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Predicting the Stability of the Solid-Solution $Sc_{1-x}Ln_xAsO_4$ and $Tb_xLn_{1-x}AsO_4$ Orthoarsenates

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Urusov's crystal-energy theory of isomorphous substitutions is used to calculate mixing energies (interaction parameters) and critical decomposition temperatures (stability temperatures) of solid solutions in the $Sc_{1-x}Ln_xAsO_4$ (Ln = Sm–Lu, Y) (I) and $Tb_{1-x}Ln_xAsO_4$ (Ln = Y, Tm) (II) systems with zircon structure. Based on the obtained calculation results, for systems (I), a diagram is presented to estimate the stability regions of solid solutions and predict the substitution limits based on the temperature, or the decomposition temperature depending on the given substitution limits. They are characterized by the presence of regions of thermodynamical stability, instability, and metastability of solid solutions. In systems (II), solid solutions are thermodynamically stable above the critical temperatures and metastable below the critical temperatures. Within the limits of the method error, the calculation results for systems (II) do not contradict the experimental data described previously in the literature. The present results can be useful in choosing the ratio of components in 'mixed' matrices, the amount of activator in luminescent, laser and other practically important materials, as well as in matrices for immobilization of toxic and radioactive waste.

У рамках кристалоенергетичної теорії ізоморфних заміщень В. С. Урусова розраховано енергію змішування та критичні температури розпаду (стабільности) твердих розчинів у системах $Sc_{1-x}Ln_xAsO_4$ (Ln = Sm–Lu, Y) (I) і $Tb_{1-x}Ln_xAsO_4$ (Ln = Y, Tm) (II) зі структурою циркону. Для систем (I) представлено діяграму термодинамічної стабільности твердих розчинів, яка уможливлює прогнозувати границі заміщень залежно від температури або температуру розпаду за заданими границями заміщень. Для них є характерною наявність областей термодинамічної стабільности, нестабільности та метастабільности твердих розчинів. У системах (II) вище критичних температур тверді розчини є термодинамічно стабільними, а нижче — метастабільними. У межах похибки методи результати розрахунку для систем (II) не суперечать експериментальноним даним, описаним раніше в літературі. Результати роботи можуть бути корисними під час вибору співвідношення компонентів у «змішаних» матрицях, кількости активатора в люмінесцентних, лазерних та інших практично важливих матеріялах, а також у матрицях для іммобілізації токсичних і радіоактивних відходів.

Key words: solid solution, energy of mixing, isomorphous substitutions, orthoarsenates of rare-earth elements, scandium, terbium.

Ключові слова: твердий розчин, енергія змішання, ізоморфні заміщення, ортоарсенати рідкісноземельних елементів, скандій, тербій.

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1. INTRODUCTION

Even though the rare-earth element (REE) orthoarsenates in composition and crystalline structure are analogues of the REE orthophosphates and orthovanadates, which are currently being intensively studied as phosphors, lasers, light emitters, catalysts, ionic conductors, matrices for radioactive waste [1], much less attention is paid to orthoarsenates, apparently, due to the toxicity of arsenic compounds. However, it is known that REE orthoarsenates possess ferroelectric [2] and electroluminescent [3] properties and can be used as matrices for immobilization of toxic wastes of arsenic and selenium [4, 5].

Recently, luminescent materials have been intensively studied, which contain not only isomorphically substituted activator ions, including REEs, but also two or more different REE ions in the lattice of the ‘host’ structure, the so-called ‘mixed’ phosphors, *e.g.*, $M_5Sc_{1-x}AsO_9{:}xSm^{3+}$ [3] or $Sc_{0.93-x}Ln_xVO_4{:}Eu^{3+}{}_{0.07}$ [6] compositions. Besides, according to Refs. [4, 5], during the immobilization of arsenic or selenium, they are absorbed by compounds of one or more REEs, resulting in the formation of REEs’ orthoarsenates’ solid solutions. These solid solutions are slightly soluble in water and have relatively high incongruent melting temperatures (1830–2000°C) [7] that corresponds to the requirements for immobilization matrices, although there is information about the beginning of decomposition of solid solutions at lower temperatures of about 1550 K [8].

Since the waste of nuclear reactors contains up to 35 wt.% of the oxides of radioactive isotopes of various REEs, as well as uranium, plutonium, americium [9], they can also be immobilized in the composition of solid solutions based on REEs’ orthoarsenates.

Thus, in the above cases, orthoarsenates can be used in the form of solid solutions that makes it possible to control purposefully their properties. However, in the literature, there is practically no information on the state diagrams of $Ln_{1-x}Ln'_xAsO_4$ systems, where Ln, Ln' are REEs, which are the physicochemical basis for choosing the composition of solid solutions of orthoarsenates and the conditions for their solid-phase synthesis. As a rule, there is information about certain compounds, such as $Pr_{0.502}Nd_{0.478}As_{0.981}O_{4.039}$, $La_{0.427}Pr_{0.487}As_{0.948}O_{4.138}$, $Er_{0.493}Yb_{0.512}As_{0.989}O_{4.006}$ [8], $Nd_{0.65}Sm_{0.35}AsO_4$ [10, 11], $Nd_{0.95}Sm_{0.05}AsO_4$, $Nd_{0.35}Sm_{0.65}AsO_4$ [11], $Ce_{0.47}La_{0.20}Nd_{0.18}AsO_4$ [1]. At the same time, to study the dependence of practically important properties on the composition of a solid solution, knowledge of substitution limits is necessary, since a regular change in properties occurs in single-phase regions of systems. In addition, when using materials made from solid solutions, it is necessary to know the areas of their stability in order to avoid the possibility of decomposition during synthesis, utilization, and storage. However, due to the toxicity of arsenic compounds, experimental studies are difficult, and, therefore, it is rational their combination with calculating methods, as has long been carried out, for example, in studying the isomorphous substitution of radioactive substances for immobilization.

Therefore, the present research aimed to predict the limits of substitutions and stability regions of the systems of $Sc_{1-x}Ln_xAsO_4$ (Ln = Sm–Lu, Y) and $Tb_xLn_{1-x}AsO_4$ (Ln = Tm, Y) solid solutions with zircon-type structure.

The choice of these solid solutions is since Sc compounds are one of the most effective luminescent materials in related orthovanadate systems [12, 13], and the experimental results are available in the literature for $Tb_xLn_{1-x}AsO_4$ (Ln = Tm, Y) systems, which will allow us to estimate the reliability of calculation results.

2. CALCULATING APPROACH AND RESULTS

2.1. Theoretical Analysis

The main task in calculating the substitution limits of solid solutions using the Urusov's crystal-energy method [14–16] is to determine the mixing energy Q (interaction parameter). In the general case, the mixing energy, according to V. S. Urusov, consists of three contributions due to the difference in the sizes of substituting structural units or interatomic distances in the components (Q_R), the difference in the degree of ionicity of the chemical bond (Q_ε), and the difference in their crystal structures ($\Delta H_{\text{II-I}}/x_1$), where $\Delta H_{\text{II-I}}$ enthalpy of the polymorphic transition from the structure of the substituting component to the structure of the substitutable one:

$$Q = Q_R + Q_\varepsilon + \Delta H_{\text{II-I}}/x_1.$$

In this paper, we study mutual substitution of REEs in the group of $Sc_{1-x}Ln_xAsO_4$ systems, both components of which have the zircon structure. Therefore, the third summand in the above equation is equal to 0. The second summand of the equation, according to Ref. [16], must be taken into account in cases where the size factor is large enough and the difference in electronegativities of the ions substituting each other is greater than 0.4, or the difference in the degrees of ionicity of the chemical bond in the components of the systems is larger than 0.05. In this case, the above values are approximately by an order of magnitude smaller, and the dimensional parameter is of 0.0607 or less (Tables 1 and 2). Therefore, considering Q_ε is desirable.

Given the difference in the sizes of the substituted structural units and the differences in the degrees of ionicity of the chemical bond in the components, the mixing energy will be determined by the equation:

$$Q = Q_R + Q_\varepsilon = Cmnz_mz_x(\Delta R/R_1)^2 + 1390mz_mz_x\alpha(\Delta\varepsilon)^2/(2R_1)\ [\text{kJ/mole}]\ [14\text{–}16];$$

here, $C = 112.6$ kJ is a constant calculated from the equation $C = 20(2\Delta\chi + 1)$ [16] based on the difference in electronegativities (χ) of cations and anion; the value $\chi(AsO_4^{4-}) = 3.758$ was accepted equal to $\chi(O^{2-})$ as recommended in Ref. [18]; $m = 2$—the number of formula units in the pseudobinary approximation of components; $n = 5.3$—effective co-ordination number according to S. Batsanov, since in the zircon-type structure the cation is surrounded by six

TABLE 1. Initial data and calculation results of mixing energies [J/mole] and critical decomposition temperatures [K] of $Sc_{1-x}Ln_xAsO_4$ solid solutions (Ln = Sm–Lu, Y).

Ln	R, Å	$\Delta R/R_1$	Q_R, J/mole	χ	ε_{Ln}	$\Delta\varepsilon$	Q_ε, J/mole	T_{cr}, K
Sm	3.688	0.0607	39579	1.410	0.720	0.002	14	2363
Eu	3.678	0.0578	35887	1.433	0.715	0.003	32	2142
Gd	3.662	0.0532	30402	1.386	0.724	0.006	130	1815
Tb	3.652	0.0503	27178	1.410	0.720	0.002	14	1622
Dy	3.634	0.0451	21849	1.426	0.716	0.002	14	1304
Ho	3.629	0.0437	20514	1.433	0.715	0.003	32	1224
Er	3.609	0.0379	15430	1.438	0.714	0.004	58	921
Tm	3.599	0.0351	13234	1.455	0.710	0.008	230	790
Yb	3.587	0.0316	10726	1.479	0.706	0.012	518	640
Lu	3.577	0.0287	8848	1.431	0.716	0.002	14	528
Sc	3.477	—	—	1.415	0.718	—	—	—
Y	3.618	0.0405	17619	1.340	0.722	0.004	58	1052

TABLE 2. Initial data and calculation results of critical decomposition temperatures of $Tb_xLn_{1-x}AsO_4$ (Ln = Tm, Y) solid solutions.

Ln	R, Å	$\Delta R/R_1$	Q_R, J/mole	χ	T_{cr}, K
Tm	3.599	0.01472	2330	1.455	139
Y	3.618	0.00940	949	1.340	56
Tb	3.652	—	—	1.410	—

tetrahedral arsenate anions located at two significantly different distances; z_m, z_x—charge modules of structural units (Ln^{3+} and AsO_4^{3-}); R—interatomic distance 'cation–the central atom of the oxoanion'; R_1—the smaller interatomic distance; $\alpha = 1.73$—the reduced Madelung constant calculated by means of the Hoppe's formula; $\Delta\varepsilon$—differences in the degrees of ionicity of the chemical bond in the components, calculated from the difference in χ of REE cations and anion taken from [17]. The choice of the scale [17], in contrast to the scales of other authors, was due to the fact that the values of χ change in it with regular periodicity, increasing in series Ce^{3+}–Eu^{3+} from 1.348 to 1.433 and Gd^{3+}–Yb^{3+} from 1.386 to 1.479 with a sharp drop during transitions Eu^{3+}–Gd^{3+} from 1.433 to 1.386 and Yb^{3+}–Lu^{3+} from 1.479 to 1.431, due to the structure of REE electron shells. In addition, on the scale of χ [17], there are shown the values for χ of scandium and oxygen. $\Delta R/R_1$—a relative size difference of the substituted structural units (dimensionless parameter) calculated by the Ln^{3+}–AsO_4^{3-} distance values [20] or by cubic roots from the volumes of unit cells [1, 2].

The accuracy of calculating the critical temperature is of ±100 K, according to [15].

Since the size parameter values in all cases are less than 0.1 (Tables 1 and 2), according to recommendation [14–16], the critical decomposition temperatures of solid solutions were calculated in the approximation of regular solutions using the equation: $T_{cr} = Q/(2kN)$, where k is the Boltzmann constant, N is the Avogadro number. Moreover, the decomposition temperature T_d at a given substitution limit x or the substitution limit x at the decomposition temperature are according to the Becker equation [21]: $-(1-2x)/\ln[x/(1-x)] = kN\,T_d/Q$.

2.2. Calculation Results

As can be seen from the data given in Table 1, the calculated values of mixing energies and critical decomposition (stability) temperatures of solid solutions of REE orthoarsenates of the composition $Sc_{1-x}Ln_xAsO_4$ with a zircon-type structure naturally decrease along the Sm–Lu series that is due to a decrease in the size of substituting structural units. The mixing energy and critical temperature for the $Sc_{1-x}Y_xAsO_4$ system are between the corresponding values for the $Sc_{1-x}Ho_xAsO_4$ and $Sc_{1-x}Er_xAsO_4$ systems, because the crystal-chemical ionic radius Y^{3+} has a value (of 1.040 Å) that is intermediate between close to each other radii of Ho^{3+} (1.041 Å) and Er^{3+} (1.030 Å) ions [22].

The effect of differences in the degrees of ionicity of the chemical bond in the components on the critical decomposition temperature of solid solutions is within the error of the calculation method (±100 K) and can be neglected. Slight differences in the degrees of ionicity of the chemical bond in the components of the systems, namely, equal to 0.002–0.012 for $Sc_{1-x}Ln_xAsO_4$ (Ln = Sm–Lu, Y) (Table 1), are since the $\chi(Sc^{3+}) = 1.415$, and it is very close to the χ of elements of the middle of the REE series: Sm^{3+} (1.410), Eu^{3+} (1.433), Tb^{3+} (1.410), Dy^{3+} (1.426). A similar situation exists for $Tb_xLn_{1-x}AsO_4$ systems (Ln = Tm, Y), since electronegativity of the Tb^{3+} cation (1.410) has a slight distinct from χ of the Tm^{3+} (1.455) and Y^{3+} (1.340) cations (Table 2). Therefore, the critical temperature values shown in Tables 1 and 2 are given without considering the effect of differences in the degree of ionicity of the chemical bond.

According to the calculated values of T_d, their dependence on REE numbers for substitution limits $x = 0.01$, $x = 0.03$, $x = 0.05$, $x = 0.10$, $x = 0.20$ (Fig. 1) was constructed. The critical decomposition temperatures of the solid solutions were calculated in the regular solid-solution approximation for the composition with $x = 0.5$.

Using the graphical dependences, as in Ref. [23], it is possible to estimate the decomposition temperature of limited series of solid

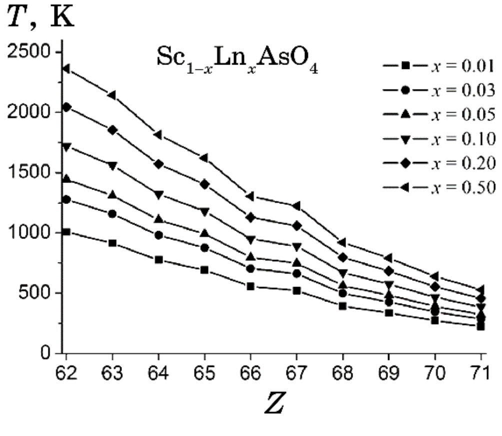

Fig. 1. Diagram of the thermodynamical stability of $Sc_{1-x}Ln_xAsO_4$ solid solutions, Ln = Sm (Z = 62)–Lu (Z = 71) (Z—REE atomic number).

solutions by setting the substitution limit or to evaluate the substitution limit of Sc by REE by setting the decomposition temperature. In the second case, the isotherm intersection point, which is drawn from the given decomposition temperature with the vertical, that is drawn from the REE number, allows us to determine the composition interval, in which the substitution limit is located; thus, interpolation between the two nearest curves gives the substitution limit. It is possible to clarify the substitution limit by constructing, for a specific system, the dependence of decomposition temperatures calculated by means of the Becker equation on the composition, which will be almost symmetrical in the approximation of regular solid solutions.

Unfortunately, as far as we know, there is no data in the literature on the temperature, at which the decomposition of $Sc_{1-x}Ln_xAsO_4$ solid solutions would cease upon cooling due to kinetic difficulties (spontaneous quenching of samples). However, it can be assumed that it is close to the temperature, at which the components interact during the solid-phase synthesis of orthoarsenates. According to the data from Ref. [8], the completion of $ScAsO_4$ synthesis occurred at a temperature of 1073 K, and of $LnAsO_4$ at 973 K during calcination for 24 hours. Consequently, it can be assumed that, in solid solutions of $Sc_{1-x}Ln_xAsO_4$ systems, the transition of samples to a metastable state due to kinetic difficulties during cooling occurs approximately in the temperature range from 1073 K (near the $ScAsO_4$ composition) to 973 K (near the $LnAsO_4$ composition).

It follows from the calculation results that, in $Sc_{1-x}Ln_xAsO_4$ systems with REEs from Sm to Ho, there are unlimited solid solutions in the region of systems adjacent to the thermodynamically stable $ScAsO_4$ composition at temperatures above critical (2363–1224 K; Table 1, Fig. 1). As the temperature decreases in the region between T_{cr} and about 1073 K, the solutions become thermodynamically unstable and can decompose, forming limited regions. This occurs, if the diffusion rate and time are large enough for stable nuclei of a new phase to arise and begin to grow. At temperatures lower than 1073 K, these solid solutions become metastable.

In systems with REEs from Er to Lu, the critical decomposition temperatures (790–528 K) are significantly lower than the temperature of 1073 K. Therefore, unlimited solid solutions synthesized at temperatures higher than 1073 K should not decompose upon cooling, and they will be stable at temperatures higher than critical one or metastable at lower temperatures. The difference of degree in the critical temperature for the $Sc_{1-x}Y_xAsO_4$ system (1052 K) from the temperature of spontaneous quenching (1073 K) does not exceed the calculation error; therefore, predicting the decomposition temperature of an unlimited series of solid solutions in this system is difficult.

To our knowledge, there is no information in the literature on mixing energies, substitution limits, and thermodynamical stability of solid solutions of the REE orthoarsenates $Sc_{1-x}Ln_xAsO_4$ with zircon-type structure found experimentally. This does not allow comparing the calculation results with the experimental data for the systems under study. At the same time, polymorphic transitions in solid solutions of the $Tb_xY_{1-x}AsO_4$ and $Tb_xTm_{1-x}AsO_4$ systems at temperatures below 30 K were previously studied [24, 25]. It was found that, in the $Tb_xY_{1-x}AsO_4$ system, the temperature of the phase transition from tetragonal symmetry to rhombic one increases regularly from 5.8 to 27.3 K when x varies from 0.32 to 1, and in the $Tb_xTm_{1-x}AsO_4$ system, when x changes from 0 to 1, it increases from 6.1 to 25.5 K [24, 25]. This indicates in the first case a wide range of formation of solid solutions, and in the second case, the presence of unlimited miscibility of components at temperatures of about 30 K.

From these experimental results, it follows that, in the $Tb_xTm_{1-x}AsO_4$ system, the critical decomposition temperature of solid solutions is less than 30 K. In the $Tb_xY_{1-x}AsO_4$ system, it should be even lower, since the sizes of crystal-chemical ionic radii (for the co-ordination number of 8) of Tb (1.18 Å) and Y (1.159 Å) differ to a lesser extent than Tb (1.18 Å) and Tm (1.134 Å) [22].

Therefore, we have also carried out calculations for the $Tb_xY_{1-x}AsO_4$ and $Tb_xTm_{1-x}AsO_4$ systems. The results of critical decomposition temperatures for these systems (56 and 139 K, respectively; Table 2), considering the accuracy of the calculation method (close to 100 K), are consistent with the results of Refs. [24, 25].

3. CONCLUSIONS

The crystal-chemical approach in the approximation of regular solid solutions was used to calculate the mixing energies and critical decomposition (stability) temperatures for solid solutions of $Sc_{1-x}Ln_xAsO_4$ (Ln = Sm–Lu, Y) and $Tb_{1-x}Ln_xAsO_4$ (Ln = Y, Tm) systems with zircon-type structure. With increasing in REEs' charge nuclei, the calculated mixing energy and critical decomposition temperature for solid solutions naturally decrease that is caused by the decrease in ionic radii in the lanthanide series from Sm to Lu. The differences of the degrees of ionicity of the chemical bond in the components of the systems are small and do not affect practically the calculation results. The mixing energy and critical temperature for the $Sc_{1-x}Y_xAsO_4$ system are between the corresponding values for the $Sc_{1-x}Ho_xAsO_4$ and $Sc_{1-x}Er_xAsO_4$ systems due to insignificant differences in the radii of their cations.

The obtained diagram of thermodynamical stability allows one to evaluate the stability of $Sc_{1-x}Ln_xAsO_4$ solid solutions in a wide range of compositions and temperatures, as well as to predict the substitution limits for limited series of solid solutions at a given decomposition temperature, or their decomposition temperature at a given substitution limit.

In $Sc_{1-x}Ln_xAsO_4$ systems with REEs from Sm to Ho, unlimited solid solutions are thermodynamically stable at temperatures above critical one (2363–1224 K). By lowering the temperature in the range between the T_{cr} and about 1073 K, these systems have become thermodynamically unstable and decompose, forming a limited range of solid solutions. At lower temperatures, these solid solutions become metastable. In systems with REEs from Er to Lu, unlimited solid solutions are thermodynamically stable at temperatures above critical one (790–528 K); at temperatures lower than critical one, they become metastable and will not decompose.

The obtained results for the critical decomposition temperatures (56 and 139 K) in $Tb_{1-x}Ln_xAsO_4$ (Ln = Y, Tm) systems are consistent with the experimental results described previously within the accuracy of the calculation method.

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