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Discrete Temperature Values in the Sintering Process as a BaTiO₃-ceramics Properties Parameter

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Abstract:

In this paper, we develop the new physical-mathematical time scale approach-model applied to BaTiO₃-ceramics. At the beginning, a time scale is defined to be an arbitrary closed subset of the real numbers R , with the standard inherited topology. The time scale mathematical examples include real numbers R , natural numbers N , integers Z , the Cantor set (i.e. fractals), and any finite union of closed intervals of R . Calculus on time scales (TSC) was established in 1988 by Stefan Hilger. TSC, by construction, is used to describe the complex process. This method may be utilized for a description of physical, material (crystal growth kinetics, physical chemistry kinetics - for example, kinetics of barium-titanate synthesis), bio-chemical or similar systems and represents a major challenge for nowadays contemporary scientists. Generally speaking, such processes may be described by a discrete time scale. Reasonably it could be assumed that such a "scenario" is possible for discrete temperature values as a consolidation parameter which is the basic ceramics description properties. In this work, BaTiO₃-ceramics discrete temperature as thermodynamics parameter with temperature step h and the basic temperature point a is investigated. Instead of derivations, it is used backward differences with respect to temperature. The main conclusion is made towards ceramics materials temperature as description parameter.

Keywords: BaTiO₃-ceramics; the Discrete scale of temperature; TSC.

1. Introduction

Timescale calculus (TSC), as a relatively new physical-mathematical method, is shown in [1-3]. Therefore, in scientific records, we have analyzed that is evident a relatively small number appropriate applications or numerical methods for solving such nonlinear problems. A good choice for solving numerical or practical problems described by the system of nonlinear differential equations is the multi-step differential transformation method - MSDTM [4], [5]. The advantage of the method is that it does not require perturbation or linearization and works as a semi analytical-numerical method that provides a solution in terms of easily computable convergent series.

As it is well known, in Nature exist several examples of kinetics: classical mechanics (as a synonym of dynamics), fluid equations, plasma and chemical kinetics, particularly in chemical physics and physical chemistry and biology kinetics [6-13]. Up to now, we performed, with this method, investigations within the organic bio-material processes. From

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the other side, in the area of non-organic materials, we investigate BaTiO₃-ceramics [14-21] as a complex material example that is often in different applications.

BaTiO₃-based ceramics is one of the most popular and the most extensively investigated ferroelectric material, widely used for multilayer capacitors (MLCCs), PTC thermistors, varistors and dynamic random access memories (DRAM) in integrated circuits due to their ferroelectric and/or semiconducting properties which can be tailored to meet the particular requirements of devices; almost more than 300 applications.

Barium-titanate, is a typical representative of the crystallographic perovskites family, named after the mineral perovskite, CaTiO₃ each member having the same basic, cubic structure.

Below its Curie temperature, $T_c \sim 120^\circ\text{C}$ barium-titanate exhibits properties typical of ferroelectrics, i.e. hysteresis between polarization and electric field, the pyroelectric and piezoelectric effect. Also, it is a semiconductor with positive temperature coefficient of resistivity.

BaTiO₃ has become one of the most important electroceramic materials among all the ferroelectric materials. It differs from other ferroelectric materials: it exhibits three phase changes, two below T_c and one above T_c the cubic perovskite phase, which is centrosymmetric, sTab. and non-polar.

The single crystals growth time kinetics process is usually time-consuming, while the ceramic microstructures complexities properties prediction from those of the corresponding single crystal are very uncertain. Consequently, empirical observations usually lead to the new devices based on ceramics, even before getting some partial understanding of the underlying physical mechanisms. Barium-titanate ceramics synthesis methods were mentioned in a lot of papers. Here, just a part is used: conventional solid-state reaction, sol-gel, hydrothermal, co-precipitation, polymeric precursor and other consolidation methods as well as a mechanic - activated synthesis. All of these, sintering time and other parameters, are the future research and analysis subject, which are planned for further works.

In the literature, there are two known approaches to the concept of nature systems discrete time [22, 23]. The first approach is a primary physical, and it is assumed the existence of time particles - chronons. The second approach is biological - the discrete time is understood as a crystal time. In the literature, it is also the well known concept of temperature over the imaginary time [24]. Therefore, the assumption that the temperature of the system has its own scale and positive discrete value is accepTab.. This is basic idea for investigation in this paper.

As it is mentioned above, the multi-step difference transformation method (MSDETM), a generalization of MSDTM in the sense that it supplies solution even if $h \rightarrow 0+$, is formulated. It is based on the transformation of functions to the corresponding Taylor series. Also, for the fitting data of the Taylor series, an equation model assuming thermomechanical condition is formed: the density of the used BaTiO₃-ceramics by pressing pressure influence and sintering temperature which *exists* as a ceramics material natural temperature scale. Here, the temperature is considered as the basic consolidation parameter, like the time, which is also a fundamental consolidation parameter.

2. Analysis of methods and experimental data

2.1. Standard experimental procedures and BaTiO₃-ceramics natural variables relations

The samples were prepared from commercial, pure BaTiO₃ powder (MURATA) with the CeO₂ additive.

The presented powders process preparing is fully applied to CeO₂ doped BaTiO₃ powder consolidation. It was done by MURATA technology but PENTRONIX – PTX –

GASBARRE consolidation is also available.

Sintering was performed in an electric tunnel furnace (CT-10 Murata) at temperatures from 1190°C to 1370°C samples have been located in special containers (saggers), and were set for two hours sintering over different pressures, as it will be shown in Tab. I. It is evident that samples BaTiO₃ doped by 0.3 wt% CeO₂ were prepared by using conventional solid-state procedure, the usual technical detail important for referent comparison.

In the next subsection displays the necessary mathematical basis for a new type of fitting experimental results in Section 3. In the following chapter will discuss some types discrete or continuous depending on the function ρ (density of ceramics) from T sintering temperature and p is pressing pressure. The applied multistep model can operate with sintering temperature T as both discrete or continuous variable.

2.2. On a class of multi-step methods

Differential transform methods can be efficiently and economically applied to high non-linear problems since it reduces the size of computational work. The multistep differential transform method (MSDETM) yields a continuous representation of the approximate solution, which allows better information of the solution over the time interval. So, such method is suitable for describing the dynamics of sintering processes. Here, it is applied on BaTiO₃-ceramics sintering.

The multistep differential transform method (MSDTM) is based on backward difference calculus. The first backward difference of a discrete real function, for $h > 0$, $f_D(t)$: $h\mathbf{Z} \rightarrow \mathbf{R}$ is defined by

$$(\nabla_h f_D)(t) := \frac{f_D(t) - f_D(t-h)}{h}, \quad (1)$$

Then there exists analog of Taylor's series and appropriate transformations, for $f_D(t)$. k -th backward difference at the point t_0 element of $h\mathbf{Z}$ is:

$$F_D(k) = \frac{(\nabla_h^k f_D)(t_0)}{k!}, \quad (2)$$

provided

$$(t-t_0)_h^{(k)} := h^k \frac{\Gamma\left(\frac{t-t_0}{h} + 1\right)}{\Gamma\left(\frac{t-t_0}{h} + 1 - k\right)} \quad (3)$$

the h -factorial function Taylor's series is ($K \in \mathbf{N}_0$):

$$f_D(t) = \sum_{k=0}^K F_D(k) (t-t_0)_h^{(k)}. \quad (4)$$

For $h \rightarrow 0_+$, Eqs. (2) and (4), respectively tends to

$$F(k) := \frac{(f^{(k)}(t_0))}{k!}, \quad (5)$$

and

$$f(t) = \sum_{k=0}^K F(k)(t-t_0)^k. \quad (6)$$

Also, the (continuum limit) $(t-t_0)_h^{(k)} \rightarrow (t-t_0)^k$ is valid.

Consider following nonlinear initial value problem of first-order difference equation:

$$\nabla_h f_D(t) = G_D(t, f_D) \quad (7)$$

subject to the initial condition $f_D(t_0=0) = c_0$; with real functions $G_D(t, f)$ and $f_D(t)$, MSDETM is formulated as follows. Let $\{0, \Delta t, \dots, T\}$ $m=1, 2, \dots, M$, $\Delta t = T/M = l \cdot h$ ($l \in \mathbf{N}$), be the discrete set over which we want to find the solution of the initial value problem (7). Set of nodes $\{0, \Delta t, \dots, T\}$ define M equal size sub-intervals $[t_{m-1}, t_m]$, $m=1, 2, \dots, M$, $t_0=0$. A sequence of approximate solutions $f_{Dm}(t)$, $m = 1, 2, \dots, M$ are given by:

$$f_D(t) = \begin{cases} f_{D1}(t) & t \in [0, t_1], \\ f_{D2}(t) & t \in [t_1, t_2], \\ \vdots & \\ f_{DM}(t) & t \in [t_{M-1}, t_M], \end{cases} \quad (8)$$

in the sense:

$$f_D(t) = \sum_{k=0}^K F_D(k)(t-t_0)_h^{(k)}, \quad (9)$$

with initial conditions:

$$f_{Dk}(t_{k-1}) \equiv F_D(0, k), \quad k = 2, 3, \dots, M \quad (10)$$

The main steps of the MSDETM, are: (1) We apply the difference transformation to the problem (7), the result is a recurrence relation for $F(k, m)$; (2) Solving this relation over each time sub-interval $[t_{m-1}, t_m]$, $m = 1, 2, \dots, M$, bearing in the mind initial conditions, and using the difference inverse transformation one can obtain the solution of the problem. With $\Delta t = T$, MSDETM reduces to the DETM. With small values of h , *i.e.* $h \rightarrow 0_+$ in (1), and $\Delta t = \text{const}$, in (8), MSDETM reduces to the MSDTM in the spirit of TSC. The sintering time is set to be fixed ($t_s = 2h$). Obtaining Taylor series of given function is the essence of the considered method.

3. Results and Discussion

In this paper, we considered that the ceramics, in this case, electronic ceramics materials have its own consolidation temperature and pressing pressure over the discrete scale. These are material properties, which are optimal for the concrete material consolidation processes. The temperature in the literature is formally known as an inverse imaginary time

[24]. This idea is more accurately expressed in the paper [26] and is the basis for this work. For BaTiO₃-ceramics the following equation of thermomechanics state will be considered $\rho = \rho(T, p, t)$, where t as sintering time keeps constant, $t = t_s$, so that:

$$\rho = \rho(T, p, t_s), \quad (11)$$

ρ is the density of ceramics, T sintering temperature, and p is pressing pressure. Experimental data are given in Tab. I. In our experiment, t_s is set to 2 hours.

Let us assume that ceramics, as a material property, has its own temperature and pressing pressure over the discrete scale. In addition to discrete polynomial, the discrete exponential function [27]:

$$e_{h\alpha}(x, x_0) := (1 + \alpha \cdot h)^{\frac{x-x_0}{h}}. \quad (12)$$

will be used. Let $h \rightarrow 0+$, then:

$$e_{h\alpha}(x, x_0) \rightarrow e^{\alpha(x-x_0)}.$$

Also, there exists corresponding discrete logarithm function:

$$\log_{h\alpha}(x, x_0) := h \cdot \log_{1+\alpha h}(x/x_0). \quad (13)$$

In the process of fitting considered as discrete and continuous exponential, polynomial, logarithm, power functions and their combinations, bearing in mind the that the maximum number of parameters is 15. The fitting was done in the MATLAB environment.

Tab. I Experimental data for technological parameters: sintering temperature T , pressing pressure p (for $t_s = 2h$) and BaTiO ₃ -ceramics density ρ [25]:		
T [°C]	p [MPa]	ρ [10^3 kg/m ³]
1190	86	5.4
1190	105	5.3
1190	130	5.4
1190	150	5.5
1240	86	5.5
1240	105	5.6
1240	130	5.6
1240	150	5.6
1290	86	5.5
1290	105	5.4
1290	130	5.2
1290	150	5.5
1370	86	5.2
1370	105	5.6
1370	130	5.4
1370	150	5.3

Other experimental conditions in Tab. I are: the used samples sintered for $2h$, doped with additives of 0.3 wt% CeO₂. Two basic types of functions of T and p have the best fitting

characteristics: ordinary polynomial and mixed polynomial. In the second, better case it is shown that the temperature of sintering has a discrete physical size, i.e., that ceramics has its own characteristic temperature scale. Concrete the best fitted two-dimensional functional dependency - mixed polynomial ($x = T, y = p, z = \rho$) is:

$$\begin{aligned} f(x, y) = & p_{00} + p_{10}(x-a) + p_{01}y + p_{20}(x-a)(x-a-h) + \\ & p_{11}(x-a)y + p_{02}y^2 + p_{30}(x-a)(x-a-h)(x-a-2h) + \\ & p_{21}(x-a)(x-a-h)y + p_{12}(x-a)y^2 + p_{03}y^3, \end{aligned} \quad (14)$$

where p_{ij} , $i, j = 0, 1, 2, 3$, h and a are fitting parameters. With $a=0$ and $h=0$ we get pure polynomial appearance. In equation (14) instead of variable y (p) are used the logarithmic and exponential functions ($\ln(p/p_0)$, $\exp(p/p_0)$). The variable $x(T)$, which is examining whether discrete or continuous, For variable $x(T)$ being tested whether discrete or continuous, are possible following substitutes: $(x-a) \rightarrow e_{\text{hd}}(x, a)$, $(x-a-h) \rightarrow e_{\text{hd}}(x, a+h)$, $(x-a-2h) \rightarrow e_{\text{hd}}(x, a+2h)$, $(x-a) \rightarrow \log_{\text{hd}}(x, a)$, $(x-a-h) \rightarrow \log_{\text{hd}}(x, a+h)$, $(x-a-2h) \rightarrow \log_{\text{hd}}(x, a+2h)$.

Tab. II Values of fitting parameters for experimental data gives in Tab. I- mixed polynomial.

Parameters	Values	Units
a	1278	$^{\circ}\text{C}$
h	97.48	$^{\circ}\text{C}$
p_{00}	-2.041	MPa
p_{01}	0.1988	$\text{kg}/(\text{m}^3\text{MPa})$
p_{02}	-0.001715	$\text{kg}/(\text{m}^3(\text{MPa})^2)$
p_{03}	$4.818 \cdot 10^{-6}$	$\text{kg}/(\text{m}^3(\text{MPa})^3)$
p_{10}	-0.02441	$\text{kg}/(\text{m}^3\text{C})$
p_{11}	0.0004211	$\text{kg}/(\text{m}^3\text{CMPa})$
p_{12}	$-1.766 \cdot 10^{-6}$	$\text{kg}/(\text{m}^3\text{C}(\text{MPa})^2)$
p_{20}	0.0001233	$\text{kg}/(\text{m}^3\text{C}^2)$
p_{21}	$1.711 \cdot 10^{-7}$	$\text{kg}/(\text{m}^3\text{C}^2\text{MPa})$
p_{30}	$5.246 \cdot 10^{-7}$	$\text{kg}/(\text{m}^3\text{C}^3)$

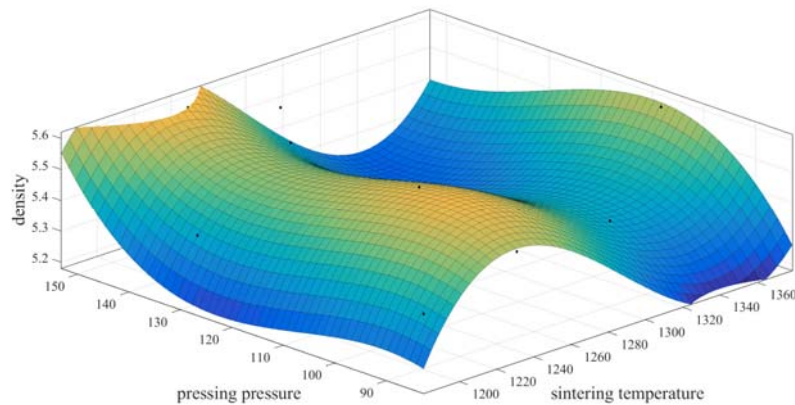


Fig. 1. Two-dimensional fitted surface, whose is given by the equation (14) and parameter values from the Tab. II.

Goodness of fit in the second case are: $SSE= 0.1024$, $R_{\text{square}} = 0.7903$, $\text{Adj } R_{\text{square}} = 0.0773$ and $RMSE=0.1204$ (SSE - sum squared error, $RMSE$ - root mean square error, R_{square} - coefficient of determination, $\text{Adj } R_{\text{square}}$ - adjusted R_{square}). Results of fit shown in Tab. II and Fig. 1.

For pure polynomial appearance, goodness of fit given by values $SSE= 0.1135$, $R_{\text{square}} = 0.6309$, $\text{Adj } R_{\text{square}} = -0.1094$ and $RMSE=0.1433$.

The main conclusions of these results that there are two material properties of doped BaTiO_3 -ceramics - basic point temperature $a = 1278^\circ\text{C}$ and the temperature step $h = 97.48^\circ\text{C}$, in the terms of backward difference calculus. Thus, the temperature 1278°C with the temperature step 97.48 produces ceramics of optimal density.

4. Conclusions

BaTiO_3 -ceramics discrete temperature properties, with two material constants - basic temperature point a and temperature step h , are investigated. It is a new contribution, although empirically, in the ceramics sciences. In this sense, TSC, the differential-difference calculus, and MSDETM represent a good basis for the use of a new mathematical apparatus for studying materials science, concretely in this paper electronics ceramics materials.

The result of the application of MSDETM method is founding an optimal point in the (temperature, temperature step) space which traces a way of employing this method in the optimization of the technological process of barium-titanate and other ceramics sintering.

5. References

1. Bohner M., Peterson A., "Dynamic equations on time scales", Birkhauser, Boston, 2001.
2. Bohner M., Peterson A., Eds. "Advances in Dynamic Equations on Time Scales". Birkhauser, Boston, 2003.
3. Atici F. M, Sengul S., "Modeling with fractional difference equations", J. Math Anal Appl., 369(1) (2010) 1-9.
4. Odibat M. Z., Bertelle C., Aziz-Alaoui M. A., Duchamp G. H. E., "A multi-step differential transform method and application to nonchaotic or chaotic systems", Comput Math Appl., 59(4) (2010) 1462-1472.
5. Alawneh A., "Application of the Multistep Generalized Differential Transform Method to Solve a Time-Fractional Enzyme Kinetics", Discrete Dyn. Nat. Soc., 7 (2013) 592938.
6. Whittaker E. T., "A Treatise on the Analytical Dynamics of Particles and Rigid Bodies", Cambridge University Press, 1993.
7. Lifshitz E. M., Pitaevskii L. P., Sykes J. B., Franklin R. N., "Physical Kinetics". Butterworth-Heinemann, 1981.
8. Tsallis C., "Nonextensive statistics: Theoretical, experimental and computational evidences and connections", Brazilian Journal of Physics, 29 (1999).
9. Alexeev B. V., "Generalized Boltzmann Physical Kinetics", Elsevier, 2004.
10. Gorelik G. E., Pavlyukevich N. V., Levdansky V. V., Leitsina V. G., Rudin G. I., "Physical Kinetics and Transfer Processes in Phase Transitions", Begell House, 1995.
11. Krainov V. P., Hendzel K., "Qualitative Methods in Physical Kinetics and Hydrodynamics", Springer, 1992.
12. Steinfeld J. I., Francisco J. S., Hase W. L., "Chemical Kinetics and Dynamics", 2nd ed., Prentice-Hall, 1999.

13. Resat H., Petzold L., Pettigrew M. F., "Kinetic modeling of biological systems", *Methods Mol. Biol.*, 2009;541:311-35.
14. Hertl W., "Kinetics of Barium Titanate Synthesis". *J. Am. Ceram. Soc.*, 71, 10 (1988) 79-83.
15. Testino A., Buscaglia V., Buscaglia M. T., Viviani M., Nanni P., "Kinetic Modeling of Aqueous and Hydrothermal Synthesis of Barium Titanate (BaTiO_3)", *Chem. Mater.*, 17 (2005) 5346-5356.
16. Vijatović M. M., Bobić J. D., Stojanović B. D., "History and Challenges of Barium Titanate: Part I", *Science of Sintering*, 40 (2008) 155-165.
17. Vijatović M. M., Bobić J. D., Stojanović B. D., "History and Challenges of Barium Titanate: Part II", *Science of Sintering*, 40 (2008) 235-244.
18. Mitić V. V., Nikolić Z. S., Ristić M. M., "The influence of pressing pressure of ferroelectric characteristics of BaTiO_3 -ceramics", Annual Meeting of the American Ceramic Society, Ohio, Cincinnati, May 1-3, 1995.
19. Chiang S. K., Lee W. E., Readey D. W., "Evolution of the core-shell grain structure in temperature-sTab. doped BaTiO_3 ", Proc. Industry University Advanced Materials Conf. Denver C. 1989.
20. Jordović B., Mitić V., Nikolić Z. S., "Effects of sintering time and temperature on BaTiO_3 -ceramic microstructured characteristics", *Acta stereologica.*, 13 (2) (1994) 381-388.
21. Mitić V., Nikolić Z. S., Ristić M. M., "The frequent characteristics of BaTiO_3 -ceramics as a function of sintering temperature", International Conference on the Science, Technology and Applicatios of Sintering, Penn State of University, September 24-27, 1995.
22. Jaroszkiewicz G., "Principles of Discrete Time Mechanics", University Printing House, Cambridge CB2 8BS, United Kingdom, 2014.
23. Eds Marsden J E, Sirovich L, Wiggins S. "The Geometry of Biological Time". Second Edition, Springer Verlag, New York, 2001.
24. Mahan G., "Many-particle physics", Kluwer Academic/Plenum Publishers, 2000.
25. Mitić V. V., "Structure and Electric Properties of BaTiO_3 -Ceramics", Zadužbina Andrejević, Beograd, 2001.
26. Z. Vosika Z, Mitić V. V, Vasić A., Lazović G., Matija L., Kocić Lj., " Multistep Generalized Transformation Method Applied to Solving Equations of Discrete and Continuous Time-Fractional Enzyme Kinetics", *Communications in Nonlinear Science and Numerical Simulation* (2016).
27. Hilger S., "Differential and Difference Calculus - Unified", *Nonlinear Anal.*, 30, 5 (1997) 2683-2694.

Садржај: У овом раду се примењује нови физичко математички приступ на BaTiO_3 -керамику заснован на рачуну временских скала (TSC). Временска скала се дефинише као неки затворени подскуп реалних бројева R , који поседује стандардну унутрашњу топологију. Типични математички примери временских скала су скуп реалних бројева R , скуп природних бројева N , целих бројева Z , Канторов скуп (фрактали) и свака коначна унија затворених интервала скупа R . TSC је 1988 формулисао Стефан Хилгер. По конструкцији, TSC описује сложене процесе. Он се може користити за моделовање физичких материјала (кинетику раста кристала, физико-хемијске кинетику, на пример, синтезу баријум титаната), биохемијских или сличних система и представља, као такав, велики изазов за савремену науку. Генерално говорећи, многи процеси могу бити описани дискретном временском скалом. Један од таквих могућих "сценарија" јесте дискретна температурна скала са карактеристичном бројном

вредношћу температурног корака као консолидационим параметром који представља особину материјала. У овом раду, ВаТiО₃-керамика је описана дискретном температурном скалом где су температурни корак h и основна полазна тачка a , њени термодинамички параметри. Уместо извода по температури, користе се задње разлике. Основни закључак рада је да керамички материјали могу поседовати нове температурне параметре који су карактеристике конкретног материјала.

Кључне речи: ВаТiО₃-керамика, дискретна температурна скала, TSC.

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