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Optimization of the compositions area of radiotransparent ceramic in the $SrO\text{-}Al_2O_3\text{-}SiO_2$ system

Abstract. *This work presents the results of optimization of the compositions area of radiotransparent ceramic. Theoretical calculation of free Gibbs energy proves the possibility of the formation of strontium anorthite phase for every composition of Sheffe plan. As a result of laboratory samples test, graphic dependences "composition – property" was obtained, the choice of the most technologically advanced composition area and sintering temperature for manufacturing the radiotransparent ceramic was substantiated. The optimal composition of the Sr-anorthite ceramics is characterized by the next level of properties: water absorption (W = 0.17 %), dielectric permittivity (ε = 5.15), mechanical strength ($\sigma_{compression}$ = 176 MPa).*

Streszczenie. *W pracy przedstawiono wyniki optymalizacji powierzchni radiotransparentnych kompozytów ceramicznych. Teoretyczne wyznaczenie wartości entalpii swobodnej stwarza możliwość obliczenia parametrów anorytu strontu dla wszystkich kompozytów Scheffe'a. Badania laboratoryjne próbek pozwoliły na otrzymanie zależności graficznych określających właściwości kompozytu. Określono wartość powierzchni kompozytu oraz temperatury spiekania, która jest optymalna do wytworzenia radiotransparentnego materiału ceramicznego. Wyznaczono również dodatkowe wielkości charakterystyczne, którymi charakteryzuje się optymalny ceramiczny kompozyt anorytowy: absorpcja wody (W = 0.17 %), przenikalność dielektryczna (ε = 5.15) oraz wytrzymałość mechaniczna ($\sigma_{compression}$ = 176 MPa). (**Optymalizacja powierzchni radiotransparentnych kompozytów ceramicznych wykorzystywanych w układach $SrO\text{-}Al_2O_3\text{-}SiO_2$**).*

Keywords: radiotransparent ceramic. simplex-plan, thermodynamic analysis, strontium anorthite, dielectric permittivity, mechanical strength, water absorption.
Słowa kluczowe: radiotransparentne materiały ceramiczne, analiza termodynamiczna, anoryt strontu, przenikalność dielektryczna, absorpcja wody.

Introduction

Uninterrupted work of aircraft, rocket and aerospace systems in many ways depends on the quality, reliability and durability of using construction materials. Thus, dielectric parts of electronic equipment (radomes in particular) must be characterized by minimal values of dielectric characteristics (dielectric loss tangent on the range 10^{-4}–10^{-2}), dielectric permittivity (ε) less than 10), high erosion resistance (dust particles, rain drops) and heat resistance. In addition, resistance to high level of vibration.

One of the most perspective materials is a strontium anorthite ceramic. Applying of this material is possible because of the combination of crystal phase – strontium anorthite, required dielectric (tg $\delta = (1\div2)\cdot10^{-4}$, $\varepsilon = 6.5$) and high mechanical properties in conditions of high temperature exposure. In modern industries this kind of ceramic is used as a constructive, dielectric and refractory materials. Generally, the required level of sintering for strontium anorthite ceramics achieves by long grinding of raw materials and firing and also high sintering temperature.

Kinetics of phase formation was studied in a number of papers by authors like Bansal N.P., Sung Y.M., Chinn R.E., Kim C.Y. and others. Russian researches in their work [1] also made an accent on technology and manufacturing of these materials and also on prospect of their applying.

Work by Song Chen, De-Gui Zhu, Xu-Sheng Cai [2] presents a development in area of obtaining a low-temperature Sr-anorthite ceramic, which is obtained at 900°C. However, presented technology of obtaining a ceramic material involves a two-time firing with preliminary heat treatment of kaolin at 1400°C.

The possibility of low-temperature synthesis (1350°C) of strontium anorthite ceramic was proved by us in a previous research [3]. The probability of the formation of $SrO\cdot Al_2O_3\cdot 2SiO_2$ compound was confirmed by thermodynamic calculation of free Gibbs energy, which remains to be the only universal physical-chemical theory today. The result of the research was the possibility of obtaining the material at 1350°C, which is characterized by dielectric permittivity value $\varepsilon = 6.29$, which complies with the requirements for radio transparent materials. Therefore, next step of the research is experimental determination of the optimal compositions area, which will provide consistently high levels of operational properties. It is expedient to solve the task with the applying of simplex-lattice method of planning with using of incomplete 3rd order Sheffe plan.

Thus, the purpose of this work is a thermodynamic evaluation of possibility of the solid-phase interaction of oxide area of the $SrO–Al_2O_3–SiO_2$ system with the strontium anorthite formation, and also conducting the experiment and determination of the "composition-property" dependency.

Experimental part

Thermodynamic calculation allows to determine fundamental possibility and probability of the reaction with the formation of new phases for seven points of simplex-plan. It will allow to substantiate technological parameters of purposeful synthesis of material with specific properties before the energy-intensive experiment.

To solve the task of optimization of the ceramic composition and establishment of the dependency "composition-properties", a simplex-lattice method of planning the experiment with incomplete 3rd order Sheffe plan was used. As an independent factors reviewed a content of silica, alumina and strontium oxides in mixes compositions. Factor space area is limited by the content of oxides, wt. %: SiO_2 – 30÷50, Al_2O_3 – 25÷45, SrO – 25÷45.

The possibility of synthesis of strontium anorthite $SrO\cdot Al_2O_3\cdot 2SiO_2$ for the seven simplex-plan points in $SrO–Al_2O_3–SiO_2$ system (Fig. 1) was estimated for the reactions of obtaining from oxides.

(1) $$SrO + Al_2O_3 + SiO_2 \rightarrow SrO\cdot Al_2O_3\cdot Si_2O_8\ (700\text{–}1700K)$$

and also with the formation of intermediate compounds Sr_2SiO_4 and $SrSiO_3$ in following sequence:

(2) $$2SrO + SiO_2 \rightarrow Sr_2SiO_4\ (700-1300K);$$

(3) $Sr_2SiO_4 + SiO_2 \rightarrow 2SrSiO_3\ (1300\text{–}1500K)$;

(4) $SrSiO_3 + Al_2O_3 + SiO_2 \rightarrow$
$\rightarrow SrO \cdot Al_2O_3 \cdot Si_2O_8\ (1500\text{–}1700K)$.

Calculation of free Gibbs energy (ΔG_T^o , kJ/mol) was carried out by integration Gibbs-Helmholtz equation:

$$\Delta G = \Delta H_p + T(\partial \Delta G / \partial T)_p,$$

considering the following polymorphic phase transformation

(5)
$$SiO_2(\beta-\text{quartz}) \xrightarrow{846K} SiO_2(\alpha-\text{quartz}) \xrightarrow{1143K} SiO_2(\alpha-\text{tridimite}),$$
$$SrAl_2Si_2O_8(\text{hexagonal}) \xrightarrow{1323K} SrAl_2Si_2O_8(\text{monoclinic})$$
$$\gamma-Al_2O_3 \xrightarrow{1500K} \alpha-Al_2O_3$$

Prediction of solid-phase reaction on temperature range 700–1700 K was carried out considering the compositions of oxide mixes, that were shown in table 1.

Most part of the initial thermodynamic data (table 2) was taken from reference tables [4-5], and from the work [6] for strontium anorthite.

Table 1. Chemical composition of studied compositions.

Point	Chemical composition of compositions, mass. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	SrO	L.O.I.
1	25.042	20.971	0.045	0.01	0.053	37.288	16.616
2	44.913	22.634	0.077	0.018	0.057	22.278	10.068
3	26.926	40.472	0.024	0.011	0.102	22.251	10.213
4	26.954	31.54	0.022	0.011	0.08	28.519	12.874
5	35.942	22.616	0.027	0.014	0.07	28.54	12.845
6	35.905	31.558	0.028	0.014	0.08	22.272	10.143
7	32.287	27.526	0.025	0.013	0.069	27.629	12.451

Table 2. Initial thermodynamic data of the compounds in $SrO–Al_2O_3–SiO_2$ system

Compound	$-\Delta H^\circ_{298}$, kJ/mol	$-\Delta G^\circ_{298}$, kJ/mol	Cp = f(T), J/(mol·K)		
			a	$b \cdot 10^3$	$-c \cdot 10^{-5}$
$SrAl_2Si_2O_8$ (hexagonal)	4235.79	4292.05	244.22	58.66	–
$SrAl_2Si_2O_8$ (monoclinic)	4235.79	4292.05	274.97	48.99	–
SiO_2 (β-quartz)	911.07	856.67	46.94	34.31	11.30
SiO_2 (α-quartz)	910.44	856.05	60.29	8.17	–
SiO_2 (α-tridimite)	905.84	851.78	57.07	1.10	–
γ-Al_2O_3	1637.98	1542.12	106.68	17.79	25.5
α-Al_2O_3	1670.63	1577.28	114.82	12.81	35.45
SrO	590.64	581.02	51.65	4.69	7.56
$SrSiO_3$	1632.92	1568.24	112.02	19.21	30.31
Sr_2SiO_4	2303.26	2228.58	154.04	28.05	31.48

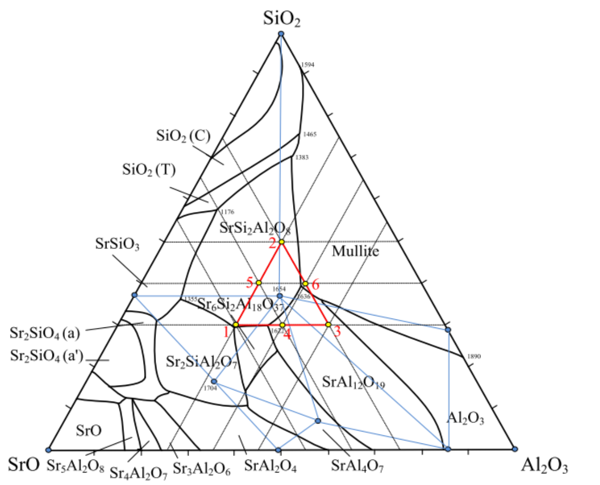

Fig.1. Location of simplex-lattice plan on ternary system $SrO\text{-}Al_2O_3\text{-}SiO_2$

Thermodynamic evaluation of the $SrO \cdot Al_2O_3 \cdot 2SiO_2$ formation carried out for the oxide compositions of simplex-plan, submitted in mole fractions. The calculation showed, that the reaction flow with simultaneous formation of strontium anorthite and accompanying compounds (strontium silicates and alumina-silicates, mullite) has almost identical values of free Gibbs energy, with a variant where only $SrO \cdot Al_2O_3 \cdot 2SiO_2$ is formed, and excessive oxides doesn't react with each other. Thus, in future for all points of simpex-plan, ΔG_T^o value (kJ/mol) presented for last mentioned reactions without a formation of accompanying phases. Graphic interpretation of dependency of the Gibbs free energy from the temperature for strontium anorthite shown in Fig. 2.

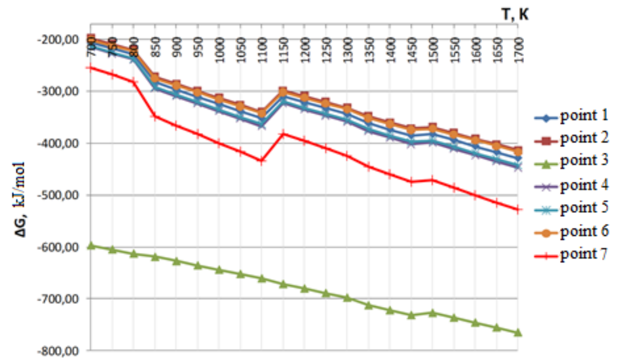

Fig.2. Graphic dependency of the ΔG, kJ/mol for strontium anorthite that was obtained from oxide (according to reaction 1)

Presented data shows that for all investigated points, the possibility of the monoclinic strontium anorthite formation $SrO \cdot Al_2O_3 \cdot 2SiO_2$ is rather high and less than -200.

Despite kJ/mol. The most preferred are reactions of formation for points 3 and 7, because they characterized by the most negative value of ΔG_T^o. For others points of planned experiment dependencies of free Gibbs energy almost identicalthe minimal ΔG_T^o value for points 3 and 7, these compositions can be characterized by lower dielectric properties, because they contain maximal amount of Al_2O_3 (~28…45 wt. %). According to calculated data, a little more than a half of this amount of Al_2O_3 goes on the formation of strontium anorthite. The rest of alumina oxides is in the products of reaction and it remains to be unbound.

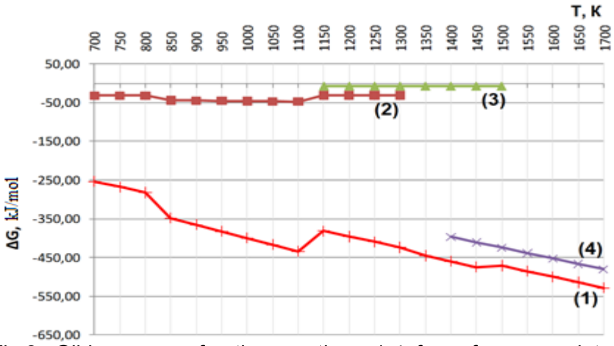

Fig.3. Gibbs energy for the reactions 1-4 for reference point of simplex-plan in a temperature range 700–1700 K

Also, a thermodynamic calculation of the strontium anorthite formation with the formation of intermediate compound according to reactions 2-4 was carried. For all investigated compositions value of ΔG_T^o of reactions is negative. However, the formation of intermediate crystal phases Sr_2SiO_4 and $SrSiO_3$ has a much lower possibility than a direct flowing of reaction. For all points of simplex plan, the value of free Gibbs energy is almost identical, that is why Fig. 3 shows a dependency of ΔG_T^o only for one composition (point No 7) for reactions 2-4, and also for reaction 1 for comparing.

Figure data shows that the reaction flow through the formation of intermediate compounds is unlikely, especially at temperature up to 1400 K. However, even above this temperature during the strontium anorthite formation from oxides according to reaction (1) values of free Gibbs energy is more negative.

Thus, received data of theoretical calculation of thermodynamic possibility of the formation of strontium anorthite $SrO·Al_2O_3·2SiO_2$ confirmed this possibility for all points of simplex plan. More preferable is the reaction flowing without a formation of intermediate compounds Sr_2SiO_4 and $SrSiO_3$.

Next step of the research is a manufacturing of samples and determination of optimal amount of each from phase forming oxides (SiO_2, Al_2O_3, SrO), that will provide minimal values of dielectric properties and high level of physical-mechanical properties. As a feedback water absorption *W* (%), dielectric permittivity (ε) and compressing strength $\sigma_{compression}$ (MPa) was set.

For manufacturing a laboratory samples as a raw material quartz of Vishnevetzkogo field and technical products such as alumina G-00 and strontium carbonate were used. Samples were prepared by moist pressing method, their form and proportions comply with GOST 24409-80. Fast firing was carried at the temperatures 1250–1450°C with exposure 5 hours.

For synthetic materials the measurement of compression strength was carried using the press GMS-50, dielectric permittivity with using digital measure of inductance of capacity and resistance E 7-8, water absorption was determined by boiling. As a measurement result the arithmetic average of three parallel tests was taken (table 3).

Table 3. Samples properties, sintered at different temperatures

No of sample	1250°C			1350°C			1450°C		
	W, %	ε	$\sigma_{compression}$, MPa	W, %	ε	$\sigma_{compression}$, MPa	W, %	ε	$\sigma_{compression}$, MPa
1	30.83	11.08	19	0.76	7.11	96	0.00	6.89	168
2	10.75	24.52	156	0.17	5.15	176	0.10	5.23	273
3	24.55	20.15	23	24.73	14.02	36	25.64	18.6	58
4	26.53	16.43	15	29.00	14.83	56	26.83	7.49	97
5	17.32	27.39	47	0.20	6.09	105	0.00	6.22	233
6	22.38	22.30	39	22.40	14.03	53	23.05	17.26	111
7	23.58	19.82	34	22.20	8.42	82	20.55	6.58	107

Presented data shows at temperature 1250°C the required level of sintering of materials is not reached – water absorption and dielectric permittivity values is much higher than acceptable limit, while the strength characteristics are acceptable only for samples of raw composition No 2.

In case of firing at 1350°C for all points of simplex plan value of dielectric permittivity decreasing and mechanical strength increasing. For samples No 1, 2, 5 the value of water absorption is decreasing (< 1%). Temperature increasing up to 1450°C doesn't affect water absorption much, however, affected dielectric properties in two ways: value of dielectric permittivity for samples No 1, 4, 7 is decreased, for others – increased. Increasing of temperature affected only mechanical characteristics in a positive way, however, samples No 1 and 5 showed signs of high-temperature deformation.

As a result of processing the experimental data of planned experiment, the dependency "composition-property" were established. Fig. 4 shows graphical view of obtained dependencies for compositions, that were sintered at temperature 1350°C. Isolines shows an equal values of properties.

Obtained dependencies shows that compositions with minimal amount of alumina oxide (25 wt. %) has a minimal value of water absorption. Dependency "composition – dielectric permittivity" has a similar trend – with decreasing of amount of alumina oxide the necessary level of a value ($\varepsilon < 10$) achieved, and minimal value of permittivity achieved at amount of Al_2O_3 25 wt. %. Higher mechanical strength of samples provides at amount of SiO_2 40–50 wt. % and Al_2O_3 25–30 wt. %. Area of optimal values of measured properties shifts to the area of stoichiometric composition of strontium anorthite $SrO·Al_2O_3·2SiO_2$, which can indicate a complete conversion of raw materials.

Complex analysis of presented data allows to suggest, that developed compositions of radio transparent ceramic No 2, No 5 required a necessary level of properties. Optimal composition is No 2, sintered at temperature 1350°C, which is characterized by minimal water absorption (0.17 %), minimal dielectric permittivity (5.15) and maximal mechanical compression strength (176 MPa).

Conclusions

As a result of theoretical studies for all composition of the simplex plan, the possibility of obtaining a strontium anorthite ceramic in a temperature range 700–1700K was determined. Obtained data indicates that the reaction of $SrO·Al_2O_3·2SiO_2$ synthesis more likely flows without a formation of intermediate compounds (Sr_2SiO_4 and $SrSiO_3$). Raw material compositions No 3 and No 7 has a minimum value of free Gibbs energy. However, these compositions contain a large amount of Al_2O_3, and after $SrO \cdot Al_2O_3 \cdot 2SiO_2$ synthesis part of the alumina oxides remains unbound. Such excess of Al_2O_3 leads to increasing of sintering temperature and decreasing of electro-physical properties, which confirmed by experimental data from laboratory samples test.

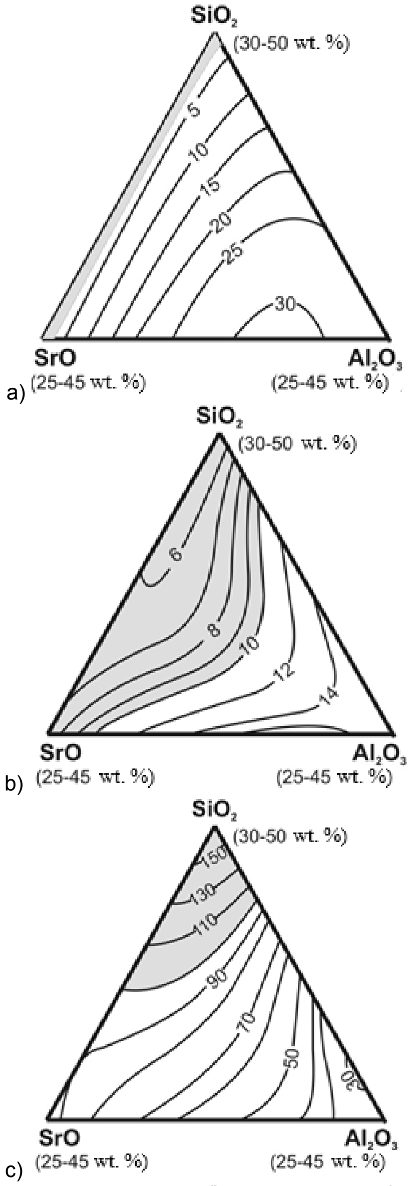

Fig.4. "Composition – property" dependencies for developed compositions of radio transparent ceramics, sintered at temperature 1350°C: a) water absorption (W, %); b) dielectric permittivity (ε); c) compression strength ($\sigma_{compression}$, MPa)

Realization of the experiment allowed to determine the most technological area of the compositions for the obtaining of radio transparent ceramic that provides maximum level of sintering (0.17–0.20%) and mechanical strength (105–175 MPa) and also low values of dielectric permittivity (5.15–6.09) at sintering temperature 1350°C. The optimum ratio of raw materials is: quartz:strontium carbonate:alumina = 50:25:25.

Thus, as a result of theoretical and experimental researches the compositions area for radio transparent ceramic was optimized and the best composition with the water absorption – 0.17%, dielectric permittivity value – 5.15 and mechanical strength – 175 MPa was chosen.

The results will be useful for creation and improvement of operational characteristics and durability of new polyfunctional radio transparent materials.

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