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THERMAL ANALYSIS OF THE YSe-Y_2Se_3 SYSTEM

SUMMARY. The solidus-liquidus area of the phase diagram of the YSe-Y_2Se_3 system is constructed by the visual-polythermal (VPTA) and simultaneous-thermal (STA) analyses. While finding the Y_2Se_{3-x} compound in the polycrystalline state, the endothermic effect is first registered at t = 1,325 ± 5 ^0C; ΔH = 18 ± 2 kJ / mol (43 J/g). The effect is identified as the polymorphic transition from the Y_2Se_{3-x} (ST Sc_2S_3) orthorhombic structure into the high-temperature modification of ξ-Y_2Se_3, most probably of a cubic structure. The transition is reversible, it is reproduced when being cooled. The eutectoid transformation temperature in the Y_2Se_3–based solid solution is equal to 1,275 ± 5 ^0C. The heat effect of eutectic melting is registered in the thermal analysis of the Y_2Se_{3-x} compound. The total melting enthalpy of all the Y_2Se_{3-x} crystals is approximately 70 ± 15 kJ/mol (169 J/g). According to the VPTA, the eutectic temperature between the YSe and Y_2Se_3 phases is 1,380 ± 15 ^0C; according to the STA, it is 1,350 ± 7 ^0C. The eutectic composition is assumed to be 57.5 at. % Se; according to the STA, the melting enthalpy of the eutectics is 43.2 ± 5 J/g. The melting temperature of YSe is 2,110 ± 35 ^0C.

KEYWORDS. Lanthanon selenides, phase diagram, phase transformation heat.

The $4d^15s^2$ yttrium is the first 4d element and demonstrates similarity to rare-earth elements by its properties [1-2]. According to the data published, in the YSe-Y_2Se_3 system, the series of compounds is formed: YSe of the cubic structure, the phase of the $Y_{0.75}Se$ structure, Y_3Se_4 of the orthorhombic structure, Y_5Se_7 of the monoclinic structure, and Y_2Se_3 of the orthorhombic structure. The conditions of the phase occurrence in the YSe-Y_2Se_3 system diagram are not registered [1].

Yttrium selenides demonstrate semiconducting properties [1], [3]. The YSe and Y_3Se_4 selenides have the metal type conductivity, while Y_2Se_3 (Sc_2S_3 type) and YSe_2 are semiconductors. The impurities influence considerably the quality of semiconductors and their properties. To investigate the properties of the yttrium selenide phases, the study of the phase diagram of the YSe-Y_2Se_3 system is of the utmost importance. The phase diagram of the YSe-Y_2Se_3 system has not been studied before.

The thermal technique was used in the physicochemical analysis for a long time as a traditional method [4], [5]. One of its variations is the visual-polythermal analysis which allows studying the samples at high temperatures. The VPTA method makes it possible to register an aggregative change in a sample, as the sample surface condition is monitored. Modern methods of thermal analysis, such as STA, allow determining quantitative heat effects, the change in the sample weight when heating, with a high accuracy and sensitivity, which is impossible to obtain by the VPTA method [6].

The purpose of the paper was to construct the solidus – liquidus area in the phase diagram of the YSe-Y_2Se_3-system by the methods of simultaneous thermal and visual-polythermal analyses.

The experiment. The samples were prepared from yttrium metal of the *Itm-1* grade and selenium of *22-4* extra-pure grade. The dimensions of yttrium chips were as follows: the thickness was 0.01-0.05 mm, the calculated surface area of 1 g of chips was 100-120 cm^2. The 5 g sample weights of yttrium and selenium with these dimensions were placed in the 10 ml quartz ampoule, which was vacuumed and sealed in. Starting with 570 K, every 24 hours the temperature was raised by 50 K until it reached 1,270 K, at this temperature the ampoule was cured during 100 hours [5], [6]. The mixture was ground and melted using a high-frequency unit in tantalic (50-54 at. % Se) or graphite (56-60 at. % Se) crucibles. The sample was melted twice for 1 minute and then cooled. The sample of 60 at. % Se composition was heated in selenium vapor [7]. The samples were annealed during 15 minutes at 1,770 K.

The visual-polythermal analysis was used for the high-temperature thermal study. In analyzing the test samples, the incipient melting and the complete melting were visually registered [8], [9].

The simultaneous thermal analysis was carried out using the *STA 449 F3 Jupiter* appliance. The sample under study was a single polycrystalline. Each sample was previously fit to the crucible form. The sample weights were 100-150 mg. Extra pure helium was used as the inert media. The heat schedule was 40 K/min. until 1,200 ^{0}C was reached. After reaching the point of the estimated thermal effects, the heat schedule was changed to 10 K/min. The sample was melted, cooled until completely crystallized, and re-melted. The X-ray phase analysis (RPA) was carried out using the *DRON-3* diffractometer in copper filtered radiation (Cu Kα-radiation, Ni-filter).

Results and discussion. The phase composition of the samples was determined by the RPA method. The samples mostly were the mixture of the phases of two structures and were formed by the solid solution (SS) on the basis of the YSe phase (the structure type (ST) was $Y_{0.75}Se$; a = 1.145 nm) and the Y_2Se_3 phase of the orthorhombic structure (a = 1.147 nm; b = 0.817 nm; c = 2.438 nm) (Table 1).

The melting ranges for the samples of the YSe — Y_2Se_3 system were determined by the VPTA method (Table 1). The incipient melting in samples containing from 54 to 59 at. % Se occurred at the temperatures close to 1,360-1,370 ^{0}C, which indicated the existence of a eutectic horizontal in the system. The temperatures of the complete melting of the samples – the liquidus temperatures – were approximated by the second-degree polynomial. Depending on the chosen type of the polynomial, the concurrence of lines was observed in the segment of 57-58 at. % Se (Fig. 3). Such a solidus-liquidus area is characteristic of the eutectic diagrams [3] (Fig. 3). The maximum position on the liquidus curve for the 3Y:4Se composition was not registered. As the VTPA does not enable all the range of changes in the enthalpy to be monitored while the sample is heated, but it enables only the aggregative changes to be registered, the STA of the system samples was carried out.

Table 1

The temperatures and melting conditions for the samples of the YSe-Y_2Se_3 system determined by the VPTA method

Sample composition at. % Se	Phase composition (annealed at 1,500 ^0C)	Melting range, ^0C		Visible transition behavior
		Incipient melting	Complete melting	
50	SS YSe (ST $Y_{0.75}Se$) a = 1.139 nm	2,070	2,110	Fast melting
51	SS YSe (ST $Y_{0.75}Se$) a = 1.140 nm	1,980	2,030	Melting from the sides, transition into the liquid state
53	SS YSe (ST $Y_{0.75}Se$) a = 1.145 nm	1,460	1,810	Appearance of melt in the sample pits, increase in melt when heated, melt formation with spots of solid phase, melt
54	SS YSe (ST $Y_{0.75}Se$) — 65% a = 1.145 nm; SS Y_2Se_3 (ST Sc_2S_3) — 35% a=1.148 nm b=0.819 nm c=2.44 nm	1,380	1,720	The same melting conditions as for 53 at. % Se sample
56	SS YSe (ST $Y_{0.75}Se$) — 35 % a = 1.145 nm; SS Y_2Se_3 (ST Sc_2S_3) — 65 % a=1.148 nm b=0.819 nm c=2.44 nm	1,380	1,460	Melting within a narrow range
59	SS YSe (ST $Y_{0.75}Se$) — 15 % a = 1.145 nm; SS Y_2Se_3 (ST Sc_2S_3) — 85 % a=1.148 nm b=0.819 nm c=2.44 nm	1,380	1,460	Melting within a narrow range
60	SS Y_2Se_3 (ST Sc_2S_3) a = 1.147 nm; b = 0.817 nm; c = 2.438 nm	1,460	1,490	Melting within a narrow range

The samples of 57-60 at. % Se (this substance does not interact with graphite crucibles) were studied by the STA method. After the heat treatment, all the samples had the appearance of typical melted ones.

The endothermic effect was first recorded at t = 1,325 ^{0}C; 18 ± 2 kJ/mol (43 J/g), while the Y_2Se_{3-x} compound was in a polycrystalline state (Fig. 2). The effect was identified as the polymorphic transition from the Y_2Se_{3-x} (Sc_2S_3 ST) orthorhombic structure to the ξ-Y_2Se_3 high-temperature modification, most probably of the cubic structure. The transition was reversible, it was reproduced when being cooled. The nature of this effect was confirmed by its behavior in the two-phase area. The effect temperature went down to 1,275 ± 5 ^{0}C. Constructing the Tamman's triangle demonstrated that the effect area reduced in proportion to the decrease in the Y_2Se_3 phase content.

When the thermal analysis of the Y_2Se_{3-x} composition was carried out, the endothermic effects of melting the eutectic and primary crystals were registered. The total melting enthalpy of the Y_2Se_{3-x} crystals of any type was 70 ± 15 kJ/mol. (169 J/g) (Table 2). This melting heat should be considered approximate, as the sample was in the inhomogeneous phase condition.

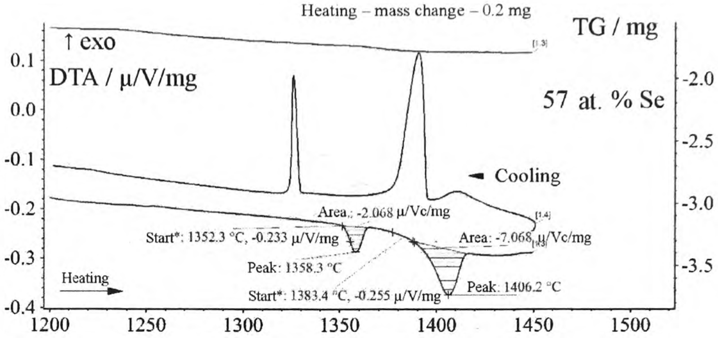
Table 2

Temperatures and enthalpies of phase transitions in the YSe-Y_2Se_3 systems

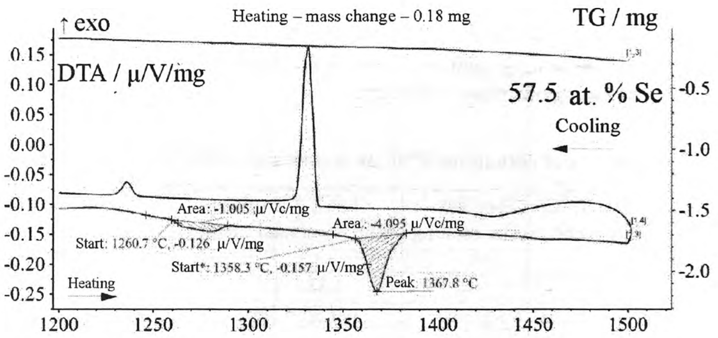
Sample composition, at. % Se	T, ^{0}C; Δ H of the eutectic crystal melting	T, ^{0}C; Δ H of the primary crystal melting	T, ^{0}C; Δ H of the polymorphic transition
57	1,352 ^{0}C; — 21.8 J/g	1,383 ^{0}C; — 75.6 J/g	-
57.5	1,358 ^{0}C; — 43.18 J/g-	-	1,260 ^{0}C; — 1.27 J/g
58	1,353 ^{0}C; — 27.73 J/g-	-	1,270 ^{0}C; — 8.05 J/g
59.7	- 21.34 J/g	1,353 ^{0}C; — 148 J/g	1,305 ^{0}C; — 9.68 J/g

In the STA of the samples with the composition of 57, 58, and 59.7 at. % Se, the heat effects were registered on the liquidus curve (Fig. 1). In the area of the Y_2Se_3 compositions, a eutectic was observed. According to the VPTA and STA data, the liquidus temperatures correlated within the measurement accuracy. The data were approximated by a second-degree polynomial, which met the axis of 60 at. % Se at 1,510 ± 10 ^{0}C. The value is assumed the melting point for the Y_2Se_3 phase. Meeting the eutectic horizontal occurs at 57.5 at. % Se.

According to the VPTA data, the eutectic temperature between the YSe and Y_2Se_3 phases was equal to 1,380 ± 15 ^{0}C; according to the STA data, it is was 1,350 ± 7 ^{0}C. The eutectic composition is was considered equal to 57.5 at. % Se; according to the STA data, the enthalpy of melting is was 43.2 J/g.



a



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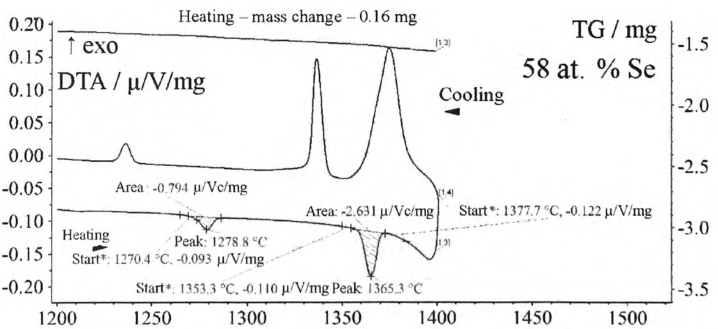

c

Fig. 1 (a,b, c). The heating patterns for the samples of the YSe-Y_2Se_3 system. The *STA 449 F3 Jupiter* appliance. The sample weights are 174 mg (58 atm % Se), 124 mg (57 atm % Se), 141 mg (57.5 atm % Se). The helium medium. The heating mode is 10 K/min.

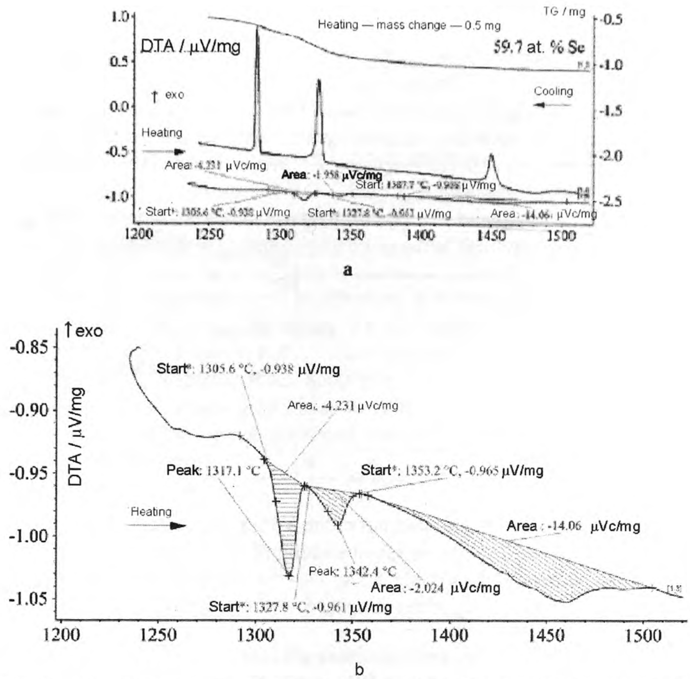

Fig. 2 (a, b). The heating patterns of the samples of 59.7 at. % Se composition, the sample weight is 119 mg

According to the Efimov-Vozdvizhensky's (1), Kordes' (2), and Vasilyev's equations (3), the eutectic position was calculated [10] (Table 3), based on the eutectic melting point of 1,625 K determined by the STA method and the melting points of the system components. According to the VPTA data, the YSe melting point was 2,380 K. The Y_2Se_3 melting point determined by the run of the liquidus curve in the YSe-Y_2Se_3 system diagram was 1,780 K. While the eutectic point was substituted into the empirical formulas, the calculated values of the eutectic composition fell in the interval of the selenium concentrations from 57 to 58 at. %, which correlated with the experimental data.

Table 3

Calculation of the eutectic composition in the YSe-Y_2Se_3 system

The melting point of the components	T_e	The eutectic composition calculated		
		1	2	3
$Y_{0.75}Se$ = 2,380 K Y_2Se_3= 1,780 K	1,625 K	57.9 at. % Se	57.8 at. % Se	58.2 at. % Se

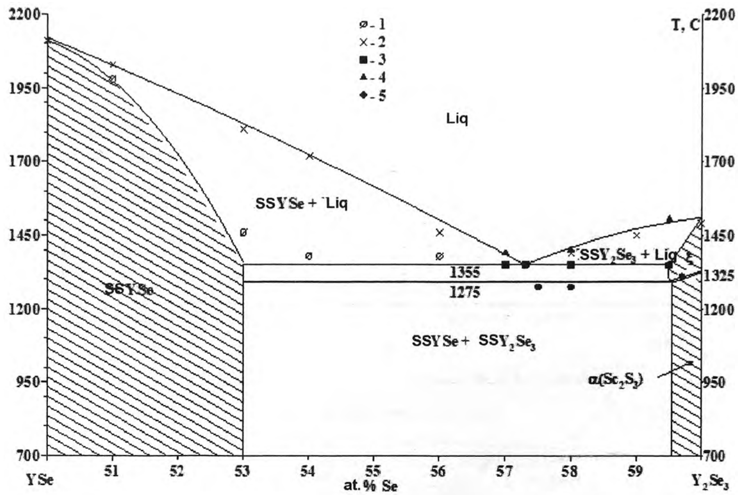

Fig. 3. The phase diagram of the YSe-Y_2Se_3 system.
VPTA: 1 — the incipient melting of the sample;
2 — the complete melting of the sample. STA: 3 — the incipient melting of the sample;
4 — the complete melting of the sample; 5 — the polymorphic transition

Conclusion. The YSe-Y_2Se_3-system phase diagram was of the eutectic type. The eutectic temperature between the phases YSe and Y_2Se_3 was 1,350 ± 5 °C, the eutectic composition was considered equal to 57.5 at. % Se. According to the STA data, the enthalpy of eutectic point was 43.2 ± 5 J/g. While the Y_2Se_{3-x} compound was in a polycrystalline state, the endothermic effect was first recorded at t = 1,325 °C± 5 °C; ΔH = 18 ± 2 kJ/mol (43 J/g), which was supposed to be due to the polymorphic transition into Y_2Se_3. The total enthalpy of melting for the Y_2Se_{3-x} crystals of all types was approximately 70 ± 15 kJ/mol. (169 J/g).

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