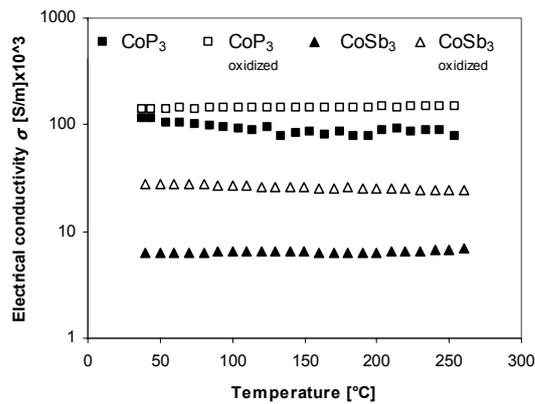


Fig. 9. Electrical conductivity of CoSb<sub>3</sub> and CoP<sub>3</sub> before and after oxidation in air. (617°C, 24 hours)

the basis of kinetic parameters and assumed model are shown in fig. 8.

An experiment on oxidation kinetics of polycrystalline samples of CoSb<sub>3</sub> and CoP<sub>3</sub> were carried out at 610C in air for 1 day. It demonstrated that CoP<sub>3</sub> is more resistant and its oxidation stops after surface passivation. In case of CoSb<sub>3</sub> weight gain was observed during all the time of experiment. Estimated rate constants for the reaction in this conditions are for CoP<sub>3</sub>  $k=2 \times 10^{-8}$  mm/s and for CoSb<sub>3</sub>  $k=2 \times 10^{-7}$  mm/s.

#### Electric measurements

Electrical conductivity and Seebeck coefficient of the polycrystalline samples used for oxidation kinetic measurements were examined before and after oxidation (air, 610C, 1day). Results of these measurements are shown in fig. X and y. Electrical conductivity of CoSb<sub>3</sub> after oxidation is increased by a factor of 3.6 to 4.5 in wide range of temperatures. Less influence is observed for CoP<sub>3</sub> which increases its electrical conductivity by a factor of 2.5- 2.9. Seebeck coefficient of initial CoSb<sub>3</sub> equal is about -450μV/K at room temperature and its absolute value is decreased by a factor of 1.5-1.9. In case of CoP<sub>3</sub> oxidation didn't change the thermopower noticeably. These results for CoSb<sub>3</sub> and CoP<sub>3</sub> means that oxidation leads to increase of charge carrier concentration, electrons for cobalt antimonide and holes for cobalt phosphide. In both cases the power factor increased after oxidation. It may look that oxidation gives a positive effect on thermoelectric properties but we should keep in mind that for optimised material any change of electronic properties is undesirable.

#### Conclusions

We have compared oxidation behaviour of cobalt triantimonide and cobalt triphosphide in air in the temperature range of 20-850°C. From TG/DTA data starting temperature of oxidation was determined to be 380°C for CoSb<sub>3</sub> and 470°C for CoP<sub>3</sub>. Further differences were found in the reaction products and kinetic. CoSb<sub>3</sub> oxidation leads to formation of three main oxide phases: Sb<sub>2</sub>O<sub>4</sub> on the

surface and cobalt antimonates, forming inner layer. It is a two stage reaction. During the initial stage single layer of

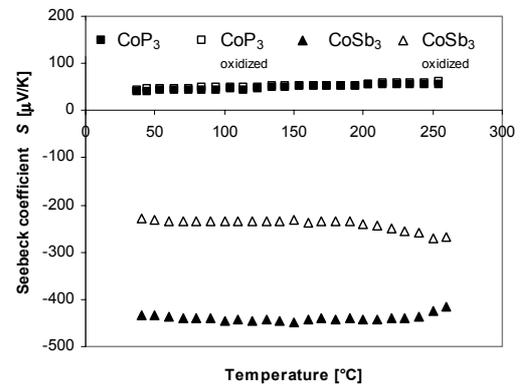


Fig. 10. Seebeck coefficient of CoSb<sub>3</sub> and CoP<sub>3</sub> before and after oxidation in air. (617°C, 24 hours)

mixed Sb<sub>2</sub>O<sub>4</sub>, CoSb<sub>2</sub>O<sub>6</sub> and CoSb<sub>2</sub>O<sub>4</sub> is formed. In II stage oxide layer splits up into outer Sb<sub>2</sub>O<sub>4</sub> layer and inner CoSb<sub>2</sub>O<sub>6</sub>/CoSb<sub>2</sub>O<sub>4</sub> layer. Kinetics of both stages is determined by reactant diffusion through the growing products layer described by the parabolic law.

CoP<sub>3</sub> oxidation leads to formation of volatile P<sub>2</sub>O<sub>5</sub> and a thin passivating cobalt metaphosphate Co<sub>2</sub>P<sub>4</sub>O<sub>12</sub> layer stopping further oxidation. Thickness of this layer was estimated to be about 0.1μm. Reaction rate constant  $k$  for CoP<sub>3</sub> in 610°C is  $k=2 \times 10^{-8}$  mm/s and it is 10x smaller than rate constant for CoSb<sub>3</sub>  $k=2 \times 10^{-7}$  mm/s

Heating in air changes significantly electrical properties of examined compounds. Especially in the case of CoSb<sub>3</sub>, where electrical conductivity  $\sigma$  increases 5 times and the absolute value of Seebeck coefficient  $S$  decreases twice.

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