

Predicting the Phase Stability of $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ ($\text{Ln} = \text{Gd}–\text{Lu}, \text{Y}$) Zircon-Structured Solid Solutions

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Abstract—The energies of mixing (interaction parameters) in the $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ ($\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}, \text{Y}$) systems have been calculated using Urusov's crystal energy theory of isomorphous substitutions. The decomposition (stability) temperatures of the solid solutions have been plotted against the atomic number of the rare-earth elements at $x = 0.01, 0.03, 0.05, 0.10, 0.20,$ and 0.50 . The present results can be helpful in a search for host and activator compositions for new luminescence, laser, and other materials based on the zircon-structured rare-earth orthophosphates.

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

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INTRODUCTION

Zircon-structured LnPO_4 rare-earth orthophosphate solid solutions are known to be potentially attractive as luminescence materials for application fields ranging from optoelectronics (in the fabrication of displays, light-emitting diodes, etc.) to biomedicine [1]. They can contain a few rare-earth elements, entering into the composition of both the host and activator [2]. The choice of ScPO_4 , also isostructural with zircon, as one of the end-members is prompted by the fact that it can be used as a key component in designing light-emitting diodes whose color can be controlled by varying the activator composition [2]. However, neither $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ phase diagrams nor solid solution limits in these systems have been studied in sufficient detail, which restricts the possibility of choosing compositions of solid solutions in appropriate systems for studies of their luminescence properties and subsequent practical application. This seems to be caused by the high cost of scandium compounds [3], which causes researchers dealing with luminescence properties to choose the composition of hosts and activators either by analogy with similar systems or by trial and error.

To the best of our knowledge, there is information only about $\text{Sc}_{1-x}\text{Tb}_x\text{PO}_4$, $\text{Sc}_{1-x}\text{Eu}_x\text{PO}_4$, and $\text{Sc}_{1-x}\text{Gd}_x\text{PO}_4$ solid solutions. Mi et al. [2] experimentally studied ScPO_4 -based solid solutions containing Tb or Tb + Eu as activators. The materials were synthesized via heat treatment at 1473 K for 4 h and then furnace-cooled. X-ray diffraction characterization showed that the $\text{Sc}_{0.97}\text{Tb}_{0.03}\text{PO}_4$ sample was single-phase. How-

ever, tetragonal cell parameters and volumes were reported for the incorporation of Tb^{3+} ($x = 0.03$ and Eu^{3+} ($x = 0.02$) ions into the structure of ScPO_4 . As would be expected, they increase from $a = 6.578(7)$ Å, $c = 5.796(3)$ Å, and $V = 250.5(5)$ Å³ for ScPO_4 to $a = 6.595(7)$ Å, $c = 5.807(4)$ Å, and $V = 252.6(2)$ Å³ for $\text{ScPO}_4 : 0.03\text{Tb}^{3+}/0.02\text{Eu}^{3+}$, suggesting that terbium substitution for scandium reaches about $x = 0.03$.

$\text{Sc}_{1-x}\text{Gd}_x\text{PO}_4$ sample prepared in 10 at % steps [4] were annealed at 1173 and 1773 K for 48 h, followed by cooling. X-ray diffraction and differential thermal analysis indicated the formation of narrow ranges (<5 at %) of solid solutions based on both constituent phosphates. The low degrees of gadolinium and terbium substitutions for scandium seem to be the result of the ionic radius of scandium (0.885 Å) being substantially smaller than the ionic radii of gadolinium (1.078 Å) and terbium (1.063 Å) (here and in what follows, we use ionic radii from Shannon [5]).

Preliminary calculations for $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ are desirable as well because substitutions are possible in both a narrow and broad range. The reason for this is that the relative difference between replaced structural units ranges rather widely: from 0.13 to 0.22. In such cases, both unlimited and limited miscibility of components is possible at intermediate and high temperatures [6].

The utility of using calculational approaches is supported by information reported by Zagumennyi et al. [7], who described an attempt to grow neodymium-doped (1 at %) $\text{Sc}_{1-x}\text{Y}_x\text{VO}_4$ single crystals by the

Czochralski technique using three compositions of growth charges, containing 10, 20, and 30 at % ScVO_4 and, accordingly, 90, 80, and 70 at % YVO_4 . As a result, in all three cases they obtained single crystals containing just 1 at % Sc.

The use of calculational techniques for assessing isomorphous substitution limits in such cases would allow one to restrict the consumption of expensive reagents and considerably reduce the investigation duration. Moreover, it is not always taken into account that solid solutions synthesized at high temperatures may be unstable. They may decompose during cooling from the synthesis temperature or under service conditions. This would lead to degradation of materials based on such solid solutions.

Given the above, the purpose of this work is to predict substitution and stability limits of $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ ($\text{Ln} = \text{Gd-Lu, Y}$) solid solutions.

CALCULATIONAL APPROACH AND RESULTS

At present, there is no generally accepted approach for calculating the energy of mixing of rare-earth orthophosphate-based solid solutions, even though knowledge of this energy allows one to assess both isomorphous substitution limits in systems and their thermodynamic stability. Previously, to characterize thermodynamic parameters and assess the long-term stability of monazite solid solution hosts as ceramics for radionuclide immobilization as part of nuclear waste disposal, Neumeier et al. [8] compared the energies of mixing obtained for $\text{La}_{1-x}\text{Ln}_x\text{PO}_4$ ($\text{Ln} = \text{Eu, Gd}$) by various groups between 2007 and 2017 using ab initio [9], strain energy [6], drop calorimetry [10], ab initio/strain energy [11], and drop solution [8] methods. In the case of $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$, their values were, 13.4, 5.2, 14 ± 8 , 6.2, and 2.5 ± 2.6 kJ/mol, respectively; in the case of $\text{La}_{1-x}\text{Gd}_x\text{PO}_4$, they obtained 16.5, 6.77, 24 ± 9 , 8.6, and 11.4 ± 3.1 kJ/mol, with averages of 8.3 and 13.5 kJ/mol in the two systems. Clearly, the most reliable results are provided by the average. At the same time, whereas in the $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$ system the value closest to the average (8.3 kJ/mol) is that obtained by the ab initio/strain energy method (6.2 kJ/mol), the value closest to the average (13.5 kJ/mol) in the $\text{La}_{1-x}\text{Gd}_x\text{PO}_4$ system is that obtained by the drop solution method (11.4 kJ/mol); that is, preference can be given to none of the methods.

In view of this, the energy of mixing in the $\text{La}_{1-x}\text{Ln}_x\text{PO}_4$ ($\text{Ln} = \text{Ce-Dy}$) systems was calculated using a fundamentally different method [12], developed by Urusov [13, 14] based on the crystal energy theory of isomorphous miscibility. The method provided energies of mixing in $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$ and $\text{La}_{1-x}\text{Gd}_x\text{PO}_4$ closer to the above averages: 9.8 kJ/mol (average of 8.3 kJ/mol) and 13.9 kJ/mol (average of 13.5 kJ/mol). In view of this, we used Urusov's method in this study.

If the components of a system are isostructural, according to Urusov [14] the enthalpy of mixing is

$$\Delta H_{\text{mix}} = 1390mZ_mZ_x x_1 x_2 [\alpha(\Delta\varepsilon)^2/2R_1 + C'n(\Delta R/R_1)^2], \text{ kJ/mol.}$$

It can be represented as the sum of two contributions related to the difference in the degree of ionicity (ΔH_ε) and the sizes of the substituting structural units (ΔH_R):

$$\Delta H_{\text{mix}} = \Delta H_\varepsilon + \Delta H_R = 1390mZ_mZ_x x_1 x_2 \alpha(\Delta\varepsilon)^2/2R_1 + CmZ_mZ_x x_1 x_2 n(\Delta R/R_1)^2.$$

Since the relative difference of the cation–tetrahedral anion ($R_{\text{Ln}} - R_1$)/ R_1 interatomic distances (Table 1) in the components of the systems is under 0.1, the energy of mixing (Q_{mix}) can be calculated in the regular solution approximation as $Q_{\text{mix}} = \Delta H_{\text{mix}}/(x_1 x_2)$ [14] (where x_1 and x_2 are the mole fractions of the components). It can also be represented as the sum of two contributions related to the difference in the degree of ionicity (Q_ε) and the sizes of the substituting structural units (Q_R):

$$Q_{\text{mix}} = Q_\varepsilon + Q_R = 1390mZ_mZ_x \alpha(\Delta\varepsilon)^2/2R_1 + CmnZ_mZ_x (\Delta R/R_1)^2,$$

where $m = 2$ is the number of structural units in the components in a pseudobinary approximation; $Z_m = Z_x = 3$ are formal charges of the replaced and common structural units in the components; $\alpha = 1.73$ is a reduced Madelung constant calculated by the Hoppe formula [15]; $C = 125.6$ kJ/mol [14] is an empirical parameter dependent on compressibility and other characteristics of the crystal; $C' = C/1390$; $n = 6$ is the coordination number of the replaced structural unit in the pseudobinary approximation of the zircon structure; R is the cation–tetrahedral anion (Ln-PO_4) interatomic distance in the structures of the components of the systems borrowed from Ref. [16]; ΔR and $\Delta R/R_1$ are the difference and relative difference between the interatomic distances in the components of the system; R_1 is the interatomic distance in the component with the smaller cation radius; and $\Delta\varepsilon$ is the difference between the degree of chemical bond ionicity in scandium phosphate and other rare-earth phosphates. The Gd-PO_4 interatomic distance was calculated from the unit-cell parameters reported by Rodriguez-Liviano et al. [17].

The degree of chemical bond ionicity, ε , in the rare-earth orthophosphates was evaluated from the difference in electronegativity (χ) between the rare-earth cations [18] and the PO_4^{3-} anion ($\chi(\text{PO}_4^{3-}) = 3.7$ [19]).

It is seen from the calculation results (Table 1) that the contributions to the energy of mixing from the size parameter $\Delta R/R_1$ decrease systematically with decreasing Ln ionic radius in the Gd–Lu series. The contributions due to the difference in the degree of chemical bond ionicity exhibit opposite behavior, except for $\text{Sc}_{1-x}\text{Lu}_x\text{PO}_4$, presumably because $\chi(\text{Lu})$ is

Table 1. Data for the calculation of the energy of mixing and critical decomposition temperature of the $\text{Sc}_{1-x}\text{Ln}_x\text{VO}_4$ solid solutions

Ln	$R, \text{Å}$	$\frac{(R_{\text{Ln}} - R_1)}{R_1}$	$Q_R,$ kJ/mol	$\chi(\text{Ln}^{3+})$	$\chi(\text{PO}_4^{3-}) -$ $\chi(\text{Ln}^{3+})$	ε_{Ln}	$\varepsilon_{\text{Sc}} - \varepsilon_{\text{Ln}}$	$Q_\varepsilon,$ kJ/mol	$Q_{\text{mix}},$ kJ/mol	T_c, K
Gd	3.561	0.0595	48.0	1.386	2.314	0.713	0.006	0.2	48.2	2880
Tb	3.537	0.0524	37.2	1.410	2.290	0.708	0.001	0.0	37.2	2220
Dy	3.526	0.0491	32.7	1.426	2.274	0.705	0.002	0.0	32.7	1950
Ho	3.512	0.0449	27.3	1.433	2.267	0.703	0.004	0.1	27.4	1640
Er	3.498	0.0408	22.5	1.438	2.262	0.702	0.005	0.2	22.7	1360
Tm	3.490	0.0384	20.0	1.455	2.245	0.695	0.012	0.9	20.9	1250
Yb	3.480	0.0354	17.0	1.479	2.221	0.692	0.015	1.4	18.4	1100
Lu	3.467	0.0315	13.5	1.431	2.269	0.704	0.003	0.0	13.5	810
Y	3.499	0.0411	22.9	1.340	2.360	0.722	0.015	1.4	24.3	1450
Sc	3.361	—	—	1.415	2.285	0.707	—	—	—	—

substantially lower than the value expected from the trend in the variation of $\chi(\text{Ln})$ [18]. However, since the differences in bond ionicity in all of the systems are very small (under 0.015), Q_R exceeds Q_ε by more than one order of magnitude and determines the total energy of mixing. Because of this, Q_{mix} decreases systematically in all cases. It should also be pointed out that the energy of mixing of the $\text{Sc}_{1-x}\text{Y}_x\text{PO}_4$ solid solutions is similar to that in the $\text{Sc}_{1-x}\text{Er}_x\text{PO}_4$ and $\text{Sc}_{1-x}\text{Ho}_x\text{PO}_4$ solid solutions, because there is only a slight difference between the crystalline ionic radii of the Y^{3+} (1.040 Å), Er^{3+} (1.030 Å), and Ho^{3+} (1.041 Å) cations [5].

The critical decomposition temperatures of the solid solutions were calculated in the regular solution approximation for the composition with $x = 0.5$ using the relation $T_c = T_{0.5} = Q/2kN$ [14], where k is Boltzmann's constant and N is Avogadro's number. As would be expected (Table 1, Fig. 1), they decrease systematically with decreasing Ln ionic radius and the T_c of $\text{Sc}_{1-x}\text{Y}_x\text{PO}_4$ approaches those of $\text{Sc}_{1-x}\text{Er}_x\text{PO}_4$ and $\text{Sc}_{1-x}\text{Ho}_x\text{PO}_4$. From the dependence of the critical decomposition temperature on the atomic number of the rare-earth elements, we can assess the stability of the continuous series of $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ solid solutions over the entire composition range at different temperatures. At $T > T_c$, the continuous series of $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ solid solutions are thermodynamically stable over the entire composition range, $0 < x < 1$. For $T < T_c$, the continuous series of solid solutions are thermodynamically unstable and may decompose into phases with limited solubility. This occurs if the diffusion rate and time are sufficient for stable nuclei of a new phase to form and grow.

Since the relative difference of the interatomic distances, $(R_{\text{Ln}} - R_1)/R_1$, is below 0.1 in all of the systems, to calculate substitution limits in regions with limited component solubility we can use the regular solution

approximation [13, 14]. The composition dependence of the decomposition temperature (T_d) for the solid solutions will then be essentially symmetric and one will be able to calculate substitution limits using the Becker equation [20]:

$$-\frac{1-2x}{\ln\left[\frac{x}{1-x}\right]} = \frac{NkT_d}{Q_{\text{mix}}}$$

If energies of mixing are known, it is easy to calculate the decomposition temperature (T_d) of solid solutions in systems with limited component solubility using the Becker equation and a given substitution limit (x). According to Urusov [14], the error of calculation is on the order of ± 100 K. The inverse problem—to find the substitution limit at a given temperature—can be solved either by trial and error or graphically. We used the latter approach.

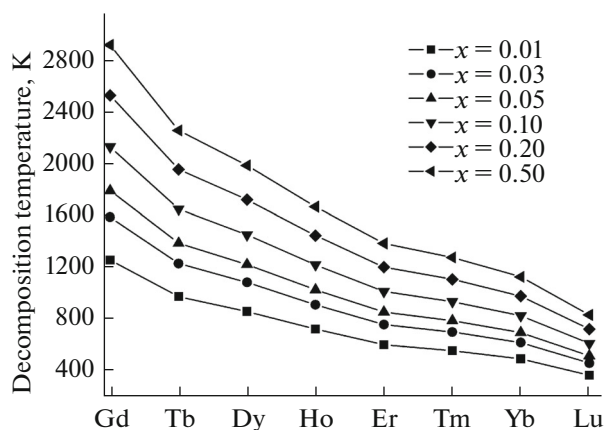


Fig. 1. Calculated decomposition temperatures of the $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ solid solutions in the Gd–Lu series at substitution limits $x = 0.01, 0.03, 0.05, 0.10, 0.20$, and 0.50 .

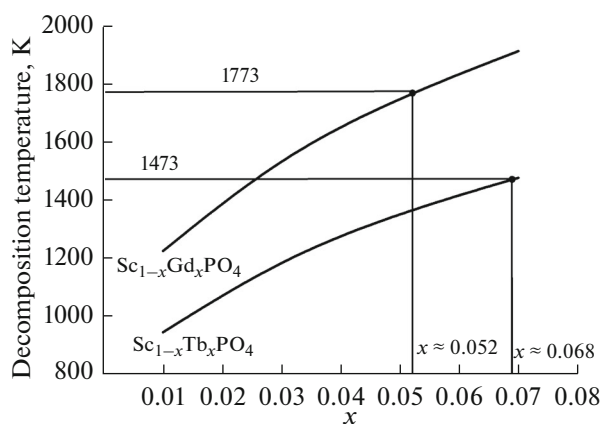


Fig. 2. Partial composition dependences of the decomposition temperature for $\text{Sc}_{1-x}\text{Gd}_x\text{PO}_4$ and $\text{Sc}_{1-x}\text{Tb}_x\text{PO}_4$ and the substitution limits found in these systems at 1773 (x \approx 0.052) and 1473 K (x \approx 0.068), respectively.

The decomposition temperatures calculated using the Becker equation were plotted for the rare-earth series at $x = 0.01, 0.03, 0.05, 0.10, 0.20,$ and 0.50 (Fig. 1). These data can be used to assess the thermodynamic stability of unlimited and the corresponding limited solid solution series. From a given temperature, we can estimate the limiting degree of rare-earth substitution for scandium. The intersection of the isotherm drawn from a given decomposition temperature with the vertical line drawn for the number of the rare earth allows us to find the substitution range. Interpolating the segment of the vertical line between two neighboring curves allows us to estimate the substitution limit. The substitution range can be found more accurately by constructing the composition dependence of the decomposition temperature calculated using the Becker equation for a particular system. Figure 2 presents portions of such dependences for the $\text{Sc}_{1-x}\text{Gd}_x\text{PO}_4$ and $\text{Sc}_{1-x}\text{Tb}_x\text{PO}_4$ systems.

To the best of our knowledge, no data on the energy of mixing for any of the $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ (Ln = Gd–Lu, Y) solid solution systems with limited component solubility are available in the literature. Clearly, this makes it difficult to assess the reliability of the present calculations. There is only information about the limiting degree of rare-earth substitutions for scandium in $\text{Sc}_{1-x}\text{Gd}_x\text{PO}_4$ ($x < 0.05$ at 1773 K [4]) and $\text{Sc}_{1-x}\text{Tb}_x\text{PO}_4$ ($x \approx 0.03$ at 1473 K [2]) samples prepared by solid-state reactions.

As seen in Fig. 2, the substitution limit obtained by us ($x \approx 0.052$) for the $\text{Sc}_{1-x}\text{Gd}_x\text{PO}_4$ system at 1773 K agrees with that reported by Chernyavsky et al. [4]: $x < 0.05$. The substitution limit calculated for the $\text{Sc}_{1-x}\text{Tb}_x\text{PO}_4$ system at 1473 K ($x \approx 0.068$) is slightly above the solid solution composition reported by Mi et al. [2]: $x = 0.03$. Unfortunately, it is not clear from Refs. [2, 4] at which temperature the composition of the solid solution is at equilibrium, because after calcina-

tion the samples were not quenched but were furnace-cooled to room temperature, where they were studied. This might lead to partial decomposition of the solid solutions and a reduction of the substitution range. It seems likely that, in both cases, the equilibrium substitution ranges at the above temperatures are slightly greater than the specified compositions and that the compositions $\text{Sc}_{0.97}\text{Tb}_{0.03}\text{PO}_4$ and $\text{Sc}_{0.95}\text{Gd}_{0.05}\text{PO}_4$ can be thought of as the lower and upper possible substitution limits, respectively, in the corresponding systems. In view of this, we suppose that the calculation results for the $\text{Sc}_{1-x}\text{Gd}_x\text{PO}_4$ and $\text{Sc}_{1-x}\text{Tb}_x\text{PO}_4$ systems are in satisfactory agreement with previously reported data obtained by instrumental characterization techniques.

CONCLUSIONS

Relying on Urusov's crystal energy theory of isomorphous substitutions, we have calculated the energies of mixing of $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ (Ln = Gd–Lu, Y) solid solutions. Across the rare-earth series from Gd to Lu, the energy of mixing decreases systematically from 48.2 to 13.5 kJ/mol and the critical decomposition temperature of the solid solutions decreases from 2880 to 810 K, respectively, which is due to the reduction in the host–substituent size mismatch.

We have presented a thermodynamic stability diagram that allows one not only to assess the stability of continuous series of $\text{Sc}_{1-x}\text{Ln}_x\text{PO}_4$ (Ln = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) solid solutions in wide composition and temperature ranges but also to predict substitution limits for limited solid solution series at a given temperature.

The calculated substitution limits in the $\text{Sc}_{1-x}\text{Gd}_x\text{PO}_4$ and $\text{Sc}_{1-x}\text{Tb}_x\text{PO}_4$ systems at 1773 and 1473 K, respectively, agree with previously reported data obtained by instrumental characterization techniques.

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