

# Approximation of temperature characteristics of Seebeck coefficients for CuNi-Ag and Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>-Ag thermopiles

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## Summary:

Determining the approximation for CuNi-Ag and Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>-Ag thermopiles based on real measurements to allow prediction of Seebeck coefficient values against temperature.

**Keywords:** energy harvesting, thermoelectricity, thick film, thermocouple, thermoelectric microgenerator

## Motivation and description of work

Thermoelectric microgenerators are one of the promising directions in the field of energy harvesting from a temperature gradient. Their operation is based on the thermoelectric phenomenon, in which the electric power is generated as a result of the temperature difference between two junctions of different materials. Such devices, due to their small scale, can be used in a wide range of applications, from powering sensors in Internet of Things (IoT) devices to industrial and medical applications, where small size and ability to operate in extreme temperature conditions are important. A key parameter characterizing thermoelectric materials is the Seebeck coefficient, which describes a material's ability to generate thermoelectric force under a temperature gradient. Optimization of this coefficient for thermoelectric microgenerators makes it possible to increase their efficiency and performance.

structures, voltage and resistance were measured as a function of temperature, from -40°C to about 160°C, cooling or heating the junction area of the structure. On this basis, the low-gradient (differential) Seebeck coefficient was determined as a function of temperature was calculated. The selected structures were aged by placing them sequentially at 150°C, 250°C and 350°C for 100 hours. After each aging step, the above-mentioned measurements were repeated.

## Results

Due to the fact that the value of the Seebeck coefficient depends on the temperature, it was decided to approximate its characteristic with a third-degree polynomial and compare experimental values with least squares approximations. The approximating function took the form presented in Eq. (1).

$$S(T) = a_3 \cdot (T - 273.15)^3 + a_2 \cdot (T - 273.15)^2 + a_1 \cdot (T - 273.15) + a_0 \quad (1)$$

Table 1. Approximation parameters for as-fired and thermally aged CuNi-Ag and Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>-Ag thermopiles.

Parameter	T-type thermocouple	CuNi-Ag on LTCC				Ca <sub>3</sub> Co <sub>4</sub> O <sub>9</sub> -Ag on alumina			
		As-fired	150°C (423 K)	250°C (523 K)	350°C (623 K)	As-fired	150°C (423 K)	250°C (523 K)	350°C (623 K)
$a_3$ [ $\mu\text{V}/\text{K}^4$ ]	-5.95E-08	-7.82E-07	-1.09E-06	7.18E-07	-1.24E-06	-1.31E-05	-3.66E-06	-6.94E-06	-4.54E-06
$a_2$ [ $\mu\text{V}/\text{K}^3$ ]	-6.65E-05	3.45E-04	3.30E-04	8.55E-05	4.67E-04	2.47E-03	1.51E-03	1.67E-03	1.18E-03
$a_1$ [ $\mu\text{V}/\text{K}^2$ ]	8.93E-02	-5.79E-03	1.33E-02	1.16E-02	-4.64E-03	-1.02E-01	-1.31E-01	-1.27E-01	-8.88E-02
$a_0$ [ $\mu\text{V}/\text{K}$ ]	3.82E+01	4.08E+01	3.93E+01	4.15E+01	4.02E+01	1.10E+02	1.12E+02	1.12E+02	1.11E+02

As part of the research, the Seebeck coefficient was modeled as a function of operating temperature, based on actual measurements. The structures that were modeled were fabricated in the form of thermopiles from pairs of CuNi-Ag materials on an LTCC substrate and Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>-Ag on an alumina substrate [1]. For these

Based on the determined approximations, the accuracy of the approximations was determined using Eq. (2), (3) and (4).

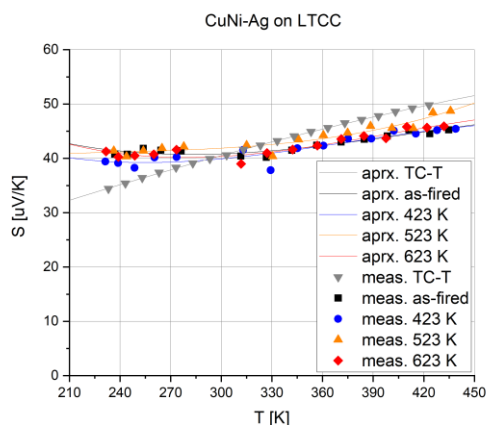
$$R^2 = 1 - \frac{\sum_{i=1}^n (S_i - \hat{S}_i)^2}{\sum_{i=1}^n (S_i - \bar{S})^2} \quad (2)$$

$$MSE = \frac{1}{n} \sum_{i=1}^n (S_i - \hat{S}_i)^2 \quad (3)$$

$$RMSE = \sqrt{MSE} \quad (4)$$

where:  $S_i$  – measured value,  $\hat{S}_i$  – value predicted by the model;  $\bar{S}$  – average value and  $n$  – number of measurements.

a)



b)

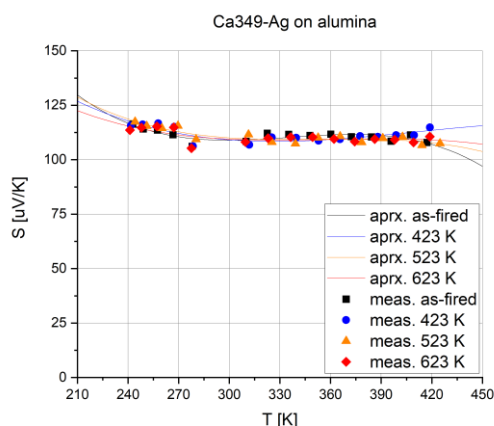


Fig. 1. Approximations with distribution of real values for (a) CuNi-Ag on LTCC; (b) Ca349-Ag on alumina

Table 2. Quality of approximation for as-fired and thermally aged CuNi-Ag and Ca349-Ag thermopiles.

Parameter	T-type thermocouple	CuNi-Ag on LTCC				Ca349-Ag on alumina			
		As-fired	150°C (423 K)	250°C (523 K)	350°C (623 K)	As-fired	150°C (423 K)	250°C (523 K)	350°C (623 K)
$\bar{S}$ [μV/K]	42.62	42.44	41.89	43.78	42.47	111.03	111.60	110.83	110.50
$R^2$ [-]	0.999	0.997	0.991	0.995	0.996	0.997	0.995	0.997	0.995
MSE [(μV/K) <sup>2</sup> ]	0.006	0.338	1.005	0.656	0.454	2.355	3.605	2.104	3.958
RMSE [μV/K]	0.078	0.581	1.003	0.810	0.674	1.535	1.899	1.451	1.989

The approximations obtained from the measurements are acceptable, although they show weaker fit than the reference values for the T-type thermocouple (standardized Cu-CuNi wire thermocouple). Determination coefficients  $R^2$  of about 0.99 show the good quality of the models' fit and confirm their ability to predict actual values. The RMSE index indicates how much, on average, the values predicted by the model can differ from the actual values. The higher RMSE values for the Ca349-Ag system are due to the wider range of data, where the average Seebeck coefficient is about 110.99 μV/K, while for CuNi-Ag it is about 42.64 μV/K (based on all measurement series). The results obtained for CuNi-Ag, can be related to the standard T-type thermocouple. The approximation determined in the same way has an  $R^2$  of 0.999 and an RMSE of 0.078 μV/K. The average Seebeck coefficient for the T-type thermocouple in the analyzed temperature range is equal to 42.62 μV/K.

The results show that the Seebeck coefficient approximation is a reasonable solution, but it should be taken into account that the third-degree polynomial is not always able to perfectly predict the results. Increasing the degree of the polynomial in the equation could allow a more accurate match between predicted and actual results. However, it can be concluded that in many applications the third-degree approximation works well for simple calculations.

## References

- [1] A. Dziejczak, S. Wójcik, M. Gierczak, S. Bernik, N. Brguljan, K. Reinhardt, S. Körner; Planar Thermoelectric Microgenerators in Application to Power RFID Tags, Sensors 2024, 24, 1646; doi: 10.3390/s24051646