Sintering and Phase Transition of the ZnTiO₃ Nano Powder Dilatometric Data Deconvolution

Nebojša Labus, Smilja Marković, Maria Vesna Nikolić, Milena Rosić, Srđan D. Matijašević

Abstract— Sintering and phase transition are often superimposed at dimensional change diagram recorded during heating. Phase transition kinetic is thus hard to deconvolute due to the superposition of the sintering and phase transition dimensional change phenomena.

Metastabile perovskite phase $ZnTiO_3$ has transition to stabile spinel Zn_2TiO_4 which occurs at 945°C with high kinetic rate. Nano powder with 40 nm particle diameter was pressed uniaxially at 200 MPa pressure without binder to form compact that will be consequently sintered. Dimensional change during heating was monitored using dilatometric thermo-mechanical analyzer TMA model SETSYS Evolution. Lever`s rule was used to calculate amount of the emerging phase during phase transition.

The compacted specimens were treated on the non-isothermal schedule up to 1050°C. Sintering phenomenon of the $ZnTiO_3$ nanopowder compact was also recorded up to 900°C with isothermal holding of 25 minutes where phase transition was avoided due to lower temperature and isothermal holding. Second run heating of the obtained sintered specimens were recorded with the heating schedule of non-isothermal heating up to 1050°C.

Kinetic of the phase transition was obtained from dilatograms recorded during sintering and from bulk on the second run heating. Furthermore, phase transition kinetics was obtained by subsequent data subtraction of the sintering curves without phase transition from the dilatation sintering curves containing phase transition.

In such a manner complex kinetics of phenomena such as sintering, linear expansion and phase transition recorded as dimensional change during heating brings the recognition of their mutual interconnected relations. Also application of these mathematical operations on dilatometric data leads to the established procedure for the sintering and phase transition data treatment.

Index Terms—Sintering, Dilatometry, Phase transition

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I. INTRODUCTION

In the following work phase transition represents change from $ZnTiO_3$ to Zn_2TiO_4. Phase transition investigated here encounters following phases on phase diagram ZnO-TiO_2: Zn_2TiO_4 (zinc orthotitanate) which has an inverse cubic spinel structure (Fd^-3m) and it is stable from room temperature to its melting (liquid) temperature. $ZnTiO_3$ (zinc metatitanate) has a hexagonal ilmenite structure (R^-3), a variant of the corundum structure where the cations are ordered into two non-equivalent oxygen sites. Zinc metatitanate is stable from room temperature to 945.8°C. $Zn_2Ti_3O_8$ was first determined by Yamaguchi et al. [1] as a low temperature form of $ZnTiO_3$ having a defect cubic spinel structure with ordered cation vacancies leading to degradation of the space group symmetry from Fd^-3m to $P4_332$.

Phase transition belongs to second order phase transition. Since it is changed from metastabile to stabile phase, it has very fast kinetic rate, comparing, for example, to anatas - rutile phase transition [2]. Phase transitions are observed usually with the means that are enabling record of the property that comes with the emerging phase. Here volume change caused by structure change is registered as linear dilatation in a function of rising temperature. This leads to a possibility of phase transition kinetics observation.

Sintering phenomenon represents densification of the powder compacted in desired form during heating. Sintering dimensional change can during heating encompass phase transition dilatataion. Also specific influence of the nano powder during sintering is influencing phase transition kinetics. It is often compared to bulk polycrystalline kinetics of the same transition. This work intention is to use dilatometry as a tool for observing phase transition and sintering phenomena indicating their interdependent mutual relations.

II. METHOD

Experiment is set to record phase transition from $ZnTiO_3$ bulk specimen and $ZnTiO_3$ nano powder during sintering. $ZnTiO_3$ nanopowder, Aldrich [CAS 112036-43-0] was used. Two specimens are used for this purpose. Specimen 1 and specimen 2, respectively. Dilatometric thermo-mechanical analyzer TMA model SETSYS Evolution device was used. Specimens were compacted at 200 MPa uniaxially with both sided actions. Transmission electron microscopy of the nano powder $ZnTiO_3$ was performed on JEOL JEM 1400 plus microscope at 120kV and 150k enlargement.

Specimen 1 is heated to 1150°C non isothermally (1st run)

and phase transition during sintering is recorded using dilatometric oven. Without extracting it from dilatometric device specimen is heated again to 1150ºC, using same temperature schedule. (2nd run).

Specimen 2 is heated non-isothermally to 900ºC and then held 25 minutes at that temperature isothermally (1st run) and thus sintering of the $ZnTiO_3$ nanopowder is recorded. It is expected and confirmed that phase transition is absent. Same specimen 2, without extraction from the dilatometric device, is than heated again, but now to 1150ºC non-isothermally with previously used thermal schedule (2nd run). Obtained curve contains phase transition of $ZnTiO_3$ to Zn_2TiO_4 recorded from bulk specimen. All diagrams have been recorded on three heating rates - 20, 10 and 5ºC/min rate.

Stage of cooling is recorded as well with 20ºC/min rate. It is important to note that during cooling no intensive dimensional change is present. This implies that phase transition is irreversible.

III. RESULTS AND DISCUSSION

Nano dimensional powder sintering process assumes different mechanisms of mass transport compared to micro dimensional powder sintering. Transmission electron micrograph on Fig. 1 represents powders dimensional and morphology introspection. Powder particles are dimension bellow 40 nm, what is declared by the producer.
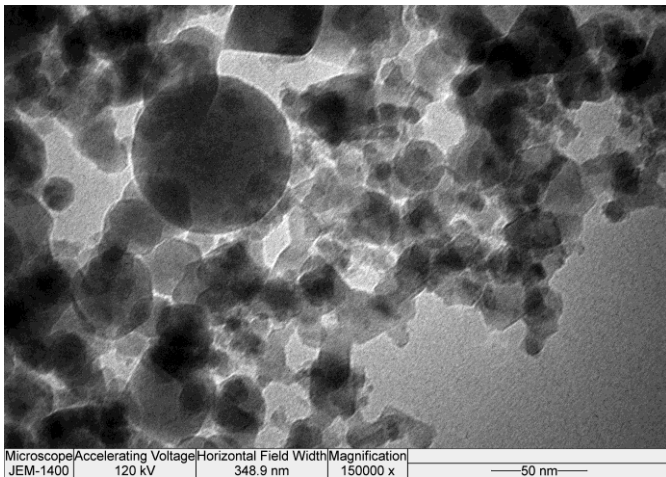

Fig. 1. TEM images of the nanopowder $ZnTiO_3$.

At Fig. 2 temperature experimental setup with whole interval dilatation curves and temperature programs are presented. Sintering phenomenon reaches 18% shrinkage while bulk specimen dimension change is represented with 3% shrinkage event. Phase transition record is marked with red square for bulk specimen and blue square for the powder sintering specimen.
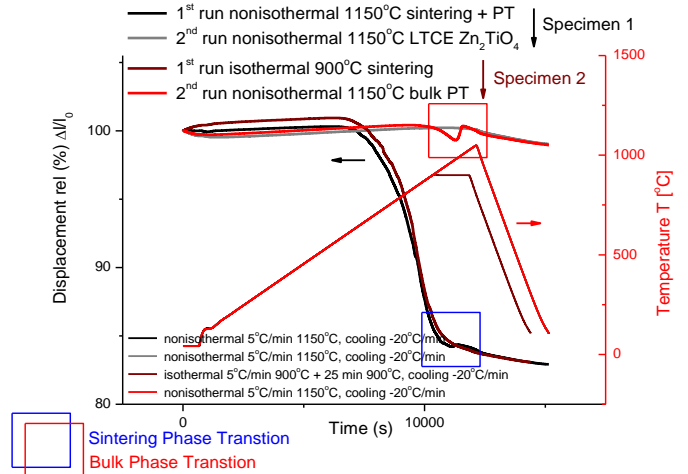

Fig. 2. Dilatometric curves and temperature programs for two specimens and four runs for the 20ºC/min speed, containing phase transition dilatation for bulk and powder specimen. Experimental setup.

Metastabile perovskite phase $ZnTiO_3$ reforms to stabile spinel Zn_2TiO_4 at 950ºC with high kinetic rate. The phase transition dimensional change diagram is consisted of sintering shrinkage and phase transition here on named as sintering. Obtained non-isothermally sintered specimens at were then second run treated with same schedule. Sintering phenomenon of the $ZnTiO_3$ nano-powder compact was also recorded up to 900ºC with isothermal holding of 25 minutes. Here phase transition was avoided with lower temperature and isothermal holding. Second run heating, of isothermally obtained specimens at 900ºC, was recorded with non-isothermal heating schedule to 1050ºC. This has led to the dilatometric curve record of the $ZnTiO_3$ phase transition in polycrystalline bulk specimen, now recorded without sintering, here on named - bulk.

All before mentioned was recorded for three different heating rates - 5ºC/min, 10ºC/min and 20ºC/min. It is presented all together and critical points are circled, red for the phase transition from bulk specimen, and blue circle for phase transition from powder during sintering Fig 3.
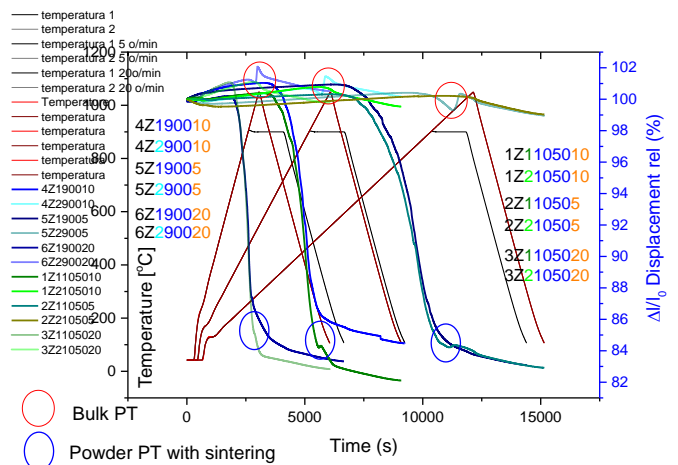

Fig. 3. Dilatometric curves, right axes and temperature programs left axes, heating rates 5, 10 and 20ºC/min.

It is worth to emphasize that on the presented diagrams phase transition during sintering 20ºC/min rate is not well distinguished, and also those final densities for 10ºC/min and 20ºC/min for non-isothermal sintering and isothermal are significantly different.

Extraction of the observed region with phase transition has been done in the 800ºC to 1100ºC, Fig. 4. Interval of the shrinkage curve heated isothermally is extracted as well. Heating rates 5, 10 and 20ºC/min.
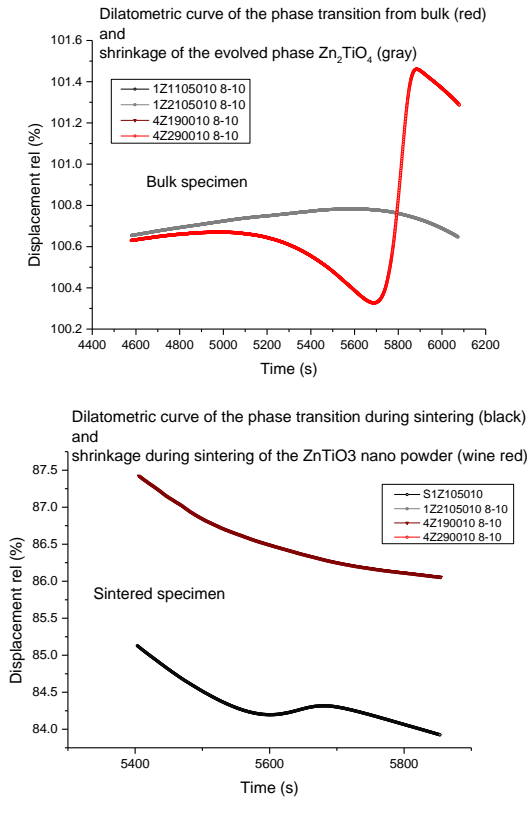

a)

b)

Fig 4. Dilatometric curves of phase transition $ZnTiO_3$ to Zn_2TiO_4 extracted phase transition interval a) observed in a bulk specimen (red), thermal expansion of the Zn_2TiO_4 phase (gray). b) Dilatometric curves of the phase transition and sintering (black), and sintering phenomenon without phase transition (wine red).
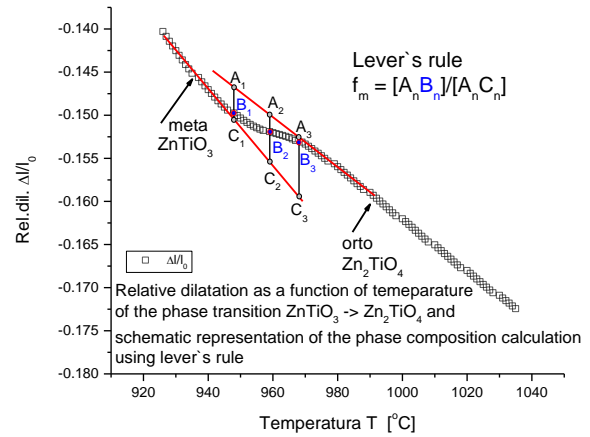

Fig 5. Relative dilatation as a function of temperature of the phase transition $ZnTiO_3$ -> Zn_2TiO_4 and schematic representation of the phase composition calculation using lever`s rule

Lever law is used in a XRD determination of the solvus curves - solid solubility curve on a phase diagram. It assumes that phases are in equilibrium during phase transition at each temperature. It also supposes that weight fraction of the observed phase amount varies linearly with composition from 0 to 1 [3].

At the dilatogram diagram, linearity, even with the sintering curve included, represents linear thermal expansion of the starting phase and can be fitted with linear function. Intensive deflexion from linearity is caused by phase transition dilatation. When phase transition is finished new phase again reaches linearity. Dimensional difference is caused by phase interchange and it is proportional to phase composition during phase transition. So, the distances AB, AC have to be determined and their relation AB/AC suites phase composition during phase transition, f=AB/AC, Fig 5. It is obvious that three sets of data are formed by the series made for each experimental point. Linear C data set, linear A data set and experimental set of curve B. All data sets have to posses same number of points since the subtraction ought to be performed. A and C sets have to be constructed. B is experimental dilatation. Than A minus B values make one column of Y. Similarly, A minus C forms second Column of Y and finally ratio AB/AC, third. AB/AC column plot in a function of temperature or time, represents kinetic curve of the phase transition.
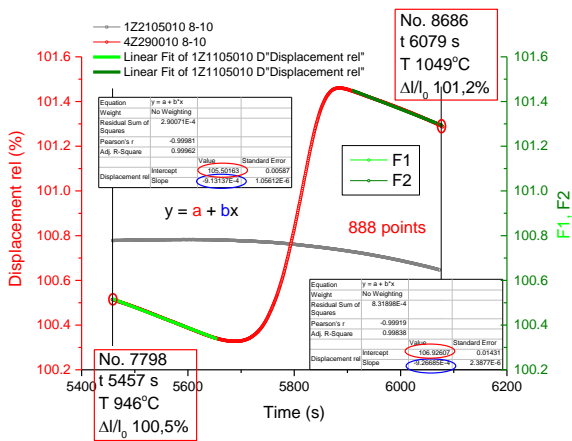
Fig 6. Linear fitting and interpolation of the inserted linear functions

At Fig. 6, phase transition curve was fitted in the linear regions before and after phase transition, light green and olive green portions of the red curve. Linear parameters of the line denoted as y= ax + b, where a is slope and b represents intercept. Number of points on the dilatometric curve in the observed interval is pointed out, it equals 888 points. Functions F1 and F2 are inserted to the graph with the interpolation of the linear functions points to the number of points that are resembling experimental dilatometric curve.

Procedure steps using Origin software after interval extraction consists of:

1. Detecting characteristic values of points and labeling them as starting and end point - No., t seconds, Temperature T, displacement shrinkage %

2. Determent of the number of points that interval consists of, here 888 points.

3. Determent of the interval that represents straight line on the begging and end of the graph that you want to fit linear. Origin software - Data, -> Mark data range, or Data selector, markers left and right positioned on the graph by cursor, Enter.

4. Linear fit of the beginning, left part, of the red curve and of the end, right part - linear fit tool – Analysis, -> Fitting -> Linear fit. Determent Y=a+bX relation from data sheet. Slope a and intercept b.

5. Adding a function graph F1 and F2 consisted of straight lines. The function insertion uses a and b parameters determined for left and right part of dilatometric curve, here light green and olive green parts. Graph -> Add Function Graph -> F2(x) = 3,31697-0,00254 * x where (example) 3,31697 is intercept b and 0,00254 is slope a parameter. -> Add. Number of points will be set to 100. Auto X range and Display curve – checked.-> Apply

6. Interpolation of the number of points on the F1 and F2 to experimental number, here 888. F1 select -> workbook -> Name of the data set image of F1, F1-C2 Enter. Graph of FuncCopy will be plot. Select function you want to Interpolate. Go to Workbook button. -> Workbook , C2-Y column Sheet 1, Analysis-> Mathematics -> Interpolate/Extrapolate -

> Open dialog -> Input C2 Y, method Linear, Number of points determined at 2 (888). Decheck Auto, X minimum enter the left minimal value determined at 1. here (5457 s), Decheck Auto, X maximum same procedure now X maximum here (8686 s), Output new sheet, -> Ok.

7. Organize workbook of the experimental data with interpolated values columns and subtract columns AB and AC, and AB/AC according to the levers rule. Plot the function AB/AC as a function of time or temperature that represents phase composition.
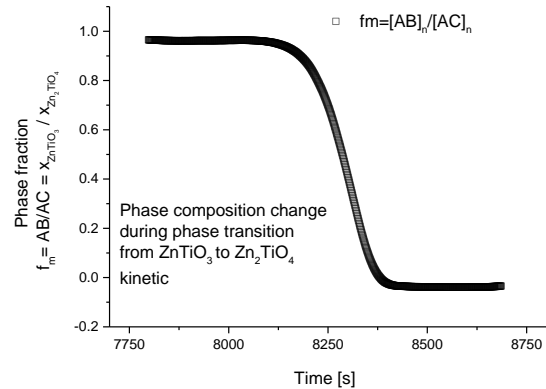

Fig 7. Dilatometric curve that represents phase composition change during phase transition from $ZnTiO_3$ to Zn_2TiO_4.

Sigmoidal curve obtained by the described procedure is presented at Fig 7. It represents disappearing of starting phase $ZnTiO_3$ and appearance of the evolving phase Zn_2TiO_4. This curve allows us to observe and, furthermore, even to discuss the kinetic of the phase transition.
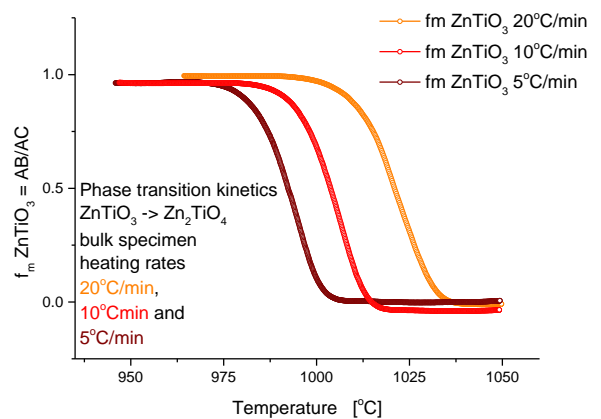

Fig 8. Phase transition kinetic from bulk specimen, three heating rates: 20°C/min 10°C/min and 5°C/min.

Phase transition from bulk specimen as a function of temperature, three heating rates, 20 10 and 5 °C/min, orange 20°C/min, red 10°C/min and wine 5°C/min represented at Fig. 8. Since the temperature is a linear function of the time, due to non isothermal heating schedule, temperature scale is used. Change of the phase composition represents phase transition

kinetic. Note that temperature of the curve center is the point with highest rate of phase transition. If the temperature of the phase transition observed, with higher heating rate, temperature of the phase transition is higher - 20°C/min 1021°C, 10°C/min 1004°C, 5°C/min 993°C. It is as well higher than expected 945°C for the phase diagram of $ZnTiO_3$ [4]. Nano-dimensions are introducing difference, as well as composition, since it is $ZnTiO_3$ pure.
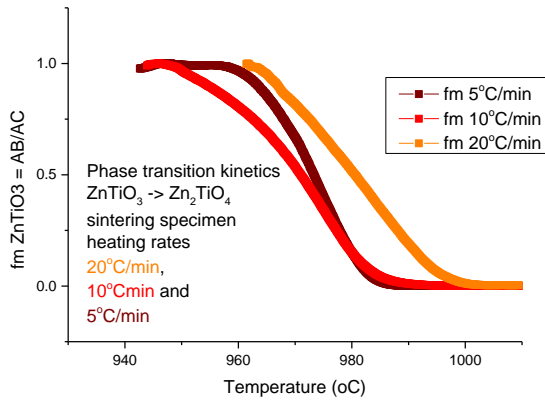

Fig 9. Phase transition kinetic from powder sintered specimen, three heating rates: 20 °C/min 10°C/min and 5°C/min.

It is obvious that curves at Fig. 9 for the phase transition kinetic for the sintered specimen do not resemble heating rate rise trend. Also, the shape is more irregular mutually for the different heating rates and also different regarding the bulk specimen curves.

Mathematical procedures enabling comparison of the data were necessary since data obtained by levers rule are different in their appearance due to physical phenomena they include. First, all values must be positive. Then, second, to compare them they must be in the zero to one values interval. Third, if the function is monotonically increasing than it should be converted to monotonically decreasing due to the convention that we observe disappearing phase.

Minimal value for the every set of data was determined by applying column statistic tool. Determined value is than added to all values in the column what has led to all values of the function are positive

1. fm > 0

Maximal value for the every set of data was determined by applying column statistic tool. Determined maxima value is used to divide all values with, what has led to the norming boundary condition - all values are inside of [0,1] set

2. fm [0,1]

Column values were finally inverted by subtracting them from 1. Parent phase disappearance shape is thus established. Function is presented as monotonically decreasing when this trend is absent due to final sintering stage influence.
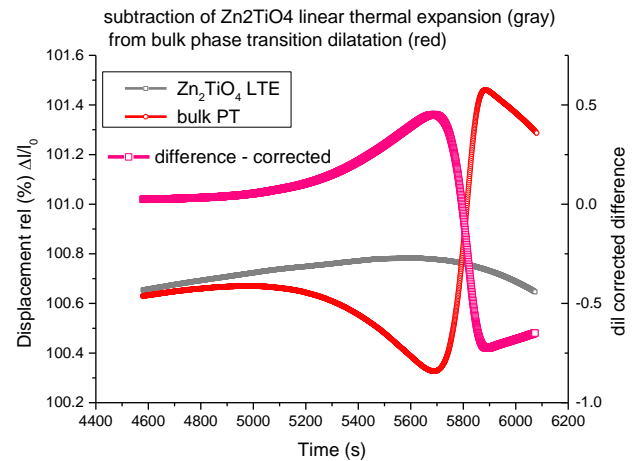
3. fm = 1- [col]

Fig 10. Correction by subtraction for the bulk specimen.

Dilatometric curves should be corrected mainly for the dilatation of the carrier system and pushing rod material enlargement. In the device with two samples, in the differential dilatometry, this procedure is done during the experiment. Here, we have decided to subtract linear dilatation of the Zn_2TiO_4 bulk sample, from phase transition recorded from bulk.

Specimen that was heated to 1050°C passed through phase transition Fig. 10, (red). Specimen was second time heated to the same temperature and this second curve represents linear thermal expansion of the evolved phase Zn_2TiO_4 (gray). This set of values will be subtracted from curve with phase transition obtained from bulk specimen (red). Pink curve represents difference – corrected curve (pink). Number of points that are going to be subtracted is often equal, and if it is not - interpolation to the number of points present in the experimental phase transition curve is performed.
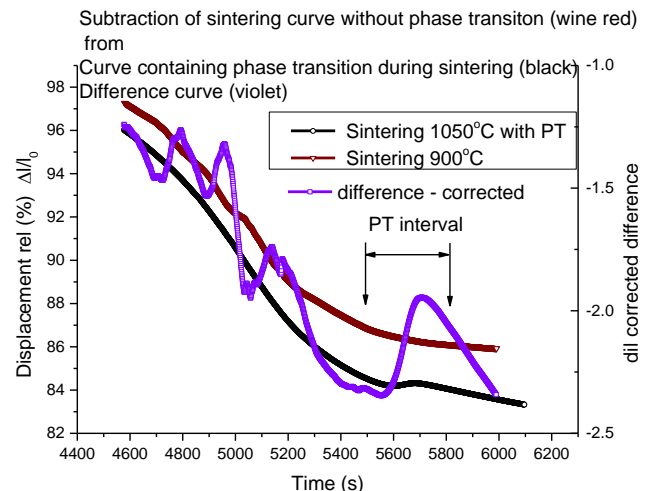

Fig 11. Correction by subtraction for the powder -sintered.

Correction by subtraction of sintering curve 900°C without phase transition (wine red) from sintering curve 1050°C that is containing phase transition during sintering (black) is performed, figure 11. Difference corrected curve is obtained (violet). Large interval was presented to show that difference

curve (violet) consists of irregularities, Fig. 11. Observed Phase Transition interval (PT interval) was extracted. The absence of stability for the resulting curve origins from sintering phenomenon when nano-powder is used. High shrinkage rates and overall large shrinkage is present due to rearrangement of highly agglomerated powder and also from intensive recrystallization and grain growth. It should be mentioned that sintering curve at 900°C was obtained by combination of non-isothermal and isothermal temperature program sequence. Yet, correction calculation was performed.

From the difference corrected curve, by the levers rule usage, the kinetic phase transition curves for bulk and sintering specimens are obtained, Fig. 12.
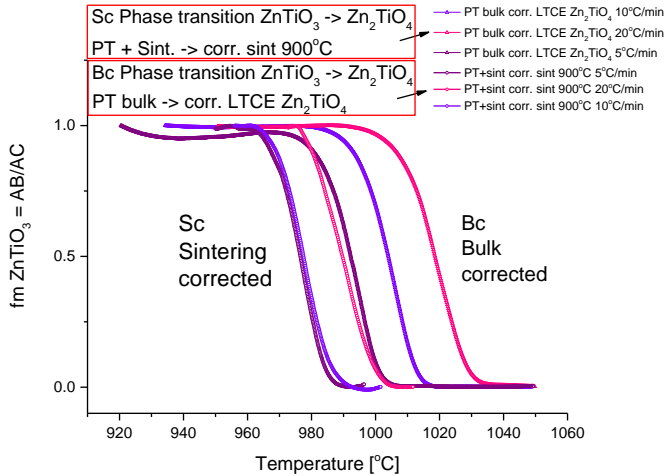

Fig 12. Phase transition kinetics comparison: Corrected curves for phase transition from Bulk and Sintered specimens.

At fig.12, obtained corrected curves for Bulk and Sintering are presented separately from experimental curves at fig. 9 and 10. Pink, violet and purple colors are subscribed to 20, 10 and 5°C/min heating rate, respectively. Sintering corrected curves does not follow heating rate sequence. This fact is expected since experimental curves are distributed in the same manner. Sintering corrected specimens' curves for heating rates 10°C/min and 5°C/min are close each other. Bulk corrected curves are well distributed following the rise of the heating rate parameter.

It is interesting to make a phase transition kinetics comparison: Bulk vs. Sintered and also Experimental vs. Corrected, Fig. 13. All curves are presented together. Good match of the bulk curves between experimental and corrected is visible. Sintered are showing deviations between experimental and corrected. Deviation is in the position of the curve, as well as in the shape. This implies great influence of sintering phenomenon on the phase transition, thermodynamically as well as kinetically. Temperature scale disproportion implies activation energy difference, while curve shape implies kinetic difference.
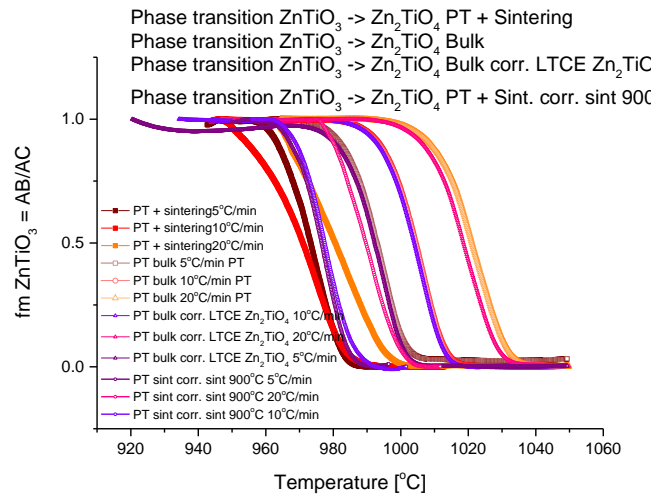

Fig 13. Phase transition kinetics comparison: Bulk and Sintered, Experimental vs. Corrected.

Although the previous comparison has led to some of the conclusions we have presented, quantitative comparison needs fitting function and overlapping measure determination of the constructed function with experimental curve. We have chosen Sigmoid shape - Boltzmann fitting function. Formula of the fitting function is given in the equation (1). Boltzmann fitting function has two constant values for the y = A1 and A2. Maximal rate represents X0, and ((A1+A2)/2), set of values. Shape of the curve, on the Fig. 14, gives good resemblance comparing to other offered functions in the Origin software package [6]. Although shape represents rise of the emerging phase, constants A1 and A2 enable as well diminishing shape. Fitting function resembles Johnson-Mehl-Avrami-Kolmogorov (JMAK) expression for the model of the kinetics for the isothermal phase transformations [5]. Their phenomenological model is often used for crystallization process and solid phase transition kinetic description.
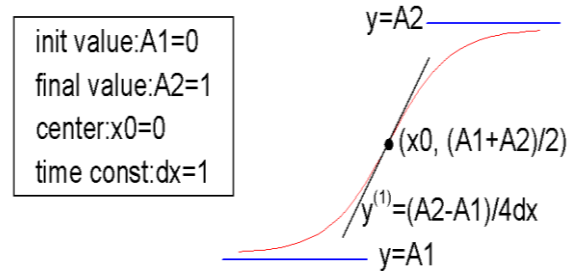

Fig 14. Sigmoid shape - Boltzmann fitting function for phase transition kinetic process.

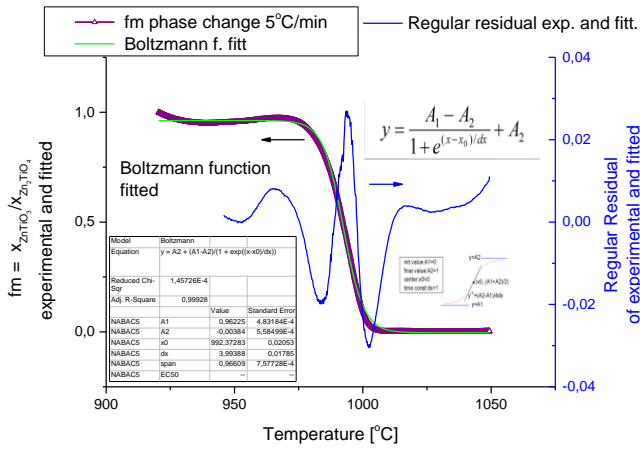$$y = \frac{A_1 - A_2}{1 + e^{(x-x_0)/dx}} + A_2$$

(1)

Fig 15. Phase transition curve, Boltzmann fitting function – Bulk, corrected, 5ºC/min.

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Example of the fitting function is presented on Fig 15. Fitting function (light green thin) for the experimental set of data (purple bold). Regular residual curve quantifies resemblance (blue, right axes). Table inserted represents fitting function parameters listed in a report data sheet of the fitting procedure. Residuals are the measure of discrepancy with the experimental curve and they also are listed in a report data sheet.
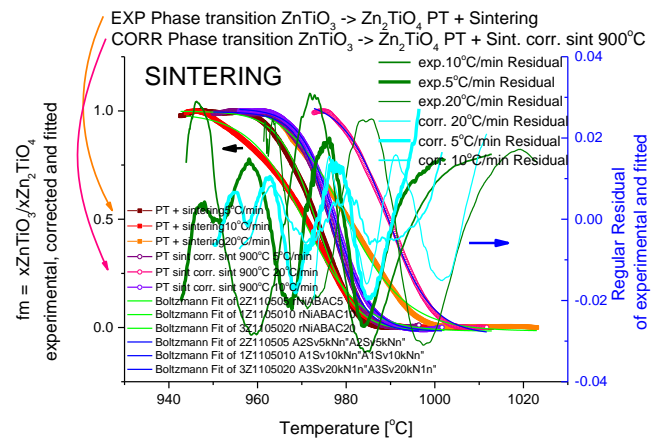

Fig 16. Bulk phase transition curve, 5, 10, 20ºC/min, experimental and corrected, Boltzmann function fitted – Residuals

Curves presented at Fig. 16 of experimental and corrected curves are bold with symbols in the colors previously used. Fitted function is green thin line for experimental and blue thin line for corrected curves, all on left axes. It is visible that residuals (cyan and olive, thickness refers to a heating rate, right axe) for the experimental and corrected curves are mutually resembling, Fig. 16. This implies that corrected curves are following fitting equation just as good as experimental. Only 20ºC /min are somewhat shifted. This can be subscribed to the fact that at larger heating rates stress - strain relation is not negligible.

Fig 17. Sintering phase transition curve, 5, 10, 20ºC/min, experimental and corrected, Boltzmann function fitted – Residuals

Same procedure of fitting for experimental and corrected curves with Boltzmann function is performed at sintering phase transition curve, Fig. 17, left axes. Residual functions for experimental (olive) and corrected (cyan) are showing intensive difference for the corrected and experimental, right axes. If the fitted functions are observed for experimental (green thin) and corrected (blue thin), it is obvious that shape of the curve that represents phase transition with correction is showing more resemblance with the sigmoid shape. Thus, the made correction is more reasonable.
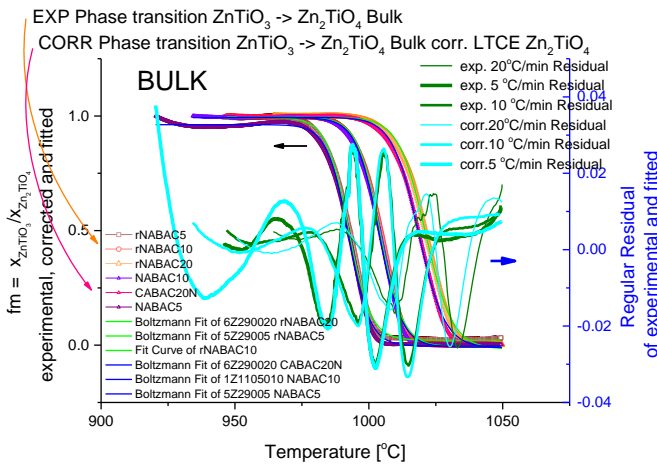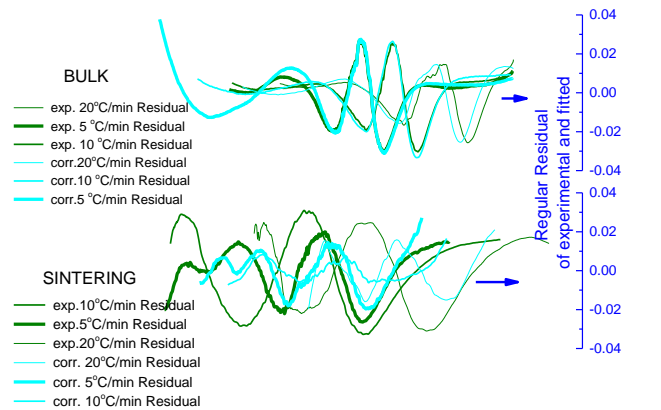

Fig 18. Fitting function Residuals comparison Boltzmann function fitted – Residuals, Sintering phase transition curve, 5, 10, 20ºC/min, experimental and corrected, Bulk phase transition curve, 5, 10, 20ºC/min, experimental and corrected.

Fitting function Residuals comparison experimental and corrected – Bulk and Sintered brings a reason that if we are comparing just residuals, Fig. 18, the conclusion drawn is that the sintering correction brings large misfit comparing to the bulk. The misfit is for the sintering residuals, as well for the different heating rates presented with different thickness of the line. Experimental curves misfit for the sintering residuals are significant (Sintering, olive, different thickness).

IV. Conclusion

Physical differentiation of the sintering shrinkage and Phase transition phenomena dilatation has been compared with mathematical data manipulation of the sintering curve and phase transition subtraction. It is found that data manipulation procedure does not give the reliable results.

Although a thorough procedure for the phase transition kinetic data achieving from the dilatometric data and fitting procedure with sigmoidal function has been established.

Acknowledgment

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