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Thermodynamic physico-chemical modelling and calculation for the synthesis process of modern functional materials

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Abstract. The method of thermodynamic modeling of phase and chemical transformations for synthesis conditions of multicomponent functional materials is presented. Calculation of the phase transformations taking place in the conditions of synthesis and operation of ceramic materials on the basis of the system $\text{SiO}_2 – \text{K}_2\text{O} – \text{Na}_2\text{O} – \text{Al}_2\text{O}_3 – \text{Fe}_2\text{O}_3 – \text{CaO} – \text{MgO} – \text{TiO}_2 – \text{P}_2\text{O}_5 – \text{SO}_3$ in the field of temperatures from 0 to 2000° C is carried out. The sequence of phase and chemical transformations between components of synthesizable material and their reaction products, depending on temperature, is founded.

1. State of the problem
It is required that modern functional materials have very different exploitation characteristics, such as strength, thermal and chemical stability, moisture absorption, rheology, etc. Nature of the phase and chemical transformations which occur during the synthesis from raw materials and composition of the product define these characteristics [1, 2]. Due to presence of multiple phases, many components, complexity and interconnection of the interactions and transitions, which take place during the synthesis, and wide range of values of state parameters, the detailed experimental research within the wide range of temperatures, compositions, and different conditions of synthesis is a very complex problem, which to date is generally unresolved [1-3].

In some cases it is correct and sufficiently effective to apply methods of the thermodynamic physico-chemical modelling. These methods have principal advantages in comparison to experimental methods, letting to obtain more detailed data about the whole complex of interrelated phase and chemical transformations corresponding to functional materials and products synthesis [4-9].

However, this method turns out to be effective, i.e. yielding reliable, quantitatively justified data, only when several conditions are met [5-7]. First of all, the modelling and computational apparatus used to describe these systems should be correct, effective, and adequate to the real system. In second, thermodynamic characteristics of the initial compounds and possible interaction products should be valid. In third, interpretation, analysis, and generalization of the results obtained from thermodynamic modelling should be correct.

2. Objects and methods of investigation
As the main object of the investigation it has been considered the process of synthesis cranial base of the ceramic tiles. At the first stage of investigation, the physico-chemical modelling of the synthesis of material, which meets certain criteria, has been undertaken. Then, based on the modelling results, it has been required to correctly interpret these results, reveal mechanism of the occurring processes, and discover principles of influence of the state parameters, such as temperature, moisture content,
synthesis atmosphere, on the phase and chemical transformations during the synthesis. As it is known, ceramics is synthesised via annealing of the raw materials till the certain temperature—the annealing temperature. As a result of the interaction of the components in the raw material, which takes place under elevated temperatures, the phase and chemical composition of the annealed product becomes different from the initial, and the product acquires such properties, as hardness, strength, etc. It is namely phase and chemical composition of the synthesised product defines its exploitation properties.

Subject to the forgoing, the primary object of investigation is the raw material of the ceramic synthesis. As the basis of modelling, the raw material of a typical complex composition has been used (including all the main and auxiliary components). Its composition has been defined using analytical methods, and the main compounds have been recalculated into their oxide forms. As a result, oxide composition of the raw material corresponded to the following ten-component system, which is the set of compounds-components fully and unambiguously describing both composition of the raw material, and the product:

\[ \text{SiO}_2 – \text{K}_2\text{O} – \text{Na}_2\text{O} – \text{Al}_2\text{O}_3 – \text{Fe}_2\text{O}_3 – \text{CaO} – \text{MgO} – \text{TiO}_2 – \text{P}_2\text{O}_5 – \text{SO}_3 \]

The investigation has been undertaken with help of the methods and databases of thermodynamic modelling, which have been developed earlier, and which meet the requirements described earlier [5-9]. The equilibrium composition has been calculated under the different synthesis conditions, namely, in the temperature interval from room temperature to 2000 °C (taking into account the possible overheating).

The considered conditions correspond to the annealing stage of the ceramic tiles production process.

In the table below, the initial data in mass and mole expressions are given, taking into account losses during the annealing. Using mole composition is viable from the point of view of the chemical and phase transitions analysis.

**Table.** The chemical (oxide) composition of the press-powder tiles

| Substance | SiO₂ | K₂O | Na₂O | Al₂O₃ | Fe₂O₃ | CaO | MgO | TiO₂ | P₂O₅ | SO₃ | Loss on ignition |
|-----------|------|-----|------|-------|-------|-----|-----|------|-------|-----|-----------------|
| Content   |      |     |      |       |       |     |     |      |       |     |                 |
| mass.%    | 55.20| 2.25| 0.45 | 13.68 | 3.19  | 9.72| 3.25| 0.79 | 0.15  | 0.49| 10.83           |
| mol/kg    | 9.187| 0.239| 0.073| 1.342 | 0.199 | 1.733| 0.806| 0.099| 0.011 | 0.117| –               |

It is possible to allocate two areas types within the ceramic materials synthesis, in which the conditions of synthesis and nature of the phase and chemical interactions differ principally. It’s the homogeneous area of ceramic mass (which is completely separated from the surrounding atmosphere) and the heterogeneous area ceramic mass contact with the environment (the atmosphere of synthesis).

Certainly, the main interactions are the first type ones—in the thickness of the ceramic mass (press-powder) between its components. They determine, mainly, the final phase-chemical composition of synthesizable material. Therefore the main purpose of this work is to study these homogeneous interactions in the thickness of the ceramic mass in a wide range of temperatures corresponding to different stages of functional (ceramic) materials synthesis.

3. Modelling results analysis

Let's consider the transformations taking place in the bulk of ceramic mass. Under these conditions interaction for components takes place without atmosphere, and it is impossible for gases to evolve as a result of interactions, because the processes take place in the bulk of the solid phase.

As soon as sulphur dioxide is a gas, its presence in the system is nominal and is taken into account
as amounts of sulphur and oxygen in the system, rather than sulphur dioxide itself.

Temperature influence on the phase and chemical transformations in the temperature range considered, obtained as a result of the thermodynamic modelling of the system under investigation, is presented in the Figure.

**Figure.** Temperature influence of the phase transitions in the bulk of the pottery fragment

Let's consider the sequence of transformations, which take place when the temperature is rising.

Under the room temperature complex compounds form from simple oxides as a rule: \( \text{Al}_2\text{SiO}_5, \text{CaSO}_4, \text{Ca}_4\text{P}_2\text{O}_9, \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}, \text{CaTiSiO}_5, \text{CaMg(SiO}_3)_2, \text{Fe}_2\text{O}_3, \text{KAlSi}_3\text{O}_8, \text{NaAlSi}_3\text{O}_8, \text{SiO}_2. \)

Comparison of the initial composition and the data obtained allows to conclude, that the following transformations take place in the system.

Magnesium oxide MgO interacts the most actively with calcium oxide and silicon oxide. It manifests through the formation of silicate of calcium and magnesium \( \text{CaMg(SiO}_3)_2 \):

\[
\text{MgO} + 2\text{SiO}_2 + \text{CaO} \rightarrow \text{CaMg(SiO}_3)_2
\]

Iron does not form complex compounds and remains in the form of iron (III) oxide — hematite.

All sulphur, being initially in the form of sulphur trioxide, reacts with calcium oxide, and yields calcium sulphate:
Phosphorus (V) oxide reacts with calcium oxide to form complex calcium phosphate $\text{Ca}_4\text{P}_2\text{O}_9$. The process completely consumes phosphorus (V) oxide:

$$\text{P}_2\text{O}_5 + 4\text{CaO} \rightarrow \text{Ca}_4\text{P}_2\text{O}_9$$  \hspace{1cm} (3)

Titanium oxide reacts with calcium and silicon oxides and completely transforms titanium and calcium silicates:

$$\text{TiO}_2 + \text{SiO}_2 + \text{CaO} \rightarrow \text{CaTiSiO}_5$$  \hspace{1cm} (4)

Sodium present in the system in the form of sodium oxide reacts with alumina and silicon oxides, entirely binding into sodium silicoaluminate:

$$\text{Na}_2\text{O} + 6\text{SiO}_2 + \text{Al}_2\text{O}_3 \rightarrow 2\text{NaAlSi}_3\text{O}_8$$  \hspace{1cm} (5)

Potassium oxide fully binds into potassium silicoaluminate by reacting with alumina and silicon oxides:

$$\text{K}_2\text{O} + 6\text{SiO}_2 + \text{Al}_2\text{O}_3 \rightarrow 2\text{KAlSi}_3\text{O}_8$$  \hspace{1cm} (6)

As it has been shown earlier, calcium oxide yields calcium sulphate, calcium phosphate, and magnesium and calcium silicates, in accordance with reactions (1)-(4). This shows high reactivity of calcium oxide.

Remainder of calcium oxide reacts with alumina and silicon oxide, forming $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$:

$$3\text{CaO} + 3\text{SiO}_2 + \text{Al}_2\text{O}_3 \rightarrow \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$$  \hspace{1cm} (7)

Alumina oxide has high reactivity as well. As it has been described earlier, it reacts with sodium, potassium, calcium, and silicon oxides according to equations (5)-(7), and excess of it forms alumina silicate $\text{Al}_2\text{SiO}_3$ together with silicon oxide:

$$\text{SiO}_2 + \text{Al}_2\text{O}_3 \rightarrow \text{Al}_2\text{SiO}_5$$  \hspace{1cm} (8)

Silicon, which did not bind with the compounds mentioned above, remains in the form of silicon dioxide $\text{SiO}_2$.

In this way, the reactions (1)-(8) describe how initial oxides interact at the room temperature.

When the temperature rises, some of the substances undergo structural and chemical transformations to yield new compounds.

Thus, at 392 K complex calcium aluminosilicate $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ becomes thermally unstable, and reacting with silicon dioxide and alumina silicate $\text{Al}_2\text{SiO}_3$ forms a simpler aluminosilicate $\text{CaAl}_2\text{Si}_2\text{O}_8$. This transformation is described via the following reaction:

$$2\text{Al}_2\text{SiO}_3 + \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{SiO}_2 \rightarrow 3\text{CaAl}_2\text{Si}_2\text{O}_8$$  \hspace{1cm} (9)

At the temperature 424 K alumina silicate $\text{Al}_2\text{SiO}_3$ undergoes phase transition from kyanite to andalusite.

At the temperature 446 K potassium aluminosilicate $\text{KAlSi}_3\text{O}_8$ undergoes another phase transition.

The further temperature rise till 456 K results in the changes considered below. With no regard for the stoichiometric relationships these changes are described using the following transition:

$$\text{Al}_2\text{SiO}_3 + \text{Ca}_4\text{P}_2\text{O}_9 + \text{CaTiSiO}_3 + \text{CaMg(SiO}_3)_2 \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{MgPO}_4 + \text{SiO}_2 + \text{Al}_2\text{TiO}_5$$  \hspace{1cm} (10)

As the result of this transition complex calcium phosphate $\text{Ca}_4\text{P}_2\text{O}_9$ and calcium-titanium silicate $\text{CaTiSiO}_3$ are completely consumed.

Data analysis shows that there are two independent transformations in the system. Let's consider them both separately.

The first transformation involves calcium-titanium silicate $\text{CaTiSiO}_3$. At the temperature 456 K it
becomes thermally unstable and decays reacting with Al\textsubscript{2}SiO\textsubscript{5} and forms calcium aluminosilicate CaAl\textsubscript{2}Si\textsubscript{3}O\textsubscript{8} together with titanium aluminate Al\textsubscript{2}TiO\textsubscript{5}. During this transformation the excessive silicon yields free dioxide:

\[ 2\text{Al}_2\text{Si}_3\text{O}_5 + \text{CaTiSi}_3\text{O}_5 \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{Al}_2\text{TiO}_5 + \text{SiO}_2 \]  

The second transformation from those mentioned above takes place because calcium phosphate becomes thermally unstable, and reacts with calcium-magnesium silicate to yield magnesium metaphosphate, and the excess of unstable calcium and silicon oxides:

\[ \text{Ca}_4\text{P}_2\text{O}_8 + \text{CaMg(Si}_3\text{O}_8\text{)}_2 \rightarrow \text{Mg(PO}_3\text{)}_2 + 5\text{CaO} + 2\text{SiO}_2 \]  

Calcium and silicon oxides then react with aluminosilicate Al\textsubscript{2}SiO\textsubscript{5} and form calcium aluminosilicate CaAl\textsubscript{2}Si\textsubscript{3}O\textsubscript{8} according to the following reaction:

\[ \text{CaO} + \text{SiO}_2 + \text{Al}_2\text{Si}_3\text{O}_5 \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 \]  

Merging (12) and (13) results in:

\[ 5\text{Al}_2\text{Si}_3\text{O}_5 + 3\text{SiO}_2 + 2\text{Ca}_5\text{P}_2\text{O}_8 + \text{CaMg(Si}_3\text{O}_8\text{)}_2 \rightarrow \text{Mg(PO}_3\text{)}_2 + 5\text{CaAl}_2\text{Si}_2\text{O}_8 \]  

From the reaction (14) it follows that in order for all calcium oxide, excess of which forms as a result of the reaction (12), to bind into calcium aluminosilicate CaAl\textsubscript{2}Si\textsubscript{3}O\textsubscript{8} it is necessary the presence of silicon dioxide in the system. This reaction consumes the silicon dioxide.

In this way, reactions (11) and (14) describe transformations in the system at 456 K.

Further temperature rise results in phase transition of the sodium aluminosilicate NaAlSi\textsubscript{3}O\textsubscript{8} from albite to analbite.

At the temperature 627 K calcium-magnesium silicate CaMg(Si\textsubscript{3}O\textsubscript{8})\textsubscript{2} becomes thermodynamically unstable in the presence of aluminosilicate Al\textsubscript{2}SiO\textsubscript{5} and as the result of their interaction forms calcium aluminosilicate CaAl\textsubscript{2}Si\textsubscript{3}O\textsubscript{8} and magnesium silicate MgSiO\textsubscript{3}. This reaction goes to complete disappearance of aluminosilicate Al\textsubscript{2}SiO\textsubscript{5} from the system:

\[ \text{Al}_2\text{Si}_3\text{O}_5 + \text{CaMg(Si}_3\text{O}_8\text{)}_2 \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{MgSiO}_3 \]  

Further temperature rise to 906 K results to phase transition of quartz to trimidite.

At the temperature 966 K calcium-magnesium silicate CaMg(Si\textsubscript{3}O\textsubscript{8})\textsubscript{2} becomes unstable and reacts with the complex alumina and titanium oxide Al\textsubscript{2}TiO\textsubscript{5} and silicon dioxide. As the result of this interaction calcium aluminosilicate CaAl\textsubscript{2}Si\textsubscript{3}O\textsubscript{8}, calcium and titanium silicate CaTiSiO\textsubscript{3} and magnesium silicate MgSiO\textsubscript{3}:

\[ 2\text{CaMg(Si}_3\text{O}_8\text{)}_2 + \text{SiO}_2 + \text{Al}_2\text{Ti}_3\text{O}_5 \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{CaTiSi}_3\text{O}_5 + 2\text{MgSiO}_3 \]  

This reaction goes until Al\textsubscript{2}TiO\textsubscript{5} completely reacts.

Further temperature rise to 1065 K results to potassium aluminosilicate KAlSi\textsubscript{3}O\textsubscript{8} decaying to yield simpler aluminosilicate KAlSi\textsubscript{2}O\textsubscript{6} and silicon dioxide:

\[ \text{KAlSi}_3\text{O}_8 \rightarrow \text{KAlSi}_2\text{O}_6 + \text{SiO}_2 \]  

Further changes in the system occur only at the temperature 1559 K when the phase transition of potassium aluminosilicate NaAlSi\textsubscript{3}O\textsubscript{8} takes place.

At the temperature 2018 K calcium-magnesium silicate becomes unstable in the presence of martite. As the result of their interaction forms the double calcium-iron oxide CaFe\textsubscript{2}O\textsubscript{4}, magnesium silicate MgSiO\textsubscript{3}, and free silicon dioxide:

\[ \text{CaMg(Si}_3\text{O}_8\text{)}_2 + \text{Fe}_2\text{O}_3 \rightarrow \text{CaFe}_2\text{O}_4 + \text{MgSiO}_3 + \text{SiO}_2 \]  

After the reaction (18) part of the calcium-magnesium silicate remains in the system, because the amount of iron oxide is insufficient for the complete disappearance of the silicate.

Further temperature rise to 2000 °C does not result in chemical changes of the chemical composition.
4. Conclusion
In this way, justified quantitative data are obtained and principle of the temperature influence on the phase and chemical transitions in the ceramic mass are obtained by methods of thermodynamic modeling of phase-chemical transformations, thus allowing to control the technological synthesis process.

Rigorous interrelation between stage, i.e. temperature, and corresponding phase and chemical transformations, and the composition of the synthesized material is established.

The temperature impact on the sequence of phase transitions of the complex oxides and silicates, forming the resulting ceramic material, is attained.

References
[1] Materials Handbook for refractories, traditional and advanced ceramics 1989 Ceramic Ind. J. 1 21–124
[2] Egész Á and Gömze L A 2015 Qualification Methods of Al₂O₃ Injection Molding Raw Materials. J. Phys.: Conf. Series 602 012023
[3] Smith W R Computational aspects of chemical equilibrium in complex systems 1980 Theor. Chem. Adv. Perspect. 5 185–259.
[4] Cox J D, Wagman D D and Medvedev V A 1989 CODATA key values for thermodynamics (N.Y.: Hemisphere Pub. Corp.)
[5] Veiko V P, Slobodov A A and Odintsova G V 2013 Availability of methods of chemical thermodynamics and kinetics for the analysis of chemical transformations on metal surfaces under pulsed laser action Laser Physics 23 066001.
[6] Olekhnovich R O, Glazacheva E N, Uspenskii A B, Slobodov A A, Uspenskaia M V 2015 Proc. XV Intern. Multidisc. Sci. Geoconf. 2 N 3 207-214
[7] Slobodov A, Uspenskiy An, Ralys R and Kremnev D 2015 Thermodynamic modelling of phase-chemical transformations as the method for study of rheological properties of substances Építőanyag – J. Silic. Based Compos. Mater. 67 159–163
[8] Uspenskiy An, Slobodov A A, Kremnev D, Sochagin A and Klepova A N 2016 Phase-chemical problems of technology optimization and cleaning - thermodynamic research and modeling Proc. XVI Intern. Multidisc. Sci. Geoconf. 1 769-776
[9] Ralys R V, Uspenskiy A A and Slobodov A A 2016 Deriving properties of low-volatile substances from isothermal evaporation curves J. Non-Equilibrium Thermodynamics 41 3-11.