Наносистеми, наноматеріали, нанотехнології
Nanosistemi, Nanomateriali, Nanotehnologii
2019, т. 17, № 4, сс. 701–710

PACS numbers: 61.68.+n, 64.75.Jk, 64.75.Nx, 65.40.G-, 82.33.Pt, 82.60.Lf

Predicting the Substitution of Rare-Earth Elements with Cerium in the Solid Solutions Based on Nanoscale Ln_2SiO_5 (Ln = Tb–Lu, Y)

E. I. Get'man and S. V. Radio

Vasyl' Stus Donetsk National University,
21, 600-richchia Str.,
UA-21021 Vinnytsia, Ukraine

Mixing energies (17.2–44.9 kJ/mole), critical temperatures of decomposition (1029–2700 K), and decomposition temperatures for systems of nanoscale REE oxyorthosilicates $Ln_{1-x}[(SiO_4)_{0.5}O_{0.5}]$:$Ce_x$ (Ln = Tb–Lu, Y) for compositions with $x = 0.01$, 0.02, 0.05, 0.10, and 0.20, which have luminescent properties, are calculated by means of the crystal-chemical method within the regular-solution approximation. A diagram is presented, which allows to determine decomposition temperature with a given equilibrium substitutional limit (x) or substitutional limit with a given temperature as well as to assess areas of stability, instability, and metastability of solid solutions.

Кристалохемічною методою у наближенні реґулярних розчинів розраховано енергії змішання (17,2–44,9 кДж/моль), критичні температури розпаду (1029–2700 К) і температури розпаду для складів $Ln_{1-x}[(SiO_4)_{0,5}O_{0,5}]$:$Ce_x$ з $x = 0,01$, 0,02, 0,05, 0,10 та 0,20 для систем нанорозмірних оксиортосилікатів рідкісноземельних елементів ряду Tb–Lu та Y, які мають люмінесцентні властивості. Представлено діяграму, яка уможливлює графічно визначати температуру розпаду за заданою рівноважною границею заміщення (x) або границю заміщення за заданою температурою розпаду, а також оцінювати області стабільности, нестабільности та метастабільности твердих розчинів оксиортосилікатів рідкісноземельних елементів, заміщених Церієм.

Кристаллохимическим методом в приближении регулярных растворов рассчитаны энергии смешения (17,2–44,9 кДж/моль), критические температуры распада (1029–2700 К) и температуры распада для составов $Ln_{1-x}[(SiO_4)_{0,5}O_{0,5}]$:$Ce_x$ с $x = 0,01$, 0,02, 0,05, 0,10 и 0,20 систем наноразмерных оксиортосиликатов редкоземельных элементов ряда Tb–Lu и Y, обладающих люминесцентными свойствами. Представлена диаграмма, позволяющая графически определять температуру распада по заданному равновесному пределу замещения (x) либо предел замещения по заданной температуре распада, а также оценивать области стабильности, нестабильности и метастабильности твёрдых растворов оксиортосиликатов редкоземельных элементов, замещённых церием.

Key words: solid solution, energy of mixing, isomorphous substitution, oxyorthosilicate of rare-earth elements, cerium.

Ключові слова: твердий розчин, енергія змішання, ізоморфні заміщення, оксиортосилікати рідкісноземельних елементів, Церій.

Ключевые слова: твёрдый раствор, энергия смешения, изоморфные замещения, оксиортосиликаты редкоземельных элементов, церий.

(Received 3 June, 2019)

1. INTRODUCTION

The solid solutions of nanoscale oxyorthosilicates Ln_2SiO_5 (Ln = Tb–Lu, Y) doped with rare-earth elements (REE) are known to be potentially attractive as materials for luminophores, scintillators, lasers, light-emitting diodes and other purposes [1–5]. In particular, solid solution based on lutetium oxyorthosilicate doped with cerium, which composition can be presented as $Lu_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$, has better spatial resolution and sharpness of image than famous luminophore $Gd_2O_2S:Tb$ that was used in recent decades in most medical imaging methods [3]. Solid solutions based on other REE oxyorthosilicates might have practically important properties as well. That is the reason they are actively investigated now.

Currently, there is an urgent task to find optimal quantity of dopant (value of x) as luminescence intensity, wavelength and other properties change significantly depending on composition of the solid solution. Information about substitutional limits as well as solid solutions stability at different temperatures is necessary for studying dependence of the properties on solid-solution composition. That gives possibility to avoid decomposition during synthesis, service and storage. But in the literature, there is only information about phase diagrams of systems involving $Ln[(SiO_4)_{0.5}O_{0.5}]$ and their substitutional limits at temperatures higher than 1873 K [6, 7]; at the same time, nanoscale low-temperature modifications of Tb–Lu and Y oxyorthosilicates that crystallize in $P2_1/c$ space group, which were found relatively recently, are stable at temperatures lower than 1173–1373 K [1]. As cerium oxyorthosilicate crystallizes in space group $P2_1/c$ too, formation of solid solutions in $Ln_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ (Ln = Tb–Lu, Y) systems at temperature range of 1173–1373 K can be expected.

As is known, composition influence on luminescent properties of

Lu_2SiO_5 and Y_2SiO_5 oxyorthosilicates doped with cerium were studied only. System $Lu_{1-x}[(SiO_4)_{0.5}O_{0.5}]$:$Ce_x$ was studied at composition range from 0.1 to 12 at.% of cerium [8]. It was found that maximum luminescence intensity (12 a.u.) exists at cerium concentration being close to 1% ; it is considerably weaker at lower (4 a.u.) and higher concentrations (approximately 3 a.u.). Such a considerable decrease in luminescence at same time with increase of dopant can be caused by luminescence quenching as well as transition from homogeneous form of the solid solution to heterogeneous. Unfortunately, it was only reported that, by X-ray powder diffraction, phase purity of oxyorthosilicate was proved, but the evidence was not presented. Furthermore, medium size of crystallites was $\cong$ 30 nm; in this case, X-ray phase analysis would be ineffective. Besides that, in the $Y_{1-x}[(SiO_4)_{0.5}O_{0.5}]$:$Ce_x$ system studied in composition range $x = 0.00125$–0.04, dependence of luminescence radiance intensity on the quantity of dopant is similar to previous system at $x = 0.005$ [9]. Unfortunately, results of X-rays phase analysis are not presented as well; so, it is impossible to define whether composition range $x = 0.00125$–0.04 is a homogeneous solid solution or it includes two-phase area as well.

Experimental defining of solubility areas in REE oxyorthosilicates in solid phase is a separate task, which needs special equipment, expensive reagents and increase of research time. Besides that, their disadvantages are challenge at achieving equilibrium at both relatively low temperatures because of low diffusion rate and high ones as a result of decomposition of solid solutions at cooling because of high diffusion rate. Implementing calculation approaches, which are deprived of above-mentioned disadvantages, can be beneficial in this case.

So, the purpose of this study is to predict phase stability and substitutional limits in luminescent materials based on the solid solution of nanoscale REE oxyorthosilicates $Ln_{1-x}[(SiO_4)_{0.5}O_{0.5}]$:$Ce_x$ (Ln = Tb–Lu, Y).

2. THEORETICAL APPROACH

The calculation was carried out relying on Urusov's crystal-chemical method [10–12] for pseudo-binary systems $(Ln_{1-x}Ce_x)[(SiO_4)_{0.5}O_{0.5}]$. The Becker equation was used for calculation of substitutional limit (x) at given temperature of solid-solution decomposition (T_p) or decomposition temperature at given substitutional limits [13]:

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

where R is universal gas constant, Q_{mix} is mixing energy (or interaction parameter). It can be used, if size parameter does not exceed 0.1 [10–12]. In all the above systems, value of size parameter calculated among primitive cell volumes ($\delta = (V^{1/3}{}_{\mathrm{Ce}} - V^{1/3}{}_{\mathrm{Ln}})/V^{1/3}{}_{\mathrm{Ln}}$) is lower than 0.059

(see Table 1); that is why implementation of the Becker equation is justified. Authors [1] described the low-temperature modifications of $Ln[(SiO_4)_{0.5}O_{0.5}]$ and give cell parameters only for compounds of other REE of yttrium subgroup, but not for $Lu[(SiO_4)_{0.5}O_{0.5}]$. Therefore, volume of low-temperature modified primitive cells $Lu[(SiO_4)_{0.5}O_{0.5}]$ was defined in this study with extrapolation of primitive cells of low-temperature modifications of $Ln[(SiO_4)_{0.5}O_{0.5}]$ by dependence, given in [1], on ionic radius of REE (by R. Shannon). According to Urusov's theory, if system components are isostructural, energy of mixing can be defined as the sum of two contributions due to the difference in size of replaceable structural units (Q_δ) and the difference in the degree of ionicity of chemical bond in systems' components Q_ε:

$$Q_{\text{mix}} = Q_R + Q_\varepsilon = Cmnz_m z_x \delta^2 + 1390 m z_m z_x \alpha (\Delta\varepsilon)^2/(2D).$$

In this equation, C is a constant that equals 112.6 kJ calculated from $C = 20(2\Delta\chi + 1)$ [12] by degree of difference between cation and anion electronegativities $\Delta\chi$ [14, 15]; m is the number of formula units in pseudo-binary approximation at the calculation of 1 mole of substituted structural unit ($1 + 0.5 + 0.5 = 2$); n is coordination number of the substituted structural unit in the pseudo-binary approximation ($n = 7$ (6 SiO_4^{4-} tetrahedra and O^{2-}) in the first cation site, and $n = 6$ (3 SiO_4^{4-} tetrahedra and three O^{2-}) in the second one, *i.e.*, on average $n = 6.5$); z_m, z_x are formal charges of the substituted and common structural units in the components $z_m = 3$, $z_x = 4\cdot0.5 + 2\cdot0.5 = 3$; size parameter is calculated for each system according to volume of primitive cells given in [1, 16]; α is a given Madelung constant that equals 1.9 calculated by Hoppe's formula [17]:

$$(\alpha/n)^2 + \alpha = 1.81,$$

where $n = 6.5$ is coordination number in pseudo-binary approximation of structure. Degrees of iconicity in the chemical bond ε were evaluated from the difference in electronegativity (χ) of anions and REE cations given in [15]. The value χ for SiO_4^{4-} anion was taken equal to χ for O^{2-} anion, $\chi(SiO_4^{4-}) = \chi(O^{2-}) = 3.7$ [15, 19]. D is average interatomic distance cation–anion in pseudo-binary approximation, calculated for earlier studied structures of this structural type, $Gd[(SiO_4)_{0.5}O_{0.5}]$. Distance cation–tetrahedral anion was taken into account as a sum of distances (Gd–O + Si–O) and distances cation–oxygen not bonded with silicon atom (Gd–O) for two positions of gadolinium [16].

For first position, surrounding of cation is 6 tetrahedra and 1 oxygen; the average distance equals $[6\cdot(2.49 - 1.63) + 2.35]/7 = 3.86$ Å.

For second position, surrounding of cation is 3 tetrahedra and 3 oxygens; average distance equals $[3\cdot(2.39 + 1.63) + 3\cdot2.30)]/6 = 3.15$ Å.

TABLE 1. Calculation of mixing energies and critical decomposition temperatures of $Ln_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ solid solutions.

Ln	V, Å^3	δ	Q_R, J/mole	χ_{Ln}	$\Delta\varepsilon$	T_{cr}, K	T, K [1]	
							Synthesis of Ln_2SiO_5	Phase transition in Ln_2SiO_5
Ce	455.2			1.348				
Tb	409.2	0.03610	17237	1.410	0.012	1029	1323	1373
Dy	404.0	0.04058	21780	1.426	0.014	1300	1323	1373
Ho	397.5	0.04610	28109	1.433	0.016	1678	1273	1348
Er	395.6	0.04781	30233	1.438	0.017	1805	1273	1323
Tm	389.7	0.05312	37322	1.455	0.020	2228	1273	1323
Yb	387.0	0.05558	40859	1.479	0.025	2439	1223	1273
Lu	384.0	0.05841	44947	1.431	0.015	2700	1173	1173
Y	397.4	0.04624	28280	1.340	0.002	1688	1323	1348

Average distance on two positions of cation equals 3.5 Å. According to recommendation [11], if the difference in degree of chemical ionicity is less than 0.05, the contribution of Q_ε in the total energy of mixing can be neglected. Since $\Delta\varepsilon$ is less than 0.025 (Table 1), $Q_{\text{mix}} \approx Q_R$ was taken.

3. RESULTS AND DISCUSSION

Some input data, calculation results, and final temperatures of synthesis by sol–gel method, temperatures of polymorphic transition according to data [1] are given in Table 1. According to the data, in all the systems, values of the volume parameter do not exceed 0.1 (maximum value is 0.058). Therefore, according to [11], dependence of temperatures of solid-solution decomposition *vs.* composition of the systems will be practically symmetrical, and decomposition temperatures (T_p) can be calculated by the Becker equation of regular solid solutions.

The calculation of critical temperatures of solid solutions decomposition T_{cr} was carried out by the equation [11] as follows: $T_{cr} = Q_{\text{mix}}/2kN$, where k is Boltzmann constant, N is Avogadro number. According to Table 1, their values naturally increase with the increase of REE number that is caused by increase of differences in volumes of the substituted structural units. For the $Y_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ system, the values of mixing energy and critical decomposition temperature practically equal to respective values for the $Ho_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ system; the reason is the proximity of ion radiuses Y^{3+} and Ho^{3+}.

Based on the calculated decomposition temperatures of regular solid solutions by Becker equation, we constructed their dependences on the

REE numbers (Fig. 1) for substitutional limits $x = 0.01$ (curve *a*), 0.02 (curve *b*), 0.05 (curve *c*), 0.10 (curve *d*), and 0.20 (curve *e*) for limited solid-solutions series.

These can be used for graphical calculating of REE substitutional limit for cerium at a given temperature, or based on substitutional limit,—for decomposition temperature, accordingly [18, 19]. These tasks are solved more accurately with calculation of each system using Becker equation. Calculated equilibrium substitutional limits for the most often used temperatures for REE oxyorthosilicate systems (REE = Ho–Lu, Y) are given in Table 2. They can be useful for studying dependence of luminescent properties on quantity of cerium for systems with both isostructural components of space group $P2_1/c$ as well as with non-isostructural ones provided that the quantity of dopant does not exceed a few percent.

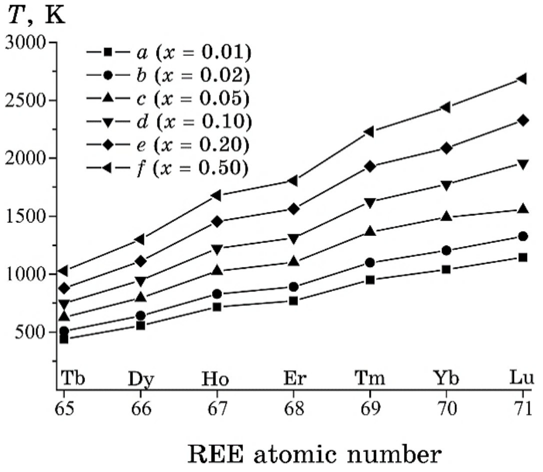

Fig. 1. Diagram of thermodynamic stability of $Ln_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ solid solutions: $x = 0.01$ (*a*), 0.02 (*b*), 0.05 (*c*), 0.10 (*d*), 0.20 (*e*), and 0.50 (*f*).

TABLE 2. Calculated substitutional limits of the most used temperatures of synthesis for REE oxyorthosilicates (Ho–Lu, Y) systems.

Ln	*T*, K									
	973	1073	1173	1273	1373	1473	1573	1673	1773	1873
Ho	0.04	0.06	0.09							
Er	0.03	0.04	0.06	0.09						
Tm	0.01	0.02	0.03	0.04	0.05	0.07	0.09			
Yb	0.007	0.01	0.02	0.03	0.04	0.05	0.06	0.08		
Lu	0.004	0.007	0.01	0.017	0.02	0.03	0.04	0.05	0.07	0.08
Y	0.04	0.06	0.08							

On the contrary to components of the systems described earlier in the study [18–19], $Ln[(SiO_4)_{0.5}O_{0.5}]$ oxyorthosilicates' solid solutions obtained with sol–gel method [1] or with solution combustion synthesis method [20–21] are subject to polymorphic transition from $P2_1/c$ to $C2/c$ space group. This influences on phase content in the systems. At temperatures of synthesis and exploitation, which are less than polymorphic transition temperature of $Ln[(SiO_4)_{0.5}O_{0.5}]$, both components in systems are isostructural, and calculation results can be used for choice of activators quantity. If temperatures of synthesis and exploitation are higher than temperatures of polymorphic transition in $Ln[(SiO_4)_{0.5}O_{0.5}]$, unlimited miscibility is prohibited, since cerium oxyorthosilicate does not undergo a polymorphic transition to $C2/c$ space group structure, and calculation results without enthalpy of polymorphic transition can be incorrect. At the same time, at small substitutional degrees (usually from fractures of percent to a few percent), polymorphic-transition enthalpy influence on energy of miscibility is negligibly small, and calculation in this case can be reliable.

Figure 1 also allows assessing areas of thermodynamic stability of solid solutions. At $T > T_{cr}$ in the area higher than curve f, unlimited solid solutions, which were synthesized at temperatures smaller than temperatures of polymorphic transition, are thermodynamically stable within the whole range of concentrations, $0 < x < 1$. Unlimited solid solutions at $T < T_{cr}$ are thermodynamically unstable and can decompose in phases with limited solubility in the area lower than curve f. In the same manner, limited solid solution series with limit value of $x = 0.01$, 0.02, 0.05, 0.10, and 0.20 in the areas higher than curves a, b, c, d, and e, correspondingly, are thermodynamically stable, and in the areas lower, they are unstable.

As it was shown [22], spontaneous quenching of solid solutions is possible in $Ln[(SiO_4)_{0.5}O_{0.5}]$ systems at cooling to temperatures lower than temperatures of polymorphic transition (1173–1373 K) (Table 1), *i.e.* solid solutions might become metastable at lower temperatures. Unlimited solid solution series in $Ln_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ (Ln = Dy–Lu) systems are thermodynamically stable at temperatures higher than the critical one; at lowering temperature in the area between T_{cr} and 1173–1373 K, they are thermodynamically unstable and can decompose. This occurs, if diffusion rate and time are high enough for appearance and beginning of new phase growth. They become metastable at lower temperatures. Critical temperature of decomposition (1029 K) in $Tb_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ system is lower than temperature of possible spontaneous quenching, unlimited solid solutions are not supposed to decompose at cooling and will be stable at temperatures higher than critical ones and metastable at lower ones. Critical temperature of decomposition (1300 K) in $Dy_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ system differs from temperatures of synthesis and polymorphous transition of its compo-

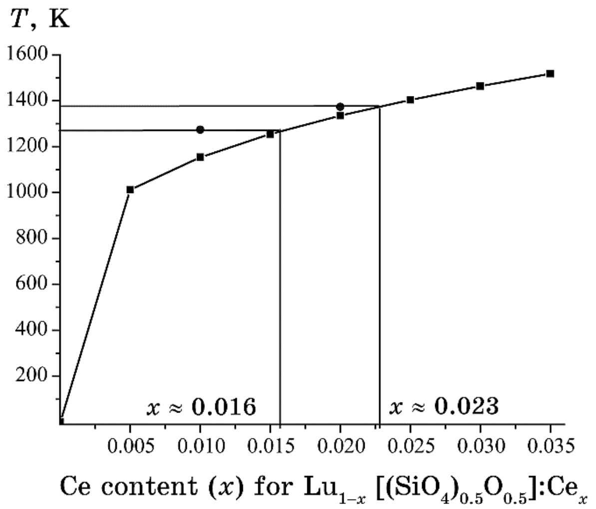

Fig. 2. Fragment of calculated decomposition-temperatures' dependence for $Lu_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ solid solution *vs.* Ce mole fraction, and experimental data for compositions with $x = 0.01$ at 1273 K [23], and $x = 0.02$ at 1373 K [24].

nents $Dy_{1-x}[(SiO_4)_{0.5}O_{0.5}]$ at a value lower than calculation error (±100 K [10–12]); that is why conclusion about possibility of decomposition and solid-solution stability in these conditions cannot be made. Critical temperatures of decomposition (1678–2700 K) in systems with REE (Ho–Lu, Y) are substantially higher than temperatures of sol–gel synthesis and polymorphous transitions; that is the reason why unlimited series of solid solutions based on nanoscale modifications cannot exist, and only limited series of solid solutions can.

As far as we know, there is no data in literature on mixing energies and substitutional limits of REE with cerium for solid solutions of nanoscale REE oxyorthosilicates with limited miscibility of components. Of course, this impedes credibility assessing of calculations. Although, there is data on compositions and temperatures of $Lu_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ solid solutions with $x = 0.01$ at 1273 K [23] and 1373 K [24]. Graphic dependence of calculated decomposition temperatures of $Lu_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ solid solutions *vs.* mole fraction of Ce (Fig. 2) shows that calculation results do not contradict experimental data, since this solid solution is in predicted area of thermodynamic stability—a bit higher than decomposition curve. Besides that, system ($x = 0.01$) is close to these calculated temperatures ($x = 0.016$ and 0.023, accordingly).

4. CONCLUSIONS

Using crystal-chemical method within the approximation of regular solutions, mixing energies (parameters of interaction) of solid solutions of low-temperature modifications of REE oxyorthosilicates $Ln_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ (Ln = Tb–Lu, Y) doped with cerium were calculated.

It was found out that, with increasing of REE number, the calculated energies of mixing and critical decomposition temperatures of solid solution increase accordingly.

A diagram of thermodynamic stability for $Ln_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ systems was constructed that allows to assess not only stability of solid solutions in a wide range of compositions and temperatures but also to predict substitutional limits with a given temperature of decomposition or temperature of their decomposition with a given substitutional limit.

Unlimited series of solid solutions in $Ln_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ (Ln = Dy–Lu) systems are thermodynamically stable at temperatures higher than the critical one, but become thermodynamically unstable and can decompose at lowering temperature in the area between T_{cr} and 1173–1373 K. For the $Tb_{1-x}[(SiO_4)_{0.5}O_{0.5}]:Ce_x$ systems, critical decomposition temperature (1029 K) is lower than the temperature of possible spontaneous quenching, unlimited solid solution should not decompose at cooling, and they will be stable at temperatures higher than critical ones and metastable at lower temperature.

ACKNOWLEDGEMENTS

The study was carried out within the Fundamental Research Programme funded by the Ministry of Education and Science of Ukraine (Project No. 0119U100025).

REFERENCES

1. J. Wang, S. Tian, G. Li, F. Liao, and X. Jing, *Mater. Res. Bull.*, **36**, No. 10: 1855 (2001); https://doi.org/10.1016/S0025-5408(01)00664-X.
2. Y. Liu, C. N. Xu, K. Nonaka, and H. Tateyama, *J. Mater. Sci.*, **36**, No. 18: 4361 (2001); https://doi.org/10.1023/A:1017953913334.
3. C. Michail, S. David, P. Liaparinos, I. Valais, D. Nikolopoulos, N. Kalivas, A. Toutountzis, D. Cavouras, I. Kandarakis, and G. Panayiotakis, *Nucl. Instrum. Methods Phys. Res. Sect. A*, **580**, No. 1: 558 (2007); https://doi.org/10.1016/j.nima.2007.05.234.
4. C. M. Michail, G. P. Fountos, S. L. David, I. G. Valais, A. E. Toutountzis, N. E. Kalyvas, I. S. Kandarakis, and G. S. Panayiotakis, *Meas. Sci. Technol.*, **20**, No. 10: 104008 (2009); https://doi.org/10.1088/0957-0233/20/10/104008.
5. E. Bescher, S. R. Robson, J. D. Mackenzie, B. Patt, J. Iwanczyk, and E. J. Hoffman, *J. Sol–Gel Sci. Techn.*, **19**, Nos. 1–3: 325 (2000);

https://doi.org/10.1023/A:1008785616233.

6. V. P. Barzakovsky, A. I. Boykova, N. N. Kurtseva, V. V. Lapin, and N. A. Toropov, *Diagrammy Sostoyaniya Silikatnykh Sistem: Spravochnik. Vypusk Tretiy. Troynyye Silikatnyye Sistemy* [State Diagrams of Silicate Systems: Handbook. Issue 3. Ternary Silicate Systems] (Leningrad: Nauka: 1972) (in Russian).
7. G. B. Loutts, A. I. Zagumennyi, S. V. Lavrishchev, Yu. Zavartsev, and P. A. Studenikin, *J. Cryst. Growth*, **174**, Nos. 1–4: 331 (1997); https://doi.org/10.1016/S0022-0248(96)01171-2.
8. M. W. Blair, L. G. Jacobsohn, B. L. Bennett, R. E. Muenchausen, S. C. Sitarz, J. F. Smith, D. Wayne Cooke, P. A. Crozier, and R. Wang, *Symposium HH—Nanophase and Nanocomposite Materials V*, **1056**: 1056-HH07-06 (2007); https://doi.org/10.1557/PROC-1056-HH07-06.
9. J. Wang, S. Tian, G. Li, F. Liao, and X. Jing, *J. Electrochem. Soc.*, **148**, No. 6: H61 (2001); DOI: 10.1149/1.1369376.
10. V. S. Urusov, *Fortschr. Mineral.*, **52**: 141 (1975).
11. V. S. Urusov, *Teoriya Izomorfnoi Smesimosti* [The Theory of Isomorphous Miscibility] (Moscow: Nauka: 1977) (in Russian).
12. V. S. Urusov, V. L. Tauson, and V. V. Akimov, *Geokhimiya Tverdogo Tela* [Geochemistry of Solid State] (Moscow: GEOS: 1997) (in Russian).
13. R. Becker, *Z. Metallkd.*, **29**: 245 (1937).
14. K. Li and D. Xue, *J. Phys. Chem. A*, **110**, No. 39: 11332 (2006); https://doi.org/10.1021/jp062886k.
15. S. S. Batsanov, *Russ. Chem. Rev.*, **37**, No. 5: 332 (1968); https://doi.org/10.1070/RC1968v037n05ABEH001639.
16. J. Felsche, *Rare Earths. Structure and Bonding. Vol. 13. The Crystal Chemistry of the Rare-Earth Silicates* (Berlin–Heidelberg: Springer: 1973); https://doi.org/10.1007/3-540-06125-8_3.
17. R. Hoppe, *Adv. Fluor. Chem.*, **6**: 387 (1970).
18. E. I. Get'man and S. V. Radio, *Inorg. Mater.*, **53**, No. 7: 718 (2017); https://doi.org/10.1134/S0020168517070044.
19. E. I. Get'man, S. V. Radio, L. B. Ignatova, and L. I. Ardanova, *Russ. J. Inorg. Chem.*, **64**, No. 1: 118 (2019); https://doi.org/10.1134/S0036023619010091.
20. E. G. Yukihara, L. G. Jacobsohn, M. W. Blair, B. L. Bennett, S. C. Tornga, and R. E. Muenchausen, *J. Lumin.*, **130**, No. 12: 2309 (2010); https://doi.org/10.1016/j.jlumin.2010.07.010.
21. R. E. Muenchausen, E. A. McKigney, L. G. Jacobsohn, M. W. Blair, B. L. Bennett, and D. Wayne Cooke, *IEEE Trans. Nuclear Sci.*, **55**, No. 3: 1532 (2008); https://ieeexplore.ieee.org/document/4545173.
22. E. I. Get'man, S. V. Radio, and L. I. Ardanova, *Determining Phase Stability of Luminescent Materials Based on Solid Solutions of Oxyorthosilicates* $(Lu_{1\ x}Ln_{x})[(SiO_4)_{0.5}O_{0.5}]$*, where Ln La–Yb* (in press).
23. L. Fan, M. Jiang, D. Lin, D. Zhou, Y. Shi, Y. Wu, H. Yao, F. Xu, J. Xie, F. Lei, L. Zhang, and J. Zhang, *J. Alloy. Compd.*, **720**: 161 (2017); https://doi.org/10.1016/j.jallcom.2017.05.248.
24. J. Xie, F. Zhang, S. Shen, D. Lin, L. Fan, L. Zhang, F. Lei, Y. Shi, and P. Liu, *Proc. SPIE 9796. Selected Papers of the Photoelectronic Technology Committee Conferences held November 2015 (Various, China)* (26 January 2016), p. 97960T; https://doi.org/10.1117/12.2228576.