

© ANDREI V. ELYSHEV, OLEG V. ANDREEV, GUZEL S. SHAFIKOVA,
DENIS S. ADAKHOVSKY

sheffield87@inbox.ru, andreev@utmn.ru

UDC 544.016.2

**TECHNIQUE PREDICTING THE PHASE DIAGRAMS
OF THE $Ln'_2S_3 - Ln''_2S_3$ ($Ln', Ln'' = La - Lu$) SYSTEMS,
THE $Nd_2S_3 - Er_2S_3$ SYSTEM***

SUMMARY. The technique predicting the type of the phase diagrams of the $Ln'_2S_3 - Ln''_2S_3$ ($Ln', Ln'' = La - Lu$) systems is developed. The expansion of solid solutions is calculated based on the change of the equivalent radius of the Ln^{3+} cation. The radius values can be changed within the radii range for the cations of the $\gamma-Ln_2S_3$, $\alpha-Ln_2S_3$, $\delta-Ln_2S_3$ structural types in the family of rare-earth elements. The coordination number values for the structural types are $\gamma-Ln_2S_3$ (CN 8), $\alpha-Ln_2S_3$ (CN 6), $\delta-Ln_2S_3$ (CN 6). The prediction of the phase diagram of the $Nd_2S_3 - Er_2S_3$ system is confirmed while being constructed. The complex method of simultaneous thermal analysis (STA) is first applied for studying the $Ln/2S_3 - Ln/2S_3$ systems; the STA 449 F3 Jupiter appliance with a powerful IT-complex is used. The eutectoid transformation in the solid solution based on Nd_2S_3 and the eutectic temperature are fixed by the STA method. The balance equations are formulated. The diagram of eutectic type (the eutectic composition is 75 mol. % Er_2S_3 , $T = 1770 \pm 10$ K) with $\gamma-Nd_{2.2x}Er_{2x}S_3 - 45$ mol. % Er_2S_3 , $\alpha-Nd_{2.2x}Er_{2x}S_3 - 40$ mol. % Er_2S_3 , $\delta-Er_{2x}Nd_{2.2x}S_3$ 98 — 100 mol. % Er_2S_3 solid solutions is constructed.

KEY WORDS. Prediction, phase diagram, sesquisulfides, rare-earth elements.

The Ln_2S_3 compounds of the Th_3P_4 -type structure are transparent in the spectral region from 0.5 to 20-30 μm , their band gap is $\Delta E_{opt} = 2.6-2.8$ eV [1]. As a rule, the materials with the properties required are selected from the solid solution range in the $Ln'_2S_3 - Ln''_2S_3$ ($Ln', Ln'' = La - Lu$) systems [1], [2].

There are publications on the study of the $Ln'_2S_3 - Ln''_2S_3$ elementary systems [1], [2]. Continuous $\gamma-La_{2.2x}Nd_xS_3$ ($x = 0 - 1$) solid solution is formed in the $La_2S_3 - Nd_2S_3$ system [1]. The phases of $LnLuS_3$ composition are formed in the $Ln_2S_3 - Lu_2S_3$ ($Ln = Ce, Pr, Nd$) systems [3].

The Ln_2S_3 compounds exist in a few structure types (ST), which are designated as follows: $\alpha-Ln_2S_3$ with an orthorhombic structure of the $\alpha-La_2S_3$ type, $\gamma-Ln_2S_3$ with

* The research was carried out using the CUC SANO&N equipment and was financially supported by the Ministry of Education and Science of the Russian Federation (code 3.3763.2011 (7-12)), within the Federal Target Program *Scientific and Academic Staff of Innovative Russia*. No. 14.B37.21.1184.

a cubic structure of the Th_3P_4 type, and $\delta\text{-Ln}_2\text{S}_3$ with a monoclinic structure of the $\delta\text{-Ho}_2\text{S}_3$ type. The continuous variation of cation equivalent radius occurs in the solid solution range (SS) of the $\text{Ln}'_2\text{S}_3 - \text{Ln}''_2\text{S}_3$ systems.

It is relevant to develop a technique for predicting a phase diagram of the $\text{Ln}'_2\text{S}_3 - \text{Ln}''_2\text{S}_3$ systems, based on the structure of the Ln_2S_3 compounds and variations of the cation equivalent radius in the solid solution range. There are no such data published for predicting a phase diagram of the $\text{Ln}'_2\text{S}_3 - \text{Ln}''_2\text{S}_3$ systems.

The $\text{Nd}_2\text{S}_3 - \text{Er}_2\text{S}_3$ system, which is formed from the isoformula compounds having a common sulfide-anion, is chosen as the model system. The correlation of the geometric and energetic properties of the $r\text{Nd}^{3+}$ and $r\text{Er}^{3+}$ cations ($r\text{Nd}^{3+} = 0.1109$ nm, $\chi = 1.14$; $r\text{Er}^{3+} = 0.1004$ nm $\chi = 1.24$) suggests predicting the formation of the extended solid solution range in the system. There are no data published on the study of phase equilibria for the $\text{Nd}_2\text{S}_3 - \text{Er}_2\text{S}_3$ system.

The purpose of this paper is to develop a technique for predicting the phase diagram of the $\text{Ln}'_2\text{S}_3 - \text{Ln}''_2\text{S}_3$ ($\text{Ln}', \text{Ln}'' = \text{La} - \text{Lu}$) system, based on the data on the initial compound structure and the variation of the cation equivalent radius in the solid solution range, to predict and construct a phase diagram for the $\text{Nd}_2\text{S}_3 - \text{Er}_2\text{S}_3$ system.

The technique for predicting the phase diagram of the $\text{Ln}'_2\text{S}_3 - \text{Ln}''_2\text{S}_3$ system type is based on the following initial theses formulated according to the general approaches of the physicochemical analysis:

- the phase diagram type of the $\text{Ln}'_2\text{S}_3 - \text{Ln}''_2\text{S}_3$ ($\text{Ln}', \text{Ln}'' = \text{La} - \text{Lu}$) systems depends on the structure type of the initial Ln_2S_3 compounds;

- each of the $\alpha\text{-Ln}_2\text{S}_3$, $\gamma\text{-Ln}_2\text{S}_3$, $\delta\text{-Ln}_2\text{S}_3$, $\varepsilon\text{-Ln}_2\text{S}_3$ structure types exists within certain limits of the $r\text{Ln}^{3+}$ ionic radius in the series of the Ln_2S_3 ($\text{Ln} = \text{La} - \text{Lu}$) compounds;

- the values of the equivalent radius constantly vary in the $\text{Ln}'_{2-2x}\text{Ln}''_{2x}\text{S}_3$ solid solution, which suggests predicting a potential extension of the solid solution range in the $\text{Ln}'_2\text{S}_3 - \text{Ln}''_2\text{S}_3$ systems.

The Ln_2S_3 ($\text{Ln} = \text{La} - \text{Dy}$) sesquisulfides exist as the $\alpha\text{-Ln}_2\text{S}_3$ low-temperature modifications with the orthorhombic structure of the $\alpha\text{-La}_2\text{S}_3$ type ($r\text{La}^{3+}(\text{CN}6) = 0.1032$ nm, $r\text{Dy}^{3+}(\text{CN}6) = 0.0912$ nm) (Table 1) and the $\gamma\text{-Ln}_2\text{S}_3$ high-temperature modifications with the cubic structure of the Th_3P_4 type ($r\text{La}^{3+}(\text{CN}8) = 0.1160$ nm, $r\text{Dy}^{3+}(\text{CN}8) = 0.1027$ nm) [4], [5].

The $\delta\text{-Ln}_2\text{S}_3$ structure with a monoclinic system exists for Ln: Ho, Y, Er, Tm ($r\text{Ho}^{3+}(\text{CN}6) = 0.0901$ nm, $r\text{Tm}^{3+}(\text{CN}6) = 0.0880$ nm) [4], [5].

The values of the $r\text{Ln}^{3+}$ cation radii, where the structure types of Ln_2S_3 : $\alpha\text{-Ln}_2\text{S}_3$; $\gamma\text{-Ln}_2\text{S}_3$; $\delta\text{-Ln}_2\text{S}_3$ compounds are stable, are used as the basic data for the calculation of solid solution range extension (Table 1, the right column).

In the $\text{Ln}_{2-2x}\text{Ln}_{2x}\text{S}_3$ ($x = 0 - 1$) solid solution range, the r_{eq} value of the cation equivalent radius should be considered as the factor determining the structure type and the structure stability intervals in the solid solution range.

Table 1

The crystal system, the structure type, the rLn^{3+} values for the Ln_2S_3 polymorphic modifications according to the data from [4]

Structure	Crystal system	Structure type	Ln^{3+} CN	rLn^{3+} for CN of the structure type	rLn^{3+} value limits, nm, where Ln_2S_3 compounds are stable
$\alpha-La_2S_3$	orthorhombic	$\alpha-La_2S_3$	6	0.1032	0.1032 – 0.0912
$\alpha-Ce_2S_3$	orthorhombic	$\alpha-La_2S_3$	6	0.1010	
$\alpha-Pr_2S_3$	orthorhombic	$\alpha-La_2S_3$	6	0.0990	
$\alpha-Nd_2S_3$	orthorhombic	$\alpha-La_2S_3$	6	0.0983	
$\alpha-Sm_2S_3$	orthorhombic	$\alpha-La_2S_3$	6	0.0958	
$\alpha-Eu_2S_3$	orthorhombic	$\alpha-La_2S_3$	6	0.0947	
$\alpha-Gd_2S_3$	orthorhombic	$\alpha-La_2S_3$	6	0.0938	
$\alpha-Tb_2S_3$	orthorhombic	$\alpha-La_2S_3$	6	0.0923	
$\alpha-Dy_2S_3$	orthorhombic	$\alpha-La_2S_3$	6	0.0912	
$\beta-La_2S_3$	tetragonal	$\beta-La_2S_3$	7	0.1100	0.1100
$\gamma-La_2S_3$	cubic	Th_3P_4	8	0.1160	0.1160-0.1027
$\gamma-Ce_2S_3$	cubic	Th_3P_4	8	0.1143	
$\gamma-Pr_2S_3$	cubic	Th_3P_4	8	0.1126	
$\gamma-Nd_2S_3$	cubic	Th_3P_4	8	0.1109	
$\gamma-Sm_2S_3$	cubic	Th_3P_4	8	0.1079	
$\gamma-Eu_2S_3$	cubic	Th_3P_4	8	0.1066	
$\gamma-Gd_2S_3$	cubic	Th_3P_4	8	0.1063	
$\gamma-Tb_2S_3$	cubic	Th_3P_4	8	0.1040	
$\gamma-Dy_2S_3$	cubic	Th_3P_4	8	0.1027	
$\delta-Y_2S_3$	monoclinic	$\delta-Ho_2S_3$	6	0.0900	0.0901 – 0.0880
$\delta-Ho_2S_3$	monoclinic	$\delta-Ho_2S_3$	6	0.0901	
$\delta-Er_2S_3$	monoclinic	$\delta-Ho_2S_3$	6	0.0890	
$\delta-Tm_2S_3$	monoclinic	$\delta-Ho_2S_3$	6	0.0880	

The equivalent radius is the one calculated as the arithmetic average of the cation radius values taken as the values of their coordinate numbers for this structure. The formulas to calculate the equivalent ionic radius are as follows:

For the structure of the $\alpha-La_2S_3$ and $\delta-Ho_2S_3$ types where the coordinate number of the Ln^{3+} cations is equal to 6,

$$r_{eq}(Ln'_{2-2x}Ln'_{2x})S_3 = \frac{(2-2x)Ln'(CN6) + 2xLn''(CN6)}{2} \quad (1)$$

For the structure of the Th_3P_4 type, where the coordinate number of the Ln^{3+} cations is equal to 8.

$$r_{eq}(Ln'_{2-2x}Ln''_{2x})S_3 = \frac{(2-2x)Ln'(CN8) + 2xLn''(CN8)}{2} \quad (2)$$

Each of the solid solution types (α , γ , δ) exists within the r_{eq} equivalent radius limits, which are equal to the rLn^{3+} limits of the radii of the stability structure type in the series of the Ln_2S_3 compounds.

In the α - $Nd_{2-2x}Er_{2x}S_3$ solid solution, the smaller-in-size Er^{3+} ions compress the crystal structure. The minimum limit value of the radius ($r_{eq} = 0.0912$ nm) for the α - La_2S_3 structure type is substituted into the left side of the formula (1), and the x value is calculated, $x = 0.6$ is obtained. The predicted boundary of the solid solution is of the following composition: α - $Nd_{0.8}Er_{1.2}S_3$ (60 mol.% Er_2S_3).

For the γ -structure, the minimum value of the radius ($r_{eq} = 0.1027$ nm) is substituted into the formula (2), $x = 0.63$ is obtained, the boundary composition of the solid solution is as follows: α - $Nd_{0.74}Er_{1.26}S_3$ (63 mol. % Er_2S_3).

The boundary value for the δ - Er_2S_3 structure is $x = 0.95$ (95-100 mol. % Er_2S_3). In the Nd_2S_3 — Er_2S_3 system, the difference in the structures of the α - Nd_2S_3 , γ - Nd_2S_3 , δ - Er_2S_3 initial compounds predetermines the existence of two-phase sections in the diagram. The close melting temperatures for high-melting compounds (Er_2S_3 $T_{melt.} = 1,940$ K [7] and Nd_2S_3 $T_{melt.} = 2,140$ K [6]) allow predicting the nature of a two-phase section, it is most likely eutectic. The predicted form of the phase diagram for the Nd_2S_3 — Er_2S_3 system is presented in Fig. 2a.

The technique for the physicochemical analysis of the Nd_2S_3 , Er_2S_3 compounds.

The sampling procedure for solid solutions as a powder and as-cast in the Nd_2S_3 — Er_2S_3 system is presented in [6], [7], [8].

The integrated method of simultaneous thermal analysis (STA) was first applied to study the Ln'_2S_3 — Ln''_2S_3 systems using the *STA 449 F3 Jupiter* appliance (Fig. 1) equipped with a powerful IT-complex. The STA techniques are based on the combination of differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermo-gravimetric analysis (TGA) [9], [10].

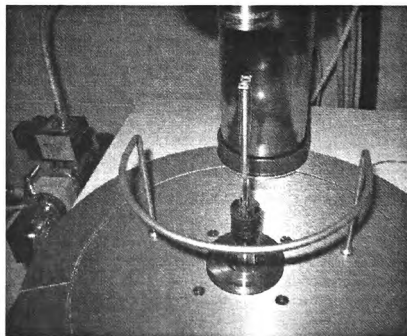
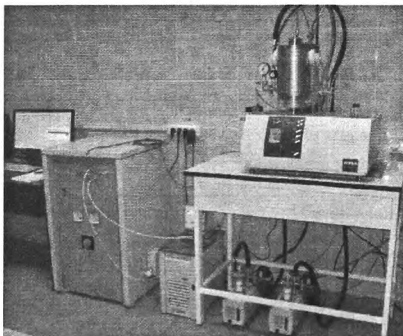


Fig. 1. The STA 449 F3 Jupiter appliance for simultaneous thermal analysis, the temperature accuracy is 0.3 °C (the Program of Innovative University Infrastructure Development, the RF Government Decree No. 219)

The sample weight for the STA was 120-140 mg. He 7.0 was used as a gas medium (99.99999% meets the Technical Specifications No. 14299304-002-2000). The temperature interval where it was expected to register the phase change peaks was studied at the sample heating rate of 10 K/min. When crystallizing, the cooling rate was also 10 K/min.

The frames were Au, Cu₂S, SrF₂, and MnS. The heat effect area was specified using the *Proteus 6 2012* software. While heat treating, the initial weights were down by 0.2-0.6% which was 0.280-0.960 mg, it could be explained by the loss of highly volatile impurities sorbed in the process of synthesis and atmospheric gases.

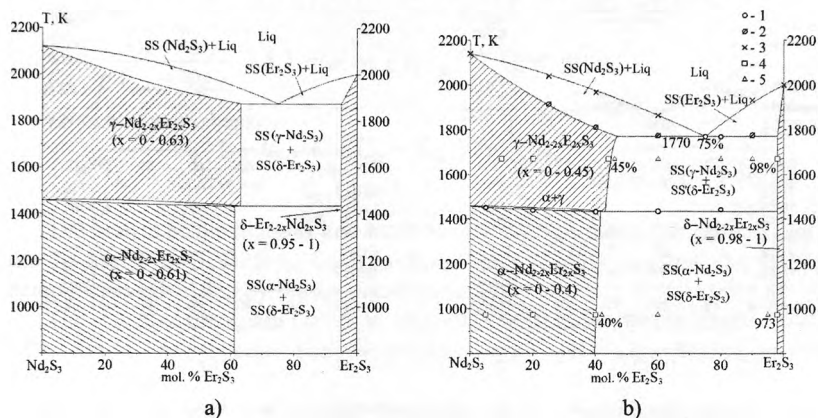


Fig. 2. The predicted (a) and constructed by the PCA methods (b) phase diagram of the Nd₂S₃ — Er₂S₃ system.

1 — The data of differential scanning calorimetry.

The VPTA results: 2 — incipient melting; 3 — complete melting.

The state of samples based on the RFA, MSA, and DMA methods is 4 — one-phase one; 5 — two-phase one.

The construction of the phase diagram for the Nd₂S₃ — Er₂S₃ system. The phase diagram for the Nd₂S₃ — Er₂S₃ system is first constructed (Fig. 2b), this is the diagram of the eutectic type with the extended solid solution range based on the α-Nd₂S₃ (0-40 mol.% Er₂S₃) and γ-Nd₂S₃ (0-45 mol.% Er₂S₃) compounds and the solid solution based on the δ-Er₂S₃ (98-100 mol.% Er₂S₃).

The type of the phase diagram fully matches the predicted one. There are differences in the solid solution extension between the prediction and the experiment. According to the RFA data, in the range from 0 to 40 mol.% Er₂S₃, all the samples annealed at 970 K have the structure of the α-La₂S₃ modification type. The u.c. parameters and the volume of the orthorhombic u.c. regularly decrease, which correlates with the ratio of ionic radii ($r_{Nd^{3+}}(\text{CN } 6) = 0.0983 \text{ nm}$, $r_{Er^{3+}}(\text{CN } 6) = 0.0890 \text{ nm}$) [5] (Fig. 3a).

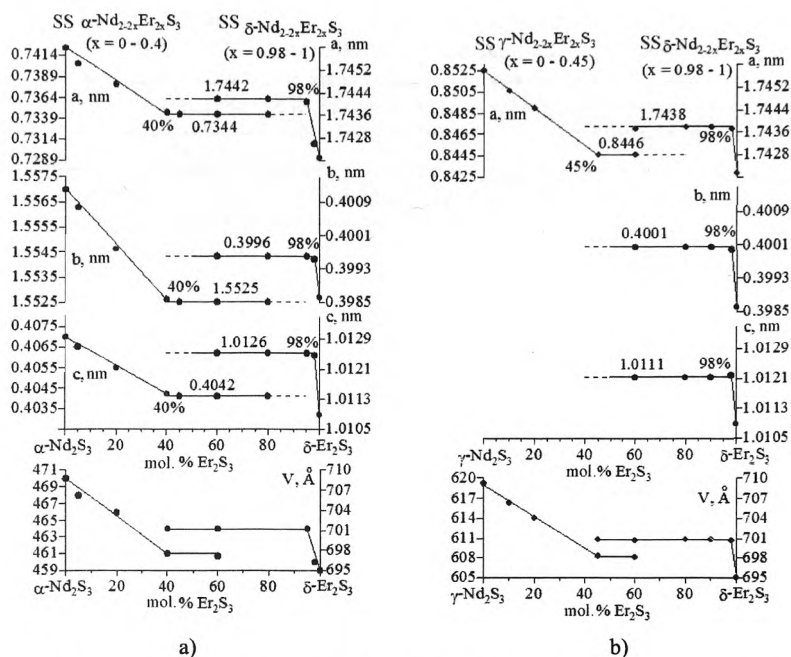


Fig. 3. The parameter variation of the orthorhombic u.c. in the solid solution (SS) range:

- α -Nd_{2-2x}Er_{2x}S₃ and δ -Er_{2x}Nd_{2-2x}S₃ for the samples of the Nd₂S₃ — Er₂S₃ system synthesized at 1,270 K and annealed at 970 K during 3,600 hours;
- γ -Nd_{2-2x}Er_{2x}S₃ and δ -Er_{2x}Nd_{2-2x}S₃ for the samples of the Nd₂S₃ — Er₂S₃ system annealed at 1,670 K during 30 min.

According to the RFA data, in the range from 0 to 45 mol.% Er₂S₃, all the samples annealed at 1,670 K have the structure of the γ -modification type. The u.c. parameters and the volume of cubic u.c. regularly decrease as well (Fig. 2b) in accordance with the changes in the ion concentration ($r_{\text{Nd}^{3+}(\text{CN } 8)} = 0.1109 \text{ nm}$, $r_{\text{Er}^{3+}(\text{CN } 8)} = 0.1004 \text{ nm}$) [5].

The extension of the solid solution based on δ -Er₂S₃ is equal to 98-100 mol.% Er₂S₃. There are only the δ -modification monoclinic system reflexes in the samples obtained as a powder and annealed at 970 K during 5 months, the as-cast samples annealed at 1,670 K during 30 min. The rapid change in the u.c. parameters against the initial δ -Er₂S₃ is observed (Fig. 3a).

In the sample of 95 mol% Er₂S₃ annealed at 1,670 K, the δ -Er_{2x}Nd_{2-2x}S₃ solid solution content is markedly less than in the sample annealed at 970 K. The dependence of the solvability value on the temperature is demonstrated in the δ -Er_{2x}Nd_{2-2x}S₃ solid solution.

The u.c. parameter increase occurring in the δ -modification solid solution range also correlates with the REE ratio of the ionic radii: $rEr^{3+}(CN\ 6) = 0.0890\text{ nm}$ and $rNd^{3+}(CN\ 6) = 0.0983\text{ nm}$ [5].

The eutectic melting peak at 1,770 K was detected in the two-phase area of the system by the STA method. The eutectic composition was calculated by the following equations (Table 2):

$$\text{Kordes} \\ \frac{C_L}{C_H} = \frac{T_H - T_E}{T_H} \div \frac{T_L - T_E}{T_L} - 77.2\text{ mol\% } Er_2S_3$$

$$\text{Vasilyev} \\ \frac{C_L}{C_H} = \frac{T_H - T_E}{T_L - T_E} - 74.2\text{ mol\% } Er_2S_3$$

$$\text{Efimov-Vozdvizhensky} \\ T = T_L - \frac{C_H[1 - C_H + x(C_H - C_e)]T_L - T_E}{C_H(1 - C_e)} - 74.2\text{ mol\% } Er_2S_3$$

The branch of the liquidus line identified by the STA method is extrapolated to the 75 mol% Er_2S_3 eutectic composition, which closely matches the eutectic composition calculated by the empirical formulas.

The eutectoid change in the Nd_2S_3 -base solid solution range was detected by the STA method. The heat effect peak has a diffuse nature, and it is specific to kinetically difficult processes.

The balance equations for phase changes were formulated (Table 2).

Table 2

**The balance equations for eutectic and eutectoid phase changes
in the Nd_2S_3 — Er_2S_3 system**

Form of phase change	Coordinates of non-variant points		Equation for phase change	ΔN_{melt} , kJ/mol
	Composition	T, K		
Eutectic melting	75 mol.% Er_2S_3	1,770 K	0.44 SS γ - Nd_2S_3 (0.46 Er_2S_3 ; 0.54 Nd_2S_3) + 0.56 SS δ - Er_2S_3 (0.98 Er_2S_3 ; 0.02 Nd_2S_3) \leftrightarrow L (0.75 Er_2S_3 ; 0.25 Nd_2S_3)	47
Eutectic transformation	42 mol.% Er_2S_3	1,435 K	0.98 SS α - Nd_2S_3 (0.41 Er_2S_3 ; 0.59 Nd_2S_3) + 0.02 SS δ - Er_2S_3 (0.98 Er_2S_3 ; 0.02 Nd_2S_3) \leftrightarrow SS γ - Nd_2S_3 (0.42 Er_2S_3 ; 0.58 Nd_2S_3)	7

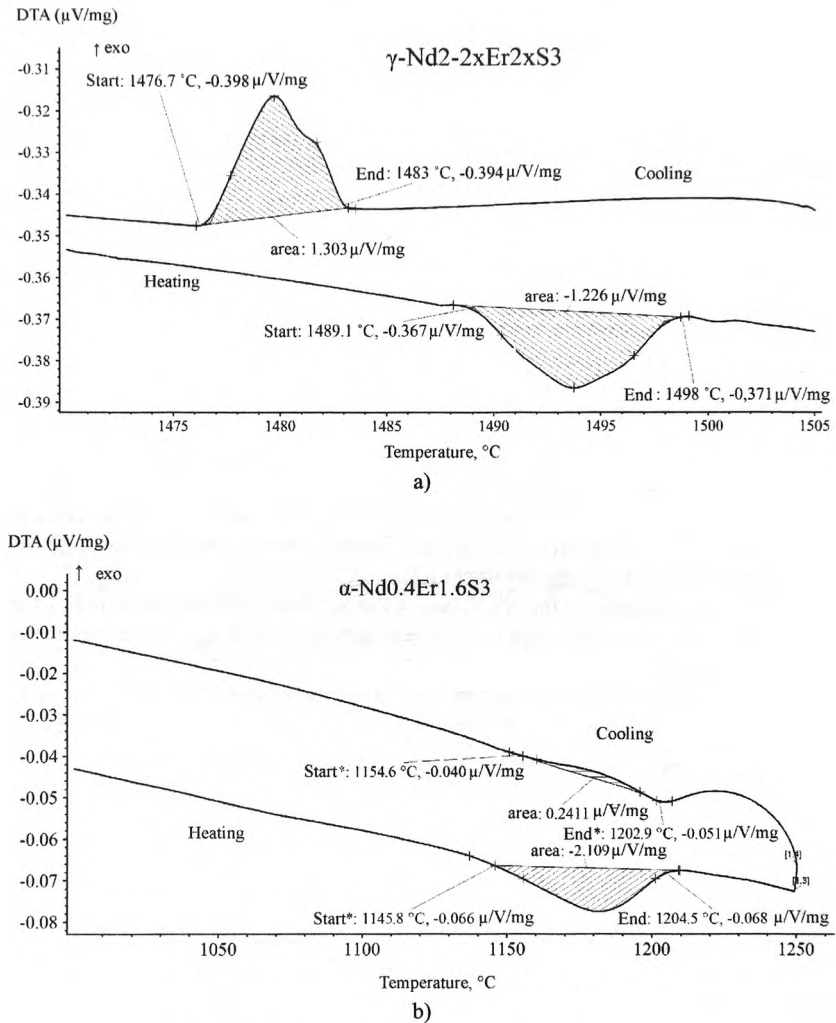


Fig. 4 The heat patterns of the Nd_2S_3 — Er_2S_3 system:

- a) the 80 mol.% Er_2S_3 sample, the phase composition is $\gamma+\delta$, the eutectic melting peak of heat effect; b) the 80 mol.% Er_2S_3 sample, the phase composition is $\alpha+\delta$, the eutectic melting peak of heat effect (Table 2)

Conclusion. The technique for the prediction of the $\text{Ln}'_2\text{S}_3$ — $\text{Ln}''_2\text{S}_3$ system phase diagram type is developed on the basis of the data on the Ln_2S_3 compound structures and the calculation of solid solution extension by variation in the values of cation equivalent radius in the solid solution.

The prediction for the phase diagram of the Nd_2S_3 — Er_2S_3 system is confirmed while being constructed. The diagram is of the eutectic type (the eutectics composition is 75 mol.% Er_2S_3 , $T = 1,770 \pm 10$ K) with the solid solutions as follows: $\gamma\text{-Nd}_{2-2x}\text{Er}_{2x}\text{S}_3$ — 45 mol.% Er_2S_3 , $\alpha\text{-Nd}_{2-2x}\text{Er}_{2x}\text{S}_3$ — 40 mol.% Er_2S_3 , $\delta\text{-Er}_{2x}\text{Nd}_{2-2x}\text{S}_3$ 98 — 100 mol.% Er_2S_3 .

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