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RESEARCH ARTICLE

**Determining the phase stability of luminescent materials based on the solid solutions of oxyorthosilicates  $(\text{Lu}_{1-x}\text{Ln}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$ , where Ln = La–Yb**

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**Objectives.** This study aimed to predict the limits of substitution and stability of luminescent materials based on low-temperature modifications of solid solutions (spatial group  $P2_1/c$ ) with lutetium oxyorthosilicates  $(\text{Lu}_{1-x}\text{Ln}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$ , where Ln represents the rare-earth elements (REEs) of the La–Yb series.

**Methods.** The V.S. Urusov's crystal energy theory of isomorphous substitutions and a crystallochemical approach in the regular solid solution approximation were used to calculate the energies of the mixing (interaction parameters) of the solid solutions.

**Results.** Using the V.S. Urusov's theory, we calculated the energies of mixing (interaction parameters) in the systems under study. The dependences of the decomposition temperatures of solid solutions on the REE number and composition ( $x$ ) were obtained and used to create a diagram of the thermodynamic stability of the solid solutions, allowing us to predict the substitution limits depending on the temperature or determine the decomposition temperature using the given substitution limits.

**Conclusions.** The results of the study can be useful when choosing the ratio of components in matrices (host materials) and the amount of the activator (dopant) in the new luminescent, laser, and other materials based on low-temperature modifications of solid solutions of "mixed" REE oxyorthosilicates  $(\text{Lu}_{1-x}\text{Ln}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$ .

**Keywords:** oxyorthosilicate, rare-earth elements, isomorphous substitution, solid solution, energy of mixing

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НАУЧНАЯ СТАТЬЯ

# Определение фазовой стабильности люминесцентных материалов на основе твердых растворов оксиортосиликатов $(Lu_{1-x}Ln_x)[(SiO_4)_{0.5}O_{0.5}]$ , где Ln = La–Yb

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**Цели.** Целью работы явилось прогнозирование пределов замещения и стабильности люминесцентных материалов на основе низкотемпературных модификаций твердых растворов (пространственная группа  $P2_1/c$ ) на основе оксиортосиликата лютеция  $(Lu_{1-x}Ln_x)[(SiO_4)_{0.5}O_{0.5}]$ , где Ln – редкоземельный элемент серии La–Yb.

**Методы.** Для расчета энергий смешения (параметров взаимодействия) для твердых растворов была использована теория изоморфной смесимости В.С. Урусова и кристаллохимический подход в приближении регулярного твердого раствора.

**Результаты.** Получены зависимости температур распада твердых растворов от порядкового номера редкоземельных элементов и состава, которые использованы для построения диаграмм термодинамической устойчивости твердых растворов, что позволило прогнозировать пределы замещения в зависимости от температуры или определять температуру распада на основе заданных пределов замещения.

**Выводы.** Результаты исследования могут быть полезны при выборе соотношения компонентов в матрице («хозяине») и количества активатора (допанта) в новых люминесцентных, лазерных и других материалах на основе низкотемпературных модификаций твердых растворов «смешанных» оксиортосиликатов редкоземельных элементов  $(Lu_{1-x}Ln_x)[(SiO_4)_{0.5}O_{0.5}]$ .

**Ключевые слова:** оксиортосиликат; редкоземельные элементы; изоморфное замещение; твердый раствор; энергия смешения

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## INTRODUCTION

Oxyorthosilicates of rare-earth elements (REEs),  $Ln[(SiO_4)_{0.5}O_{0.5}]$ , and solid solutions  $(Lu_{1-x}Ln_x)[(SiO_4)_{0.5}O_{0.5}]$  have attracted the attention of researchers, as they can be applied as materials for producing luminophores [1, 2], scintillators [3–7], lasers [8], among other purposes. Initially, they were synthesized at a temperature of 1773 K, and then single crystals were grown by the Czochralski method, as they have significantly high melting points [4]. The oxyorthosilicates obtained under these conditions crystallize in the space groups  $P2_1/c$  (for the cerium subgroup) and in  $C2/c$  (for the yttrium subgroup) into a monoclinic crystal system [3–5]. Subsequently,

the authors of [1] established that the oxyorthosilicates of the yttrium subgroup can also be obtained as a low-temperature modification (1173–1273 K) of nanosized polycrystals (space group  $P2_1/c$ ). In this case, they are isostructural crystals of the cerium subgroup.

The study of luminescent properties showed that the polycrystalline oxyorthosilicate  $Lu[(SiO_4)_{0.5}O_{0.5}]:Ce$  had better spatial resolution and image sharpness than luminophore  $Gd_2O_2Si:Tb$ , which has been used in most medical imaging methods in the last decades [6]. This luminophore can be used in X-ray mammography for visualization in both radiographic cassettes and digital detectors. It has an excellent spectral compatibility with the currently used Si-based films

and photodiodes [7]. The luminescence intensity of a polycrystalline, nanosized lutetium oxyorthosilicate obtained by solution combustion synthesis (SCS) and excited by X-rays is significantly higher ( $64 \pm 4$ ) than those of gadolinium ( $36 \pm 4$ ) and yttrium ( $44.3 \pm 1.5$ ) oxyorthosilicates obtained by the same method, but it is slightly lower than those of Gd and Y single crystals ( $94 \pm 13$  and  $97 \pm 14 \text{ s}^{-1} \text{ mg}^{-1}$ , respectively) synthesized by the Czochralski method [9].

Luminophores derived from lutetium oxyorthosilicate ( $\text{Lu}[(\text{SiO}_{4/0.5}\text{O}_{0.5})]$ ) suffer from several drawbacks. First, they contain nearly 2.6% of the radioactive isotope  $^{176}\text{Lu}$ , which undergoes beta decay and causes noise in scintillation devices. Second, lutetium is more expensive than other REEs [10].

These drawbacks can be minimized by using “mixed” oxyorthosilicates ( $\text{Lu}_{1-x}\text{Ln}_x[(\text{SiO}_{4/0.5}\text{O}_{0.5})]$ ), which contain not only lutetium but also other REEs [4, 9–12].

However, the physicochemical bases for the synthesis of “mixed” solid solutions—phase diagrams and, particularly, solubility regions of solutions based on REE oxyorthosilicates—have not been studied yet. The experimental determination of the solubility regions in a solid phase is an independent task, which requires special equipment expensive reagents, and long research periods.

Therefore, most researchers studying the luminescent properties of mixed REE oxyorthosilicates have to choose the composition of the matrices and activators either by analogy with similar systems or by trial and error.

Occasionally, researchers do not consider the fact that solid solutions synthesized at high temperatures are prone to decaying upon cooling and can change their phase compositions and properties. This can lead to the degradation of the materials that are based on these solutions in practical scenarios. Therefore, before synthesizing and studying the properties, one must evaluate the limits of isomorphous substitutions and stability of solid solutions in the corresponding systems both during their synthesis and intended use.

Accordingly, this study aims to predict the limits of substitution and stability of luminescent materials based on low-temperature modifications of solid solutions (spatial group  $\text{P2}_1/\text{c}$ ) with lutetium oxyorthosilicates ( $\text{Lu}_{1-x}\text{Ln}_x[(\text{SiO}_{4/0.5}\text{O}_{0.5})]$ , where Ln represents REEs).

## METHODOLOGY OF CALCULATION AND INITIAL DATA

The calculations were performed within the framework of the V.S. Urusov’s crystal energy theory of isomorphous miscibility [13] in regular solid solution approximation for one gram-atom number of the substituting structural units in pseudobinary ( $\text{Lu}_{1-x}\text{Ln}_x[(\text{SiO}_{4/0.5}\text{O}_{0.5})]$ ) systems.

To calculate the substitution limit ( $x$ ) for a given decomposition temperature of a solid solution ( $T_d$ ) or to define a decomposition temperature for a given substitution limit in the approximation of regular solutions, we used the Becker equation [14] as follows:

$$-(1-2x)/\ln[x/(1-x)] = RT_d/Q_{\text{mix}}, \quad (1)$$

where  $R$  denotes the universal gas constant and  $Q_{\text{mix}}$  the mixing energy (or interaction parameter). Equation 1 can be used in our case if the dimensional parameter of interatomic distances (the dimensional parameter is calculated using the values of the substitutable structural units or dimensions of the unit cells of the system components) does not exceed 0.1 [13, 15, 16]. In the systems under consideration, the value of the dimensional parameter, which is calculated using the volumes of unit cells as  $[\delta = (V_{\text{Ln}}^{1/3} - V_{\text{Lu}}^{1/3})/V_{\text{Lu}}^{1/3}]$ , does not exceed 0.066 (see the table); therefore, it is expedient to apply the Becker equation. We used the volumes of unit cells in our calculation because the literature data [1, 10, 17] (pertaining to the synthesis and investigation of the properties of nanoscale low-temperature modification of  $\text{Lu}[(\text{SiO}_{4/0.5}\text{O}_{0.5})]$ ) did not contain the information on its structural data. The authors in [1], who described the low-temperature modifications of  $\text{Ln}[(\text{SiO}_{4/0.5}\text{O}_{0.5})]$ , provided cell parameters only for the compounds of other REEs that belonged to the yttrium subgroup, and not for  $\text{Lu}[(\text{SiO}_{4/0.5}\text{O}_{0.5})]$ . Therefore, the volume of the low-temperature modification of the  $\text{Lu}[(\text{SiO}_{4/0.5}\text{O}_{0.5})]$  unit cell (approximately  $384 \text{ \AA}^3$ ) was determined by extrapolating the relationship between the volumes of low-temperature modifications of  $\text{Ln}[(\text{SiO}_{4/0.5}\text{O}_{0.5})]$  unit cells, provided in [1], and the ionic radii of REEs according to R. Shannon [18] (see Fig. 1).

In the regular solution approximation, the mixing energy can be determined by the enthalpy of mixing ( $\Delta H_{\text{mix}}$ ) as  $Q_{\text{mix}} = \Delta H_{\text{mix}}/(x_1 \times x_2)$ , where  $x_1$  and  $x_2$  denote the mole fractions of the solvent and dissolved substance, respectively. Thus, the main task while calculating the substitution limit for a given decomposition temperature of a solid solution or while determining the decomposition temperature for a given substitution limit is to estimate the enthalpy of mixing.

Normally, the enthalpy of mixing ( $\Delta H_{\text{mix}}$ ) in Equation 2 proposed by V.S. Urusov [13, 15, 16] arises because of three factors: the difference among the sizes of the substituting structural units ( $\Delta H_{\delta}$ ), different degrees of ionicity of the chemical bonds between the system components ( $\Delta H_{\epsilon}$ ), and the difference in their crystal structures ( $\Delta H_{\text{II-I}}$  denotes the enthalpy during the polymorphic transition from the structure of the substituting component to the structure of the substitutable component). One has the following:

Energies of mixing and critical decomposition temperatures of solid solutions  
 $(\text{Lu}_{1-x}\text{Ln}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$

| Ln | $V, \text{\AA}^3$ | $\delta$ | $Q_R, \text{J/mol}$ | $\chi_{\text{Ln}}$ | $\epsilon$ | $\Delta\epsilon$ | $Q_\delta, \text{J/mol}$ | $Q_{\text{mix}}, \text{J/mol}$ | $T_{\text{cr}}, \text{K}$ |
|----|-------------------|----------|---------------------|--------------------|------------|------------------|--------------------------|--------------------------------|---------------------------|
| La | 465.2             | 0.06602  | 57428               | 1.327              | 0.724      | 0.019            | 585                      | 58013                          | 3460                      |
| Ce | 455.2             | 0.05841  | 44947               | 1.348              | 0.720      | 0.015            | 365                      | 45312                          | 2700                      |
| Pr | 445.1             | 0.05045  | 33528               | 1.374              | 0.716      | 0.011            | 196                      | 33724                          | 2010                      |
| Nd | 439.3             | 0.04577  | 27719               | 1.382              | 0.714      | 0.009            | 131                      | 27850                          | 1660                      |
| Pm | 431.9             | 0.03998  | 21058               | 1.391              | 0.712      | 0.007            | 79                       | 21137                          | 1260                      |
| Sm | 424.4             | 0.03390  | 15134               | 1.410              | 0.708      | 0.003            | 15                       | 15149                          | 900                       |
| Eu | 417.9             | 0.02860  | 10776               | 1.433              | 0.704      | 0.001            | 2                        | 10778                          | 640                       |
| Gd | 414.0             | 0.02538  | 8484                | 1.386              | 0.712      | 0.007            | 79                       | 8563                           | 510                       |
| Tb | 409.2             | 0.02141  | 5967                | 1.410              | 0.708      | 0.003            | 15                       | 5982                           | 360                       |
| Dy | 404.0             | 0.01706  | 3834                | 1.426              | 0.706      | 0.001            | 2                        | 3836                           | 230                       |
| Ho | 397.5             | 0.01158  | 1767                | 1.433              | 0.704      | 0.001            | 2                        | 1769                           | 100                       |
| Er | 395.6             | 0.009961 | 1305                | 1.438              | 0.703      | 0.002            | 6                        | 1311                           | 80                        |
| Tm | 389.7             | 0.004925 | 317                 | 1.455              | 0.700      | 0.005            | 40                       | 357                            | 20                        |
| Yb | 387.0             | 0.002600 | 85                  | 1.479              | 0.695      | 0.010            | 162                      | 247                            | 10                        |
| Lu | 384.0             | –        | –                   | 1.431              | 0.705      | –                | –                        | –                              | –                         |

Note: The volumes of the unit cells of cerium and promethium oxyorthosilicates are defined as the arithmetic mean of the volumes of the unit cells of lanthanum and praseodymium oxyorthosilicates, as well as of neodymium and samarium, respectively.

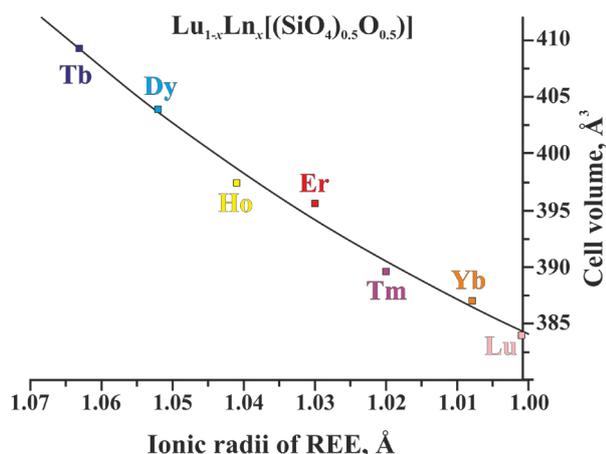


Fig. 1. Dependence of the volumes of the unit cells of low-temperature modifications of  $\text{Ln}[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$  on the ionic radii of REE.

$$\Delta H_{\text{mix}} = \Delta H_\delta + \Delta H_\epsilon + x_2 \Delta H_{\text{II-I}} = Cx_1x_2mnz_mz_x\delta^2 + 1390x_1x_2mz_mz_x\alpha(\Delta\epsilon)^2/(2r) + x_2\Delta H_{\text{II-I}} \quad (2)$$

However, to the best of our knowledge, no data in the literature pertains to the enthalpies of polymorphic transitions  $\Delta H_{\text{II-I}}$  for the oxyorthosilicates of REEs. This equation can still be used for performing calculations in cases wherein the system components are isostructural (i.e., at  $\Delta H_{\text{II-I}} = 0$ ) or wherein the amount of the dissolved substance is significantly low (at  $x_1 \approx 1$  or at  $x_2 \ll 1$ ) [13, 15].

While performing calculations in systems with isostructural components, the  $\Delta H_{\text{mix}}$  value consists of two

factors (see Equation 3): the difference in the sizes of the substituting structural units ( $\Delta H_\delta$ ), and different degrees of ionicity of the chemical bonds between the system components ( $\Delta H_\epsilon$ ). One has the following:

$$\Delta H_{\text{mix}} = \Delta H_\delta + \Delta H_\epsilon = Cx_1x_2mnz_mz_x\delta^2 + 1390x_1x_2mz_mz_x\alpha(\Delta\epsilon)^2/(2r), \text{ (kJ/mol)} \quad (3)$$

Therefore, the energy of mixing can also be determined as the sum of two factors as follows:

$$Q_{\text{mix}} = Q_\delta + Q_\epsilon = Cmnz_mz_x\delta^2 + 1390mz_mz_x\alpha(\Delta\epsilon)^2/(2r) \quad (4)$$

In this equation, C denotes a constant equal to 112.6 kJ and is calculated as  $C = 20(2\Delta\chi + 1)$  [16] by using the electronegativity difference between cations and anions,  $\Delta\chi$  [19–20] in a pseudobinary approximation. The term  $m$  denotes the number of formula units in the pseudobinary approximation, calculated per mole of a substitutable structural unit ( $1 + 0.5 + 0.5 = 2$ ). The term  $n$  denotes the coordination number of a substitutable structural unit in the pseudobinary approximation of the structure (at the first cation position ( $n = 7$ ), there are 6  $\text{SiO}_4^{4-}$  tetrahedra and one  $\text{O}^{2-}$  ions; at the second position ( $n = 6$ ), there are 3  $\text{SiO}_4^{4-}$  tetrahedra and three  $\text{O}^{2-}$  ions; i.e., on average  $n = 6.5$ ). The terms  $z_m$  and  $z_x$  denote the formal charges of the substitutable and common structural units of the components, respectively:  $z_m = 3$ , as  $z_x = 4 \times 0.5 + 2 \times 0.5 = 3$ . The term  $\delta$  denotes a dimensional parameter, which is calculated for each

system using the volumes of the unit cells, as shown in [1, 21]. The term  $\alpha$  denotes a reduced Madelung constant equal to 1.9 and is calculated by the Hoppe's formula [22] as follows:  $(\alpha/n)^2 + \alpha = 1.81$ , where  $n = 6.5$  is a coordination number in the pseudobinary approximation of the structure. The degrees of ionicity of the chemical bond  $\varepsilon$  were determined using the electronegativity difference ( $\Delta\chi$ ) between the REE anions and cations, as provided in [19]. The  $\chi$  value of the  $\text{SiO}_4^{4-}$  anion according to the recommendation provided in [20] was assumed to be equal to that of the oxide anion, i.e., 3.7 [19]. The term  $r$  denotes the average interatomic "cation–anion" distance in the pseudobinary approximation, and it was calculated for one of the previously studied structures of this structural type, i.e.,  $\text{Gd}[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$ . The "cation–tetrahedral anion" distances for two positions of gadolinium were considered as the sum of distances ( $\text{Gd–O} + \text{Si–O}$ ) and the "cation–oxygen" distance ( $\text{Gd–O}$ ), not bounded to silicon [21]. In the first position: the cation was surrounded by 6  $\text{SiO}_4^{4-}$  tetrahedral ions and 1 oxygen atom, and the average distance was  $[6 \times (2.49 + 1.63) + 2.35]/7 = 3.86 \text{ \AA}$ . In the second position: the cation was surrounded by 3  $\text{SiO}_4^{4-}$  tetrahedral ions and 3 oxygen atoms, and the average distance was  $[3 \times (2.39 + 1.63) + 3 \times 2.30]/6 = 3.15 \text{ \AA}$ . The average distance between the two positions of the cation was  $r = 3.5 \text{ \AA}$ .

## RESULTS AND DISCUSSION

Some initial data and calculations results are presented in the table. From the table, it is evident that the values of size parameter ( $\delta$ ) do not exceed 0.1, with the maximum value being 0.066. Consequently, according to [13], the dependence of the decomposition temperatures of solid solutions on the system composition will be almost symmetric, and the  $T_d$  values can be calculated using the Becker equation for regular solid solutions.

As the REE number increases, the contributions to the total energy of mixing  $Q_R$  consequently decreases, as explained by the decreasing difference in the size of the replacing structural units—REE ions. Their electronegativity values ( $\chi_{\text{Ln}}$ ) vary non-monotonically unlike their ion radii: they grow with increase in the REE number in the La–Eu series, sharply decrease during the transition to Gd, and then again increase with increase in the REE number in the Gd–Yb series. The electronegativity of Lu, as in the case of Gd, is also significantly low. Such a change in the  $\chi_{\text{Ln}}$  of REEs leads to a situation wherein the differences in the degrees of ionicity of the chemical bonds vary within the range of 0.001–0.019 and do not significantly affect the total energy of mixing, which decreases with increase in the REE number. As recommended in [13], if  $\Delta\varepsilon < 0.05$ , the contribution of  $\Delta H_\varepsilon$  to the mixing energy can be neglected.

The critical decomposition temperatures  $T_{\text{cr}}$  of the solid solutions were calculated as  $T_{\text{cr}} = Q_{\text{mix}}/2kN$  [13], where  $k$  denotes the Boltzmann constant and  $N$  the Avogadro number. As can be seen from the table and Fig. 2 (curve for  $x = 0.50$ ), their  $T_{\text{cr}}$  values, as expected, decrease with increase in the REE number.

Using the values of the decomposition temperatures of solid solutions calculated by the Becker equation, we plotted the dependences of the decomposition temperature on the REE number (see Fig. 2) for the substitution limits  $x = 0.01, 0.03, 0.05, 0.1, \text{ and } 0.2$ . These dependences can be used to define the substitution limit for lutetium, replaced by REE, based on the given temperature or to calculate the decomposition temperature by using the substitution limit [23–24]. In the first case, we must draw an isotherm from the given temperature to the intersection with the vertical line of this REE. From the point of the intersection, one can estimate the range of  $x$  values, within which the substitution limit is located. The substitution limit should be refined by interpolating the vertical segment between the decomposition temperature and REE number dependences, which are the closest to the intersection points. In the second case, the position of a point on the vertical line of given REE is determined by its composition, after which a horizontal line is drawn up to the intersection with the temperature axis. These problems can be solved more precisely by plotting the dependence of the decomposition temperature of the solid solution on the composition ( $x$ ) for each system by using the Becker equation.

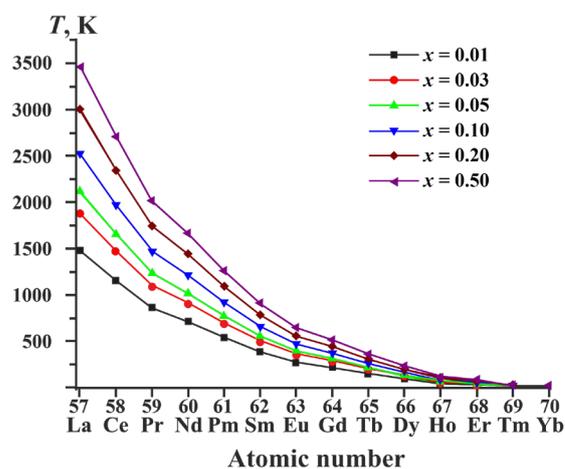


Fig. 2. Thermodynamic stabilities of the solid solutions of  $(\text{Lu}_{1-x}\text{Ln}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$  systems.

However, in contrast with the previously described systems [23–24], the component  $\text{Lu}[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$ , which serves as a basis for solid solution formation, undergoes a polymorphic transition from the  $\text{P2}_1/\text{c}$  space group to  $\text{C2}/\text{c}$  at 1173 K in the case of synthesis by the sol–gel method [1], or at 1273 K in the case of synthesis by SCS [10, 17]. This affects the phase relationships in the systems. At the synthesis temperature or operation temperature lower

than the temperature of the polymorphic transition of  $\text{Lu}[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$ , both the components in the systems are isostructural, and the results can be used both to select the ratio of components in solid solutions and the number of activators.

However, if the synthesis temperature or operating temperature exceeds the temperature of the polymorphic transition of  $\text{Lu}[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$ , a complete miscibility does not work, as the oxyorthosilicates of the cerium subgroup, unlike  $\text{Lu}[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$ , do not undergo a polymorphic transition to a structure with the C2/c space group, and the calculation results without regard to the enthalpy of polymorphic transition may be incorrect. Simultaneously, when choosing the amount of the activator to be introduced at low substitution rates (usually from a fraction of percent to several percent), the contribution of the enthalpy of polymorphic transition to the enthalpy of mixing will be negligible, and the calculation results in this case can be considered indubitable.

Noteworthy, when choosing the conditions for obtaining solid solutions, one should consider that the temperatures of the polymorphic transitions of REE oxyorthosilicates exceed the temperatures of their synthesis by the sol-gel method by only 50–75 K [1], thereby requiring highly accurate temperature regulation.

From the diagram, one can estimate the regions of thermodynamic stability of solid solutions. Thus, at  $T > T_{\text{cr}}$  (i.e., in the region above the curve for  $x = 0.50$ , see Fig. 2) the unbounded solid solutions, synthesized at temperatures below the polymorphic transition temperatures, are thermodynamically stable over the entire concentrations range, i.e.,  $0 < x < 1$ . However, in the region below the curve for  $x = 0.50$  ( $T < T_{\text{cr}}$ ), the unbounded solid solutions are thermodynamically unstable and can decay into phases with partial miscibility. Similarly, the solid solutions with  $x = 0.01, 0.03, 0.05, 0.10,$  and  $0.20$  are thermodynamically stable in the regions above the curves but are unstable in the regions below them.

With decrease in the temperature, the structural units of a solid solution become less mobile owing to the decrease in the diffusion rate while the solubility regions become smaller [13]. This phenomenon proceeds until the diffusion rate becomes so low that the solubility regions practically stop decreasing, meaning that spontaneous hardening occurs and solid solutions become metastable. If we assume that the quenching temperature is close to the minimum temperature at which the components in the solid phase start interacting and thus forming a solid solution, then we can estimate the temperature of spontaneous hardening and the region of metastability in the system. REE oxyorthosilicates and solid solutions based on them are usually synthesized

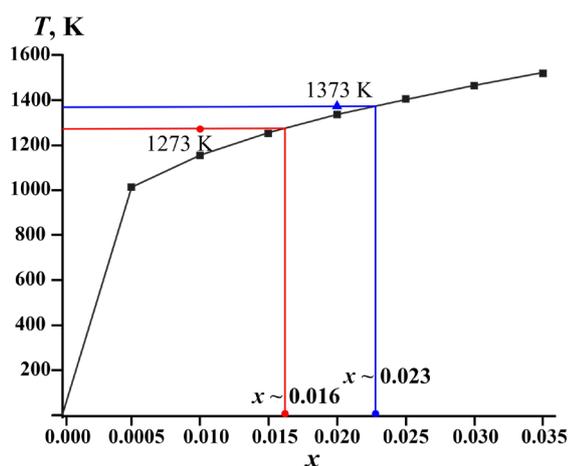
at temperatures ranging from 1773 K (using the conventional solid phase method with oxides of the corresponding elements as initial reagents [5]) to 1173 K (using the sol-gel method [1]). The latter agrees with the Tammann's rule, according to which the structural units during heating begin to interact in a mixture of solids at a temperature approximately 50% of the melting point [25]. Below the Tammann temperature, the mobility of the structural units is so low that the formation or decomposition of the solid solutions does not occur. Considering that the melting points of REE oxyorthosilicates range from 2170 K to 2320 K [26], one can assume that when solid solutions cool down to the temperature below  $\sim 1173$  K, the mobility of the structural units will be insufficient for the thermodynamically unstable solid solutions to decompose; i.e., the solid solutions will become metastable.

Therefore, in  $(\text{Lu}_{1-x}\text{Ln}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$  systems containing REEs from La to Nd, the solid solutions, which are thermodynamically stable at temperatures above the critical temperature (3460–1660 K, see the table and Fig. 2), become thermodynamically unstable and can decay when the temperature decreases within the range between  $T_{\text{cr}}$  and  $\sim 1173$  K. This occurs if the diffusion rate and time are sufficient for the stable nuclei of a new phase to emerge and start growing. At temperatures below 1173 K, the solid solutions will not decay, meaning that spontaneous hardening occurs and the solid solutions become metastable.

In systems containing REEs from Sm to Yb, the critical decomposition temperatures (900–10 K) are significantly lower than the Tammann temperature; therefore, unbounded solid solutions do not decay upon cooling and are stable at temperatures higher than the critical temperatures and metastable at temperatures lower than the critical temperatures.

The difference between the critical temperature in a system with Pm (1260 K) and the spontaneous quenching temperature ( $\sim 1173$  K) is close to the calculation error ( $\pm 100$  K); therefore, it becomes difficult to predict the decomposition temperature of an unbounded solid solution in this system.

To the best of our knowledge, the literature contains no data pertaining to the energies of mixing and the limits of substitution of lutetium by REEs for solid solutions of REE oxyorthosilicates with partial miscibility of components. Therefore, it becomes difficult to assess the validity of the calculations performed. However, there are data on the compositions and temperatures during the synthesis of solid solutions  $(\text{Lu}_{1-x}\text{Ce}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$ , where  $x = 0.01$  at 1273 K [27] and  $x = 0.02$  at 1373 K [28]. The graphical dependence of the calculated decomposition temperatures of the solid solutions  $(\text{Lu}_{1-x}\text{Ce}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$  on the mole fraction of Ce (see



**Fig. 3.** Fragment of the dependence of the calculated decomposition temperatures of the solid solutions in the  $(\text{Lu}_{1-x}\text{Ce}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$  system on the mole fraction of Ce. Also presented are the experimental data for the compositions wherein  $x = 0.01$  at 1273 K [26] and  $x = 0.02$  at 1373 K [28].

Fig. 3) shows that when  $x = 0.01$  at 1273 K [27] or/and  $x = 0.02$  at 1373 K [28], the calculation results do not contradict the experimental data. This means that these solid solutions are in the region of thermodynamic stability as predicted by us. Both the compositions of the  $(\text{Lu}_{1-x}\text{Ce}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$  system, i.e., with  $x = 0.01$  and  $x = 0.02$ , synthesized at 1273 and 1373 K [27–28], are located in the regions of solid solutions, which, according to the calculation results, extend to  $x = 0.016$  and  $x = 0.023$ , respectively, at these temperatures.

## CONCLUSIONS

A crystallochemical approach in the regular solution approximation was used to calculate the energies of mixing (interaction parameters) of solid solutions, which were based on the low-temperature modification of lutetium oxyorthosilicate  $\text{Lu}[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$  and modified with REEs for compositions with  $x = 0.01, 0.03, 0.05, 0.10, 0.20,$  and  $0.5$ . With increase in the REE number, the calculated energies of mixing and the critical decomposition temperatures of the solid solutions decreased, as explained by the decrease in the REE ionic radii in the series

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from La to Yb. It was shown that the contribution of a system component to the energy of mixing, caused by the difference in the sizes of the substituting structural units, was significantly greater than the one caused by the differences in the degrees of ionicity of the chemical bonds in the components, and hence the latter could be neglected.

The thermodynamic stability diagrams of  $(\text{Lu}_{1-x}\text{Ln}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$  systems were shown, allowing to estimate not only the stability of solid solutions in a wide range of compositions and temperatures, but also to determine the substitutions limits for a bounded series of solid solutions at a given decomposition temperature or calculate the decomposition temperature at a given substitution limit.

In  $(\text{Lu}_{1-x}\text{Ln}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$  systems containing REEs from La to Nd, the solid solutions, which are thermodynamically stable at temperatures above the critical decomposition temperatures 3460–1660 K, become thermodynamically unstable and can decay to form the bounded regions of solid solutions at temperatures between  $T_{\text{cr}}$  and  $\sim 1173$  K. Below  $\sim 1173$  K, they do not decay and are metastable.

In systems containing REEs from Sm to Yb, the critical decomposition temperatures (900–10 K) are significantly lower than  $\sim 1173$  K; therefore, unbounded solid solutions do not decay upon cooling and remain stable at temperatures higher than the critical ones and metastable at temperatures lower than the critical ones.

The calculation results for the  $(\text{Lu}_{1-x}\text{Ce}_x)[(\text{SiO}_4)_{0.5}\text{O}_{0.5}]$  system did not contradict with the experimental data obtained earlier by instrumental investigation methods for solid solutions wherein  $x = 0.01$  at 1273 K and  $x = 0.02$  at 1373 K [26–27]. This means that these solid solutions are located in the region of thermodynamic stability as predicted by us.

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### Authors' contribution

All authors equally contributed to the research work.

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