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Thermodynamic analysis of solid phase reactions in $SrO–Al_2O_3–SiO_2$ system

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On the basis of thermodynamic calculations the values of the Gibbs energy of formation reactions of strontium anorthite from various raw materials in the temperature range of 773–1973 K were estimated. The study of $SrO–Al_2O_3–SiO_2$ system indicates the prospects of its further investigation for development of the radio transparent ceramic materials.
Keywords: Thermodynamic analysis, radio transparent materials, strontium feldspar, Gibbs energy.

На основе термодинамических расчетов определены значения энергии Гиббса реакции образования стронциевого анортита из различных сырьевых материалов в диапазоне температур 773–1973 К. Изучение системы $SrO–Al_2O_3–SiO_2$ указывает на возможность ее дальнейшего исследования для разработки радиопрозрачных керамических материалов.

Аналіз твердофазових реакцій у системі $SrO–Al_2O_3–SiO_2$. *Г.В.Лісачук, Р.В.Кривобок, А.В.Захаров, О.Ю.Федоренко, М.С.Притківа.*

На основі термодинамічних розрахунків окреслено значення енергії Гіббса реакції утворення стронцієвого анортиту з різних сировинних матеріалів у діапазоні температур 773–1973 К. Вивчення системи $SrO–Al_2O_3–SiO_2$ вказує на можливість її подальшого дослідження для розробки радіопрозорих керамічних матеріалів.

I. Introduction

High-temperature and radio transparent materials for rocket and space technology, in particular for radomes of aircraft, based on compounds of ternary system $SrO–Al_2O_3–SiO_2$ were created nowadays. It is known that ceramic materials based on the ternary system $SrO–Al_2O_3–SiO_2$ have low values of dielectric permittivity and dielectric loss tangent in a wide frequency band of electromagnetic wave and temperature range [1–4].

The ternary system $SrO–Al_2O_3–SiO_2$ was studied by Deere, Starzhevsky, Gottwald, Volker, Shukla and et al. According to them, in this system there is the following three-way compounds: strontium feldspar (anorthite) $SrO{\cdot}Al_2O_3{\cdot}2SiO_2$ ($SrAl_2Si_2O_8$), gehlenite — $2SrO{\cdot}Al_2O_3{\cdot}2SiO_2$ ($Sr_2Al_2SiO_7$) and $6SrO{\cdot}9Al_2O_3{\cdot}2SiO_2$ ($Sr_6Al_{18}Si_2O_{37}$).

The author of [5] amended the three-component system $SrO–Al_2O_3–SiO_2$ (Fig. 1) (the primary offset strontium anorthite crystallization region) and found that melting point of $SrAl_2Si_2O_8$ compound is 1654°C (this temperature we will use in further calculations). Previously it was thought that the melting point is equal to 1760°C.

The greatest interest in terms of creating the radio transparent ceramic material is directed to study of strontium feldspar $SrAl_2Si_2O_8$, which has high melting temperature, low coefficient of thermal expansion, low dielectric constant and dielectric loss tangent in a wide temperature and fre-

Table 1. Properties of strontium feldspar

Compound	Properties						
	ε	10^4 tgδ, 1 MGz	T_{melt}, °C	Density, g/cm^3	Crystal system	The index of refraction	
						N_g	N_p
$SrAl_2Si_2O_8$	6.2–6.8	11–50	1654°C (congruently)	3.08	monoclinic	1.586	1.574

quency range. The basic properties of strontium feldspar are shown in Table 1.

2. Experimental part

There are a few works on studying the formation of $SrAl_2Si_2O_8$, but they do not give complete picture of the condition of the thermodynamic probability of the process of its formation under heat treatment. To predict the possibility of the formation of solid-phase reactions $SrAl_2Si_2O_8$ we chose method of thermodynamic analysis. This method allows to reduce (in some cases completely eliminate) the experimental research by using calculation methods: the calculation of entropy, heat equation and the Gibbs energy for solid phase reactions, including the high temperatures conditions.

In the reference literature we have not found the initial values of thermodynamic constants (enthalpy, entropy and heat capacity equation coefficients) for $SrAl_2Si_2O_8$. In this connection, we were calculated the thermodynamic constants at the high temperatures.

Calculation of standard enthalpy

We used the methodology of formation of binary and ternary compounds, to calculate the enthalpy ΔH^0_{298}, which considers account the average gram atomic enthalpy of formation of the ternary system compounds, which proposed by V.Taranenkova [6]. V.Taranenkova found out that for similar compounds the ratio of gram-atom enthalpy of formation of this class compounds to the sum of the atoms that forms these compounds is constant. The calculation results are shown in Table 2.

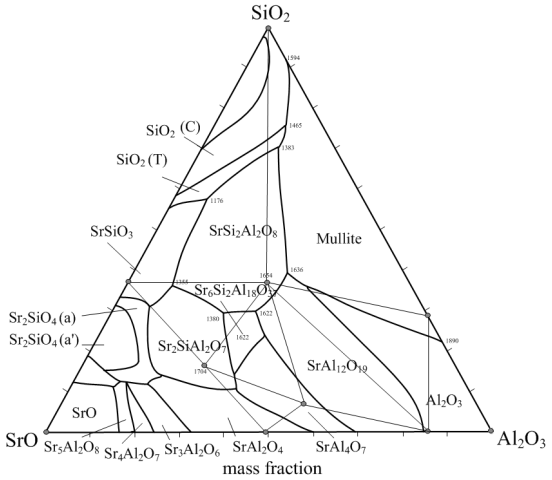

Fig. 1. Three-component systems $SrO–Al_2O_3–SiO_2$.

Calculation of standard entropy

Calculations of standard entropy were carried out according to semi-empirical formulas of Eastman and Yatsimirsky, and also formulas of Wood and Fraser according to which the entropy can be estimated by totality of values of entropy of composing mineral oxides with including of empirical correction for the difference in volume. The

Table 2. Results of enthalpy calculation

Compound	The number of atoms	$-\Delta H^0_{298}$, kJ/mol	
		Literature data	Calculation data
$Sr_4Al_2O_7$	13	4084.40	4196.01
$Sr_3Al_2O_6$	11	3535.02	3550.47
$SrAl_2O_4$	7	2310.53	2259.39
$SrAl_4O_7$	12	3949.04	3873.24
$SrSiO_3$	5	1632.92	1644.45
Sr_2SiO_4	7	2303.26	2303.23
Sr_3SiO_5	9	2971.60	2960.01
$SrAl_2Si_2O_8$	13	–	4235.79

Table 3. Results of entropy calculation

Compound	S^0_{298}, J/(mol·K)					T_{melt}, K
	by Eastman	by Yatsimirsky	by Wood	by Fraser	Average value	
$SrAl_2Si_2O_8$	201.84	173.38	217.61	204.14	199.12	1927

Table 4. Results of calculation of heat capacity

Compound	$Cp = f(T)$, J/(mol·K)			Temperature range, K
	a	$b \cdot 10^3$	$-c \cdot 10^{-5}$	
$SrAl_2Si_2O_8$	266.6	77.32	77.55	298–1927

results of these calculations are shown in Table 3.

Calculation of heat capacity

According to the method developed by N.Landiya it was determined depending equation of the heat capacity on temperature $Cp = f(T)$. The calculation was performed by the scheme according to which compound $SrAl_2Si_2O_8$ doesn't have polymorphic transformations, and it is complicated oxygen compound and consists of solid oxides and melts congruently (without decomposition). The calculation results are shown in Table 4.

Graphic interpretation of the heat capacity on temperature is shown in Fig. 2.

The figure shows that a curve of the ternary compound $SrAl_2Si_2O_8$ has nonlinear dependence in the temperature range of 573–1100 K, which is connected with the more complex structure of the ternary compound.

Calculation of the Gibbs energy

The Gibbs free energy change are calculated according to equation:

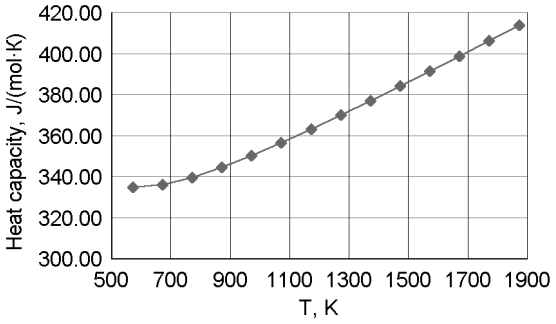

Fig. 2. Dependence of heat capacity on temperature connection $SrAl_2Si_2O_8$.

$$\Delta G_t = \Delta H_t - T \cdot \Delta S_t, \quad (1)$$

where ΔG_t — changes in the Gibbs free energy, kJ /mol; ΔH_t — change in reaction enthalpy, kJ/mol; T — reaction temperature, K; ΔS_t — entropy change of the reaction, J/(mol·K).

Methods of determining the Gibbs energy responds to the known calculation algorithm

Table 5. Thermodynamic properties of compounds

Compound	$-\Delta H^0_{298}$, kJ/mol	S^0_{298}, J/(mol·K)	$C_p = a + bT + cT^2$, J/(mol·K)			Temperature range, K	Source
			a	$b \cdot 10^3$	$c \cdot 10^{-5}$		
β–SiO_2	911.07	42.09	46.94	34.31	11.3	298–848	6
γ–Al_2O_3	1637.2	52.51	68.49	46.44	–	–	6
CO_2	393.51	213.94	44.14	9.04	8.54	298–2500	6
SrO	590.36	54.39	51.63	4.69	7.56	298–1270	10
$SrCO_3$	1218.96	97.11	86.66	35.83	14.22	298–1197	10
$Al_2Si_2O_7$	3339.67	147.28	229.5	36.82	14.56	–	10
$SrAl_2Si_2O_8$	4235.79	199.12	266.6	77.32	77.55	298–1927	Calculated by authors of the article

$\Delta G = f(T)$ in silicate systems on simple thermodynamic data.

Reference data for the calculation of the Gibbs energy are shown in Table 5.

On the basis of the thermodynamic calculations we determined the Gibbs energy value of formation reactions of strontium feldspar $SrAl_2Si_2O_8$ from the different source components — pure oxides and strontium carbonate and metakaolin in the following reactions:

$$SrSO_4 + Al_2O_3 \cdot 2SiO_2 = SrAl_2Si_2O_8 + SO_3, \quad (2)$$

$$SrSO_4 + Al_2O_3 + 2SiO_2 = SrAl_2Si_2O_8 + SO_3, \quad (3)$$

$$SrCO_3 + Al_2O_3 \cdot 2SiO_2 = SrAl_2Si_2O_8 + CO_2, \quad (4)$$

$$SrCO_3 + Al_2O_3 + 2SiO_2 = SrAl_2Si_2O_8 + CO_2, \quad (5)$$

$$SrO + Al_2O_3 \cdot 2SiO_2 = SrAl_2Si_2O_8, \quad (6)$$

$$SrO + Al_2O_3 + 2SiO_2 = SrAl_2Si_2O_8. \quad (7)$$

Calculation of probability of the formation of strontium anorthite was performed considering the polymorphic transformations of phases:

$$\gamma\text{–}Al_2O_3 \xrightarrow{1500K} \alpha\text{–}Al_2O_3,$$

$$\beta\text{–}silica \xrightarrow{848\ K} \alpha\text{–}tridymite$$

$$SrAl_2Si_2O_8 \xrightarrow{1323\ K} SrAl_2Si_2O_8$$

$$(monoclinical) \quad (hexagonal)$$

Graphic interpretation of the reactions of formation of strontium feldspar $SrAl_2Si_2O_8$ in the temperature range of 773–1973 K for 6 reactions is shown in Fig. 2.

Fig. 3 shows that the reaction of strontium anorthite formation from strontium sulfate, technical alumina and silica is accompanied by big negative value of the Gibbs energy in the investigated range of temperatures, than the rest of the reaction. But for all studied reactions the Gibbs energy change in the temperature range of

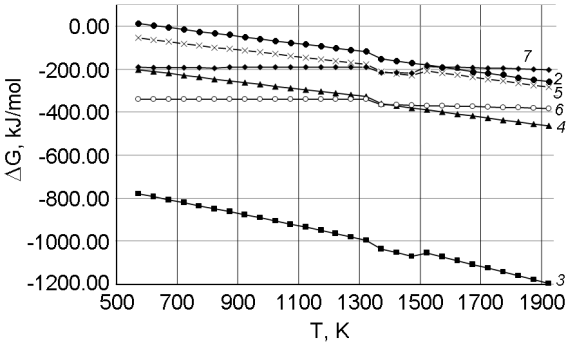

Fig. 3. Dependences of the Gibbs energy of synthesis reactions of strontium feldspar for reactions 2–7 of formation of the strontium feldspar.

773–1973 K is in the negative area, that shows the possibility of passing these reactions 2–7 of formation of strontium feldspar from a variety of raw materials.

3. Conclusions

On the basis of the performed calculation we created the thermodynamic database of ternary compound $SrAl_2Si_2O_8$ in system $SrO–Al_2O_3–SiO_2$. The method of thermodynamic analysis showed that promising raw materials for the low-temperature synthesis of strontium feldspar are strontium sulfate, technical alumina and silica in the temperature range of 773–1973 K. Studies of the thermodynamic constants of strontium feldspar indicates the prospects of its further study for the development of radio transparent ceramic materials.

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