Prediction of Substitution Limits and Thermodynamic Stability for $Y_{1-x}Ln_xF_3$ (Ln = Sm–Lu) Nanosized Materials

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Introduction

Rare-earth elements (REEs) trifluorides attract more and more attention of researchers in various fields of science and technology, such as optoelectronic devices, phosphors, lasers and others. In recent years, studies on their application in the form of nanomaterials in medicine as optical 3D devices, probes for visualization of biological objects, for intracellular labels or measurements, and in immunoassays have become topical. The interest to $Y_{1-x}Ln_xF_3$ solid solutions is because the ionic radius of yttrium is close to the ionic radii of most REEs; therefore, it is easily substituted by them. In addition, a large group of REEs trifluorides from SmF_3 to LuF_3 crystallizes in the β-YF_3 type of structure, which also favors the isomorphous substitution of Y for REEs. These crystals are considered suitable matrix materials for use in lasers or scintillators due to their high transparency in a wide wavelength range from ultraviolet to infrared. Their band gap is >10 eV. REEs trifluoride crystals have low refractive indices (about 1.5), which limits the nonlinear effects obtained by pumping a high-power laser source, as well as low phonon energies.

In this work, within the framework of the crystal-energy theory of isomorphous substitutions, the mixing energies (interaction parameters), critical decomposition temperatures (stability) and decomposition temperatures of limited solid solutions of REEs trifluorides with a structure of the β-YF_3 type in the systems $Y_{1-x}Ln_xF_3$, Ln = Sm– Lu, have been calculated.

Calculation Procedure and Initial Data

The main task in calculating the substitution limits of solid solutions using the Urusov's crystal energy method is to determine the mixing energy *Q* (interaction parameter). In this work, we study the mutual substitution of REEs in systems, both components of which are isostructural. For this case, the mixing energy can be represented as consisting of two contributions due to the difference in the sizes of the substituted structural units or interatomic distances in the components (Q_R) and the difference in the degrees of ionicity of the chemical bond (Q_ε):

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

where: C, a constant calculated from the equation $C = 20(2\Delta\chi + 1)$ based on the difference in electronegativity χ of cations and anion.

m = 4 – the number of formula units in the pseudobinary approximation of components;

n = 8.9 – effective coordination number according to S. Batsanov, since in the structure of the β-YF_3 type the cation is surrounded by anions located at two significantly different distances;

z_m, z_x – charge modulus of structural units (Ln^{3+} and F^-);

R_1 = 2.3 - smaller cation–anion interatomic distance in the β-YF_3 structure;

α = 1.6935, the reduced Madelung constant calculated by Templeton formula;

Δε – the difference in the degrees of ionicity of the chemical bond in the components, calculated from the difference in the electronegativity (EN) of REEs cations and anion;

δ - is the relative difference in the sizes of substituting structural units (Table 1) (size parameter), calculated from the cubic roots of the unit cell volumes.

The accuracy of calculating the critical temperature is less than 13%.

Since the size parameter values in all cases are less than 0.1 (Tables 1 and 2) 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 Boltzmann constant, N is the Avogadro number. And the decomposition temperature T_d at a given substitution limit x or the substitution limit x at the decomposition temperature is according to the Becker equation:

$$-(1 - 2x) / \ln[x/(1 - x)] = kN \times T_d/Q.$$

The dependence of the decomposition temperatures of solid solutions on the composition (*x*) in this case will be symmetric.

RESULTS AND DISCUSSION

Calculation results for $Y_{1-x}Ln_xF_3$ (Ln = Sm–Lu) solid solutions with β-YF_3 structure

Table 1 Initial data and results of calculating the critical temperatures of decomposition for $Y_{1-x}Ln_xF_3$ (Ln = Sm–Lu) solid solutions with β-YF_3 structure

Ln	V, Å	δ	C, kJ	Q_δ, kJ/mol	Q_ε, kJ/mol	Q_{mix}, kJ/mol	T_{cr}, K
Sm	207,371	0,0276	138,32	11,253	0,2210	11,474	685
Eu	204,325	0,0224	137,40	7,363	0,7430	8,106	484
Gd	201,572	0,0176	139,28	4,608	0,0245	4,632	276
Tb	198,414	0,0124	138,32	2,271	0,2210	2,492	149
Dy	195,225	0,0070	137,68	0,720	0,6141	1,334	80
Ho	192,796	0,0028	137,40	0,115	0,7430	0,858	51
Er	190,583	0,0010	137,20	0,015	1,2036	1,218	73
Tm	188,633	0,0045	136,52	0,295	1,9896	2,284	136
Yb	187,033	0,0073	135,56	0,772	2,9721	3,744	223
Lu	185,686	0,0099	137,40	1,438	1,0378	2,476	148
Y	191.175	-	-	-	-	-	-

Table 2 Data for the calculation of the contribution to the mixing energy due to the difference in the degree of ionicity of the chemical bond in the components of the systems

Ln	χ_{Ln}^{3+}	$\chi(F^-) - \chi(Ln^{3+})$	ε_{Ln}	Δε	Q_ε, kJ/mol
Sm	1.410	2,958	0.844	0.006	0,2210
Eu	1.433	2,935	0.839	0.011	0,7430
Gd	1.386	2,982	0.848	0.002	0,0245
Tb	1.410	2,958	0.844	0.006	0,2210
Dy	1.426	2,942	0.840	0.010	0,6141
Ho	1.433	2,935	0.839	0.011	0,7430
Er	1.438	2,930	0.836	0.014	1,2036
Tm	1.455	2,913	0.832	0.018	1,9896
Yb	1.479	2,889	0.828	0.022	2,9721
Lu	1.431	2,937	0.837	0.013	1,0378
Y	1.340	3,028	0.850	-	-

Based on the calculated values of the critical decomposition temperatures (for *x*=0.50) and the decomposition temperatures (for *x*=0.01, 0.03, 0.05, and 0.10), their dependences on REEs atomic numbers were plotted – a diagram of the thermodynamic stability of solid solutions (Figure 1).

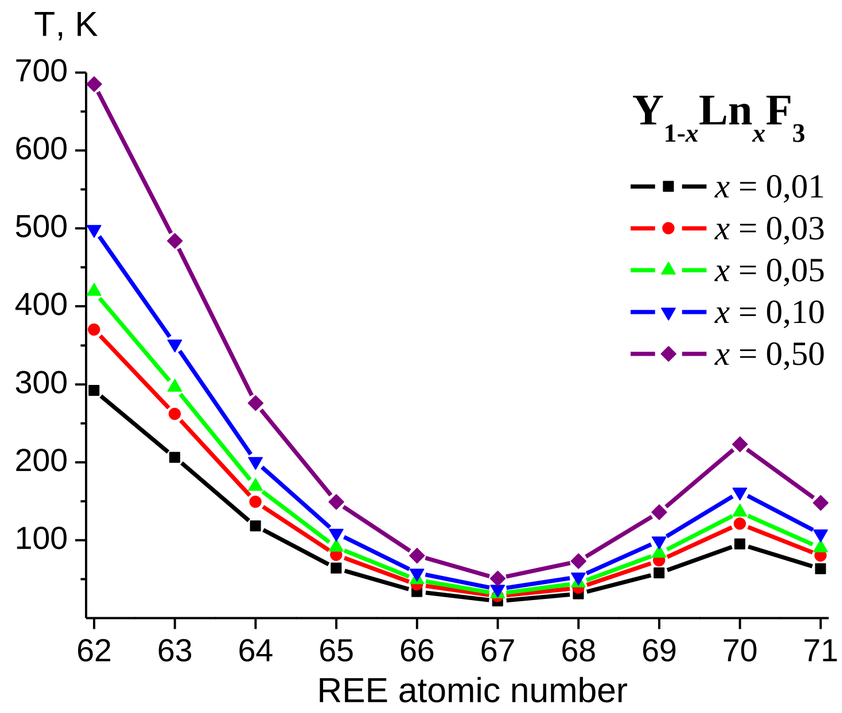

Figure 1 Dependences of the calculated decomposition temperatures (stability temperatures) of solid solutions of REEs fluorides of the composition $Y_{1-x}Ln_xF_3$ (Ln = Sm–Lu) solid solutions with β-YF_3 structure on the REEs atomic number (diagram of the thermodynamic stability of solid solutions)

Conclusions

The mixing energies (interaction parameters) and critical decomposition temperatures (stability) of solid solutions with the β-YF_3 structure of the $Y_{1-x}Ln_xF_3$, Ln=Sm–Lu systems are calculated using the crystal-energy approach in the approximation of regular solid solutions. The calculation results agree with the literature data on the temperature of synthesis of nanosized crystalline solid solutions of composition $Y_{1-x}Eu_xF_3$ (*x*=0.05, 0.10, 0.20, 0.30, and 0.40) obtained by the low-temperature hydrothermal method at 453K. The synthesis temperature of solid solutions with *x*=0.05 and 0.10 is higher calculated decomposition temperatures of solid solutions by 157 and 101K, respectively, i.e., is in the region of thermodynamic stability. The calculated decomposition temperatures of solid solutions with *x*=0.20, 0.30, and 0.40 differ from the temperature of their synthesis by only 34, 4, and 24K, respectively, i.e., their synthesis was carried out almost at the lower boundary of the temperature stability region.

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