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Dilatometric study of the $ZnTiO_3$ phase transition kinetic influenced by nano powder sintering

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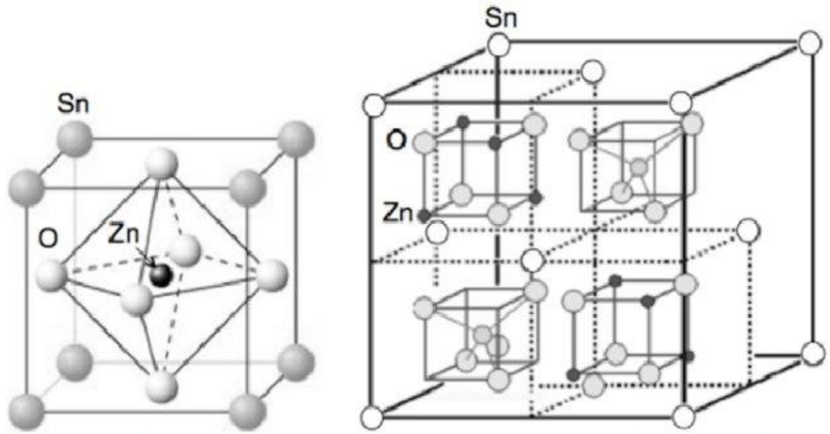
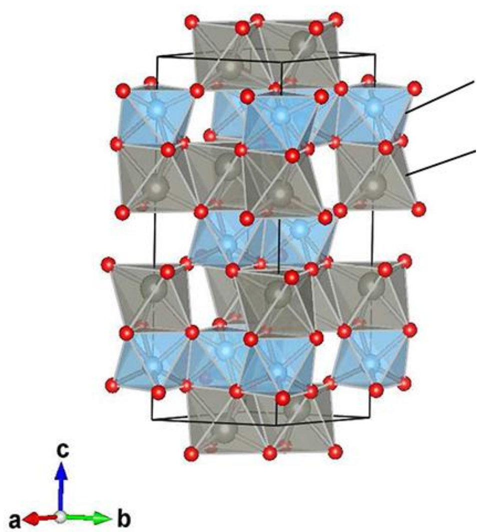
Phase transition $ZnTiO_3$ to Zn_2TiO_4

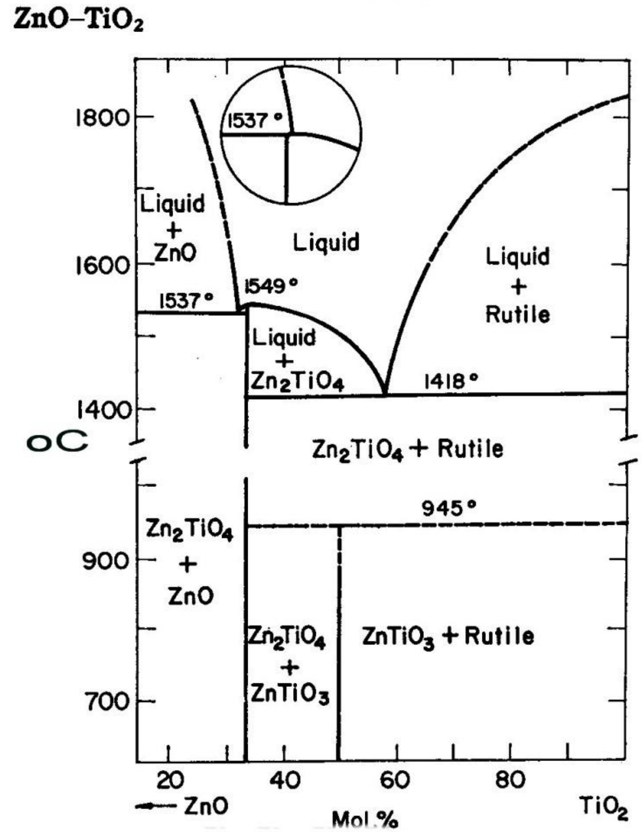


Perovskite ($ZnSnO_3$) Cubic spinel (Zn_2SnO_4)

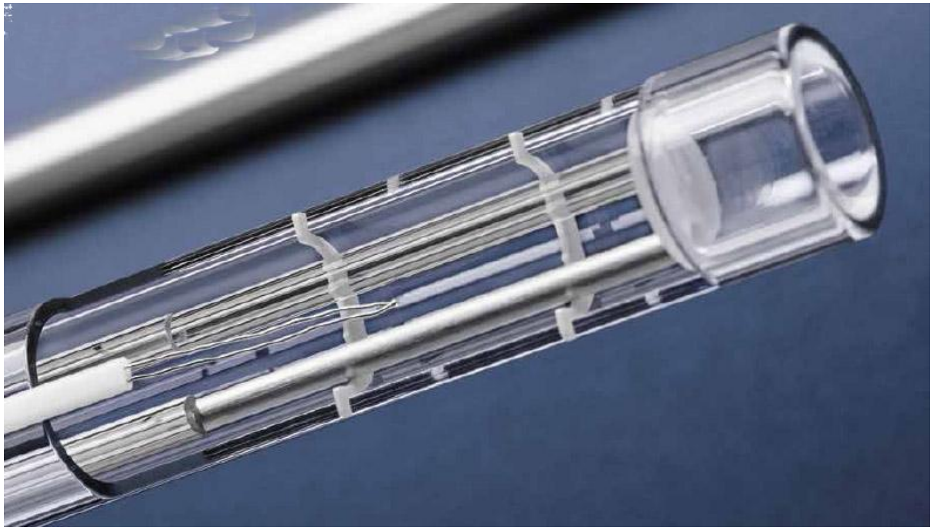
$$t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}}$$



(a) Ilmenite-type

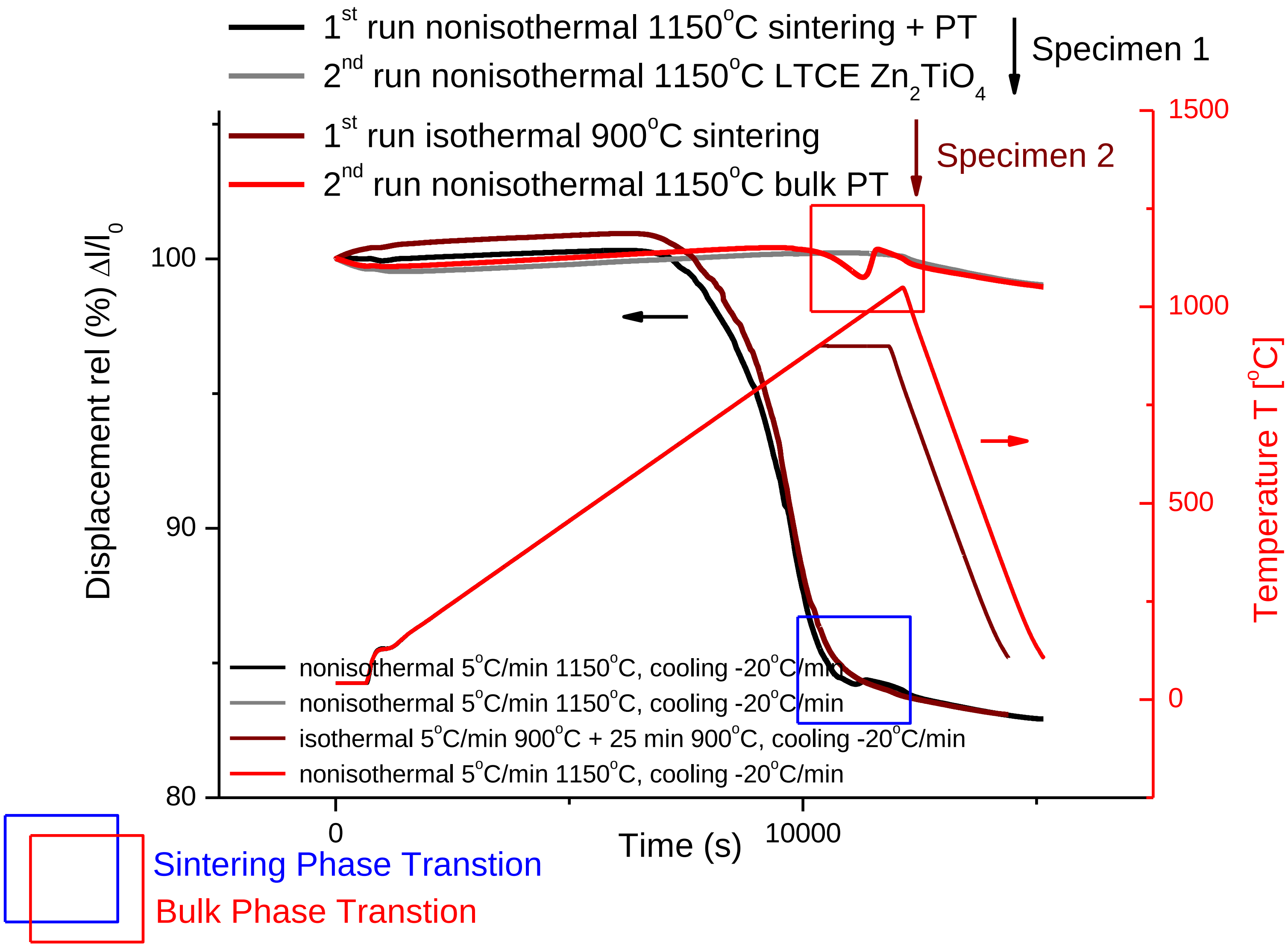


F. H. Dulin and D. E. Rase, *J. Am. Ceram. Soc.*, 43 [3] 130 (1960).

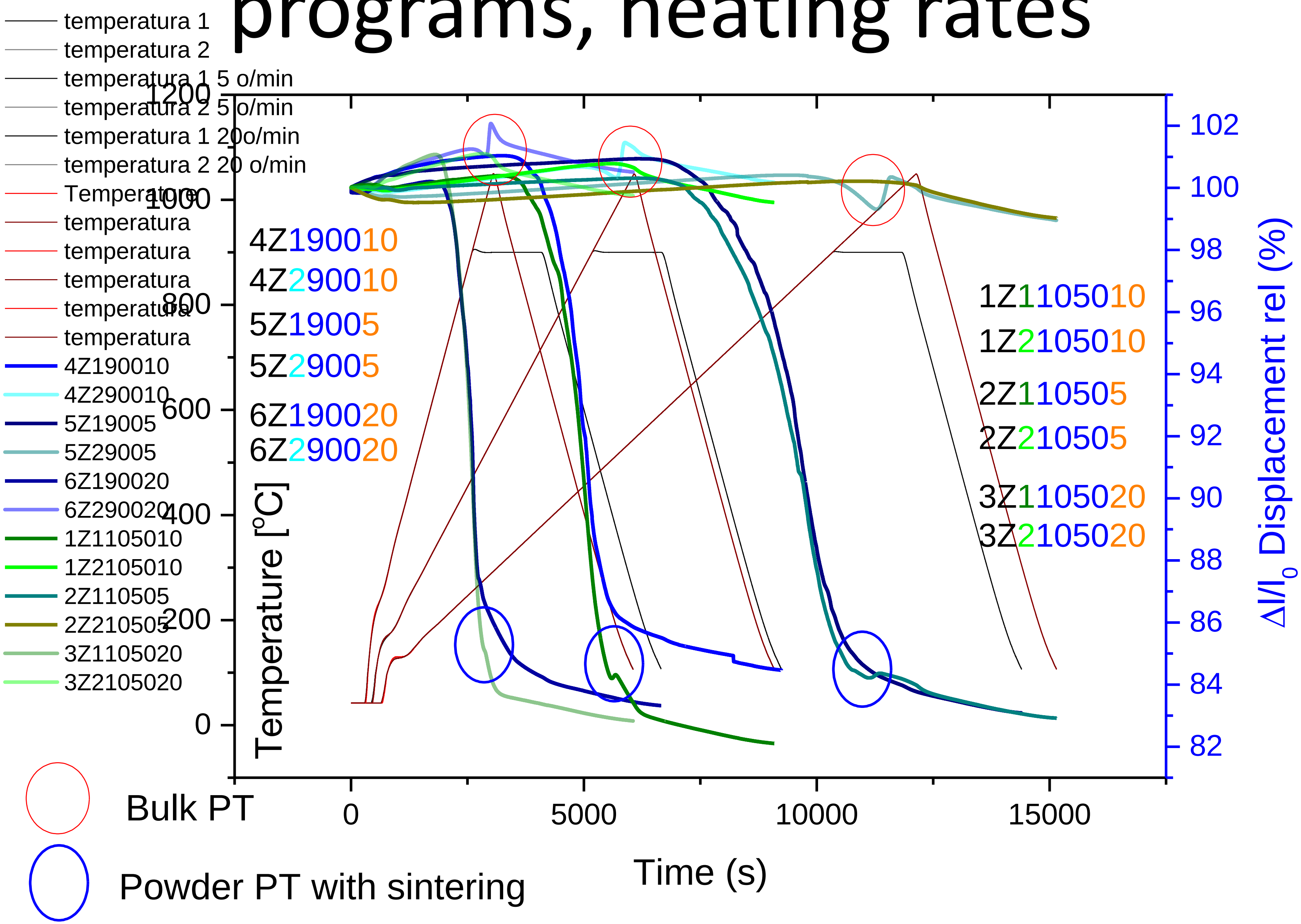


Experiment

Phase transition $ZnTiO_3$ to Zn_2TiO_4 Experimental setup

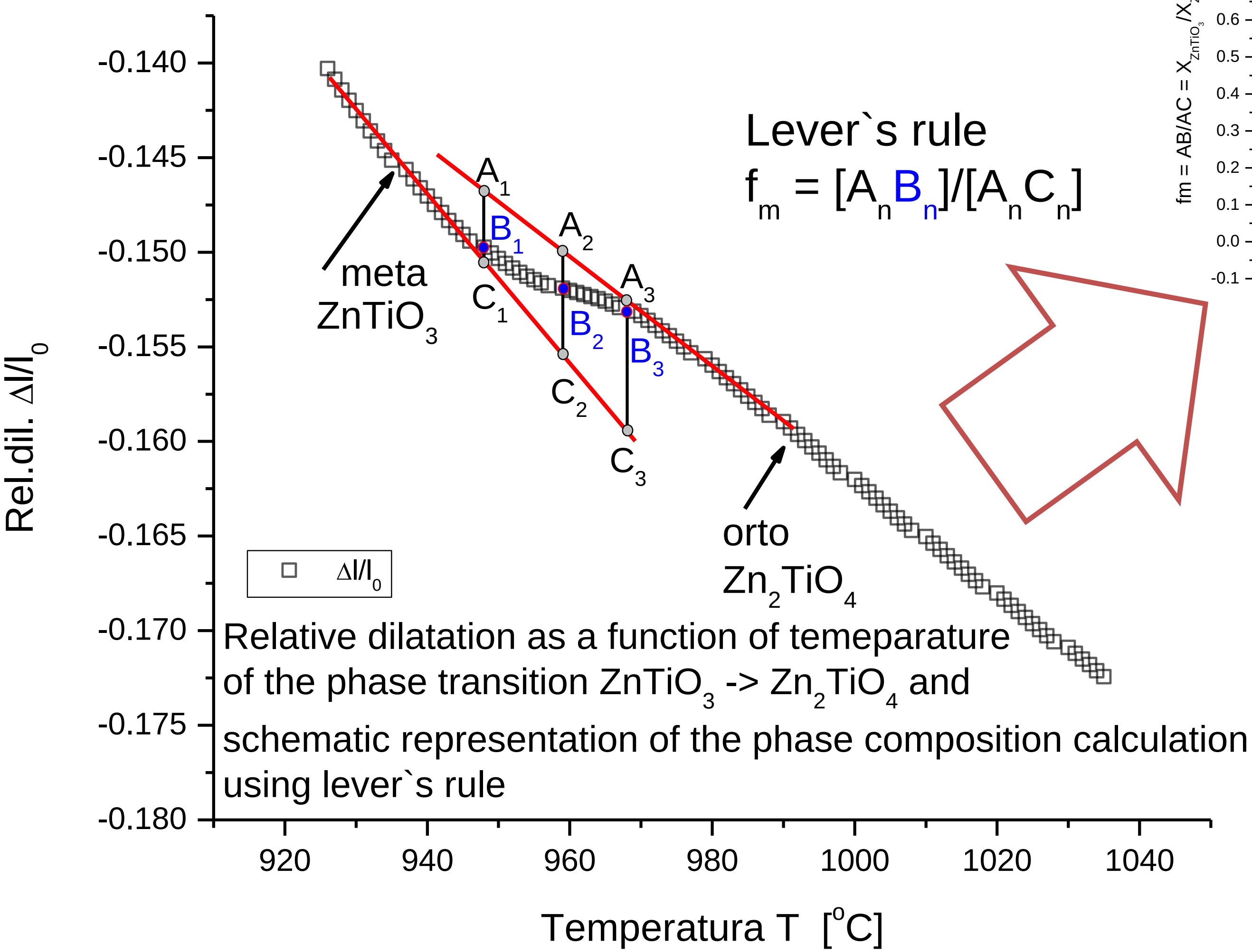


Dilatometric curves and temperature programs, heating rates

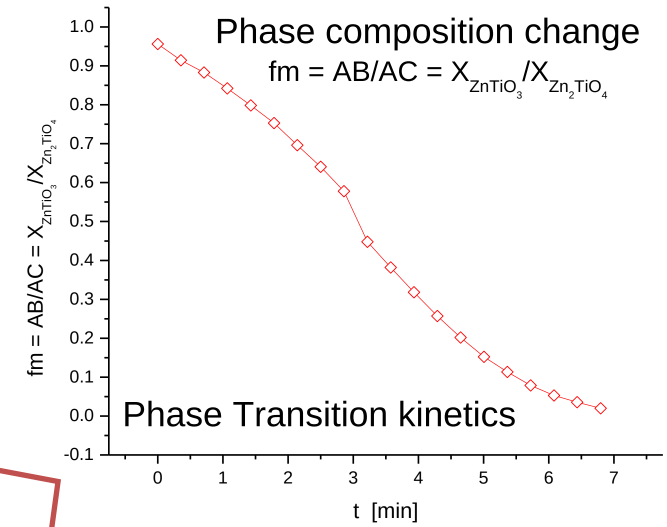


Aim

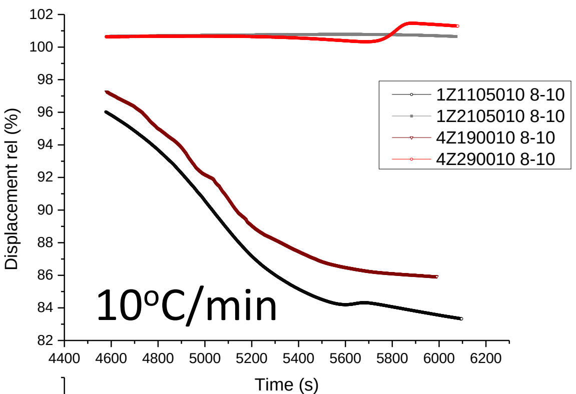
Phase transition kinetics

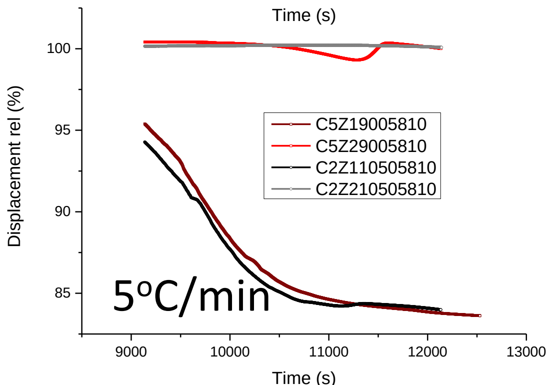


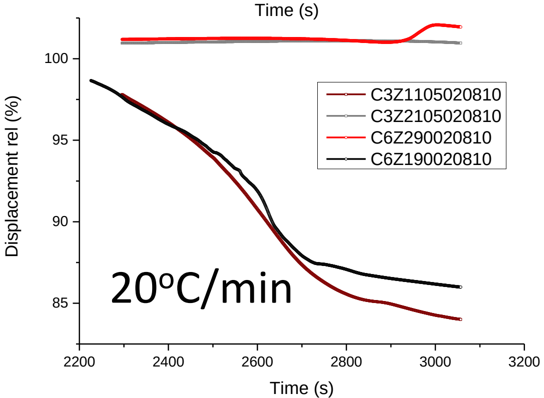
Relative dilatation as a function of temeparature of the phase transition $ZnTiO_3$ -> Zn_2TiO_4 and schematic representation of the phase composition calculation using lever`s rule

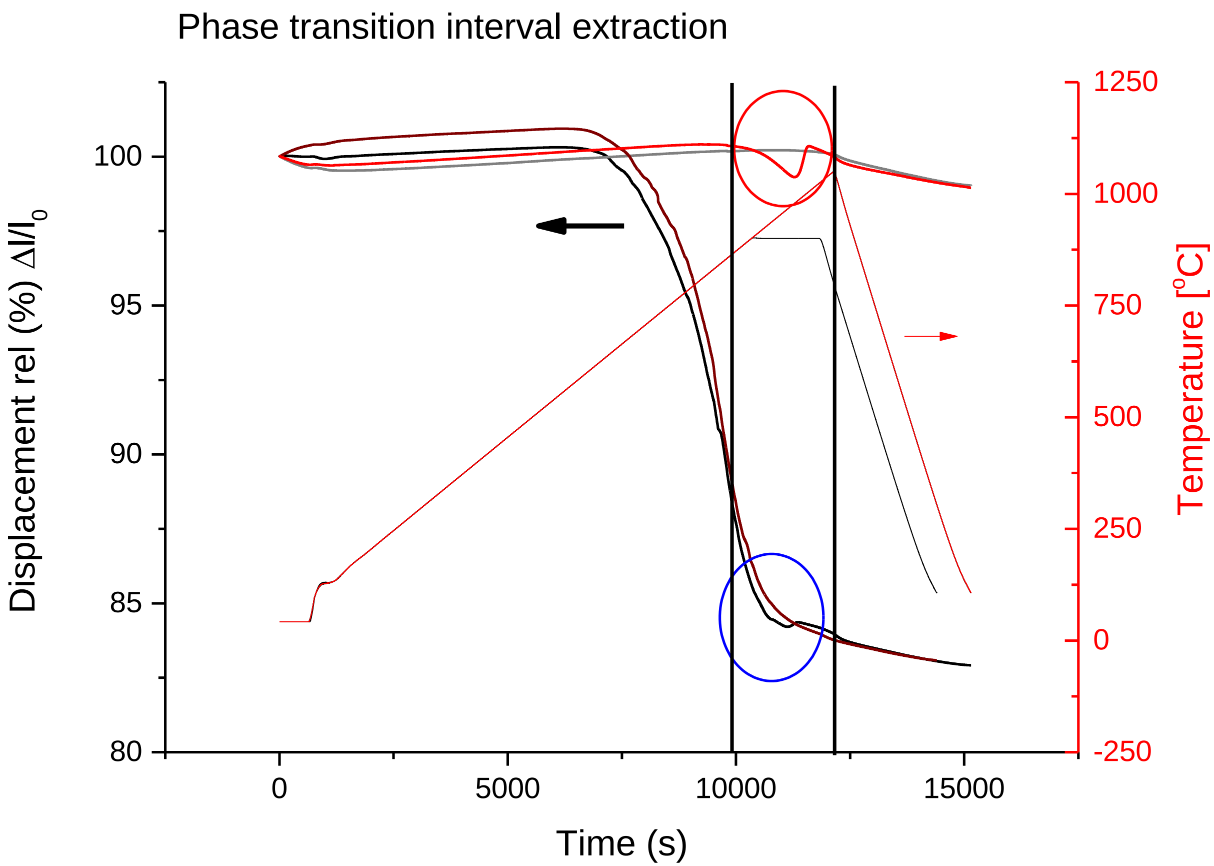


Phase transition interval extraction

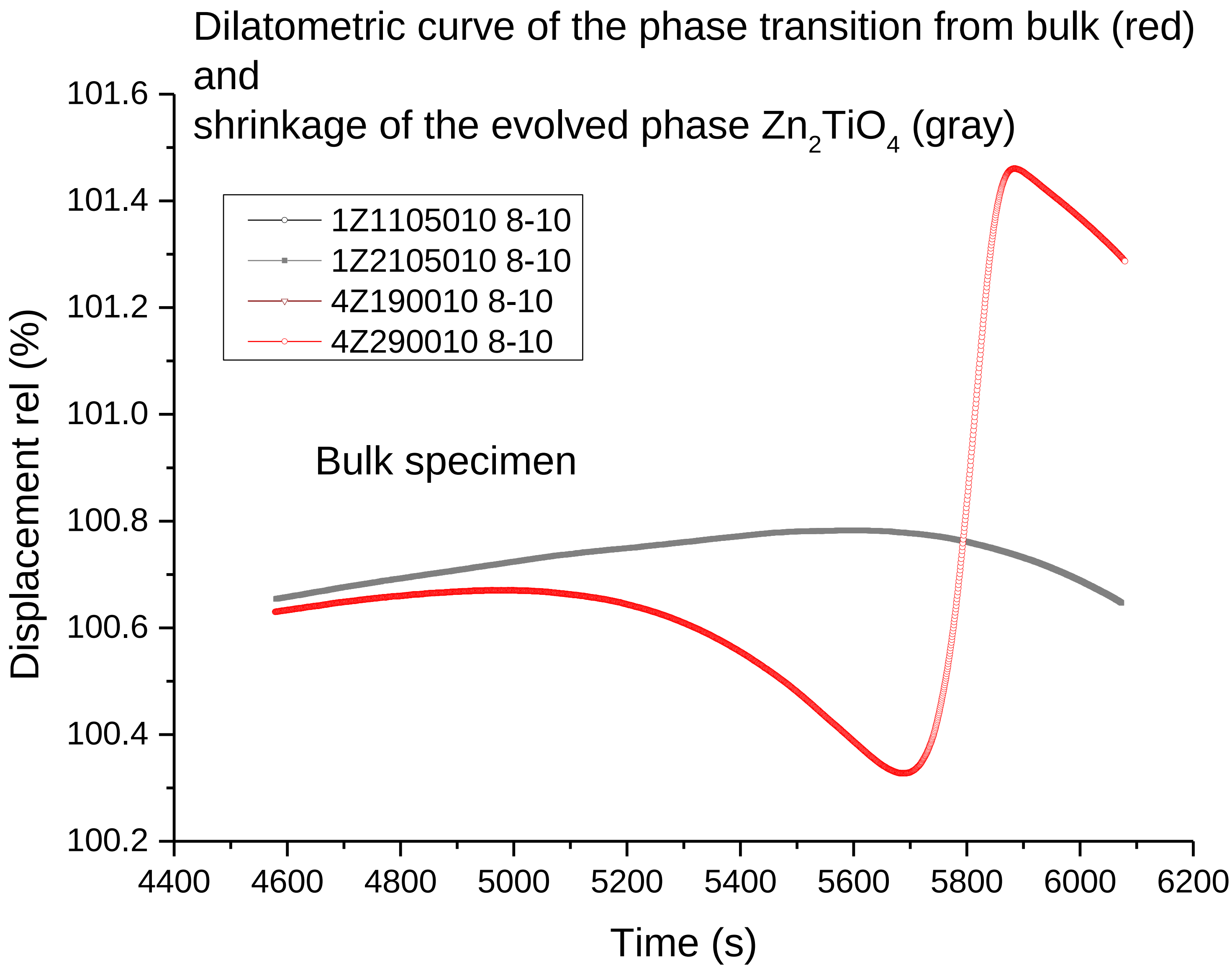






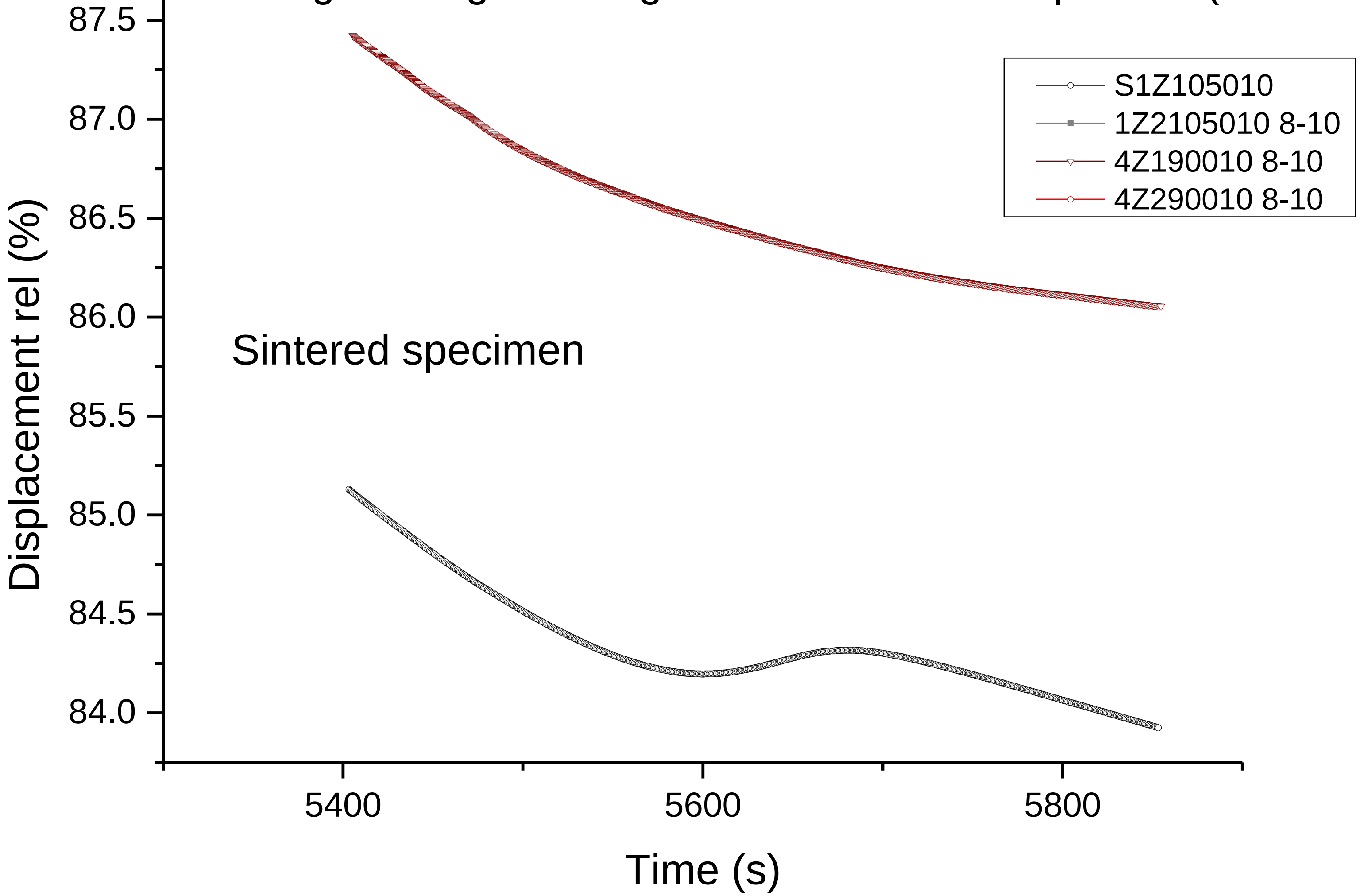


Bulk phase transition dilatation

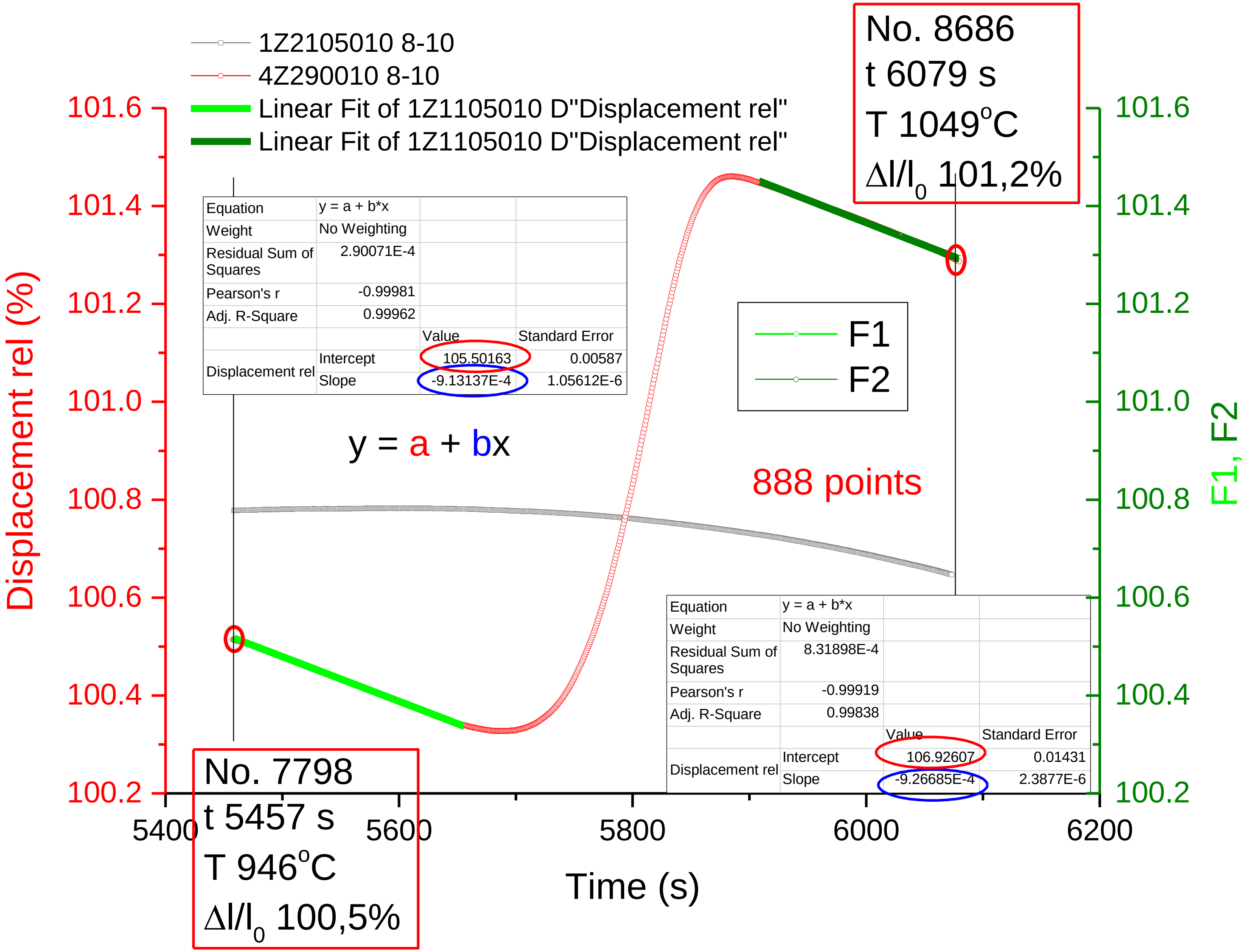


Sintering phase transition dilatation

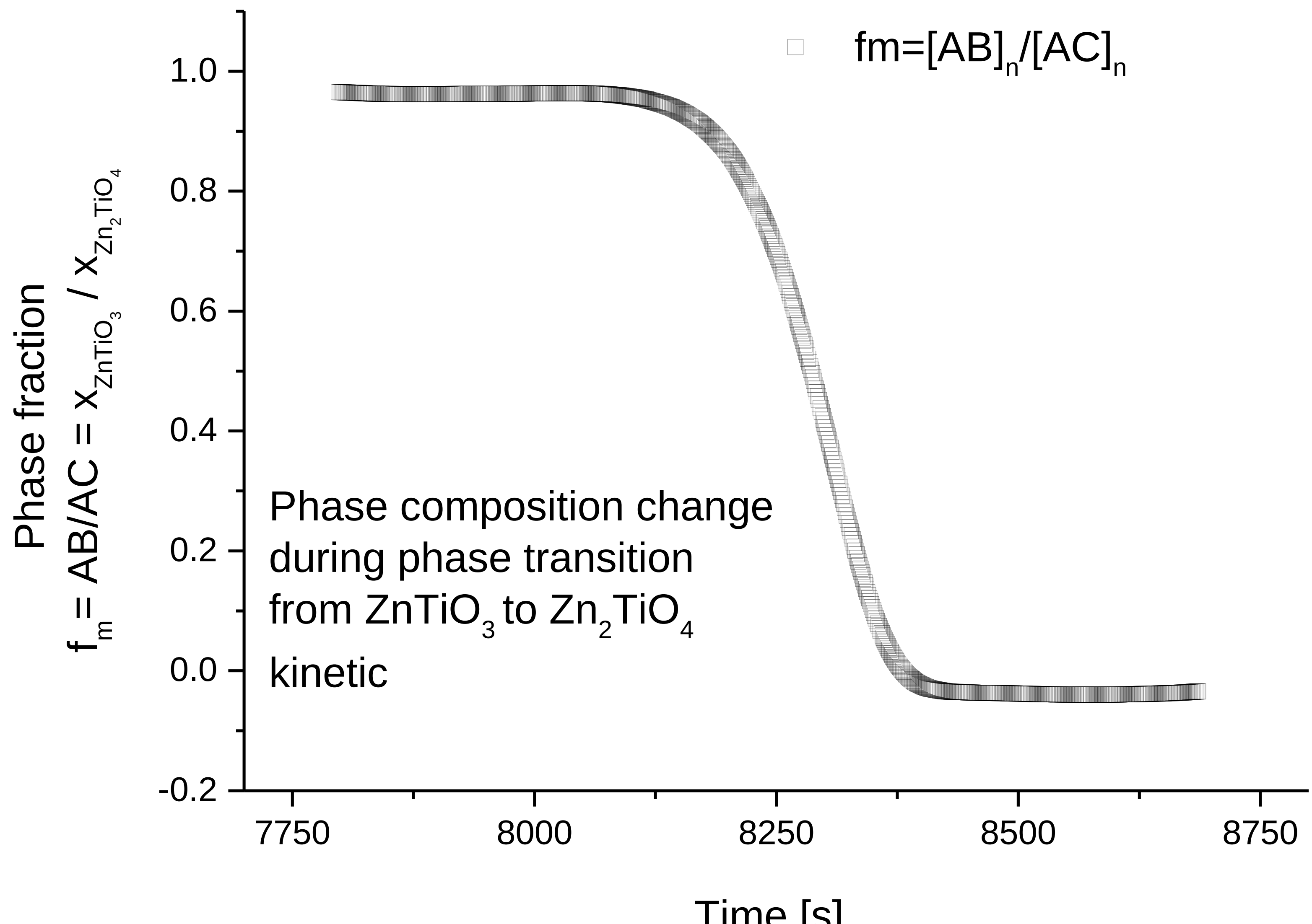
Dilatometric curve of the phase transition during sintering (black)
and
shrinkage during sintering of the ZnTiO3 nano powder (wine red)



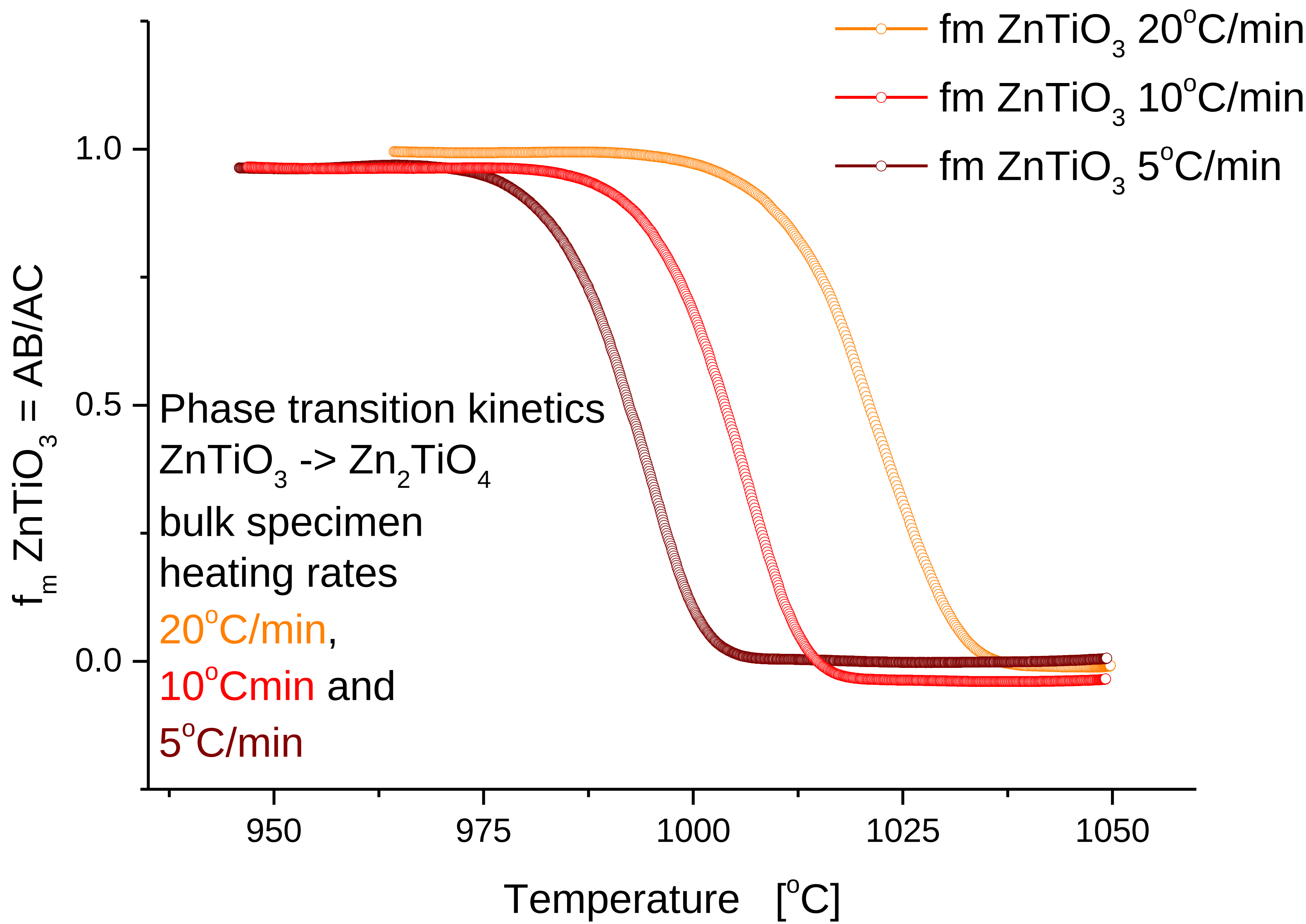
Linear fitting and interpolation of the inserted linear functions



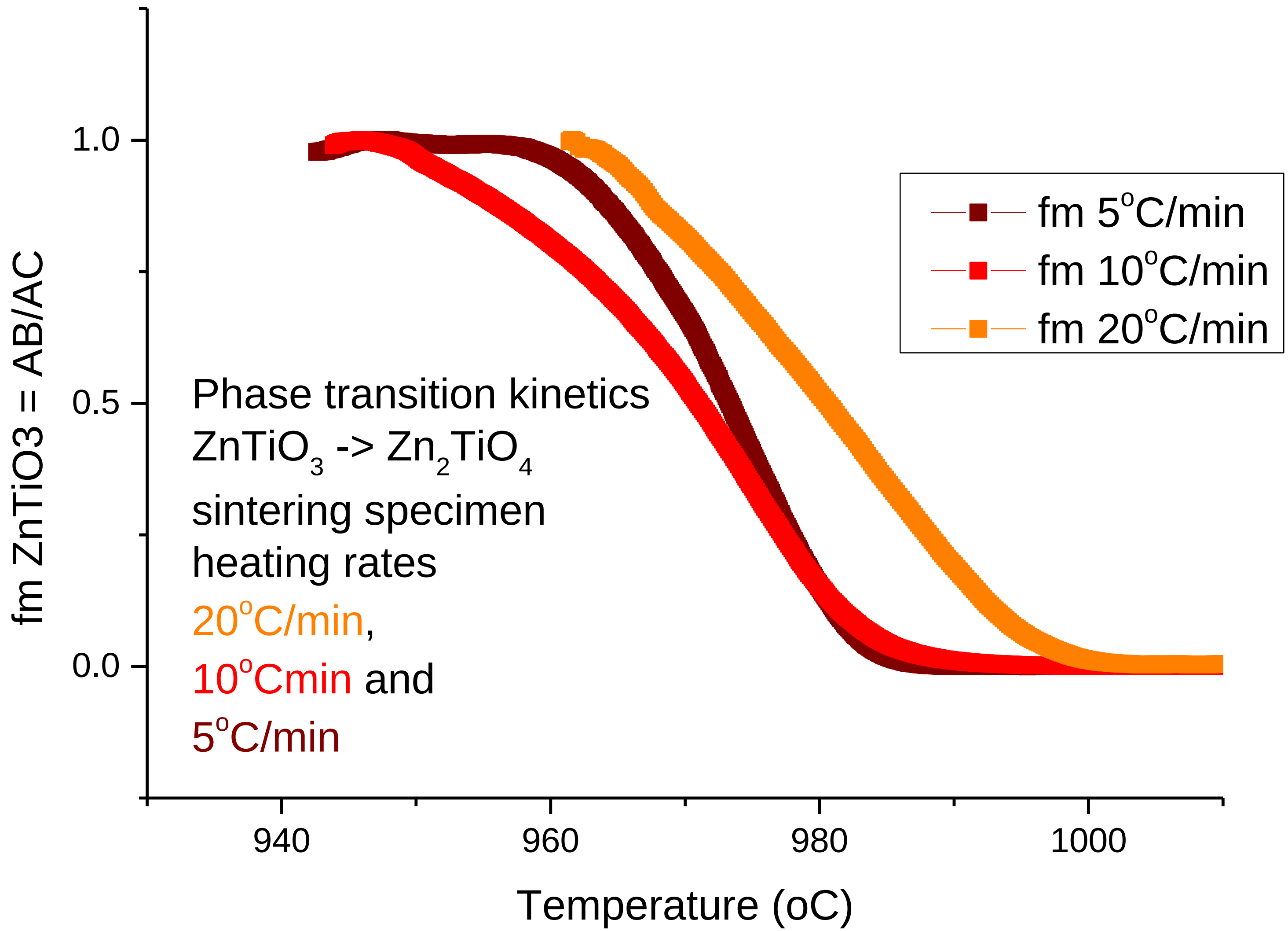
Phase composition - kinetic



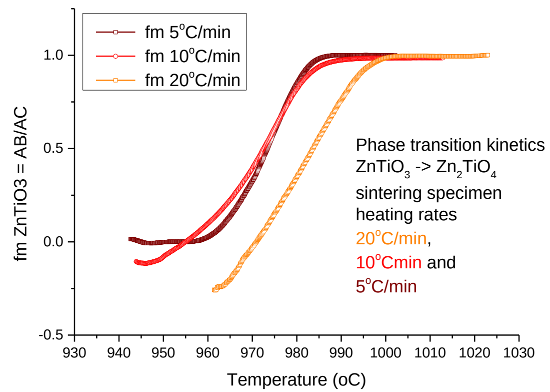
Phase transition from bulk specimen
Three heating rates



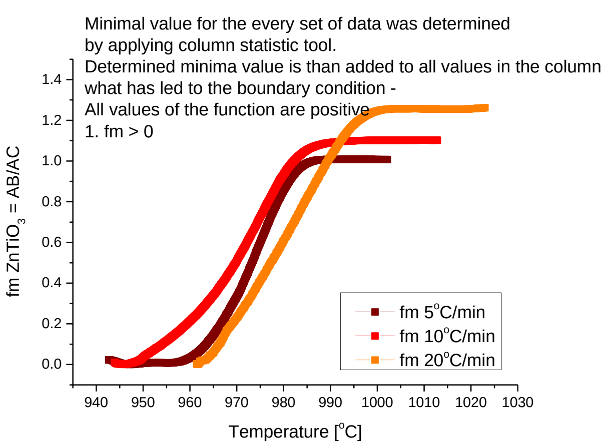
Phase transition from sintered specimen - Three heating rates



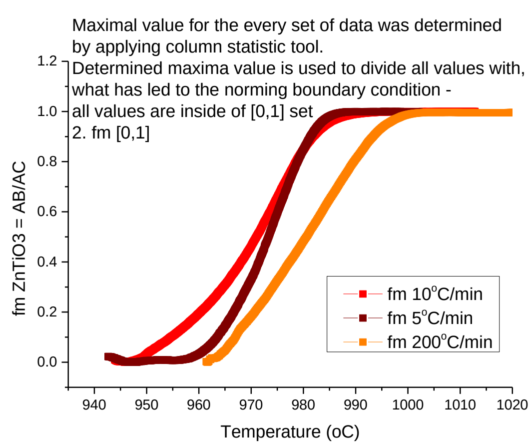
Mathematical porcedures enabeling comaprison of the data



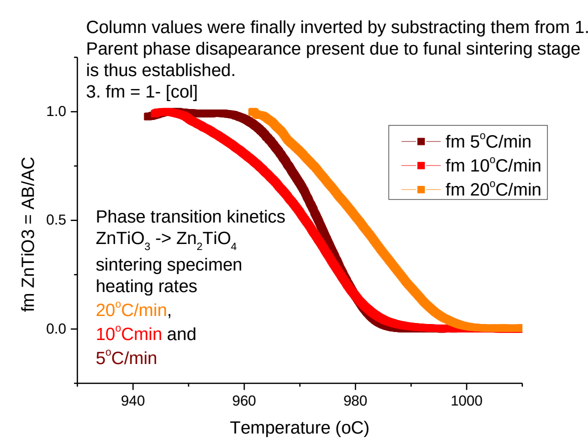
1. fm>0



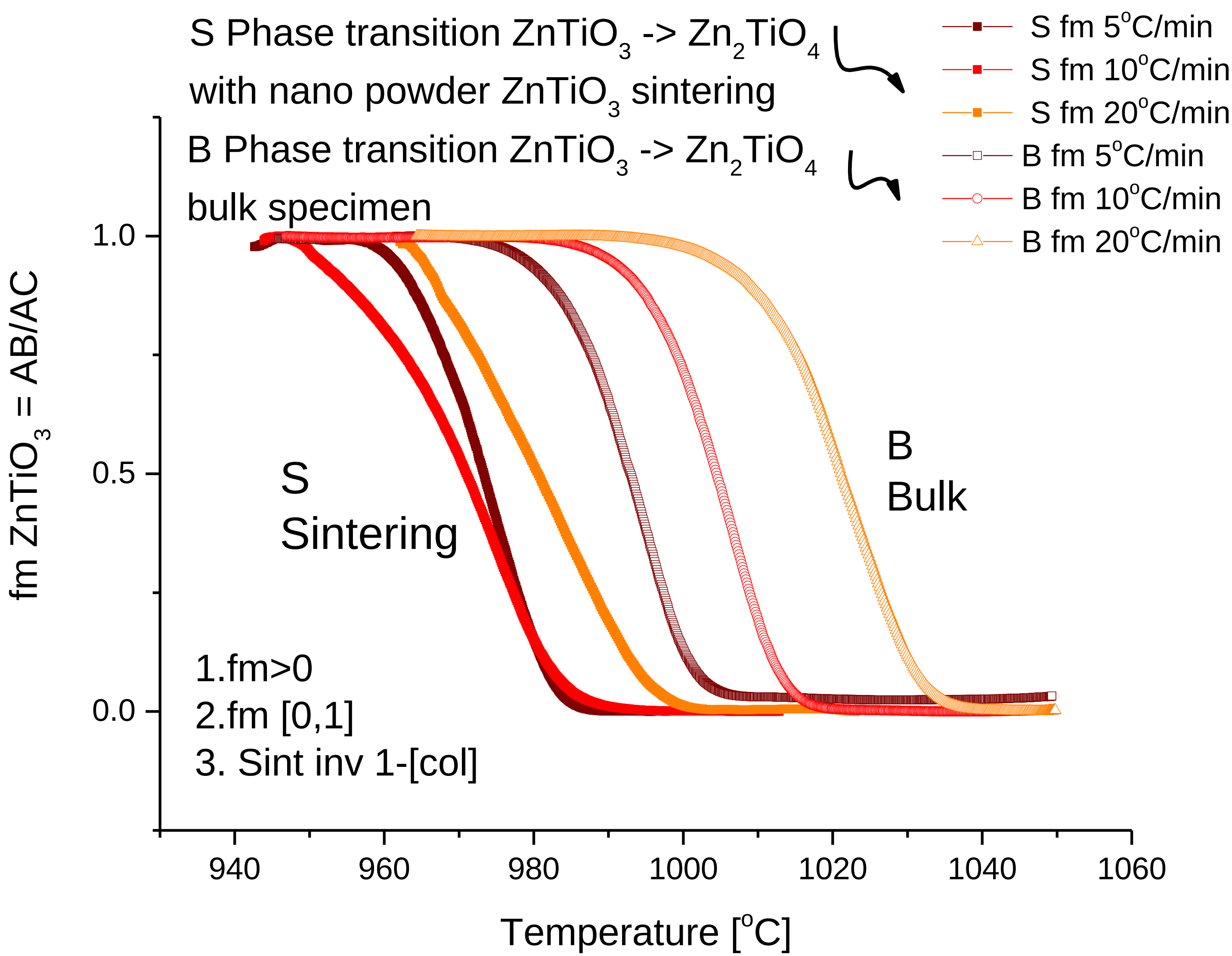
2. fm [0,1]



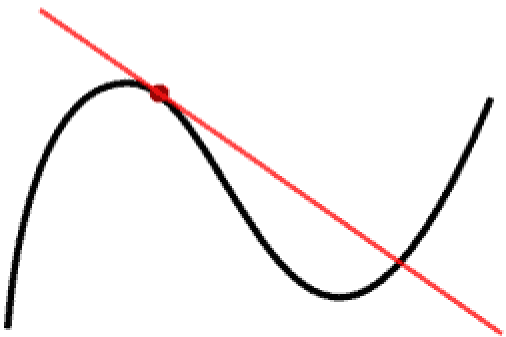
3. fm = 1 - [col]

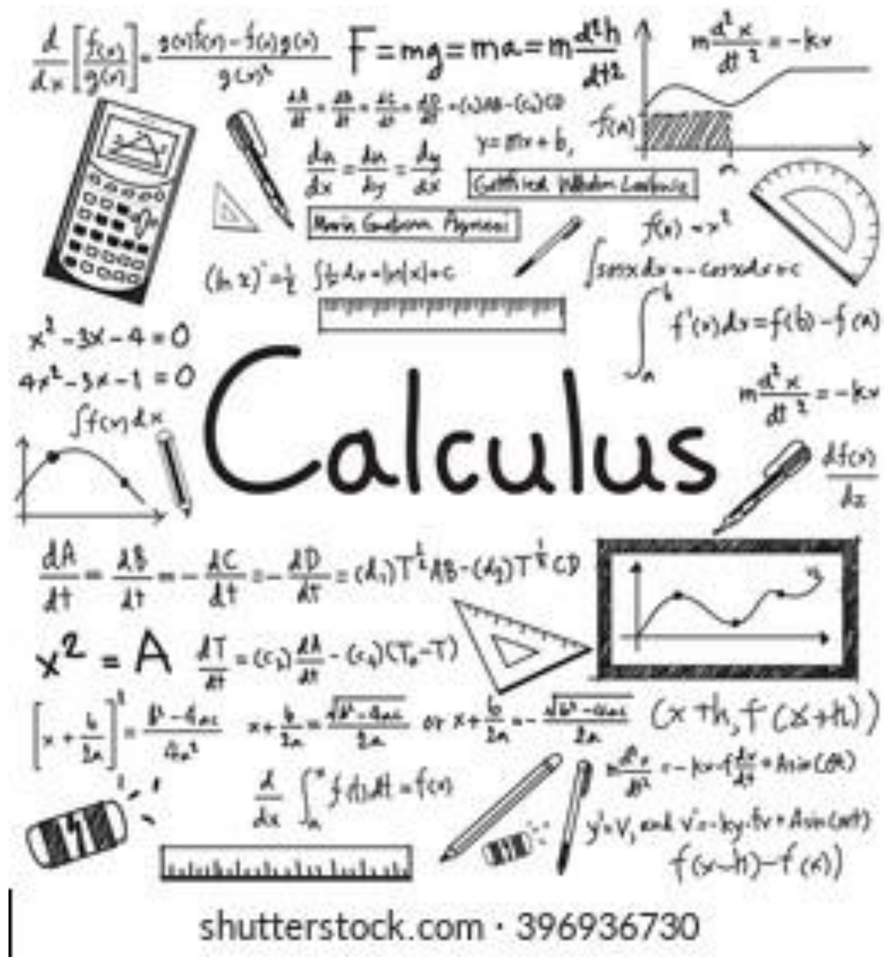


Phase transition kinetics comparision: Bulk and Sintered - Experimental



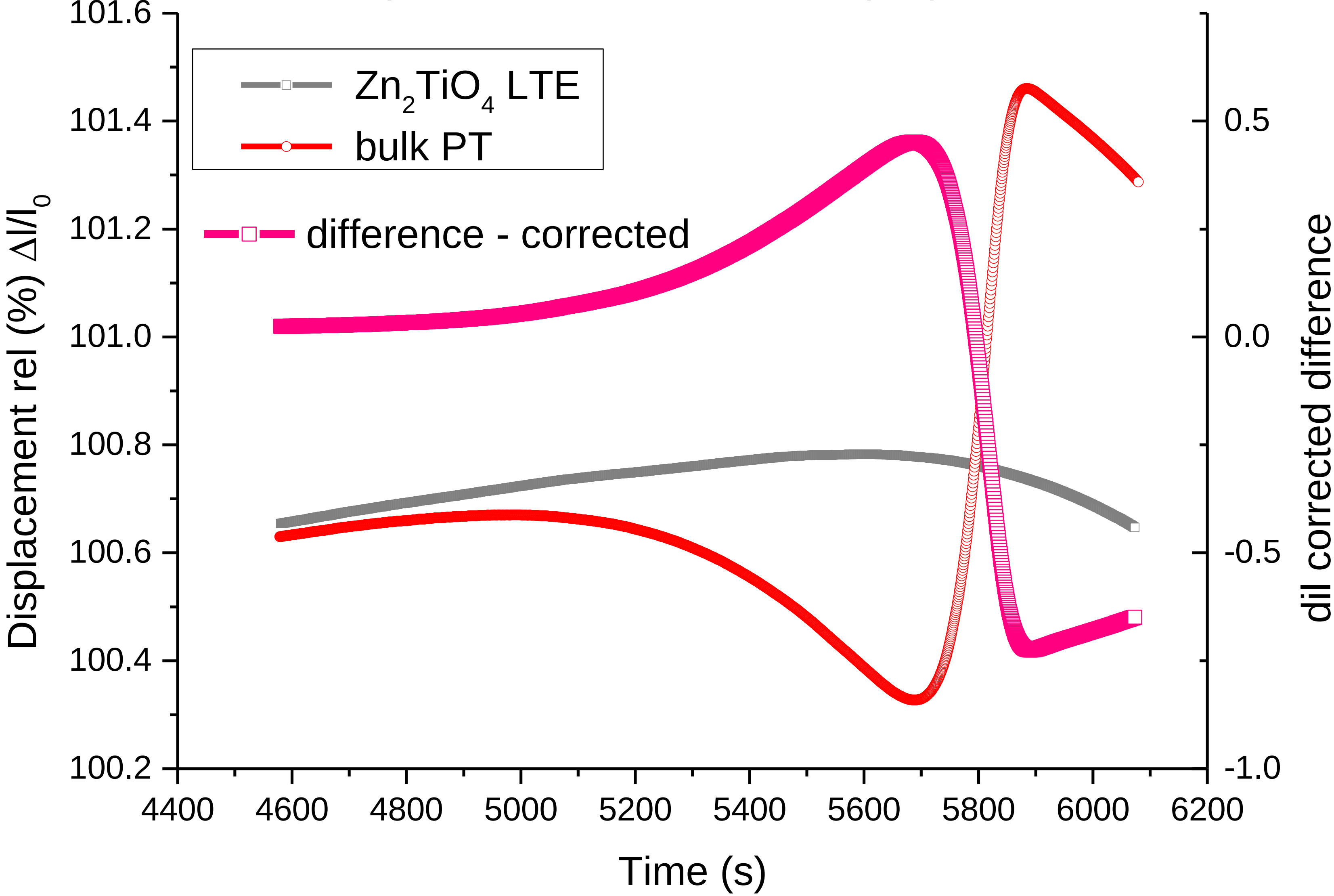
Correction Calculus



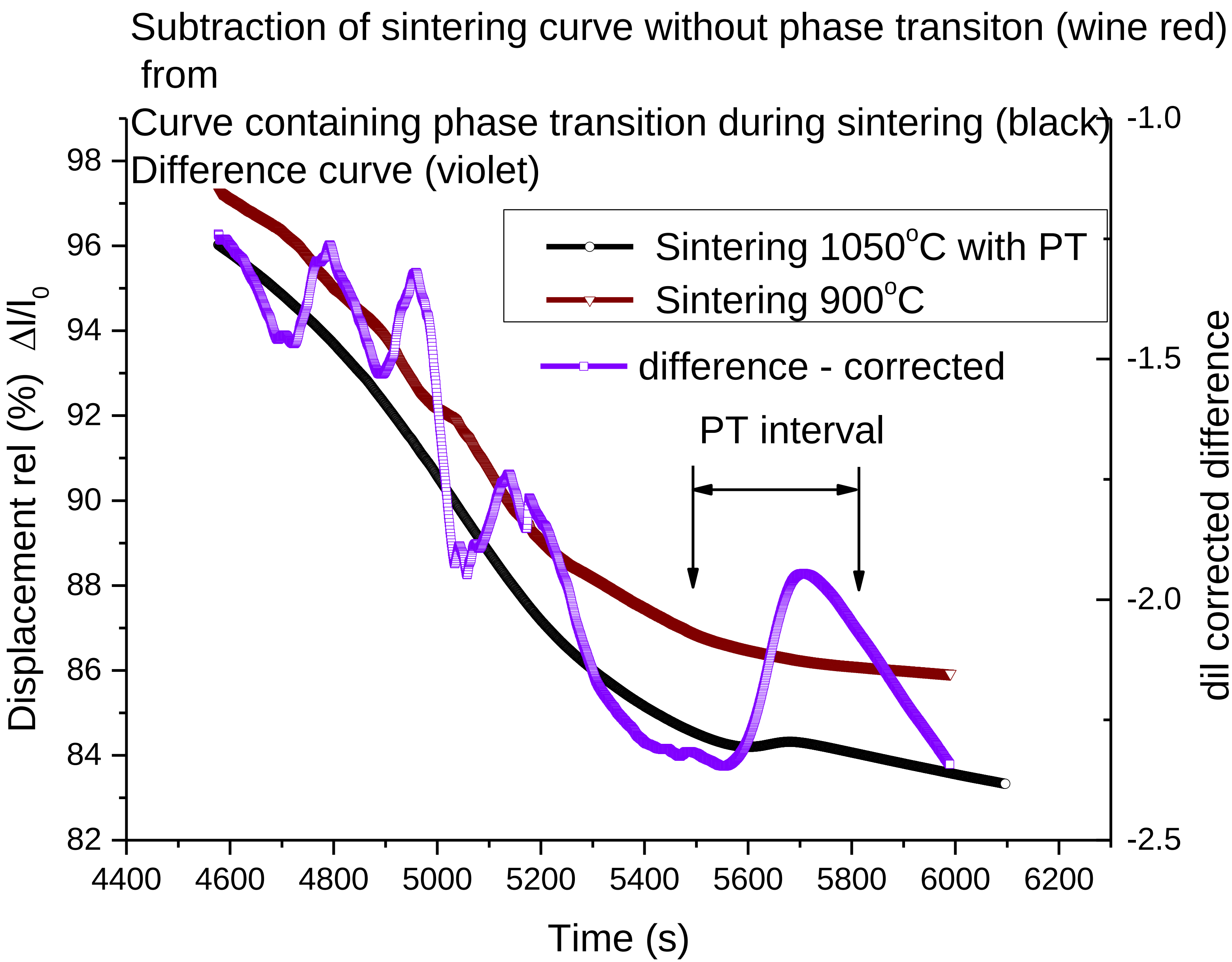


Correction by subtraction - bulk

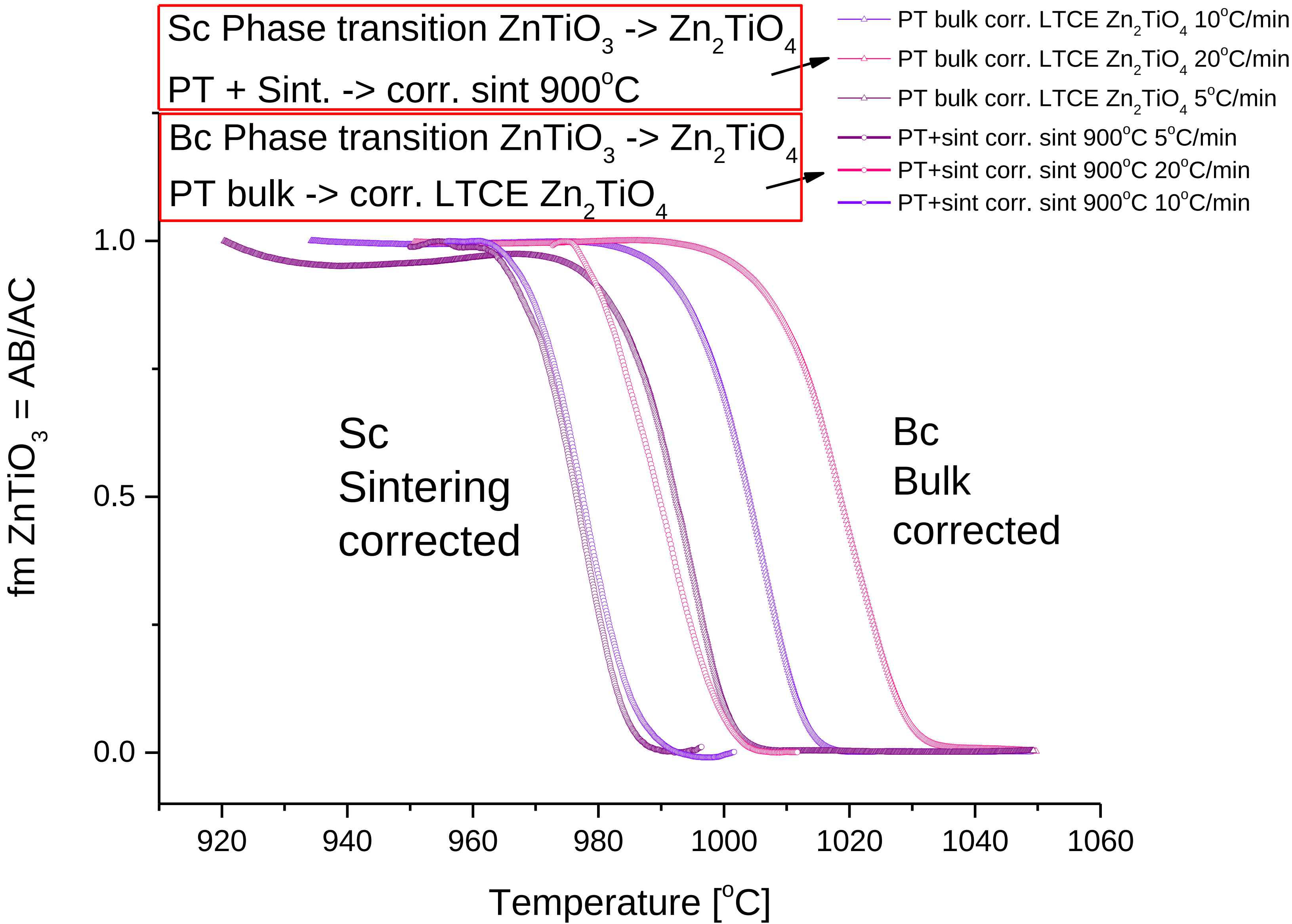
subtraction of Zn2TiO4 linear thermal expansion (gray)
from bulk phase transition dilatation (red)



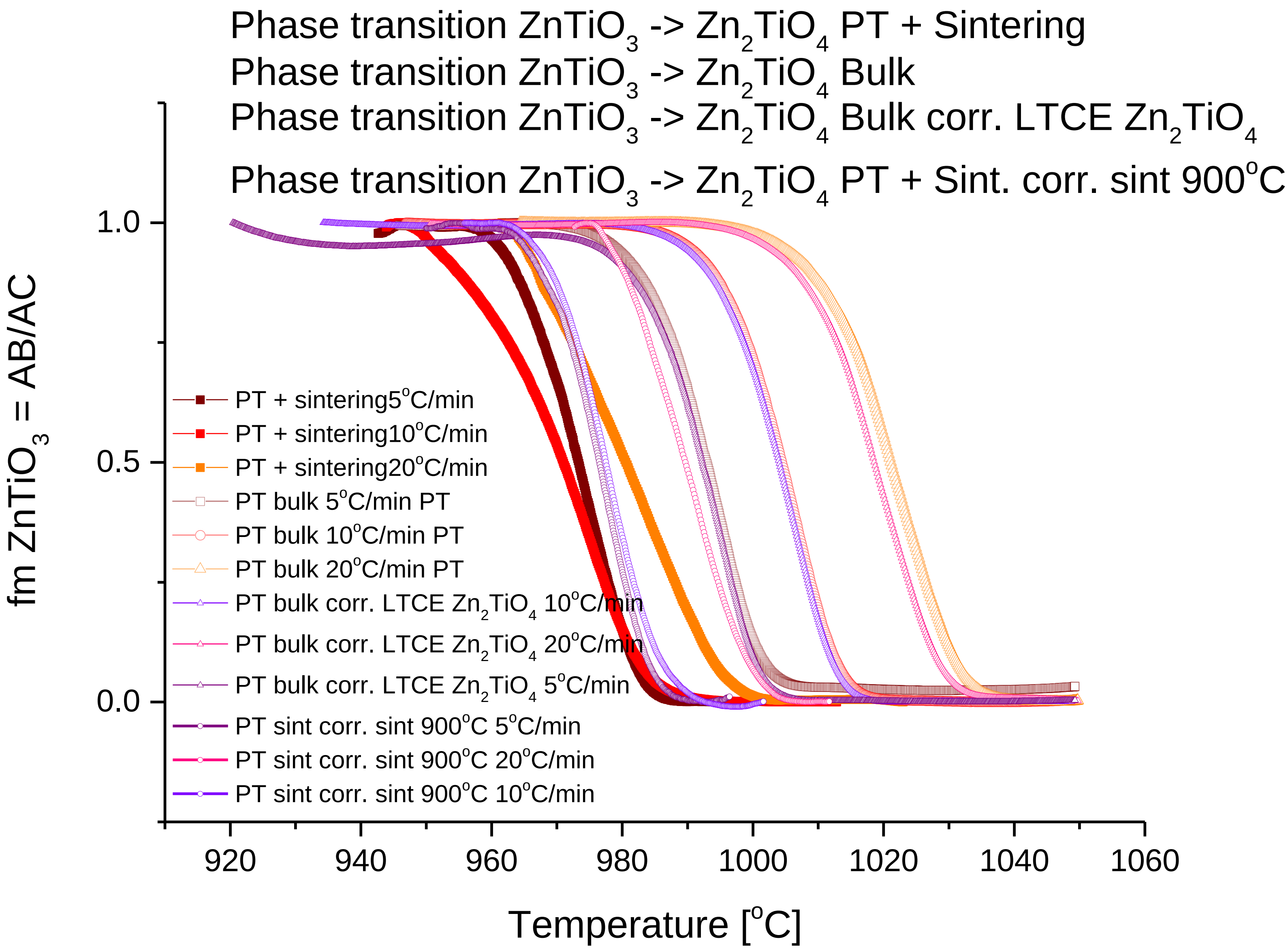
Correction by subtraction - sintered



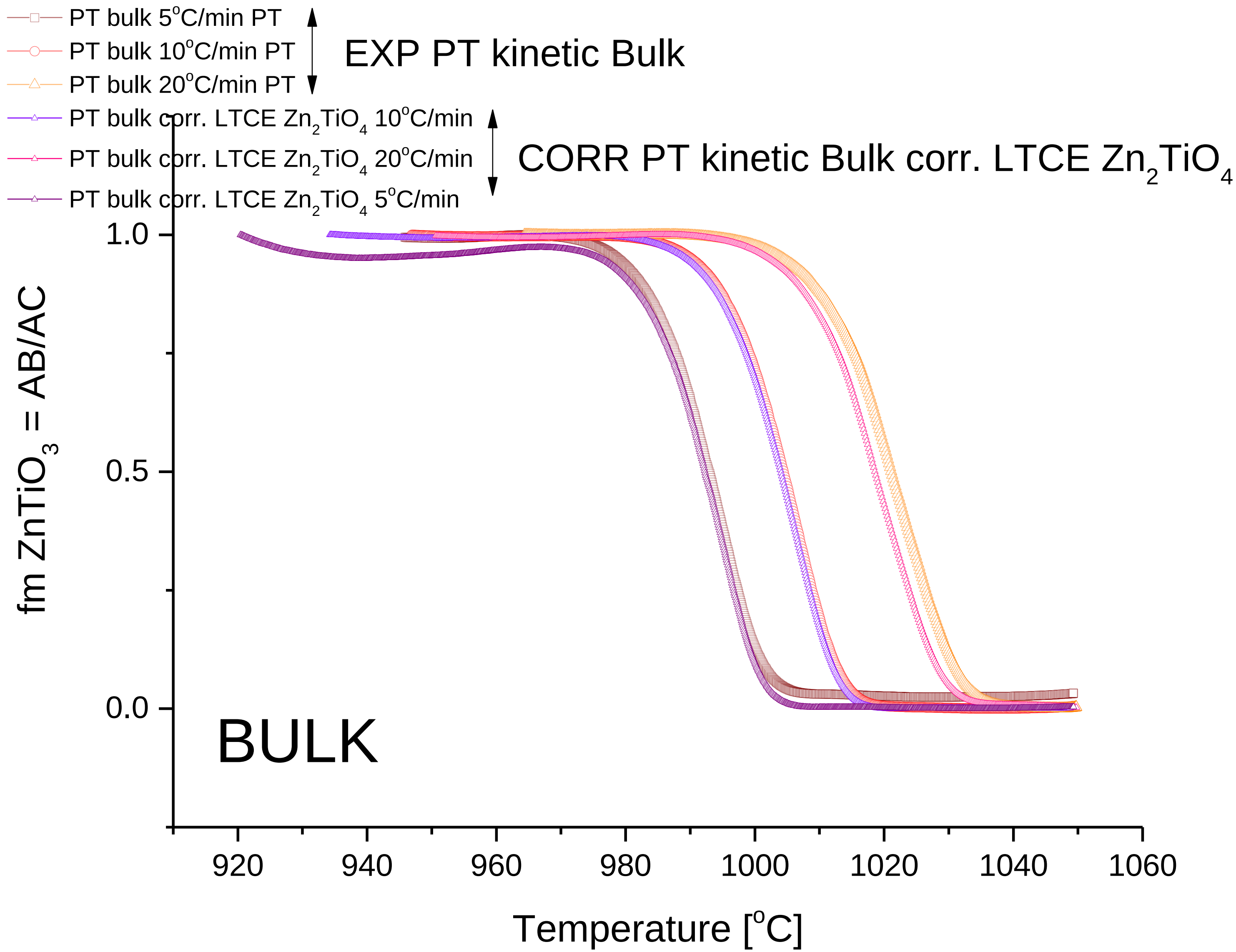
Phase transition kinetics comparision: Corrected



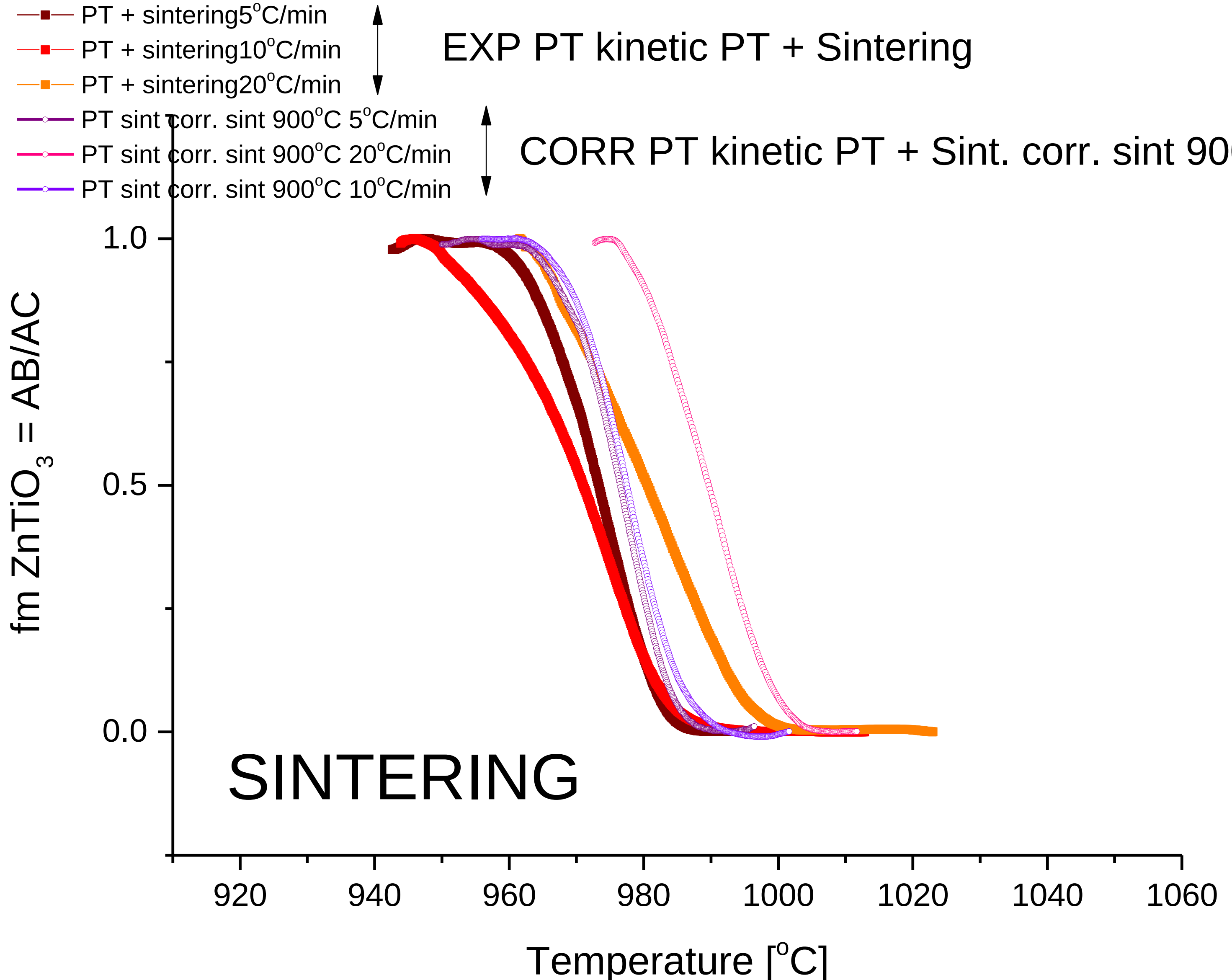
Phase transition kinetics comparison: Experimental vs. Corrected



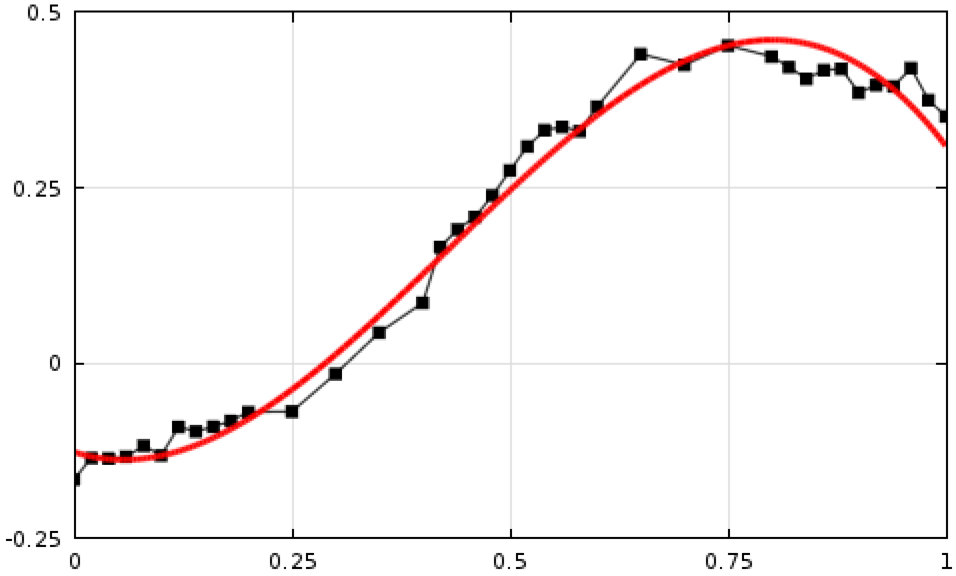
Phase transition kinetics comparison: Experimental vs. Corrected - BULK

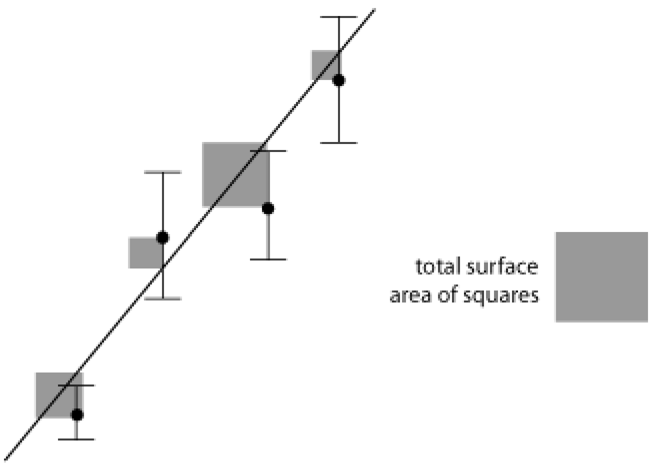


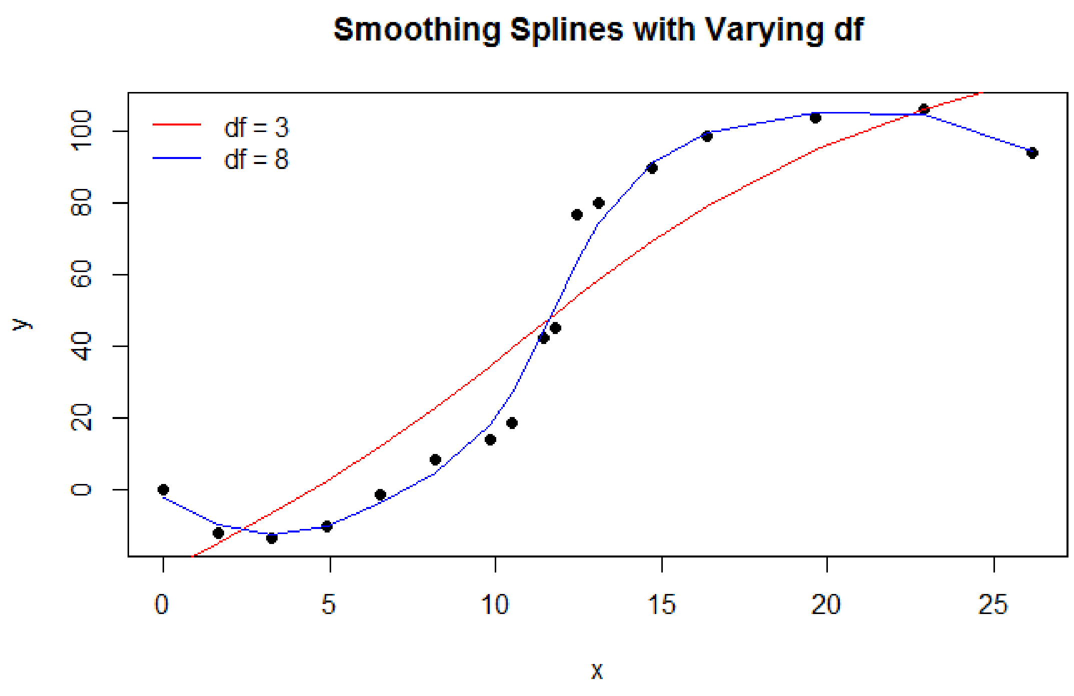
Phase transition kinetics comparision: Experimental vs. Corrected- SINTERING



Fitting

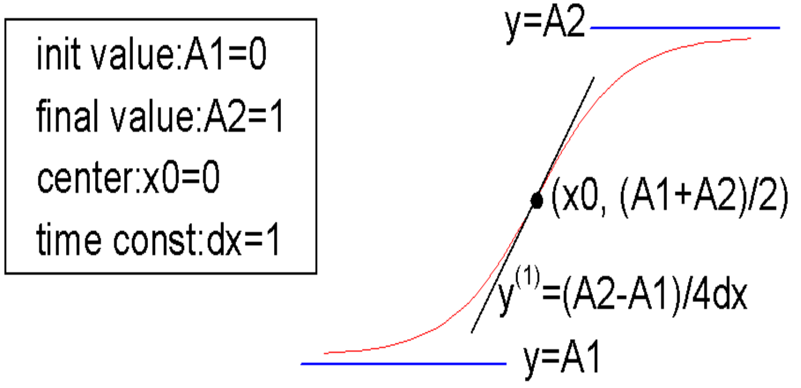

0.5
0.25
0
-0.25
0
0.25
0.5
0.75
1


total surface
area of squares


Smoothing Splines with Varying df
df = 3
df = 8
y
x
0
20
40
60
80
100
0
5
10
15
20
25

Boltzmann fitting function

$$y = \frac{A_1 - A_2}{1 + e^{(x - x_0)/dx}} + A_2$$

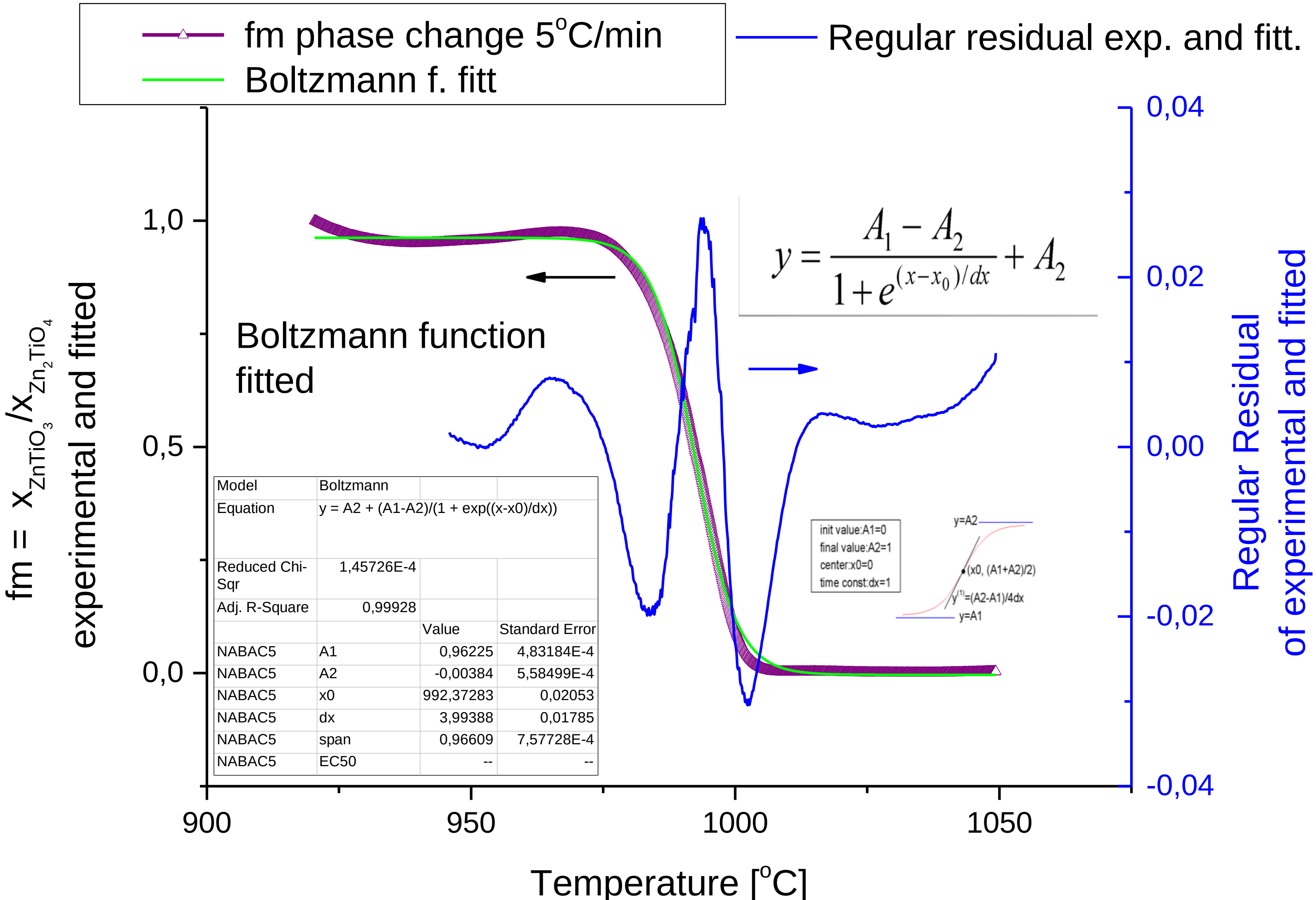


$$\frac{V^{\beta}(t)}{V} = 1 - \exp\left[-\frac{4\pi}{3}\int_0^t J\,v^3\,(t-t')^3\,\mathrm{d}t'\right]. \qquad \frac{V^{\beta}(t)}{V} = 1 - \exp\left[-\frac{\pi}{3}\,v^3\,J_{ss}\,t^4\right].$$

This is the Kolmogorov–Johnson–Mehl–Avrami (KJMA) equation.

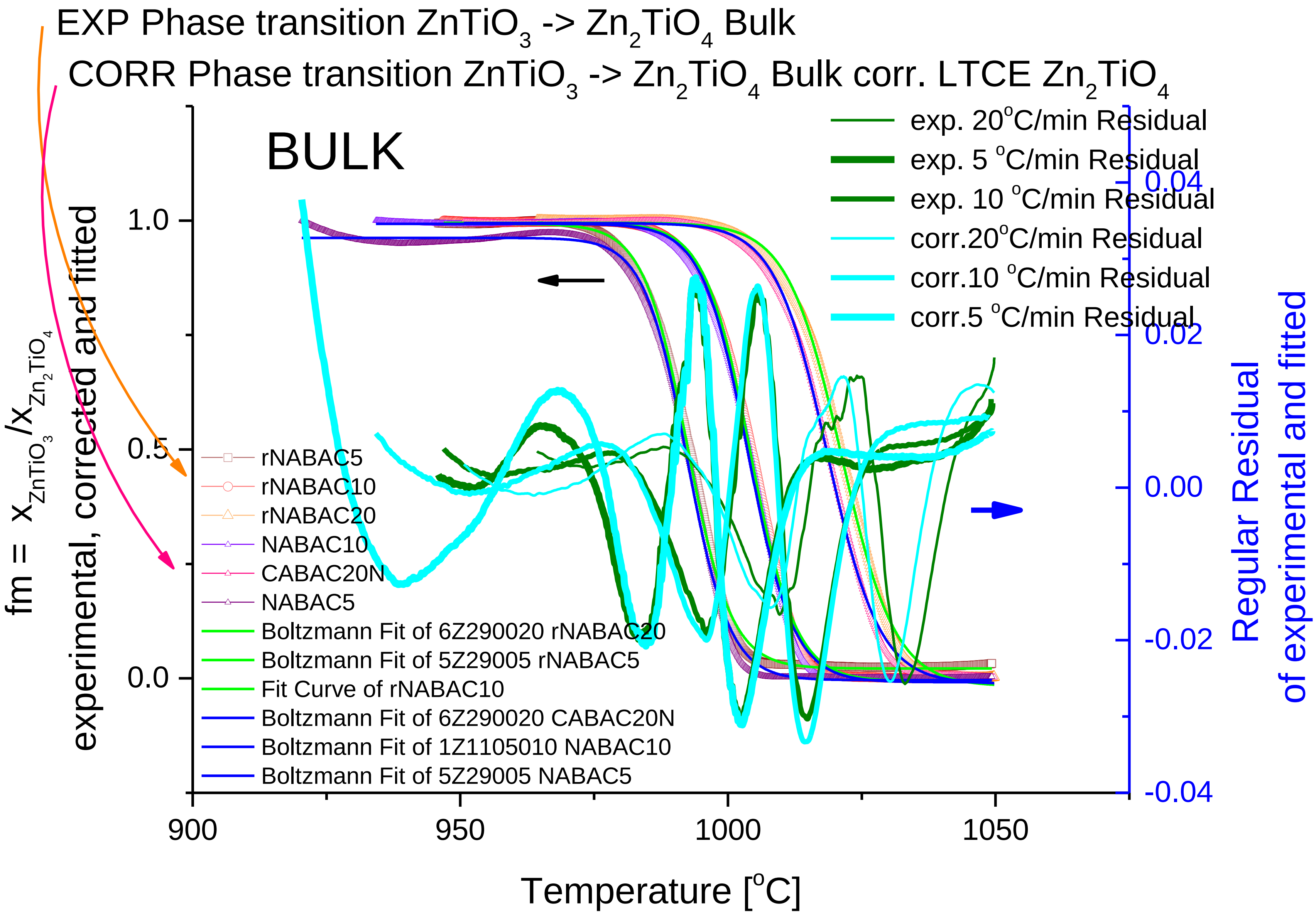
The KJMA Eq. 11.45 predicts that the volume fraction at $t = 0$ is zero, but has a sigmoidal shape with increasing slope that later gives way to an asymptote at long time with $V^{\beta}/V = 1$. The actual shape of V^{β}/V is typically calculated for two cases. The first

Phase transition curve, Boltzmann fitting function – Bulk, LTEC corrected, 5°C/min

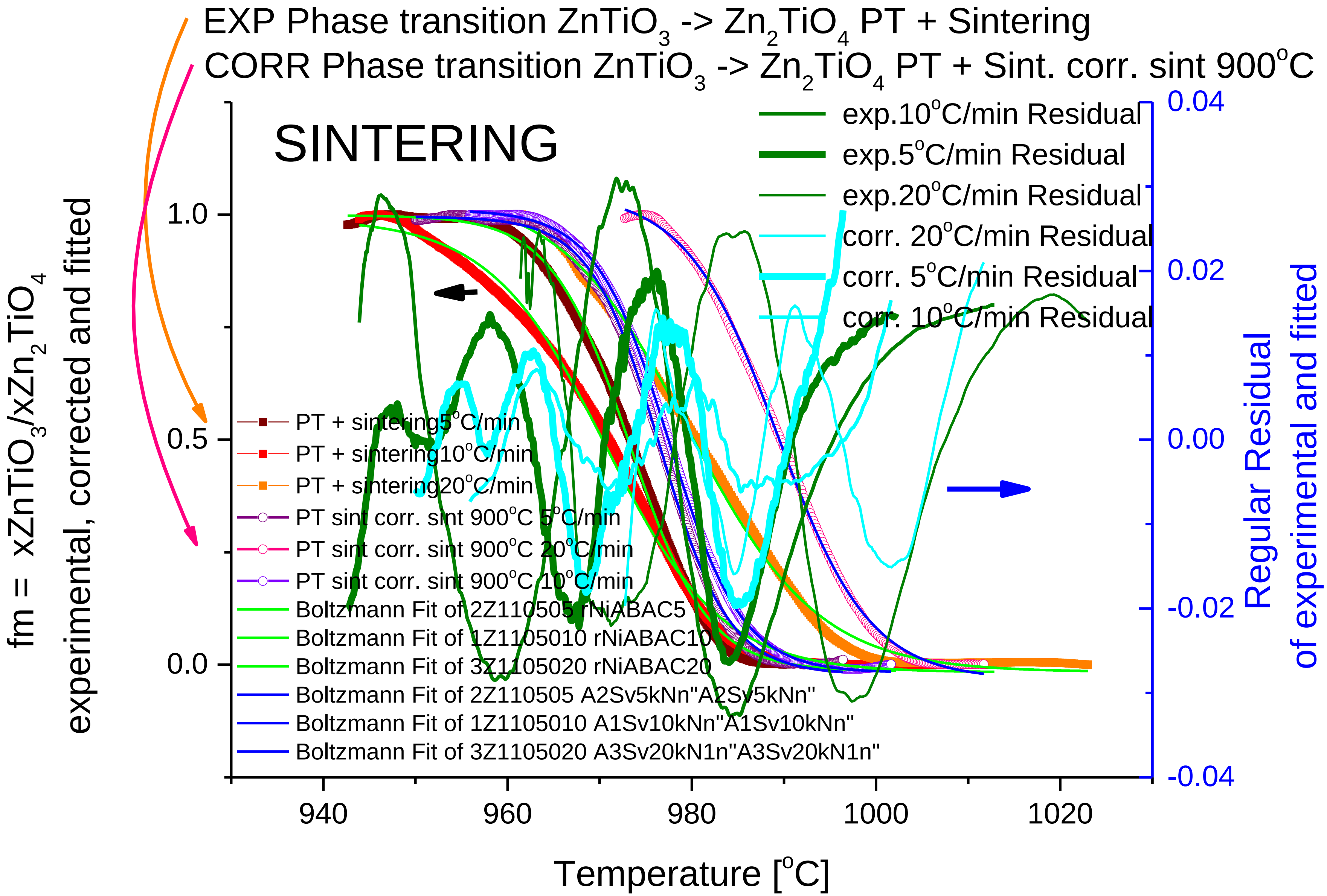


Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	1,45726E-4		
Adj. R-Square	0,99928		
		Value	Standard Error
NABAC5	A1	0,96225	4,83184E-4
NABAC5	A2	-0,00384	5,58499E-4
NABAC5	x0	992,37283	0,02053
NABAC5	dx	3,99388	0,01785
NABAC5	span	0,96609	7,57728E-4
NABAC5	EC50	--	--

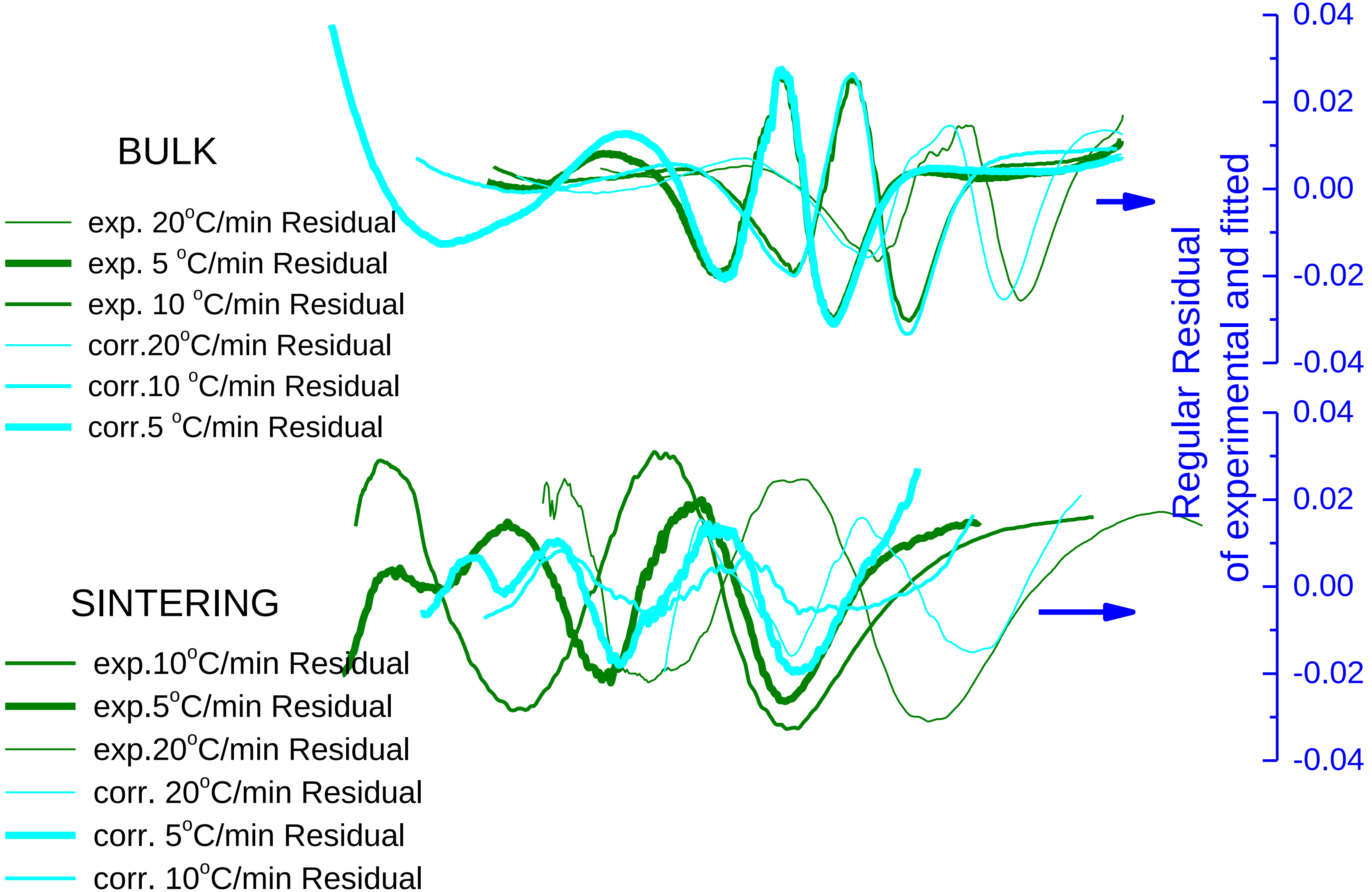
Bulk - experimental and corrected Boltzmann function fitted – Residuals



Sintering - experimental and corrected Boltzmann function fitted – Residuals



Fitting function Residuals comparision



Conclusion

- ✓Phase transition for bulk specimens temperature is a function of heating rate (possible Kissinger equation usage)
- ✓Sintering phenomenon substantially effects phase transition (temperatures are lowered by simultaneous sintering)
- ✓Correction by sintering submission does not affect temperatures of the phase transition (although kinetic of the phase transition is different)
- ✓Phase transition kinetics from dilatograms by lever`s rule is most prommsing (softvare obtained with dilatometric device does not includes this option)

THANK YOU FOR YOUR PATIENCE AND ATTENTION.