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REGULAR ARTICLE

Thermodynamics of Phase Equilibria and Reaction Sintering of Microwave Ceramic Dielectrics in the BaO – TiO₂ – MgO System

S.M. Logvinkov[1], O.M. Borysenko[2,*], R.V. Kryvobok[2], N.P. Klochko[2], H.M. Shabanova[2], A.M. Korohodska[2], V.M. Shumeiko[2], V.V. Voloshchuk[2]

[1] *O.M. Beketov National University of Urban Economy in Kharkiv, 61002 Kharkiv, Ukraine*
[2] *National Technical University "Kharkiv Polytechnic Institute", 61002 Kharkiv, Ukraine*

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A thermodynamic analysis of the subsolidus structure of the three-component BaO–TiO$_2$–MgO system was carried out in the temperature range 1200-1600 K using calculations of Gibbs free energy changes for model solid-phase exchange reactions. It was determined that MgO is thermodynamically stable with all barium titanates, while BaTi$_4$O$_9$ coexists exclusively with magnesium titanates. Triangulation of the system revealed eight elementary triangles, defining the equilibrium phase combinations. The study highlights the possibility of targeted prediction of the phase composition of new ceramic materials based on a selected concentration point within an elementary triangle, e.g., BaTi$_4$O$_9$–MgTiO$_3$–MgTi$_2$O$_5$. A rational approach of reactive sintering using pre-synthesized BaTi$_2$O$_5$ and MgTi$_2$O$_5$ is proposed to achieve the desired three-phase combination, controlling crystallite growth and optimizing structure-dependent dielectric properties. This method allows predicting volumetric changes and shrinkage, which is particularly important for the production of radio-technical ceramics. The results can be applied in designing new functional materials with tailored phase compositions and enhanced dielectric properties.

Keywords: Subsolidus structure, Triangulation, Solid-phase reactions, Reactive sintering, Elementary triangles, Dielectric properties, Phase composition, Technical ceramics.

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1. INTRODUCTION

Modern materials science of technical ceramics for radio engineering applications in Ukraine is currently in a state of crisis. The production capacities of radio ceramics suffered significant losses already in the early years of Ukraine's independence for several reasons. At the same time, much of the qualified workforce, unique technological equipment, and technical documentation were lost, and the previously existing scientific schools experienced a decline. At present, however, under the conditions of ongoing military actions, the demand for the development and establishment of domestic production of electronic reconnaissance systems and countermeasures against unmanned aerial vehicles is steadily increasing. A significant number of relevant materials science problems can be addressed through the investigation of heterophase radio ceramics within the BaO–TiO$_2$–MgO system. This system has not yet been fully explored, although some of its individual compounds and their combinations have long been used in the production of a wide range of capacitor ceramics and high-frequency dielectrics. It should also be noted that, in recent years, numerous new and more precise data have been obtained for binary subsystems, necessitating a revision of earlier knowledge regarding their liquidus and subsolidus structures.

It is known that capacitors with varying dielectric permittivity (ε) can be obtained based on polymorphic modifications of TiO$_2$ [1-3], since for anatase is close to 31; for brookite, the value depends on the orientation of the crystals: perpendicular to the axis of symmetry – 78, parallel – 89; for rutile – 173.

Pure oxides of Ba and Mg have high electrical resistance, but are of limited applicability due to the possible formation of carbonates and hydroxides in the air environment.

In the MgO–TiO$_2$ system, even higher values of the dielectric permittivity (ε) can be obtained [4-8], while in the BaO–TiO$_2$ system ultra-high values [9, 10] are achieved. These materials are used in the production of high-power capacitors, as well as ferroelectric and piezoelectric ceramics with a high degree of nonlinearity in their current–voltage characteristics.

The global experience in obtaining high-quality electroceramics within individual subsystems of the BaO–MgO–TiO$_2$ system forms the basis for developing new approaches to the fabrication of heterophase materials with predefined properties.

Among modern data on the structure of phase diagrams of individual subsystems, particular attention should be paid to the substantial revision of the nature and compositional limits of solid solutions based on magnesium titanates [8, 11-13], which form three types of crystal structures: pseudobrookite, corundum-like, and

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[*] Correspondence e-mail: oksana.borysenko@khpi.edu.ua

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spinel. The phase diagram of the MgO–TiO_2 system has been investigated for quite a long time. In early studies, only two compounds were reported: qandilite (Mg_2TiO_4) and karrooite ($MgTi_2O_5$). Later, another stoichiometric phase, geikielite ($MgTiO_3$), was identified. Magnesium dititanate $MgTi_2O_5$ crystallizes in a pseudobrookite structure, and ceramic materials based on it are effective dielectrics, finding applications in microwave technology [14, 15]. Ceramic materials derived from $MgTi_2O_5$, sintered in the presence of low-melting glasses of the Li_2CO_3–B_2O_3–SiO_2 system, exhibit a dielectric permittivity of 19.3 and a high-quality factor of 6800 GHz. Qandilite Mg_2TiO_4 is characterized by a spinel-type structure. Ceramics fabricated on its basis are widely used as dielectric materials in resonators, filters, and antennas for communication, radar, and global positioning systems operating in the microwave range [16, 17]. Ceramic synthesis based on magnesium titanate ($MgTiO_3$) is typically carried out via high-temperature solid-state reactions between magnesium oxide (MgO) and titanium dioxide (TiO_2). This approach ensures the formation of well-defined crystalline structures and enables the production of materials with exceptional dielectric properties, making them highly promising for applications in microwave technology and modern electronics [18]. Thus, the MgO–TiO_2 system holds significant importance for materials science and titanium metallurgy, while also being of interest in petrological studies.

Significant revisions have also been made to the phase diagram of the BaO–TiO_2 system [9, 10], which is of considerable interest in the field of functional ceramics due to the presence of a wide range of intermediate phases with pronounced dielectric and ferroelectric properties. The most well-known compound in this system is $BaTiO_3$, which became the first identified polycrystalline piezoelectric material. However, its piezoelectric coefficient is relatively low (~ 191 pC/N), which limits its application in piezoelectric devices. For this reason, research on $BaTiO_3$ has been largely focused on its dielectric characteristics and its use in multilayer ceramic capacitors.

In addition to $BaTiO_3$, according to [9, 10], the system contains eight intermediate phases: Ba_2TiO_4, $Ba_{11}Ti_{10}O_{31}$, $BaTi_2O_5$, $Ba_6Ti_{17}O_{40}$, $Ba_4Ti_{13}O_{30}$, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, and $BaTi_5O_{11}$. Although many of these compounds possess potential for practical applications, their investigation has remained limited to date. The main reasons are the uncertainties regarding invariant points, the temperature ranges of stability, and the lack of comprehensive data on the fundamental parameters and physical properties of these materials.

At the same time, some compounds have narrow temperature limits of thermodynamic stability, but are of great practical importance due to the ability to modify heterophase ceramic materials. This is facilitated by the difference in the electrophysical properties of the compounds, in particular, $BaTi_2O_5$ has an electrical conductivity of 10^{-6}-10^{-7} S/m at 600 °C with an activation energy of 1.75-1.86 eV and is a ferroelectric (without Fe_2O_3) with a maximum permittivity of 122 – 130 in the temperature range of 450-475 °C (the variability is due to firing at 1100 and 1225 °C). At the same time, $Ba_6Ti_{17}O_{40}$ is a typical dielectric with a permittivity of ~ 57-55 in the temperature range of 40-400 °C, and the permittivity of Ba_2TiO_4 is 40 and has low losses (0.06) when measured at a frequency of 100 kHz in samples fired at 1000 °C. Dense ceramics based on $BaTi_5O_{11}$ are promising for obtaining microwave dielectric resonators – dielectric constant of 38.9 at a frequency of 8 GHz, low dielectric losses, a temperature coefficient of resonance frequency close to zero and a high quality factor. $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ compounds have traditionally been used to obtain radioceramics and continue to be widely studied due to their very high dielectric characteristics in the microwave frequency range. Doping these compounds with some oxides (Sm_2O_3, ZrO_2, MgO) leads to a supra-additive increase in dielectric properties, which determines the development of new radioceramics technologies.

However, no information on the structure of the three-component phase diagram of the BaO – TiO_2 – MgO system has been found in reference literature and scientific articles. Thus, conducting research on the study of the subsolidus structure of the BaO – TiO_2 – MgO system, which is the physicochemical basis for the development of technical ceramics compositions, is relevant.

2. THEORETICAL PART

In three-component systems in solid-phase equilibrium, there may exist binary combinations of compounds, whose composition points are located at the ends of straight-line segments connecting them (conodes), as well as ternary combinations of compounds, whose composition points are located at the vertices of elementary triangles. The subsolidus structure of the system is determined by the entire set of elementary triangles and makes it possible to predict thermodynamically equilibrium phase combinations in any compositional region.

The procedure of determining elementary triangles is called the triangulation of the concentration triangle of a physicochemical system. This procedure is extremely complex when experimentally studying all coexisting combinations of compounds. To reduce the labor intensity of triangulation, thermodynamic prediction is employed by calculating and analyzing the changes in Gibbs energy as a function of temperature for all possible solid-phase exchange reactions between the system's compounds. In this way, the number of experiments is significantly reduced, and they are carried out mainly to verify and control the planned phase composition of mixtures. This approach is especially valuable when investigating previously unstudied systems or when revising outdated data.

In the system under consideration, seven binary compounds are stable in the subsolidus region, while ternary compounds are absent, and no binary compounds are formed in the BaO–MgO subsystem. In the MgO–TiO_2 subsystem, the stable phases are Mg_2TiO_4, $MgTi_2O_5$, and $MgTiO_3$. In the BaO–TiO_2 subsystem, the stable phases are Ba_2TiO_4, $BaTiO_3$, $BaTi_2O_5$, and $BaTi_4O_9$. The compounds $Ba_{11}Ti_{10}O_{31}$, $Ba_6Ti_{17}O_{40}$, $Ba_4Ti_{13}O_{30}$, $Ba_2Ti_9O_{20}$, and $BaTi_5O_{11}$ have insufficiently studied temperature ranges of thermodynamic stability, and it is possible that they are metastable solid solutions. We assume these are solid solutions, since the existence of these compounds has not been definitively proven, and no thermodynamic data for them are available in the literature. Thus, one can model possible variants of conode existence in this system, as shown in Fig. 1.

From the entire set of intersecting straight-line segments, the forthcoming thermodynamic analysis must identify the most stable conodes, which, according to Kurnakov's rule [19], determine the existence of only a strictly limited number of elementary triangles.

According to formula [20], investigating the subsolidus structure of this system will require writing, balancing, calculating Gibbs energy values for, and verifying the following number of equations:

$$P = \frac{V_1 \cdot V_2 \cdot (V_1 + 1) \cdot (V_2 + 1)}{4} = \frac{3 \cdot 4 \cdot 4 \cdot 5}{4} = 60.$$

where V_1 and V_2 are the numbers of binary compounds in the corresponding subsystems of the analyzed system (three compounds in the $MgO–TiO_2$ subsystem and four compounds in the $BaO–TiO_2$ subsystem); R is the total number of intersection points of all possible conode variants, which also determines the total number of model solid-phase reactions required to establish thermodynamically equilibrium combinations between the system's compounds.

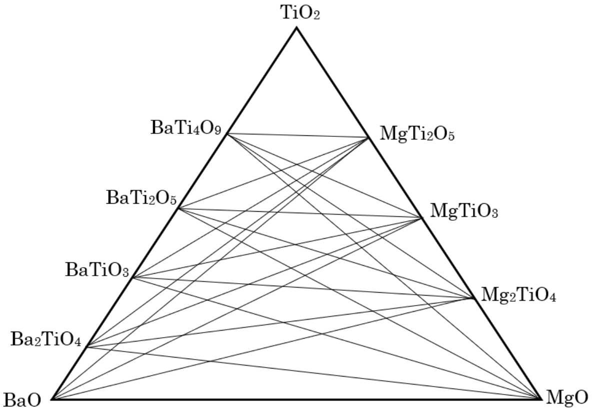

Fig. 1 – Variants of conode existence in the system

The complexity of the analyzed system, in terms of the number of possible model solid-phase reactions, amounts to 68 %. Accordingly, the complexity of the subsolidus structure of the system under consideration is 21 % relative to the maximum possible complexity.

To reduce the labor intensity of analyzing all model solid-phase reactions, it is convenient to use a methodological approach [20] that includes not only reactions of the "2 = 2" type but also reactions of the "2 = 3" type (or conversely, "3 = 2"), where the equality sign separates the number of initial reactants and interaction products.

In this work, a thermodynamic analysis of the subsolidus structure of the $BaO–TiO_2–MgO$ system was carried out in the temperature range of 1200–1600 K. The calculations were performed by comparing the Gibbs free energy values for model solid-phase exchange reactions, using the thermodynamic data presented in Table 1.

Table 1 – Thermodynamic constants of compounds [19, 22-24]

Compound	$-\Delta H^0_{298}$ kJ/mol	S^0_{298} J/(mol·K)	$Cp = a + bT + c'T^{-2}$, J/(mol·K)		
			a	$b \cdot 10^3$	$-c \cdot 10^{-5}$
MgO	601.241	26.924	42.59	7.28	6.19
TiO_2 rutile	943.492	49.915	74.6	2.092	17.698
BaO	558.15	70.29	53.304	4.35	8.301
$MgTiO_3$	1571.93	74.56	118.37	13.27	27.32
Mg_2TiO_4	2163.55	115.10	154.64	35.73	28.83
$MgTi_2O_5$	2507.89	138.91	170.21	38.49	30.75
Ba_2TiO_4	2250.99	188.43	146.15	28.03	–
$BaTiO_3$	1663.56	105.94	84.5	44.35	–
$BaTi_2O_5$	2662.09	173.55	189.2	83.68	34.396
$BaTi_4O_9$	4752.72	271.15	291.75	68.62	64.14

The dependence of the Gibbs free energy change on temperature allows the assessment of the direction of solid-phase reactions and the identification of the most favorable phase combinations [21]. The results of the calculation of the function $\Delta G = f(T)$ for the model reactions are presented in Table 2. In the course of the study, it was assumed that the character of the $\Delta G = f(T)$ dependence for the reactions under consideration is unambiguous and sufficient for drawing conclusions regarding the stability of the corresponding phase combinations. Calculations were carried out for solid-phase reactions of the "2 = 2" and "2 = 3" types.

3. RESULTS AND DISCUSSION

The analysis of the calculated Gibbs free energy values for reactions (1-4) indicates the thermodynamic stability of MgO with all barium titanates: $MgO – Ba_2TiO_4$, $MgO – BaTiO_3$, $MgO – BaTi_2O_5$, $MgO – BaTi_4O_9$.

Table 2 – The results of calculating the change in the values of Gibbs free energy depending on temperature

№	Reaction	ΔG, kJ/mol, at temperature, К		
		1200 К	1400 К	1600 К
1	$Ba_2TiO_4 + 2MgO = Mg_2TiO_4 + 2BaO$	121.180	105.804	89.448
2	$Ba_2TiO_4 + Mg_2TiO_4 = 2MgO + 2BaTiO_3$	– 43.642	– 28.526	– 13.629
3	$BaTiO_3 + Mg_2TiO_4 = 2MgO + BaTi_2O_5$	– 86.422	– 103.615	– 122.573
4	$BaTi_2O_5 + 2Mg_2TiO_4 = 4MgO + BaTi_4O_9$	– 86.090	– 58.568	– 27.702
5	$6BaO + MgTi_2O_5 + MgTiO_3 = 2MgO + 3Ba_2TiO_4$	– 414.292	– 380.119	– 344.206
6	$3BaO + MgTi_2O_5 + MgTiO_3 = 2MgO + 3BaTiO_3$	– 297.986	– 264.202	– 230.478
7	$2BaO + MgTi_2O_5 + 2MgTiO_3 = 3MgO + 2BaTi_2O_5$	– 394.665	– 413.921	– 437.562
8	$BaO + MgTi_2O_5 + 2MgTiO_3 = 3MgO + BaTi_4O_9$	– 311.922	– 301.708	– 291.153
9	$4BaO + Mg_2TiO_4 + MgTiO_3 = 3MgO + 2Ba_2TiO_4$	– 248.606	– 221.261	– 192374
10	$2BaO + Mg_2TiO_4 + MgTiO_3 = 3MgO + 2BaTiO_3$	– 171.069	– 143.983	– 116.556
11	$BaO + Mg_2TiO_4 + MgTiO_3 = 3MgO + BaTi_2O_5$	– 175.080	– 180.434	– 187.590
12	$BaO + Mg_2TiO_4 + 3MgTiO3 = 5MgO + BaTi_4O_9$	– 273.663	– 258.307	– 242.247
13	$2BaTi_2O_5 + 6MgO = Ba_2TiO_4 + 3Mg_2TiO_4$	216.487	235.758	258.775
14	$BaTi_2O_5 + 4MgO = BaO + 2Mg_2TiO_4$	168.833	170.781	174.112

This situation remains valid even for three-phase combinations that can participate in solid-phase exchange reactions according to Gibbs' phase rule (reactions of the "3 = 2" type, where "3" is the number of initial reactants and "2" is the number of interaction products). All "3 = 2" reactions (5-12) confirm this observation. Two model solid-phase exchange reactions, Nos. 13 and 14, were selected as verification reactions from the total number of possible "2 = 2" type reactions.

The ΔG values for the reactions confirm the coexistence of MgO with barium titanates and establish the exclusivity of the coexistence of $BaTi_4O_9$ with each of the magnesium titanates.

For the complete triangulation of the BaO–TiO_2–MgO system, which determines its subsolidus structure, it was necessary to analyze 12 model solid-phase reactions and perform a verification by calculating ΔG values for two additional reactions (13, 14, Table 2). Accordingly, the labor intensity of the analysis, compared to the total number of possible "2 = 2" type reactions ($R = 60$), was reduced fivefold. In practice, the reduction in labor intensity is even greater, since as the number of analyzed reactions increases, the combinatorial problems of comparing their ΔG values over different temperature ranges grow sharply, and the risk of errors increases disproportionately.

The subsolidus structure of the BaO–TiO_2–MgO system is shown in Fig. 2. According to thermodynamic calculations, this system is divided into eight elementary triangles: BaO – MgO – Ba_2TiO_4, MgO – Ba_2TiO_4 – $BaTiO_3$, MgO – $BaTiO_3$ – $BaTi_2O_5$, MgO – $BaTi_2O_5$ – $BaTi_4O_9$, MgO – $BaTi_4O_9$ – Mg_2TiO_4, $BaTi_4O_9$ – Mg_2TiO_4 – $MgTiO_3$, $BaTi_4O_9$ – $MgTiO_3$ – $MgTi_2O_5$, $BaTi_4O_9$ – $MgTi_2O_5$ – TiO_2.

The division of the BaO–MgO–ZrO_2 system into elementary triangles is consistent with Kurnakov's rule [19], giving a value of $X = 1 + 7 = 8$.

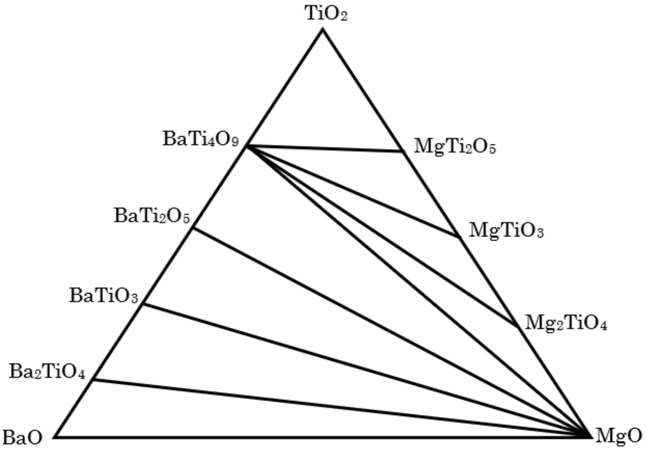

Fig. 2 – Subsolidus structure of the BaO – TiO_2 – MgO system

The subsolidus structure of the system established by triangulation (Fig. 2) provides researchers with the ability to purposefully predict the phase composition of new materials. In particular, attention should be paid to the existence of the elementary triangle $BaTi_4O_9$ – $MgTiO_3$ – $MgTi_2O_5$, which determines the thermodynamic equilibrium of this three-phase combination at any point within the concentration region inside the elementary triangle. Each of the titanates ($BaTi_4O_9$, $MgTiO_3$, $MgTi_2O_5$) possesses high dielectric properties, and their combination in various quantitative proportions in a ceramic material is reasonable, at least from the standpoint of additive effects, and may potentially exhibit a synergistic effect.

It is evident that when synthesizing a material with a phase composition corresponding to a selected point within the elementary triangle $BaTi_4O_9$ – $MgTiO_3$ – $MgTi_2O_5$, using simple oxides as starting reagents, the reactive sintering will proceed with the formation of a large number of intermediate phases. Specifically, the interaction of BaO and TiO_2 to form $BaTi_4O_9$ occurs through the preliminary formation of the titanates Ba_2TiO_4, $BaTiO_3$, and $BaTi_2O_5$ (Fig. 2), while the interaction of MgO and TiO_2 to form $MgTiO_3$ and $MgTi_2O_5$ proceeds via the intermediate formation of Mg_2TiO_4. The presence of a significant number of intermediate stages in synthesizing the targeted phase composition complicates the attainment of thermodynamic equilibrium and may require additional technological measures, at a minimum – either increasing the isothermal holding time at the planned temperature or raising the firing temperature.

It is logical to change the starting reagents and use pre-synthesized compounds to produce the ceramic material. However, using pre-synthesized $BaTi_4O_9$, $MgTiO_3$, and $MgTi_2O_5$ would eliminate solid-phase reactive interaction from the sintering mechanism, since these compounds are in thermodynamic equilibrium and do not react with each other. Strictly physical sintering may require firing temperatures close to the temperature of the ternary eutectic in this concentration region of the system, or the use of a liquid-phase sintering mechanism, potentially involving additional components, which would significantly complicate the technology and could negatively affect the final dielectric properties. It is more rational to employ reactive sintering of pre-synthesized $BaTi_2O_5$ and $MgTi_2O_5$, which will participate in a solid-phase exchange reaction:

$$BaTi_2O_5 + 2MgTi_2O_5 \rightarrow BaTi_4O_9 + 2MgTiO_3. \quad (1)$$

In this case, $BaTi_2O_5$ and $MgTi_2O_5$ will be consumed, and to obtain the targeted three-phase combination, a certain excess of $MgTi_2O_5$ will be required. Under such conditions, the growth of the crystallite size of the forming $BaTi_4O_9$ and $MgTiO_3$ will be slowed due to the preferential consumption of energy for completing the solid-phase reaction, while the reactive crystallites from the excess $MgTi_2O_5$ may thin down to the nanoscale. This is an important factor for controlling the structure-dependent dielectric properties of the synthesized material with a specified phase composition.

A similar approach of reactive sintering based on solid-phase exchange reactions to achieve the desired three-phase combinations in the material's phase composition can also be applied to other concentration regions of the system within the corresponding elementary triangles (Fig. 2). For example, for the elementary triangle $BaTi_4O_9$ – Mg_2TiO_4 – $MgTiO_3$, solid-phase interactions can be envisaged through "2 = 2" or "2 = 3" type reactions:

$$3BaTi_2O_5 + 4MgTi_2O_5 = 3BaTi_4O_9 + 2Mg_2TiO_4, \quad (2)$$

$$2BaTi_2O_5 + 3MgTi_2O_5 = 2BaTi_4O_9 + Mg_2TiO_4 + MgTiO_3. \quad (3)$$

To obtain a three-phase combination of barium titanates ($BaTi_4O_9$ and $BaTi_2O_5$) with magnesium oxide:

$$2BaTiO_3 + 4Mg_2TiO_4 = BaTi_4O_9 + BaTi_2O_5 + 8MgO. \quad (4)$$

An additional advantage of implementing this type of reactive sintering is the ability to calculate volumetric changes during the reaction, which enables the prediction of shrinkage behavior when producing radio-technical ceramics.

4. CONCLUSIONS

The thermodynamic analysis and triangulation of the $BaO–TiO_2–MgO$ system in the subsolidus region allowed the identification of eight elementary triangles, which define the stable phase combinations of the system. MgO exhibits thermodynamic stability with all barium titanates, and $BaTi_4O_9$ coexists exclusively with magnesium titanates, as confirmed by ΔG calculations for both “2 = 2” and “3 = 2” solid-phase exchange reactions.

The established subsolidus structure enables targeted prediction of phase compositions for new ceramic materials. Reactive sintering using pre-synthesized $BaTi_2O_5$ and $MgTi_2O_5$ is a rational approach for achieving desired three-phase combinations while controlling crystallite growth and optimizing structure-dependent dielectric properties. This methodology can be extended to other concentration regions within the system, allowing for precise design and processing of ceramics with tailored phase compositions and predictable volumetric and shrinkage behaviour.

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Термодинаміка фазових рівноваг та реакційного спікання мікрохвильових керамічних діелектриків у системі $BaO – TiO_2 – MgO$

С.М. Логвінков[1], О.М. Борисенко[2], Р.В. Кривобок[2], Н.П. Клочко[2], Г.М. Шабанова[2], А.М. Корогодська[2], В.М. Шумейко[2], В.В. Волощук[2]

[1] *Харківський національний університет міського господарства імені О.М. Бекетова, 61002 Харків, Україна*
[2] ***Національний технічний університет «Харківський політехнічний інституі», 61002 Харків, Україна***

Проведено термодинамічний аналіз субсолідусної будови трикомпонентної системи $BaO–TiO_2–MgO$ у температурному діапазоні 1200-1600 К із використанням розрахунків зміни енергії Гіббса для модельних твердофазних реакцій обміну. Встановлено, що MgO термодинамічно стабільний зі всіма барієвими титанатами, тоді як $BaTi_4O_9$ співіснує виключно з титанатами магнію. Тріангуляція системи виявила вісім елементарних трикутників, які визначають рівноважні фазові комбінації. Показано можливість цілеспрямованого прогнозування фазового складу нових керамічних матеріалів на основі вибраної концентраційної точки всередині елементарного трикутника, наприклад, $BaTi_4O_9$–$MgTiO_3$–$MgTi_2O_5$. Обґрунтовано раціональний підхід реакційного спікання із застосуванням заздалегідь синтезованих $BaTi_2O_5$ та $MgTi_2O_5$ для досягнення заданої трьохфазної комбінації, контролю росту кристалітів та оптимізації структурозалежних діелектричних властивостей. Метод дозволяє прогнозувати об’ємні зміни та усадку, що особливо важливо для виробництва радіотехнічної кераміки. Результати можуть бути використані при проектуванні нових функціональних матеріалів із заданим фазовим складом і покращеними діелектричними характеристиками.

Ключові слова: Субсолідусна структура, Тріангуляція, Твердофазні реакції, Реакційне спікання, Елементарні трикутники, Діелектричні властивості, Фазовий склад, Технічна кераміка.