Instructions – DC/AC

The files come in three different extensions, compatible with notepad: .RES, .SEB and .SER. The file .RES contains data for resistivity measurements, both AC and DC. The .SEB files contain all measurement points for Seebeck coefficient. The .SER files contain calculated values of Seebeck coefficients.

The typical format of the .RES file looks as follows:

```
HEOX CoCrFeMnNi 32 Cub02
27.10.2018 12:43:28
 3.88   1.43    8.30    'Sample Dimensions A x B x Length [mm]
   98    'Number of data
Point  Time [s]   Temp1[°C]  Temp2[°C]  Voltage[+V]   Current[+A]   Voltage[-V]   Current[-A]  Resistance[ohm]  Resistivity[ohm x m]
    1        10      23.639     23.561   1.76838E-01   2.60897E-05  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~   6.77809E+03     4.53103094E+00
    1        17      23.639     23.564   3.53734E-01   3.13822E-05  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~   1.12717E+04     7.53498684E+00
    1        24      23.636     23.573   5.30544E-01   3.31256E-05  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~   1.60161E+04     1.07064966E+01
    1        30      23.638     23.560   7.07710E-01   3.28047E-05  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~   2.15734E+04     1.44214414E+01
    1        37      23.641     23.567   1.06138E+00   3.41099E-05  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~   3.11164E+04     2.08007620E+01
    1        47      23.610     23.548   5.00928E-01   1.48843E-06  -4.98762E-01  -1.43735E-06   3.41682E+05     2.28408521E+02
    1        55      23.618     23.540   7.50926E-01   2.19291E-06  -7.48552E-01  -2.19149E-06   3.42003E+05     2.28622641E+02
    1        64      23.609     23.541   1.00067E+00   2.96739E-06  -9.98357E-01  -2.94914E-06   3.37871E+05     2.25860954E+02
    1        72      23.602     23.530   2.00021E+00   5.84077E-06  -1.99795E+00  -5.86077E-06   3.41678E+05     2.28405557E+02
    1        81      23.598     23.538   2.99940E+00   8.82873E-06  -2.99718E+00  -8.77577E-06   3.40628E+05     2.27703330E+02
    2      2418      41.016     40.015   1.76828E-01   2.90994E-05  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~   6.07667E+03     4.06214488E+00
    2      2425      41.020     40.030   3.53704E-01   2.73470E-05  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~   1.29339E+04     8.64608288E+00
    2      2433      41.016     40.020   5.30496E-01   3.03198E-05  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~   1.74967E+04     1.16962148E+01
    2      2441      41.024     40.032   7.07632E-01   2.95298E-05  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~   2.39633E+04     1.60190514E+01
    2      2449      41.012     40.023   1.06126E+00   2.78561E-05  ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~   3.80980E+04     2.54678360E+01
    2      2460      41.015     40.031   5.00721E-01   2.73246E-06  -4.98652E-01  -2.70269E-06   1.83872E+05     1.22915373E+02
    2      2470      41.017     40.024   7.50691E-01   4.08501E-06  -7.48383E-01  -4.02823E-06   1.84769E+05     1.23514581E+02
    2      2482      41.008     40.028   1.00039E+00   5.37246E-06  -9.98134E-01  -5.36715E-06   1.86089E+05     1.24396993E+02
    2      2491      41.010     40.042   1.99967E+00   1.07260E-05  -1.99749E+00  -1.07949E-05   1.85733E+05     1.24159365E+02
    2      2501      41.003     40.033   2.99863E+00   1.61598E-05  -2.99646E+00  -1.61688E-05   1.85442E+05     1.23964922E+02
```

Fig. 1. An exemplary .RES file.

Sample's dimensions
1st column - temperature point, since we use 5 different voltages for both AC and DC, the total number of rows is 10 - 1-5 are AC, 6-10 - DC
2nd column - time of the measurement
3rd column - temperature on the electrode with heater
4th column - temperature of the reference electrode
5th column - voltage
6th column - current
7th column - voltage for the second run with opposite polarization (only DC)
8th column - current for the second run with opposite polarization (only DC)
9th column - resistance (total)
10th column - resistivity (normalized with respect to the sample's size)

The .RES files are necessary to calculate the conductivity of our samples, and to plot the Arrhenius relation. The conductivity can be calculated as:

$$\sigma = \frac{l}{AR} \tag{1.1}$$

Since in our case, we already have the value normalized with respect to the sample's dimensions, we can use the values of resistivity from 10th column directly:

$$\sigma = \frac{1}{\rho} \tag{1.2}$$

Then, we have to use the Arrhenius equation:

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \tag{1.3}$$

Taking the natural logarithm:

$$\ln \sigma T = \ln \sigma_0 - \frac{E_a}{RT} \tag{1.4}$$

Now, what we have to do, is to plot this relation in a lnσT(1/T) coordinates. Then, we will see that the relation has a linear character, which may change with the temperature. Usually, we observe 2 or 3 separate stages, characterized by different slopes. For each stage, we should perform a linear regression, obtaining in the process the value of energy of activation, characteristic for a given stage.

In each .RES file a whole history of the measurement is saved. That means that the data can be from two different runs: from room temperature to 1000 °C, and back from 1000 °C to room temperature.

The typical format for the .SEB file looks as follows:

```
HEOX CoCrFeMnNi 32 Cub01
24.10.2018 11:02:10
  980     'Number of data
Point  Time[s]    Temp1[°C]   Temp2[°C]  DeltaT[°C] Voltage[µV]  Grad.No
    1       339       20.29       20.29        0.01      92.469        1
    2       347       21.19       20.30        0.89     -36.698        1
    3       356       21.80       20.34        1.46    -175.164        1
    4       366       22.56       20.39        2.17    -157.582        1
    5       375       23.00       20.42        2.58    -253.893        1
    6       383       23.56       20.45        3.11    -235.714        1
    7       391       24.17       20.49        3.68    -468.111        1
    8       400       24.51       20.54        3.97    -346.661        1
    9       410       25.17       20.59        4.58    -433.935        1
   10       419       25.44       20.66        4.78    -507.536        1
   11      3521       40.69       39.76        0.93    -168.489        2
   12      3530       41.42       39.80        1.63    -207.078        2
```

Fig. 2. An exemplary .SEB file.

1st column - measurement point (for each temperature point, 10 measurements are performed)
2nd column - time of the measurement
3rd column - temperature on the electrode with heater
4th column - temperature of the reference electrode
5th column - the difference between these temperatures ΔT
6th column - measured potential ΔV
7th column - number of temperature point

The Seebeck coefficient S is defined as:

$$S = -\frac{\Delta V}{\Delta T} \tag{1.5}$$

To calculate its value for a given temperature point, we have to plot the ΔV in a function of ΔT and calculate the slope of the resulting function:

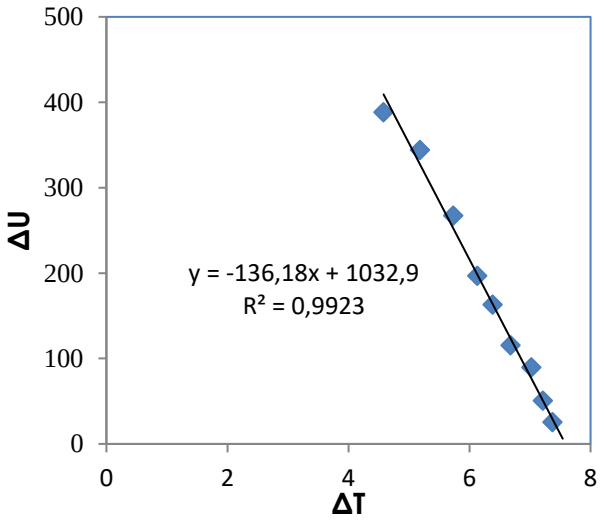


Fig. 3. An exemplary determination of Seebeck coefficient.

Similarly as previously, in each .SEB file a whole history of the measurement is saved. That means that the data is in fact for two different runs: from room temperature to 1000 °C, and back from 1000 °C to room temperature.

The results from procedure shown in the Fig. 3 are compiled for all temperature points in .SER file:

Typical format for the .SER file looks as follows:

```
HEOX CoCrFeMnNi 32 Cub01
24.10.2018 11:02:10
   98     'Number of data
Point  Temp1[K]   Seebeck Coef.[µV/K]  Linear Correlation
    1     20.29  -1.15788982647E+0002      -0.9604344083
    2     39.76  -1.19591305869E+0002      -0.9960943037
    3     58.50  -1.27278201104E+0002      -0.9986102194
    4     77.43  -1.23725613288E+0002      -0.9939513105
    5     96.75  -1.18953400778E+0002      -0.9977514413
    6    116.78  -1.57122387225E+0002      -0.7787262770
    7    136.48  -1.11472774304E+0002      -0.9956008150
    8    155.98  -1.13486457611E+0002      -0.9950321658
    9    176.40  -1.13519667196E+0002      -0.9945490583
   10    196.98  -1.14162716573E+0002      -0.9951667482
   11    217.56  -1.12525713046E+0002      -0.9969780447
```

Fig. 4. Exemplary .SER file.

1st column - temperature point
2nd column - temperature
3rd column - value of Seebeck coefficient
4th column - value of the R^2 correlation factor

A typical way of determining the potential of a given material in the thermoelectric application, is to calculate its figure of merit *ZT*:

$$ZT = \frac{\sigma S^2 T}{\kappa} \tag{1.6}$$

where: σ - electrical conductivity, S - Seebeck coefficient, T - temperature, and κ - thermal conductivity (remember about the common units!).

Except for the last property, all other can be extracted from the .RES and .SEB file. The κ can be calculated for the spinel samples 32 and 36, using the following equation:

$$\kappa\left[Wm^{-1}K^{-1}\right] = 443174T^{-1.8692} + 7.3970 \tag{1.7}$$

What is to be done:

- calculate conductivity and plot the Arrhenius relation for 4 different measurements runs (remember, we have 2 per file)

- calculate the energies of activation for each plot and for each distinct stage (if two or more different slopes are present)

- plot the temperature dependence of Seebeck coefficient for each of the measurements (remember, that the .RES files and .SER files of the same name refer to exactly the same measurement)

- using the values of σ, S, and T, as well as relations (1.6) and (1.7), calculate the ZT for samples 32 and 36.

In the report there should be:

- 4 figures with Arrhenius plots

- 4 tables with the values of energies of activation for each measurement

- 4 tables and 4 figures with $ZT(T)$ for each of the measurements - only samples 32 and 36.

- a few words of comment, maybe comparison with some literature values - "*impress me*"

32 - $(Co,Cr,Fe,Mn,Ni)_3O_4$

36 - $(Co,Cr,Fe,Mn,Mg)_3O_4$

Instructions – EIS

In the excel file "117" there are 4 sheets, each with 3 columns: frequency (f), resistivity (Z') and reactance (Z"). The results were measured at four consecutive temperature points (150, 200, 250 and 300°C, as indicated in the sheets' names) for the $(Ce,Gd,Nd,Pr,Sm)O_{2-\delta}$ material. In the next file "EIS", a solver with an implemented solution for the following equivalent circuit is prepared:

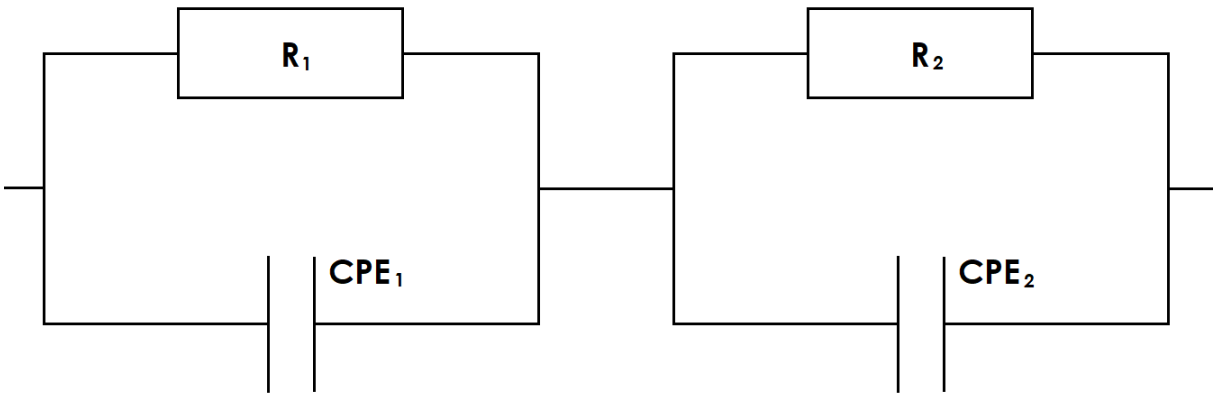


Fig. 4. Equivalent circuit for the $(Ce,Gd,Nd,Pr,Sm)O_{2-\delta}$.

As can be seen, we can distinguish two R-CPE circuits. The first of them describes the properties of the bulk, while the second of the grain boundaries in the material. The CPE abbreviation stands for the constant phase element, which describes non-ideal behavior of the capacitor:

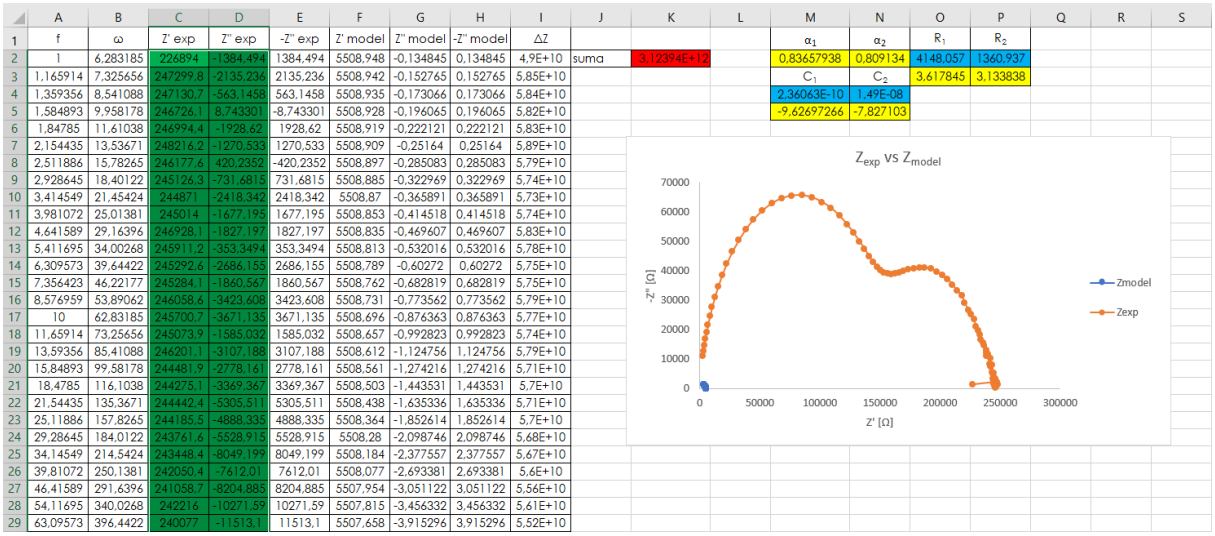
$$Z_{CPE} = \frac{1}{C(j\omega)^{\alpha}} \tag{1.8}$$

Where C – non-ideal capacity, α – constant. For the values of α equal to 1, our CPE behaves like an ideal capacitor, for the values equal to 0 – like a resistor.

In order to find the values of resistivity and capacity characteristic for the bulk and grain boundary conductivity, we have to run an optimization of our experimental results. To perform this operation,

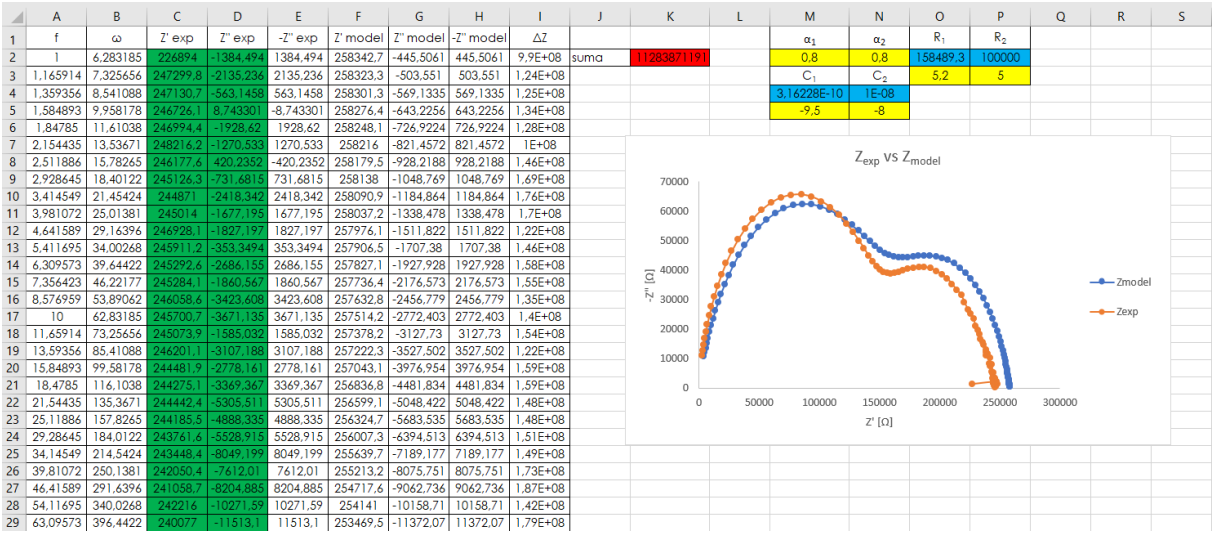
we have to copy the Z' and Z'' values from the "117" to columns C and D in "EIS" file (highlighted in green). Then, we can start the comparison of the theoretical values with the experimental ones. In columns M to P, are the starting parameters for our optimization (highlighted in yellow). All values, except for α, are given as exponents, based on which are calculated the final values (blue).

So, first, we copy the values from "117" to green columns:



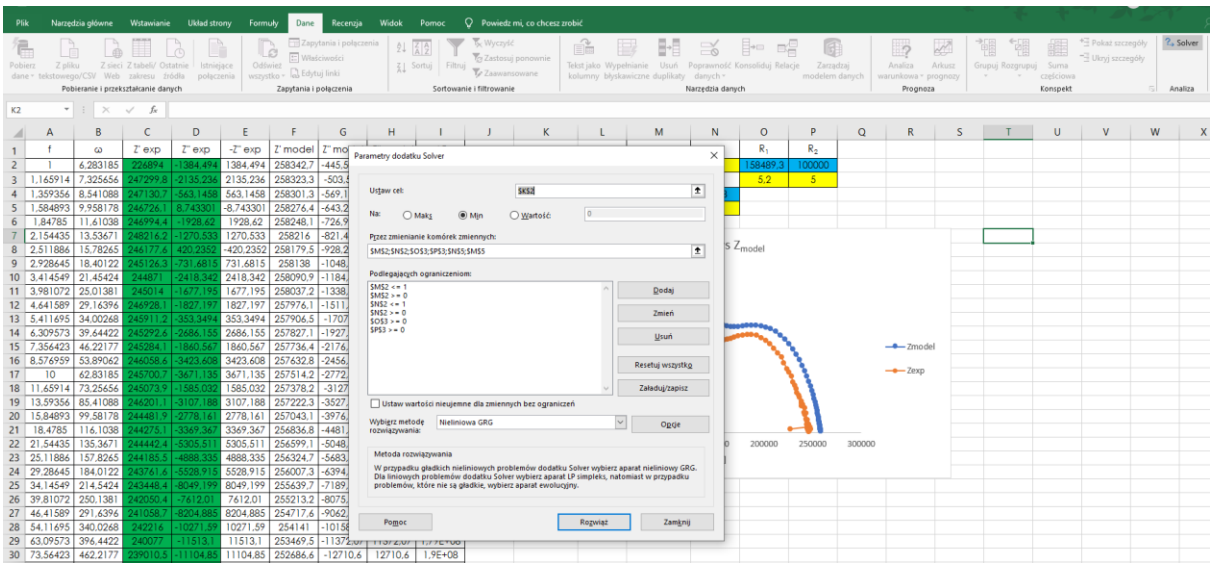
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
1	f	ω	Z' exp	Z'' exp	-Z'' exp	Z' model	Z'' model	-Z'' model	ΔZ				α_1	α_2	R_1	R_2			
2	1	6,283185	226894	-1384,494	1384,494	5508,948	-0,134845	0,134845	4,9E+10	suma	3,12394E+12		0,83657938	0,809134	4148,057	1360,937			
3	1,165914	7,325656	247299,8	-2135,236	2135,236	5508,942	-0,152765	0,152765	5,85E+10				C_1	C_2	3,617845	3,133838			
4	1,359356	8,541088	247130,7	-563,1458	563,1458	5508,935	-0,173066	0,173066	5,84E+10				2,36063E-10	1,49E-08					
5	1,584893	9,958178	246726,1	8,743301	-8,743301	5508,928	-0,196065	0,196065	5,82E+10				-9,62697266	-7,827103					
6	1,84785	11,61038	246994,4	-1928,62	1928,62	5508,919	-0,222121	0,222121	5,83E+10										
7	2,154435	13,53671	248216,2	-1270,533	1270,533	5508,909	-0,25164	0,25164	5,89E+10										
8	2,511886	15,78265	246177,6	420,2352	-420,2352	5508,897	-0,285083	0,285083	5,79E+10										
9	2,928645	18,40122	245126,3	-731,6815	731,6815	5508,885	-0,322969	0,322969	5,74E+10										
10	3,414549	21,45424	244871	-2418,342	2418,342	5508,87	-0,365891	0,365891	5,73E+10										
11	3,981072	25,01381	245014	-1677,195	1677,195	5508,853	-0,414518	0,414518	5,74E+10										
12	4,641589	29,16396	246928,1	-1827,197	1827,197	5508,835	-0,469607	0,469607	5,83E+10										
13	5,411695	34,00268	245911,2	-353,3494	353,3494	5508,813	-0,532016	0,532016	5,78E+10										
14	6,309573	39,64422	245292,6	-2686,155	2686,155	5508,789	-0,60272	0,60272	5,75E+10										
15	7,356423	46,22177	245284,1	-1860,567	1860,567	5508,762	-0,682819	0,682819	5,75E+10										
16	8,576959	53,89062	246058,6	-3423,608	3423,608	5508,731	-0,773562	0,773562	5,79E+10										
17	10	62,83185	245700,7	-3671,135	3671,135	5508,696	-0,876363	0,876363	5,77E+10										
18	11,65914	73,25656	245073,9	-1585,032	1585,032	5508,657	-0,992823	0,992823	5,74E+10										
19	13,59356	85,41088	246201,1	-3107,188	3107,188	5508,612	-1,124756	1,124756	5,79E+10										
20	15,84893	99,58178	244481,9	-2778,161	2778,161	5508,561	-1,274216	1,274216	5,71E+10										
21	18,4785	116,1038	244275,1	-3369,367	3369,367	5508,503	-1,443531	1,443531	5,7E+10										
22	21,54435	135,3671	244442,4	-5305,511	5305,511	5508,438	-1,635336	1,635336	5,71E+10										
23	25,11886	157,8265	244185,5	-4888,335	4888,335	5508,364	-1,852614	1,852614	5,7E+10										
24	29,28645	184,0122	243761,6	-5528,915	5528,915	5508,28	-2,098746	2,098746	5,68E+10										
25	34,14549	214,5424	243448,4	-8049,199	8049,199	5508,184	-2,377557	2,377557	5,67E+10										
26	39,81072	250,1381	242050,4	-7612,01	7612,01	5508,077	-2,693381	2,693381	5,6E+10										
27	46,41589	291,6396	241058,7	-8204,885	8204,885	5507,954	-3,051122	3,051122	5,56E+10										
28	54,11695	340,0268	242216	-10271,59	10271,59	5507,815	-3,456332	3,456332	5,61E+10										
29	63,09573	396,4422	240077	-11513,1	11513,1	5507,658	-3,915296	3,915296	5,52E+10										

Then, we try to set the values in yellow cells, to get our "Zmodel" plot to similar ranges as the experimental "Zexp" (just similar, not identical):

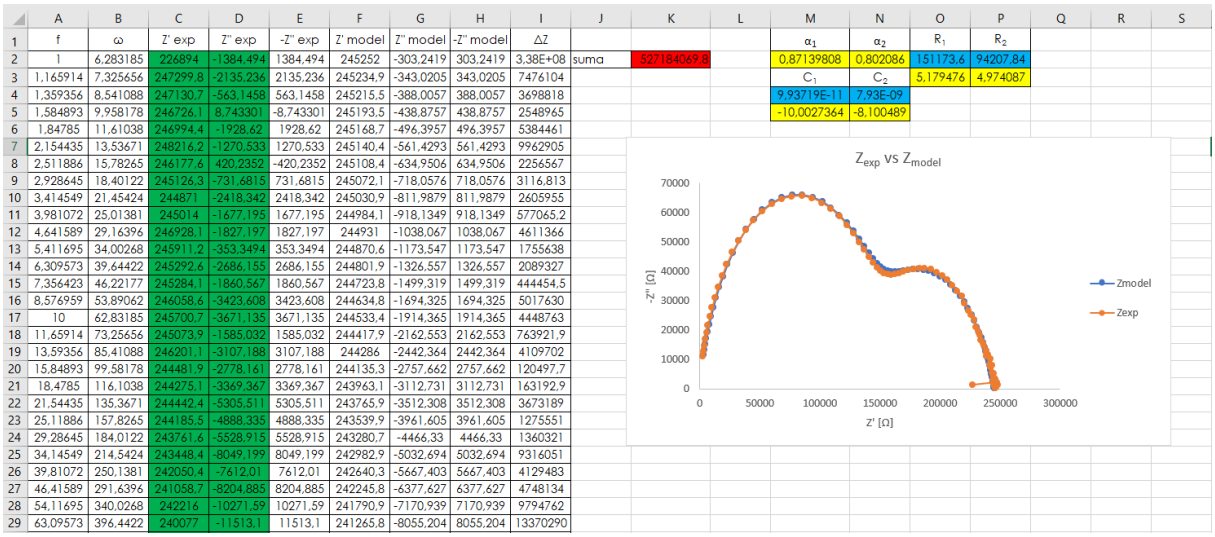


	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
1	f	ω	Z' exp	Z'' exp	-Z'' exp	Z' model	Z'' model	-Z'' model	ΔZ				α_1	α_2	R_1	R_2			
2	1	6,283185	226894	-1384,494	1384,494	258342,7	-445,5061	445,5061	9,9E+08	suma	11283871191		0,8	0,8	158489,3	100000			
3	1,165914	7,325656	247299,8	-2135,236	2135,236	258323,3	-503,551	503,551	1,24E+08				C_1	C_2	5,2	5			
4	1,359356	8,541088	247130,7	-563,1458	563,1458	258301,3	-569,1335	569,1335	1,25E+08				3,16228E-10	1E-08					
5	1,584893	9,958178	246726,1	8,743301	-8,743301	258276,4	-643,2256	643,2256	1,34E+08				-9,5	-8					
6	1,84785	11,61038	246994,4	-1928,62	1928,62	258248,1	-726,9224	726,9224	1,28E+08										
7	2,154435	13,53671	248216,2	-1270,533	1270,533	258216	-821,4572	821,4572	1E+08										
8	2,511886	15,78265	246177,6	420,2352	-420,2352	258179,5	-928,2188	928,2188	1,46E+08										
9	2,928645	18,40122	245126,3	-731,6815	731,6815	258138	-1048,769	1048,769	1,69E+08										
10	3,414549	21,45424	244871	-2418,342	2418,342	258090,9	-1184,864	1184,864	1,76E+08										
11	3,981072	25,01381	245014	-1677,195	1677,195	258037,2	-1338,478	1338,478	1,7E+08										
12	4,641589	29,16396	246928,1	-1827,197	1827,197	257976,1	-1511,822	1511,822	1,22E+08										
13	5,411695	34,00268	245911,2	-353,3494	353,3494	257906,5	-1707,38	1707,38	1,46E+08										
14	6,309573	39,64422	245292,6	-2686,155	2686,155	257827,1	-1927,928	1927,928	1,58E+08										
15	7,356423	46,22177	245284,1	-1860,567	1860,567	257736,4	-2176,573	2176,573	1,55E+08										
16	8,576959	53,89062	246058,6	-3423,608	3423,608	257632,8	-2456,779	2456,779	1,35E+08										
17	10	62,83185	245700,7	-3671,135	3671,135	257514,2	-2772,403	2772,403	1,4E+08										
18	11,65914	73,25656	245073,9	-1585,032	1585,032	257378,2	-3127,73	3127,73	1,54E+08										
19	13,59356	85,41088	246201,1	-3107,188	3107,188	257222,3	-3527,502	3527,502	1,22E+08										
20	15,84893	99,58178	244481,9	-2778,161	2778,161	257043,1	-3976,954	3976,954	1,59E+08										
21	18,4785	116,1038	244275,1	-3369,367	3369,367	256836,8	-4481,834	4481,834	1,59E+08										
22	21,54435	135,3671	244442,4	-5305,511	5305,511	256599,1	-5048,422	5048,422	1,48E+08										
23	25,11886	157,8265	244185,5	-4888,335	4888,335	256324,7	-5683,535	5683,535	1,48E+08										
24	29,28645	184,0122	243761,6	-5528,915	5528,915	256007,3	-6394,513	6394,513	1,51E+08										
25	34,14549	214,5424	243448,4	-8049,199	8049,199	255639,7	-7189,177	7189,177	1,49E+08										
26	39,81072	250,1381	242050,4	-7612,01	7612,01	255213,2	-8075,751	8075,751	1,73E+08										
27	46,41589	291,6396	241058,7	-8204,885	8204,885	254717,6	-9062,736	9062,736	1,87E+08										
28	54,11695	340,0268	242216	-10271,59	10271,59	254141	-10158,71	10158,71	1,42E+08										
29	63,09573	396,4422	240077	-11513,1	11513,1	253469,5	-11372,07	11372,07	1,79E+08										

Then, we use the "solver" plug-in ("dane" menu in excel):



All the setups are visible in the above figures. Our optimization is based on the least squares element method, implemented in the column I and summarized in our target function in cell K2 (red). After solving the task, we should get the optimized plots and final values (blue):



The value in cell O3 represents the resistivity of the bulk, while the value in cell P3 describes the resistivity of the grain boundaries. Using the eq. (1.1), we can then calculate the conductivity for both cases, and plot the Arrhenius plots according to eqs. (1.3) and (1.4). The dimensions for the sample are as follows:

- l = 0.97 mm
- A = 52.17 mm^2

What is to be done:

- Perform the optimization for all 4 temperatures, save the optimized files for each of them and attach them to the report.
- Gather all plots and optimized values and put them into the report.
- Recalculate the obtained resistivity values into conductivity and create Arrhenius plots, one for the bulk and one for the grain boundaries.
- Calculate the energies of activation for both mentioned processes.