

PHYSICAL METHODS
OF INVESTIGATION

Energies of Mixing (Interaction Parameters),
Substitution Limits, and Phase Stability of Solid Solutions
 $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$ (Ln = Ce–Yb, Sc, Y)

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Abstract—The energies of mixing (interaction parameters) and temperature ranges of stability of solid solutions $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$ (where Ln is a rare-earth element (REE), scandium, or yttrium) with the zircon structure were calculated using the crystal-energy theory of isomorphous miscibility. It was shown that, with increasing atomic number of REE in the Ce–Lu series, the calculated energies of mixing and critical decomposition temperatures of the solid solutions regularly decrease. The substitution limits at various temperatures, the thermodynamic phase stability, and the temperature of transition to a metastable state were determined. The thermodynamic stability diagram of the REE vanadate solid solutions $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$ was presented. The results of the work can be used for searching the compositions of matrices and activators of new laser and other materials.

Keywords: solid solution, orthovanadate, zircon structure, energy of mixing

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INTRODUCTION

Solid solutions of rare-earth element (REE) orthovanadates are used as materials for matrices and activators of optical quantum generators [1], luminescent materials, scintillators, optical polarizers, and light-emitting diodes [2, 3]. The most frequently used modifiers are Nd, Dy, Ho, Er, Tm, and Yb [4].

However, the physicochemical foundations of synthesizing solid solutions and growing their single crystals—state diagrams and, in particular, solubility regions based on components of these systems—are studied insufficiently. Because of this, the compositions of matrices and modifying additives in studying the laser properties of REE orthovanadates have to be chosen either by analogy with related systems, or by trial and error, which may lead to excessive consumption of expensive reagents and an increase in the duration of the studies. As an example, one can refer to a study [1], in which single crystals modified by neodymium (1 at %) were attempted to be grown by the Czochralski method from mixtures of three compositions, containing 10, 20, and 30 at % ScVO_4 and 90, 80, and 70 at % YVO_4 , respectively. As a result, the crystals obtained in all the three cases contained only ~1 at % Sc.

Moreover, it is not always taken into account that vanadate solid solutions synthesized at high tempera-

tures tend to decompose in cooling and using and can uncontrollably change the phase composition and properties. This may lead to degradation of materials based on them.

Currently, among materials for solid-state lasers, of greatest interest are REE orthovanadates. They are an alternative to yttrium aluminum garnet as they have higher thermal conductivity, larger width, and higher absorption cross section [4]. Initially, materials based on individual orthovanadates YVO_4 , LaVO_4 , and LuVO_4 were investigated [5]. Later, higher efficiency was reached using “mixed” lutetium-containing orthovanadates, or, more accurately, solid solutions, e.g., $\text{Lu}_x\text{Y}_{1-x}\text{VO}_4$ [6], which were previously insufficiently studied, probably, because of the high cost of lutetium. The possibility of the formation of solid solutions over wide concentration ranges both between components of matrices, and between the matrix and activators is due to the fact that REE orthovanadates (except lanthanum orthovanadate) are of the same structural type—zircon type.

In this context, the purpose of this work was to predict the energies of mixing, substitution limits, and phase stability of solid solutions $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$ (where Ln is a rare-earth element, Sc, or Y) with the zircon structure.

CALCULATION

Choice and Substantiation of a Method for Calculating the Energy of Mixing

Recently [7], the interaction parameters (energies of mixing) in the related systems $\text{La}_{1-x}\text{Ln}_x\text{PO}_4$ ($\text{Ln} = \text{Eu}, \text{Gd}$) that were determined by various authors in 2007–2017 have been compared. Using the ab initio (2014), strainenergy (2007), dropcalorimetry (2007), ab initio/strainenergy (2016), and dropsolution (2017) methods, the parameters for $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$ were found to be $13.4, 5.2, 14 \pm 8, 6.2,$ and 2.5 ± 2.6 kJ/mol, respectively, and the parameters for $\text{La}_{1-x}\text{Gd}_x\text{PO}_4$ were $16.5, 6.77, 24 \pm 9, 8.6,$ and 11.4 ± 3.1 kJ/mol, respectively, with the average values for these systems being 8.3 and 13.5 kJ/mol. Obviously, the most reliable results are given by the average value. However, for $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$, the closest to the average value (8.3 kJ/mol) was the value obtained by the ab initio/strainenergy method (6.2 kJ/mol), whereas for $\text{La}_{1-x}\text{Gd}_x\text{PO}_4$, the closest to the average value (13.5 kJ/mol) was the value found by the dropsolution method (11.4 kJ/mol); i.e., none of the analyzed methods cannot be preferred. Therefore, to calculate the energy of mixing in the related systems $\text{La}_{1-x}\text{Ln}_x\text{PO}_4$, we previously [8] used a fundamentally different calculation method, which was earlier developed by Urusov based on the crystal-energy theory of isomorphous miscibility [9, 10]. By this method, we calculated the energies of mixing that were closer to the average values: for $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$ and $\text{La}_{1-x}\text{Gd}_x\text{PO}_4$, they were 9.8 and 13.9 kJ/mol, respectively, with the average values for these systems being 8.3 and 13.5 kJ/mol. Therefore, in this work, we used Urusov method, a feature of which is that it takes into account not only the deformation energy in the substitution of structural units of different sizes, but also the energy determined by the difference in chemical bonds between components of systems as governed by the difference in their ionicity. This method was not previously used for calculating the REE substitutions because the accuracy (± 0.05) of the REE electronegativities on the Pauling scale was insufficient to calculate the differences in ionicity between chemical bonds in the above and related systems.

Main Formulas of the Urusov Method

If components are isostructural, the enthalpy of mixing is [9]

$$\Delta H_{\text{mix}} = 1390mz_mz_x x_1x_2 \times \left[\alpha(\Delta\varepsilon)^2/(2R) + C'n(\Delta R/R_1)^2 \right] \text{ kJ/mol.}$$

Because the relative difference of the cation–tetrahedral anion interatomic distances $\Delta R/R_1$ in components of the systems (Table 1) is less than 0.1, the energy of mixing Q_{mix} can be calculated in the approximation of regular solutions as

$$Q_{\text{mix}} = \Delta H_{\text{mix}}/(x_1x_2),$$

where x_1 and x_2 are the mole fractions of components. It can be represented as the sum of two contributions, Q_ε and Q_R , which characterize the differences in ionicity and in sizes of replaced structural units, respectively:

$$Q_{\text{mix}} = 1390mz_mz_x\alpha(\Delta\varepsilon)^2/(2R) + Cmnz_mz_x(\Delta R/R_1)^2 = Q_\varepsilon + Q_R, \text{ kJ/mol,}$$

where $m = 2$ is the number of structural units of components of the systems in the pseudobinary approximation of the zircon structure; $z_m = z_x = 3$ are the formal (integer) charges of replaced and common structural units in components, respectively; $\alpha = 1.723$ is the reduced Madelung constant calculated by the Templeton formula; $C = 113$ kJ/mol is the empirical parameter, which depends on the compressibility and other characteristics of crystal [9]; $C' = C/1390$; $n = 6$ is the coordination number of the replaced structural unit in the pseudobinary approximation of the structure; R is the $\text{Ln}-\text{VO}_4$ cation–tetrahedral anion interatomic distance [11]; ΔR and $\Delta R/R_1$ is the difference and relative difference of the interatomic distances in components of the systems, respectively; R_1 is the interatomic distance in the smaller-cation component of the system; and $\Delta\varepsilon$ is the difference in ionicity between the chemical bonds in lutetium vanadate and other REE vanadates. The ionicity ε of the chemical bond in REE vanadates was determined from the difference of the electronegativities (EN) of the cation and the anion according to the literature data [12]. The calculation was made using the EN values of REE cations that have been obtained quite recently by the valence-bond method based on the crystallographic data on more than 1000 lanthanide compounds [13]. The obtained values were normalized to the Pauling scale. The NE of Eu turned out to be significantly overestimated and, therefore, was taken to be the average value between the values for Sm and Gd. The EN of the VO_4^{3-} ion was taken to be equal to the EN of oxygen (3.76) as recommended in the literature [14].

Table 1 presents some initial data and calculation results.

Calculation of the Decomposition Temperatures of Solid Solutions

Table 1 shows that the relative differences of the cation–tetrahedral anion interatomic distances in all the systems are significantly less than 0.1. Hence, it follows [9] that the curve of the decomposition temperatures of the solid solutions versus composition is virtually symmetrical, and the solubility regions can be calculated by the Becker solution for regular solutions [16]:

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

Table 1. To the calculation of the energies of mixing (kJ/mol) and critical decomposition temperatures of solid solutions $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$

Composition	Ln	$R, \text{Å}$	$\Delta R/R_1$	EN	ε_{Ln}	$\Delta\varepsilon$	$Q_R,$ kJ/mol	$Q_\varepsilon,$ kJ/mol	$Q_{\text{mix}},$ kJ/mol	T_{cr}, K
$\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$	Ce	3.776	0.0489	1.00	0.800	0.070	29.18	29.34	58.53	3490
	Pr	3.760	0.0444	1.10	0.785	0.055	24.06	18.11	42.18	2520
	Nd	3.741	0.0392	1.12	0.780	0.050	18.75	14.97	33.72	2010
	Pm*	3.725	0.0347	1.14	0.775	0.045	14.70	12.12	26.82	1600
	Sm	3.709	0.0303	1.16	0.770	0.040	11.20	9.58	20.79	1240
	Eu	3.696	0.0267	1.18	0.766	0.036	8.70	7.76	16.46	980
	Gd	3.685	0.0236	1.21	0.760	0.030	6.80	5.39	12.19	730
	Tb	3.668	0.0189	1.19	0.764	0.034	4.36	6.92	11.28	670
	Dy	3.652	0.0144	1.25	0.752	0.022	2.53	2.90	5.43	320
	Ho	3.640	0.0111	1.25	0.752	0.022	1.50	2.90	4.40	260
	Er	3.633	0.0092	1.26	0.750	0.020	1.03	2.39	3.42	200
	Tm	3.621	0.0058	1.29	0.744	0.014	0.41	1.17	1.58	90
	Yb	3.609	0.0025	1.32	0.738	0.008	0.08	0.38	0.46	30
	Lu	3.600	—	1.37	0.730	—	—	—	—	—
$\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4^{**}$	Sc	3.502	0.028	1.415	0.721	0.005	9.57	0.15	9.60	570
	Y	3.643	0.012	1.340	0.734	0.018	1.76	1.94	3.69	220

* The interatomic distance for promethium vanadate was determined as the arithmetic mean of the distances for neodymium and samarium vanadates.

** For the systems $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$, the EN of Lu, Sc, and Y are 1.431, 1.415, and 1.340, respectively [15].

where T_d is the decomposition temperature of solid solution; Q_{mix} is the energy of mixing, which was taken to be constant in each of the systems; and R is the universal gas constant.

With increasing atomic number of REE, the contributions Q_R and Q_ε to the energy of mixing and their sums Q_{mix} regularly decrease (Table 1), which is due to a decrease in the difference between the sizes of replaced structural units and between the ionicities of the chemical bond in components. Note that the contribution Q_ε reaches 50% of Q_{mix} and is taken into account, although if the difference between the ionicities of the chemical bond in components is less than 0.05, Q_ε may be ignored [9]. In our case, Q_ε should be taken into account because the size parameter $\Delta R/R_1$ is small (<0.05).

The critical decomposition temperatures T_{cr} were calculated by the equation [9]

$$T_{\text{cr}} = Q_{\text{mix}} / (2kN),$$

where k is the Boltzmann constant, and N is the Avogadro constant.

As Table 1 shows, T_{cr} regularly decreases with increasing atomic number of REE. The energy of mixing and critical decomposition temperature for the yttrium-containing systems are close to the respective values for the holmium- and erbium-containing sys-

tems because of the insignificant differences between their ionic radii.

If the energy of mixing is known, then the decomposition temperature of the solid solution in regions with limited solubility of components can be calculated by the Becker equation from a given substitution limit. The calculation error was reported [9] to be about ± 100 K.

RESULTS AND DISCUSSION

Investigation of the Dependence of the Decomposition Temperature on the Atomic Number of REE

Using the calculated T_d values, their dependences on the atomic number of REE were constructed within the substitution limits $x = 0.01$ – 0.20 (Fig. 1), and the critical (maximal) decomposition temperatures of the solid solutions ($x = 0.5$) were presented. These dependences also allow one to evaluate the thermodynamic stability of the solid solutions.

For example, at $T > T_{\text{cr}}$ (in the region above the points $x = 0.5$), the unlimited solid solutions in the systems are thermodynamically stable throughout the concentration range $0 < x < 1$. In the region below the points $x = 0.5$ at $T < T_{\text{cr}}$, the unlimited solid solutions are thermodynamically unstable and can decompose into phases with limited solubility.

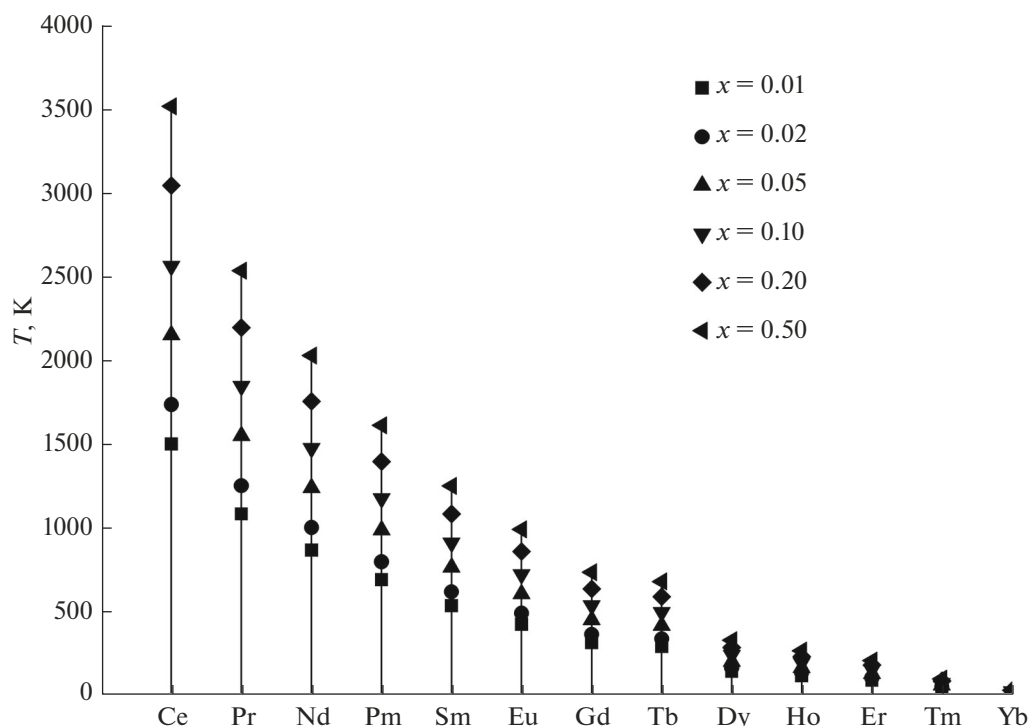


Fig. 1. Dependences of the calculated decomposition temperatures of solid solutions in the systems $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$ on the atomic number of REE (thermodynamic phase stability diagram) at $x = 0.01, 0.02, 0.05, 0.10, 0.20,$ and 0.50 .

From the other dependences, either the decomposition temperature can be estimated by specifying the substitution limit, or the limit of substitution of a REE for lutetium in the limited solid solutions can be estimated by specifying the melt temperature. In the second case, the point of intersection of the isotherm drawn from a given decomposition temperature with the vertical drawn from the atomic number of a REE enables one to find the composition range in which there is a substitution limit, and the interpolation between the two nearest points of the histogram gives the substitution limit. The substitution limit can be refined by constructing the dependence of the decomposition temperatures calculated by the Becker equation on a given composition for a specific system.

It is known that, with decreasing temperature, the mobility of structural units of a solid solution decreases (because of a decrease in the diffusion rate), and the solubility regions shrink [9]. This occurs until the diffusion rate is so low that the solubility regions virtually cease to shrink; i.e., spontaneous quenching happens, and the solid solutions become metastable. If it is assumed that the quenching temperature is close to the minimal temperature of the onset of the interaction of components in the solid phase that leads to the formation of a solid solution, then the quenching temperature and the metastability region in the system can be estimated.

Estimation of the Metastability Region of Solid Solutions of REE Orthovanadates

In the literature, there are pretty much data on the conditions of the synthesis of orthovanadates LnVO_4 and their solid solutions $\text{Ln}_{1-x}\text{Ln}'_x\text{VO}_4$ by various methods; but, in most cases, intermediate and final synthesis temperatures are presented. However, these temperatures can probably significantly exceed initial temperatures because the former depend less strongly on the synthesis method. In particular, in the synthesis in the solid phase [17, 18, 20–22] and by annealing components obtained from the liquid phase [19], the temperature is 953–1473 K; and in the synthesis by the sol–gel method [3] and by magnetron sputtering of thin film [23], it was 1273 K.

In the synthesis from the complex compounds $(\text{NH}_4)[\text{Ln}^{\text{III}}(\text{EDTA})] \cdot x\text{H}_2\text{O}$ and $(\text{NH}_4)_3[\text{V}^{\text{V}}(\text{O})_2(\text{EDTA})] \cdot 0.5\text{H}_2\text{O}$ using vacuum to remove the solvent, the reactions of the formation of REE orthovanadates and solid solutions based on them were studied by high-temperature X-ray powder diffraction analysis with stepwise increasing temperature in 100-K increments [24]. The authors considered that this procedure can give a homogeneous (with two complexes distributed at the molecular level) precursor, which ensures that the interaction temperature is lower than that in other synthesis methods.

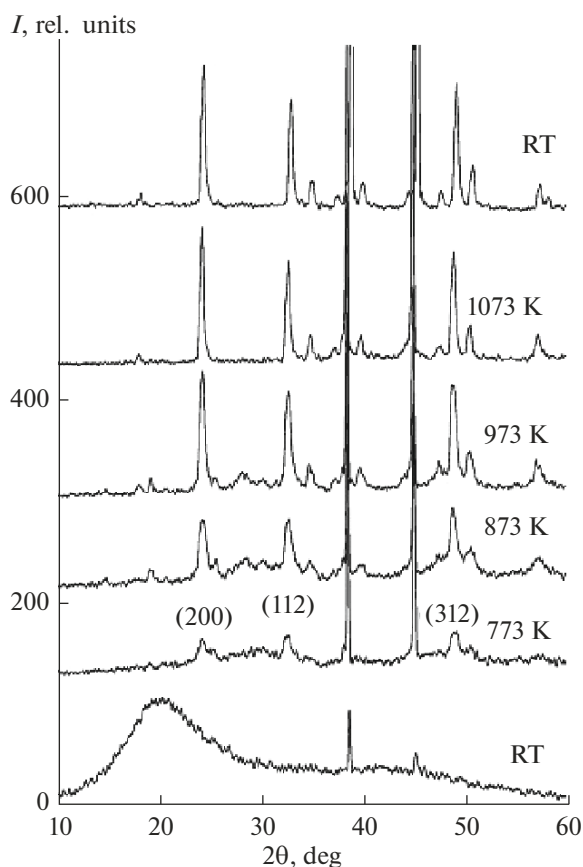


Fig. 2. X-ray powder diffraction patterns of the synthesis of YVO_4 from precursors as recorded at room temperature (RT) after annealing at 573 (two reference signals are seen), 773, 873, 973, and 1073 K, and also at room temperature again after annealing at 1073 K [24].

It was reported [24] that, as the precursors were heated to produce YVO_4 , the reaction product began to crystallize at 773 K, and the final temperature was 1073 K (Fig. 2).

However, as is seen from Fig. 2, the X-ray powder diffraction patterns at 773 K already show the lines of the reaction products (with indices (200), (312), and (112)), the intensities of which increase with a further increase in temperature. Consequently, the reaction of the formation and crystallization of YVO_4 begins not at 773 K, but at a lower temperature.

Using the intensities of the brightest reflections (200), (112), and (312) (Fig. 2), their temperature dependences were constructed (Fig. 3). The extrapolation of this dependence to the abscissa axis gives the temperature of the onset of the reaction and crystallization of YVO_4 , which is ~ 720 K.

Because of the similarity of the properties of yttrium and REE orthovanadates and also solid solutions based on them, one can believe that, near 720 K, the diffusion rate in them is such that not only can the reaction of the formation of YVO_4 occur with increasing

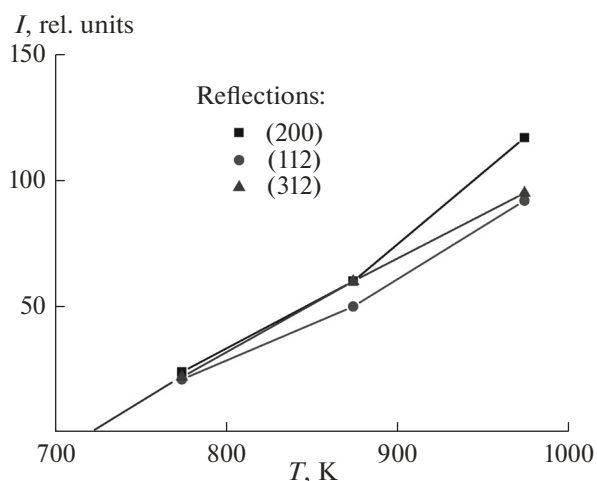


Fig. 3. Dependence of the intensity of reflections (200), (312), and (112) of the zircon structure on temperature in the YVO_4 synthesis.

temperature, but also the decomposition of solid solutions can cease on cooling below 720 K. Therefore, one can assume that, in the systems $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$ with REE from Ce to Eu, the unlimited solid solutions, which are thermodynamically stable at temperatures above the critical temperature (3490–980 K), become thermodynamically unstable and can decompose to form limited regions with decreasing temperature in the range between T_{cr} and 720 K. This occurs if the diffusion rate and time are high enough for stable nuclei of a new phase to emerge and begin to grow. At temperatures below 720 K, these solid solutions become metastable.

In the systems with REE from Dy to Yb, the critical decomposition temperatures (320–30 K) are much lower than 720 K, and the unlimited solid solutions should not decompose on cooling and are metastable. The difference of the critical temperature for the systems with Gd (730 K) and Tb (670 K) from the quenching temperature (720 K) does not exceed the calculation error; therefore, the decomposition temperature of an unlimited solid solution in these systems is difficult to predict.

Comparison of the Obtained Results with Literature Data

Previously, in the systems $\text{Lu}_{1-x}\text{Y}_x\text{VO}_4$ [6], $\text{Lu}_{1-x}\text{Sc}_x\text{VO}_4$ [25], and, probably, $\text{Lu}_{1-x}\text{Yb}_x\text{VO}_4$ [26] (which was studied mainly by Raman spectroscopy), the unlimited miscibility of components was experimentally detected. This agrees with the calculation results, according to which the critical decomposition temperatures of the solid solutions for these systems are 220, 570, and 30 K, respectively (Table 1). Hence, continuous series of solid solutions in these systems are thermodynamically stable at temperatures above the critical temperatures and are thermodynamically

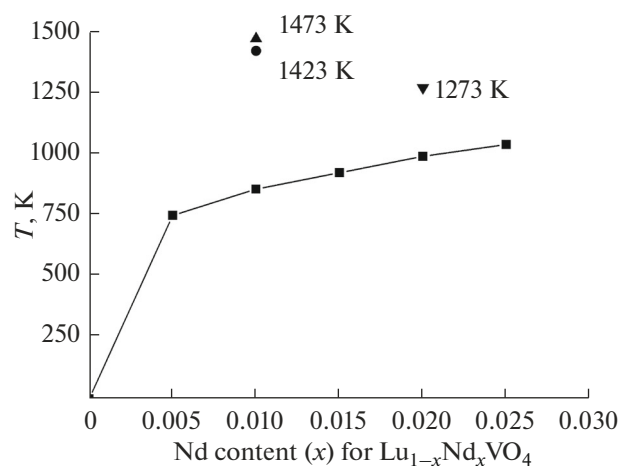


Fig. 4. Dependence of the calculated decomposition temperatures of solid solutions in the system $\text{Lu}_{1-x}\text{Nd}_x\text{VO}_4$ on the mole fraction x of Nd; and experimental synthesis temperatures for $\text{Lu}_{0.99}\text{Nd}_{0.01}\text{VO}_4$ at 1423 K [27] and 1473 K [19], and $\text{Lu}_{0.98}\text{Nd}_{0.02}\text{VO}_4$ at 1273 K [18].

metastable at temperatures below the critical temperatures.

As far as we know, in the literature, there are almost no data on the energies of mixing and substitution limits of REE for lutetium for solid solutions of orthovanadates with the zircon structure with limited miscibility of components. Of course, this complicates the estimation of the reliability of the performed calculations. However, there are data on the compositions and annealing temperatures of solid solutions $\text{Lu}_{0.99}\text{Nd}_{0.01}\text{VO}_4$ at 1423 K [27] and 1473 K [19] and $\text{Lu}_{0.98}\text{Nd}_{0.02}\text{VO}_4$ at 1273 K [18]. The graphic dependence of the calculated decomposition temperatures of solid solutions $\text{Lu}_{1-x}\text{Nd}_x\text{VO}_4$ on the mole fraction of Nd (Fig. 4) shows that the experimental points corresponding to solid solutions $\text{Lu}_{0.99}\text{Nd}_{0.01}\text{VO}_4$ (at 1423 and 1473 K) and $\text{Lu}_{0.98}\text{Nd}_{0.02}\text{VO}_4$ (at 1273 K) are much above the calculated curve of the decomposition of solid solution.

Consequently, our calculation results do not contradict experimental data in the fact that the previously obtained solid solutions [18, 19, 27] are thermodynamically stable.

Recently, many works have been published (e.g., [5, 28, 29]) that described solid solutions of lutetium orthovanadates $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$ that were produced by mild hydrothermal synthesis from tartaric acid solutions, citric acid solutions, or similar media at relatively low temperatures (from 453 K).

However, by the example of a number of systems with REE Tm, Er, Sm, and Eu, it was shown [30] that, actually, samples produced at these temperatures contain vanadium that was partially reduced to V^{4+} , and also carbonyl groups and crystal lattice defects, which are removed on heating in the temperature range 523–

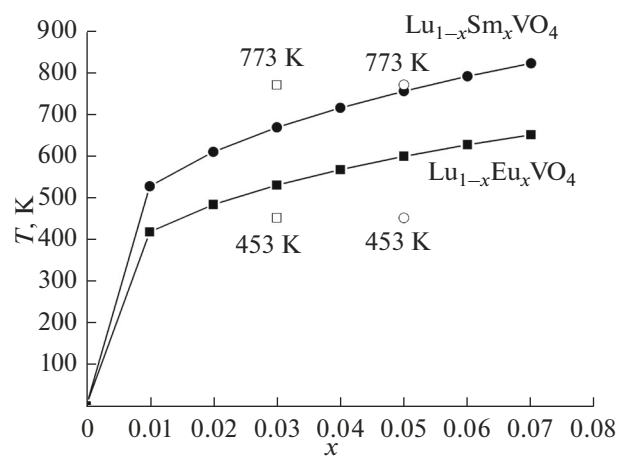


Fig. 5. Dependence of the calculated decomposition temperatures of solid solutions in the systems $\text{Lu}_{1-x}\text{Eu}_x\text{VO}_4$ and $\text{Lu}_{1-x}\text{Sm}_x\text{VO}_4$ on the mole fraction x of REE; and experimental temperatures for two stages of the synthesis of $\text{Lu}_{0.95}\text{Eu}_{0.05}\text{VO}_4$ (453 and 773 K) and $\text{Lu}_{0.97}\text{Sm}_{0.03}\text{VO}_4$ (453 and 773 K).

723 K. Therefore, to complete the synthesis of solid solutions $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$, the samples were additionally annealed at 773 K. In effect, it was assumed that the product of the synthesis at 453 K is not $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$ but a phase with different composition, albeit with the zircon structure.

For this reason, we performed calculations by the example of $\text{Lu}_{0.95}\text{Eu}_{0.05}\text{VO}_4$ and $\text{Lu}_{0.97}\text{Sm}_{0.03}\text{VO}_4$, which showed (Fig. 5) that solid solutions with such compositions at 453 K are indeed impossible to synthesize because they can be thermodynamically stable at temperatures above 600 and 670 K, respectively, as was confirmed by their synthesis at 773 K [30].

The calculation also corroborated that the synthesized [30] $\text{Lu}_{0.95}\text{Eu}_{0.05}\text{VO}_4$ and $\text{Lu}_{0.97}\text{Sm}_{0.03}\text{VO}_4$ are within regions of solid solutions, which, at the synthesis temperatures (773 K), extend to $x = 0.13$ and $x = 0.05$, respectively. Thus, calculations can be useful when experimental investigations give contradictory results.

CONCLUSION

Urusov's quantitative crystal-energy theory of isomorphous miscibility was used to calculate the energies of mixing and decomposition temperatures of solid solutions $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$ formed by the isomorphous substitution of REE, scandium, or yttrium for lutetium in orthovanadates with the zircon structure. It was shown that the contributions made to the energy of mixing by the differences in sizes in replaced structural units and in ionicity of the chemical bond in components are virtually equal. With increasing atomic number of REE, the calculated energies of mixing and critical decomposition temperatures of the

solid solutions regularly decrease, which is due to the decrease in the ionic radii of REE in the series from Ce to Lu and in the difference in ionicity of the chemical bond in components of the systems. The thermodynamic phase stability diagram of solid solutions of orthovanadates $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$ was constructed, using which either the limit of substitution of a REE for lutetium can be estimated from a given temperature, or the decomposition temperature can be estimated from a given substitution limit. The temperature of transition of the solid solutions to the metastable state was estimated. The obtained calculation results do not contradict the published experimental data on solid solutions $\text{Lu}_{1-x}\text{Ln}_x\text{VO}_4$. The results of this work can be used for creating new laser, luminescent, and other materials based on LuVO_4 modified by rare-earth elements.

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REFERENCES

1. A. I. Zagumennyi, S. A. Kutovoi, A. A. Sirotkin, et al., *Appl. Phys. B* **99**, 159 (2010).
2. L. G. Chumilina, Candidate's Dissertation in Chemistry (Krasnoyarsk, 2016), www.imet-uran.ru/emp/Chumilina/info.htm (accessed 9 September 2017).
3. X. Wei, J. Wen, S. Li, et al., *Appl. Phys. Lett.* **104**, 181904 (2014).
4. A. I. Zagumennyi, P. A. Popov, and F. Zerouk, et al., *Quantum Electron.* **38**, 227 (2008).
5. Y. Zhang, H. He, W. Zhu, et al., *Cryst. Eng. Comm.* **13**, 6471 (2011).
6. L. Guo, Zh. Wang, H. Yu, et al., *AIP Advances* **1**, 042143 (2011).
7. S. Neumeier, P. Kegler, Y. Arinicheva, et al., *J. Chem. Thermodyn.* **105**, 396 (2017).
8. E. I. Get'man and S. V. Radio, *Inorg. Mater.* **53**, 718 (2017).
9. V. S. Urusov, *Theory of Isomorphous Miscibility* (Nauka, Moscow, 1977) [in Russian].
10. V. S. Urusov, *Fortschr. Mineral.* **52**, Special Issue, 141 (1975).
11. E. I. Get'man, *Isomorphous Substitutions in Tungstate and Molybdate Systems* (Nauka, Novosibirsk, 1985) [in Russian].
12. S. S. Batsanov, *Structural Chemistry: Facts and Dependences* (Dialog-MGU, Moscow, 2000) [in Russian].
13. D. Xue, S. Zuo, and H. Ratajczak, *Physica B* **352**, 99 (2004).
14. S. S. Batsanov, *Russ. Chem. Rev.* **37**, 332 (1968).
15. K. Li and D. Xue, *J. Phys. Chem. A* **110**, 11332 (2006).
16. R. Becker, *Z. Metallkd.* **29**, 245 (1937).
17. S. L. Shchur, K. E. Levits'ka, and S. A. Nedil'ko, *Naukovi Pratsi Donets'kogo Natsional'nogo Tekhnichnogo Universitetu. Ser.: Khimiya i Khimichna Tekhnologiya*, No. 16, 21 (2011).
18. M. Higuchi, T. Shimizu, J. Takahashi, et al., *J. Cryst. Growth* **283**, 100 (2005).
19. H. Zhang, H. Kong, S. Zhao, et al., *J. Cryst. Growth* **256**, 292 (2003).
20. M. Dragomir, Dissertation (Graduate School, University of Nova Gorica, Nova Gorica, Slovenia, 2013), <http://www.ung.si/~library/doktorati/fizika/17Dragomir.pdf> (accessed September 9, 2017).
21. V. Panchal, S. Lopez-Moreno, D. Santamaria-Perez, et al., *Phys. Rev. B* **84**, 024111 (2011).
22. A. K. Cheetham and N. Sharma, U.S. Patent, No. 2016/0192219 (August 31, 2006).
23. T. Minami, T. Miyata, Y. Suzuki, et al., *Thin Solid Films* **469–470**, 65 (2004).
24. N. Deligne, V. Gonze, D. Bayot, et al., *Eur. J. Inorg. Chem.*, No. 6, 896 (2008).
25. R. J. Lundgren, L. M. D. Cranswick, and M. Bieringer, *Chem. Mater.* **19**, 3945 (2007).
26. Y. Levesque, Etude optique de matériaux laser: $\text{Yb}_x(\text{Lu}, \text{Nd})_{1-x}\text{VO}_4$. (Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Quebec, Canada, 2011) https://www.physique.usherbrooke.ca/pages/sites/default/files/memoireLevesque_Yannick.pdf (accessed September 9, 2017). [in French]
27. S. Zhao, H. Zhang, J. Wang, et al., *Opt. Mater.* **26**, 319 (2016).
28. Y. Gao, B. Feng, Q. Fang, et al., *J. Nanosci. Nanotechnol.* **12**, 8372 (2012).
29. China Patent CN 101434411 A (May 20, 2009).
30. Y. Wang, Y. Song, Y. Li, et al., *New J. Chem.* **41**, 709 (2017).

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