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Development of new compositions of ceramic masses in $SrO–Al_2O_3–SiO_2$ system

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The paper considered promises for creation of radio-ceramic ternary $SrO–Al_2O_3–SiO_2$. Predictive analysis on capabilities of synthesis of radiotransparent ceramic strontium anorthite non-stoichiometric composition was conducted with the help of theoretical research. By grapho-analysis of selected compounds there were determined the start temperature and complete melting temperature, phase composition, and the amount and chemical composition of the melt, which are formed at predetermined heat treatment conditions. Also, for creation of the radio-transparent material its dielectric characteristics and the glass phase material was calculated and the low temperature ceramic composition were recommended.

Keywords: strontium feldspar, dielectric permittivity, liquidus temperature, melt, glass phase.

Рассмотрена перспективная для создания радиопрозрачных керамик трехкомпонентная система $SrO–Al_2O_3–SiO_2$. С помощью теоретических исследований проведен прогнозный анализ возможности синтеза радиопрозрачных керамик на основе стронциевого анортита нестехиометрического состава. Путем графо-аналитических исследований выбранных составов определены температуры начала и полного плавления, фазовый состав, количество и химический состав расплавов, которые образуются при заданных условиях термообработки. Рассчитаны диэлектрические характеристики стеклофазы и материала, рекомендован низкотемпературный состав керамики для создания радиопрозрачных материалов.

Розробка нових складів керамічних мас в системі $SrO–Al_2O_3–SiO_2$. *Г.В.Лісачук, Р.В.Кривобок, А.В.Захаров, Е.В.Чефранов, Л.В.Лісачук.*

Розглянуто перспективну для створення радіопрозорої кераміки трикомпонентну систему $SrO–Al_2O_3–SiO_2$. За допомогою теоретичних досліджень проведено прогнозний аналіз можливості синтезу радіопрозорої кераміки на основі стронцієвого анортиту нестехіометричного складу. Шляхом графо-аналітичних досліджень обраних складів, визначено температури початку та повного плавлення, фазовий склад, а також кількість та хімічний склад розплавів, які утворюються при заданих умовах термообробки. Розраховано діелектричні характеристики склофази і матеріалу та рекомендовано низькотемпературний склад кераміки для створення радіопрозорих матеріалів.

1. Introduction

The most perspective field of radiotransparent materials (RTM) creation is development of ceramic materials that characterized by high uniformity of properties, heat resistance and radiotransparency. Ceramics only can act as radiotransparent materials in the dense layers of atmosphere, where their surface is heated to temperatures above 2000°C.

International experience in the field of ceramic radiotransparent materials indicates the presence of quartz, high-, aluminosilicate materials and also ceramics from Si_3N_4 and BN and others, which belong to a class of electrical ceramics. Each of these materials also has certain disadvantages and complicated energy-intensive production technology or they may have troubles in formation of products of a given type, such as the RTM manufacturing from quartz glass [1].

It should be noted, that the Scientific and Production Enterprise (SPE) "KVARSIT" and Subsidiary "UkrNDIsklo" develop and produce the radiotransparent ceramic materials in Ukraine. For example, SPE "KVARSIT" serially produces the radiotransparent heat-resistant nose cones of different shapes and sizes for air missiles that are parts of the planes' weapons such as MiG-29, Su-27, Su-30 and others; and also for missiles that are parts of anti-aircraft missile systems such as "Cube", "Buk", C-300 of all modifications. These materials are made on the base of quartz ceramics and lithium aluminosilicate glass ceramic [2].

New perspective direction of radiotransparent materials is the development based on strontium anorthite ($SrAS_2$) crystalline phase. In research works of Y.M.Sung [3, 4] the sintering and crystallization of strontium feldspar glass were investigated, and the effect of B_2O_3 and TiO_2 additives in amount of 3 wt. % on the phase composition and ceramic properties.

The scientists of BDTU (Belarus) [5] developed the composite RTM, the specialists of RHTU (Russia) [6] obtained the ceramics with high thermal stability (~ 1000°C), but technology of their manufacturing provides the high-temperature synthesis of $SrAl_2Si_2O_8$ (~ 1550÷1600°C).

Existing modern technologies of the RTM obtaining based on strontium and barium anorthites provide a complex multicycle production with the high-temperature heat treatment (above 1500°C).

Strontium anorthite exists in two polymorphic forms: monoclinic and hexagonal. The monoclinic form has a high melting point (1650°C) and low temperature coefficient of linear expansion ($2.5 \cdot 10^{-6}$ °C). Hexagonal shape is high-temperature metastable phase of strontium aluminosilicate, it shows the high temperature coefficient of linear expansion ($8 \cdot 10^{-6}$ °C) and extends at about 3 % with the opposite transformation at 600–800°C [3].

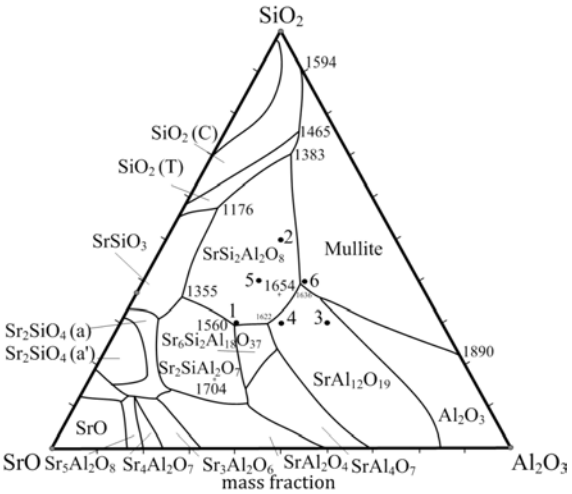

Fig. 1. Points of investigated compositions on phase diagram of $SrO–Al_2O_3–SiO_2$ system [7].

The purpose of this work is development and investigation of the new compositions of radiotransparent ceramic material of $SrO–Al_2O_3–SiO_2$ system.

The following tasks were set for achievement of this goal:

— carrying out grapho-analytical investigation and choosing the compositions, that contains a liquid phase at temperature 1250–1450°C in minimal amount 20–30 %;

— carrying out theoretical investigation of the composition properties at different temperatures;

— determination of the compositions that are suitable for applying as the low-temperature radiotransparent ceramic.

2. Experimental

2.1. Grapho-analytical investigations

In order to expand the range of known compositions of radiotransparent ceramic in ternary system $SrO–Al_2O_3–SiO_2$ we chose compositions 1–6, figurative points are shown in Fig. 1.

Chemical composition of the model ceramic masses is presented in Table 1. It should be noted, that figurative points of the model compositions 1–6 were chosen by us in primary crystallization field of strontium feldspar, mullite and strontium aluminate that suggests presence of difficult phase transitions and obtaining of several phases in products of crystallization.

Prediction of behaviour of the studied compositions for obtaining the low-temperature strontium anorthite was carried out with assistance of the predictive physicochemical analysis [8, 9]. The point of this

Table 1. Chemical composition of investigated ceramic masses

Composition code	Content of oxides, wt.%		
	SiO_2	Al_2O_3	SrO
1	30	25	45
2	50	25	25
3	30	45	25
4	30	35	35
5	40	25	35
6	40	35	25

method is to carrying out the grapho-analytic calculation in the ternary system of phase-forming oxides with the purpose of prediction of the materials phase composition and properties of melts, that formed during the heat treatment of the materials. For the model compositions the phase diagrams were plot (Fig. 2), by which temperature of melting beginning, liquidus temperature, amount of melt and solid phase composition at temperatures of 1250–1550°C were determined. Results of the grapho-analytical investigation of the composition melting process are presented in Table 2.

Analyzing the table data it is necessary to notice that composition 1, 3 and 4 in solid phase, contain compounds ($Sr_6Al_{18}Si_2O_{37}$ ($Sr_6A_9S_2$), $SrSiO_3$ (SrS), $Sr_2Al_2SiO_7$ (Sr_2AS), $SrAl_{12}O_{19}$ (SrA_6)), which are unwanted in ceramic composition, and also the high temperature of melt formation in compositions 3 and 4. For further theoretical investigations compositions 2, 5 and 6 were chosen. These compositions contain phases of strontium feldspar, mullite and quartz, that have low values of dielectric permittivity and dielectric loss tangent. The choise was justified on the basis of ability of oxide compositions form a sufficient amount of melt, that allows to decrease the temperature of strontium feldspar formation, unlike the temperature of solid-phase synthesis (1550–1600°C). For chosen the figurative points of composition 2, 5 and 6 (Fig. 2) at temperature of 1450°C the amount of melt, according to the diagram data, is 68.5, 49.5 and 37.0 %, respectively. This allows to suggest the possibility of low-temperature synthesis of the radiotransparent ceramic (in temperature range of 1250–1450°C), however for determination of the optimal amount of melt, necessary and sufficient for maximum densification of the material and intensification of strontium feldspar formation process, additional investigations are necessary.

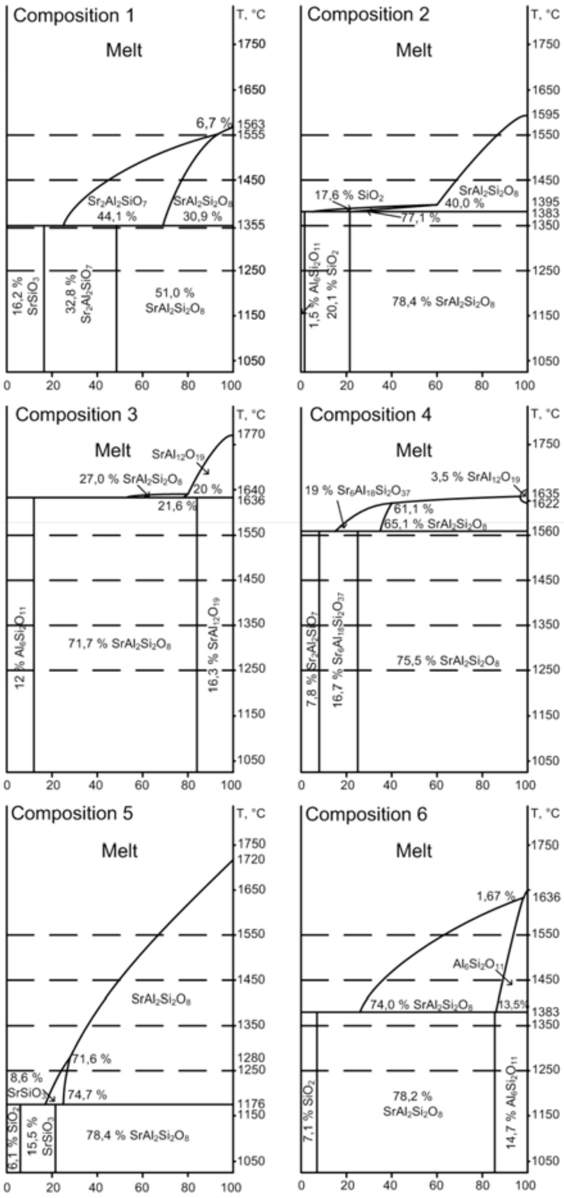

Fig. 2. Melting diagram of compositions 1–6 in $SrO_2–Al_2O_3–SiO_2$ system.

2.2. Calculation of melt properties

It is known that dielectric loss in ceramic materials depends on crystal and glass-phase characteristics and their relations. On the basis of carried preliminary calculations and compositions of the raw materials (quartz of Vishnevetsky field, alumina G-00 and strontium carbonate), chemical composition of the glass-phase which may be formed during heat-treatment at temperature range of 1250–1550°C, was calculated (Table 3).

Table 2. Physico-chemical properties of investigated compositions obtained on the basis of SrO_2–Al_2O_3–SiO_2 system

Composition code	Temperature of melt beginning, °C	Liquidus temperature, °C	Heat treatment temperature , °C	Amount of melt, %	Amount of solid phase, %	Composition of solid phase, %
1	1355	1563	1250	0	100	$SrAS_2$ (51.0) SrS (16.2) Sr_2AS (32.8)
			1350	0	100	$SrAS_2$ (51.0) SrS (16.2) Sr_2AS (32.8)
			1450	45	55	$SrAS_2$ (23) Sr_2AS (22)
			1550	91.5	8.5	$SrAS_2$ (7.5) Sr_2AS (1)
2	1383	1595	1250	0	100	$SrAS_2$ (78.4) A_3S_2 (1.5) SiO_2 (20.1)
			1350	0	100	
			1450	68.5	31.5	$SrAS_2$ (31.5)
			1550	87	13	$SrAS_2$ (13)
3	1636	1770	1250	0	100	$SrAS_2$ (71,7) A_3S_2 (12) SrA_6 (16.3)
			1350	0	100	
			1450	0	100	
			1550	0	100	
4	1560	1650	1250	0	100	$SrAS_2$ (75.5) Sr_2AS (7.8) $Sr_6A_9S_2$ (16.7)
			1350	0	100	
			1450	0	100	
			1550	0	100	
5	1176	1720	1250	24.5	75.5	$SrAS_2$ (73) SrS (2.5)
			1350	36	64	$SrAS_2$ (64)
			1450	49.5	50.5	$SrAS_2$ (50.5)
			1550	67	33	$SrAS_2$ (33)
6	1383	1650	1250	0	100	$SrAS_2$ (78.2) A_3S_2 (14.7) SiO_2 (7.1)
			1350	0	100	
			1450	37	63	$SrAS_2$ (52) A_3S_2 (11)
			1550	63	37	$SrAS_2$ (30.5) A_3S_2 (6.5)

Using a data about chemical composition and mathematic methods, proposed by N.M.Bobkova and V.I.Goleus [10, 11], dielectric properties were calculated. Also, the melt properties, as the main factors of intensity of the liquid-phase sintering of ceramics (viscosity, surface tension), and thermal coefficient of linear expansion of the glass-phase were calculated (Table 4).

In general, during a sintering of the dense ceramic materials, values of viscosity and surface tension of the melt must be in range of 10^3–10^5 Pa·sec and 300–400 N/m, which allows to accelerate the synthesis of necessary crystal phases through improving of material densification [12]. Analysis of the carried calculation shows that obtained at temperature 1250°C the melt which represents composition 5 with the values of

Table 3. Chemical composition of glass-phase, wt.%

Composition	T, °C	Content of oxides, wt.%					
		SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	SrO
2	1450	56.23	22.17	0.12	0.03	0.09	21.36
	1550	51.87	24.24	0.10	0.02	0.07	23.70
5	1250	54.57	12.57	0.13	0.07	0.33	32.33
	1350	48.9	16.39	0.09	0.04	0.22	34.36
	1450	45.62	20.47	0.06	0.03	0.16	33.66
	1550	43.35	23.28	0.05	0.02	0.12	33.18
6	1450	47.77	29.60	0.08	0.04	0.24	22.27
	1550	42.65	33.19	0.05	0.03	0.14	23.94

Table 4. Melt and glass-phase properties, that formed during heat-treatment of investigated model composition

Composition code	T, °C	TCLE, $a\cdot10^7$, K^{-1}	Melt viscosity, Pa·sec	Surface tension $\delta\cdot10^3$ N/m	ε at 10 GHz [10]	Dielectric properties [11]		
						ε at 10 GHz	ε	tgδ at 10 HGz
2	1450	44.87	$10^{3.291}$	341.1	6.37	8.67	5.23	0.0071
	1550	46.90	$10^{2.861}$	353.3	6.70	9.07	5.44	0.0078
5	1250	61.07	$10^{3.184}$	337.9	7.08	9.36	6.67	0.0024
	1350	62.36	$10^{2.75}$	352.8	7.47	9.84	6.84	0.0029
	1450	60.38	$10^{2.51}$	363,1	7.59	10.0	6.68	0.0040
	1550	58.98	$10^{2.26}$	371.5	7.68	10.2	6.57	0.0051
6	1450	44.45	$10^{3.40}$	356.9	6.83	9.26	5.21	0.0126
	1550	44.97	$10^{3.06}$	371.4	7.18	9.69	5.30	0.0162

viscosity and surface tension 103,184 Pa·sec and 337.9 N/m, respectively, and also the melt indicators of compositions 2 and 6, that formed at temperature 1450°C, with the values 103,291 Pa·sec, 341.1 N/m and 103.4 Pa·sec, 356.9 N/m, respectively, satisfy the requirements for the liquid phase synthesis.

The highest dielectric properties of the glass phase calculated using the Goleus methods, therefore data of this method were used for calculation of dielectric properties of the ceramic in general. Dielectric permittivity of the glass phase is increasing more with an increasing of temperature, than dielectric permittivity of the crystal phase, therefore the it is necessary to limit the amount of the glass phase. According to the indices of dielectric properties of the glass phase, composition 2 is more preferable than the others. The glass phase of 6-th composition, that will be formed at similar circumstances, will have the high dielectric values, therefore amount of this phase must be limited, so that values of dielectric permittivity of the ceramic composition will not be higher than 9. Dielectric values of the glass phase, that will be formed during the sintering of composition 5, does not suit the requirements.

Knowing the glass phase dielectric permittivity and the crystal phase dielectric permittivity, for calculation of dielectric permittivity of radiotransparent material the Lichtenekker's equation was used [13]:

$$\lg\varepsilon_c = y_1 \cdot \lg\varepsilon_1 + y_2 \cdot \lg\varepsilon_2,$$

where y_1 and y_2 is volume content of crystal phase and glass phase; ε_1 and ε_2 — dielectric permittivity of crystal phase and glass phase. Dielectric properties of investigated compositions of radiotransparent ceramic material are presented in Table 5.

Summarising the result, we can conclude that chosen compositions at sintering temperature of 1250–1450°C can provide the low-temperature synthesis of strontium ce-

Table 5. Dielectric properties of ceramic material

Composition code	Sintering temperature, °C	ε, 10 GHz
2	1250	6.21
	1350	6.21
	1450	8.10
	1550	8.79
5	1250	7.39
	1350	7.86
	1450	8.38
	1550	9.05
6	1250	6.56
	1350	6.56
	1450	7.75
	1550	8.67

ramic through formation of the sufficient amount of melt. However, for obtaining of the radiotransparent ceramic, for exploitation in harsh conditions, composition 2 is more preferable.

3. Conclusions

Thus, considering the information about structure of ternary system $SrO–Al_2O_3–SiO_2$, 6 points of compositions around a point of stoichiometric composition of strontium feldspar were chosen. Based on the obtained melt diagram data, 3 (three) compositions (2, 5 and 6) were chosen, where there is the presence of melt, at sintering temperature 1450°C, over 20 % and the presence of crystalline that can be used for manufacturing of radio transparent ceramic. According to the calculations of melt and glass-phase properties, the most perspective composition, compositions 2, was chosen. The indexes of melt of this composition at temperature 1450°C are: viscosity — $10^{3.291}$ Pa·sec, surface tension — 341.1 N/m, indexes of glass-phase, calculated at the same temperature: dielectric permittivity — 8.67 and dielectric loss tangent — 0.0071, and dielectric permittivity of ceramic compositions — 8.1 (at 10 HGz). Thus, for further investigation composition 2 is recommended, as it gives an opportunity of the radiotransparent materials creation, using the low-temperature synthesis.

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