ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2025.27/12805

Phase diagram of the system Na_2SO_4 – $In_2(SO_4)_3$. Comparative analysis of Na_2SO_4 – $R_2(SO_4)_3$ systems (R = Al, Ga, Fe, In, Sc, Yb)

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Abstract

Purpose: The phase diagram of the system of sodium sulfate with indium sulfate has been studied for the first time.

Experimental: Thermal and X-ray phase analysis (XRD) techniques, including high-temperature analysis, were used.

Conclusions: In the Na_2SO_4 - $In_2(SO_4)_3$ system determined a several substances. The $NaInSO_4$ compound incongruently melted at 800 °C. The $Na_3In(SO_4)_3$ compound has polymorphic transformations at 210 and 580 °C, and decomposes in the solid state at 680 °C. The compound containing 7±1 mol. % $In_2(SO_4)_3$ (ϕ phase), changing to the solid solution at 540 °C. The eutectic coordinates are 710 °C, 18 mol. % $In_2(SO_4)_3$. The solid solution region based on α-Na_2SO_4 is 11±1 mol. % $In_2(SO_4)_3$. The solid solution melting curves show a maximum at 895 °C and 3 mol. % $In_2(SO_4)_3$. According to XRD data, the $NaInSO_4$ compound crystallizes in the structural type of javapaite - $KFe(SO_4)_2$ (monoclinic space group (*C*2/m) with lattice parameters *a* = 8.024 Å, *b* = 5.069 Å, *c* = 7.211 Å, β = 90.6°), and is isostructural to compounds of similar composition with aluminum, gallium, iron, chromium, vanadium and rhodium sulfates. Low-temperature modification $Na_3In(SO_4)_3$ crystallizes in trigonal space group (*R*-3) with lattice parameters *a* = 13.970 Å, *c* = 8.871 Å), and is isostructurally similar to similar compounds with sulfates of aluminum, gallium, iron (III), vanadium, rhodium, scandium. X-ray diffraction pattern of the mid-temperature modification $Na_3In(SO_4)_3$ is indexed in monoclinic space group (*P*21/c) with lattice parameters *a* = 16.187(4) Å, *b* = 13.584(3) Å, *c* = 9.639(2) Å, β = 91.6°. The X-ray diagram of the ϕ phase is indexed in monoclinic space group (*P*21/c) with lattice parameters *a* = 7.836 Å, *b* = 14.845 Å, *c* = 4.57 Å, β = 91.14°.

Keywords: Sodium sulfate, Indium sulfate, Aluminum sulfate, Gallium sulfate, Iron sulfate, Scandium sulfate, Ytterbium sulfate, Phase diagrams, Solid solutions, Isomorphism

For citation: Proydakova V. Yu., Voronov V. V., Kuznetsov S. V., Nekrylov I. N., Zavrazhnov A. Yu., Fedorov P. P. Phase diagram of the Na_2SO_4 – $In_2(SO_4)_3$ system. Comparative analysis of the Na_2SO_4 – $R_2(SO_4)_3$ (R = Al, Ga, Fe, In, Sc, Yb). *Condensed Matter and Interphases*. 2025;27(2): 267–277. https://doi.org/10.17308/kcmf.2025.27/12805

Для цитирования: Пройдакова В. Ю., Воронов В. В., Кузнецов С. В., Некрылов И. Н., Завражнов А. Ю., Федоров П. П. Фазовая диаграмма системы Na_2SO_4 – $In_2(SO_4)_3$. Сравнительный анализ систем Na_2SO_4 – $R_2(SO_4)_3$ (R = Al, Ga, Fe, In, Sc, Yb). *Конденсированные среды и межфазные границы*. 2025;27(2): 267–277. https://doi.org/10.17308/kcmf.2025.27/12805

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1. Introduction

An urgent task of chemical materials science is the development of materials with high ionic conductivity that could serve as a substitute for scarce lithium in electrochemical energy sources [1–3]. Sodium ionic conductors, including solid solutions based on high-temperature modification of sodium sulfate, are promising [4–6]. In sulfates, an original mechanism of ionic conductivity enhancement due to rotational dynamics of sulfate ions is realized [7–8].

The investigated phase diagrams of systems with the participation of sodium sulfate indicate the formation of heterovalent solid solutions with the introduction of two-, three- and four-valent cations into the Na_2SO_4 lattice, with the formation of cation vacancies that facilitate ionic transport [6, 9-15].

The phase diagrams based on sodium sulfate with sulfates of a number of trivalent metals, namely aluminum [11], iron [12], neodymium, terbium and ytterbium [13], and bismuth [16], have been previously investigated. Preliminary results of our study of the phase diagram of Na_2SO_4 – $Ga_2(SO_4)_3$ are published in [15]. In all systems, except Na_2SO_4 – $Bi_2(SO_4)_3$, the formation of solid solutions based on high-temperature modification of sodium sulfate was revealed.

The phase diagram of the Na_2SO_4 – $In_2(SO_4)_3$ system has not been studied previously. There is a report on the existence of the compound $Na_3In(SO_4)_3$ [17]. The aim of this work is to study phase equilibria in the system of indium sulfate with sodium sulfate Na_2SO_4 – $In_2(SO_4)_3$ and to carry out a comparative analysis of phase formation in systems of sodium sulfate with trivalent metal sulfates.

Indium sulfate is characterized by polymorphism [18]. The high-temperature modification $In_2(SO_4)_3$ crystallizes in trigonal space group (R-3) while the low-temperature monoclinic has another space group $P2_1/n$.

2. Experimental methodology

Na_2SO_4 with grade "chemical purity" was calcined at 180 °C for four hours to remove crystallization water and placed in the desiccator.

Indium sulfate from LANHIT (purity 99.9 % by metal impurities) was used in this work. In addition, indium (III) sulfate was synthesized from indium bromide by heating with sulfuric acid dehydrated with thionyl chloride (the water in the sulfuric acid was bound to volatile SO_2 and HCl, which left the liquid phase):

$$2InBr_3 + 3H_2SO_4 = In_2(SO_4)_3 + 6HBr\uparrow\ (\sim 95\ \%) \quad (1)$$

$$2InBr_3 + 6H_2SO_4 = \\ = In_2(SO_4)_3 + 3Br_2\uparrow + 3SO_2\uparrow + 6H_2O\uparrow\ (\sim 5\ \%) \quad (2)$$

In turn, indium bromide was obtained by direct interaction of metallic indium and dehydrated bromine under heating.

To prepare samples with indium (III) sulfate content of 25 mol. % (compound of $Na_3In(SO_4)_3$), sodium pyrosulfate was mixed with indium oxide in stoichiometric ratios according to Eq.3:

$$3Na_2S_2O_7 + In_2O_3 \rightarrow 2Na_3In(SO_4)_3 \quad (3)$$

In turn, sodium pyrosulfate was prepared by heating sodium hydrosulfate to 250 °C (4 h):

$$2NaHSO_4 \rightarrow Na_2S_2O_7 + H_2O\uparrow, \quad (4)$$

and indium oxide was synthesized by decomposition of indium nitrate at 250 °C:

$$4In(NO_3)_3 \rightarrow 2In_2O_3 + 12NO_2\uparrow + 3O_2\uparrow \quad (5)$$

Indium (III) nitrate was prepared by dissolving indium metal (In-00) in excess concentrated nitric acid.

Solid-phase synthesis was carried out at 500 °C by sintering of sodium and indium sulfate mixtures in a porcelain mortar. In addition, compositions with low indium sulfate content (< 25 mol. %) was obtained by adding additional amounts of sodium sulfate to the reaction product (3).

Parallel studies have yielded converging results. Indium sulfate preparations are hygroscopic.

Gallium sulfate was obtained by the method described in [19]. In addition, samples in the Na_2SO_4 – $Ga_2(SO_4)_3$ and Na_2SO_4 – $Al_2(SO_4)_3$ systems were synthesized via ammonium alum, which was precipitated from concentrated sulfate solutions by adding stoichiometric amounts of ammonium sulfate. The thoroughly ground mixtures with sodium sulfate were calcined at 450 °C for 5 h.

Scandium sulfate was obtained from the oxide by interaction with concentrated sulfuric acid at 80 °C.

Thermal analysis (DTA + DTG) was carried out on a Q-1500 D derivatograph. A platinum-rhodium thermocouple, open platinum crucibles were used. Heating and cooling rates in air were 10 deg/min. The weight of the suspensions was 350-400 mg.

In addition, a second DTA technique was used. Samples weighing about 1 g were sealed in Stepanov vessels, which had small holes in the upper part to bleed excess pressure into the atmosphere. Thermographic studies were performed in heating mode at a rate of 4K/min.

Decoding of thermograms was carried out according to the method [20, 21]. The temperatures of noninvariant transformations were fixed by the onset of effects on the heating curves. Liquidus temperatures were recorded from the onset of effects on the cooling curves, as well as from maxima on the heating curves when an appropriate instrumental correction was introduced (about 10°C). Recording of thermograms was stopped when a noticeable mass loss (due to sulfate decomposition and SO_2 release) was observed.

X-ray phase analysis (XRD) was performed on a Bruker D8 Discover A25 diffractometer, Da Vinci Design, CuKα emission. X-ray diagrams were processed with EVA program version 2.1. Calculation of lattice parameters were carried out using the TOPAS version 4.2 program. The high-temperature XRD was performed using the HTK 1200N high-temperature chamber manufactured by Anton Paar. The samples were held at each temperature for about 20 min before recording XRD.

3. Results and discussion

The melting and polymorphic transition temperatures of sodium sulfate are 887 and 240 °C according to our data. Sulfates of trivalent elements decompose by reactions when heated:

$$R_2(SO_4)_3 = R_2O_3 + 3SO_2 + 1.5O_2 \qquad (6),$$

that imposes significant limitations on the study of phase equilibria with their participation. In derivatography mode (heating at a rate of 10 deg/min) decomposition of $Ga_2(SO_4)_3$ starts at 680 °C [19].

3.1. Na_2SO_4 -$In_2(SO_4)_3$ system

In this system (Fig. 1) are formed compounds $NaInSO_4$ which melts incongruently at 800 °C, $Na_3In(SO_4)_3$, which has polymorphic transformations at 210 and 580 °C and decomposes in the solid state at 680 °C, and a compound containing 7±1 mol. % $In_2(SO_4)_3$ (ϕ-phase), transforming on heating into solid solution based on α-Na_2SO_4 (α-phase). The eutectic coordinates are 710 °C, 18 mol. % $In_2(SO_4)_3$. The solid solution region based on α-Na_2SO_4 is up to 11±1 mol. % $In_2(SO_4)_3$. The

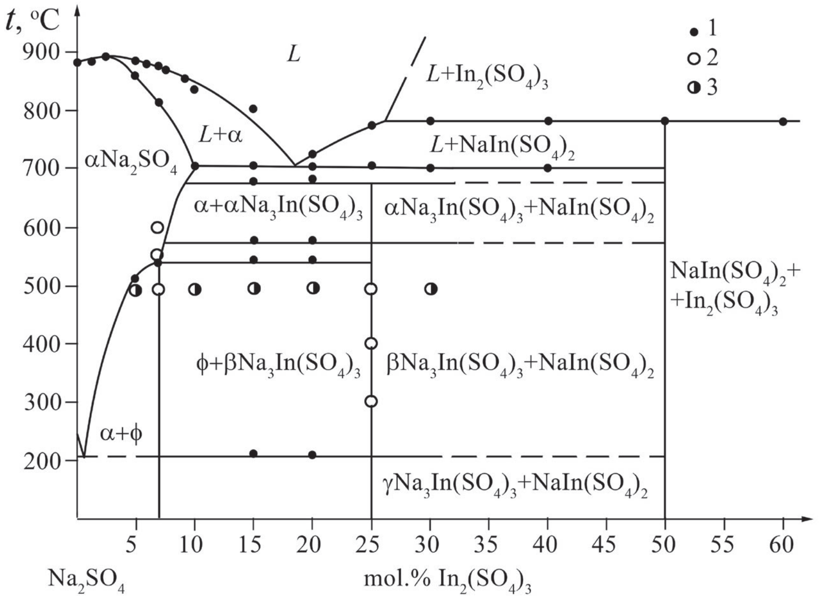

Fig. 1. Phase diagram of the system Na_2SO_4 - $In_2(SO_4)_3$. *1* – DTA data; *2* – single-phase samples; *3* – two-phase samples according to XRD data

solid solution melting curves show a maximum at 895 °C and 3 mol. % $In_2(SO_4)_3$.

The $Na_3In(SO_4)_3$ compound was known [17], while the $NaInSO_4$ compound and the ϕ-phase seem to be described for the first time. X-ray diffraction patterns of the compounds and high-temperature XRD data are presented in Fig. 2, 3 and in the Tables S1-S3 of the electronic application.

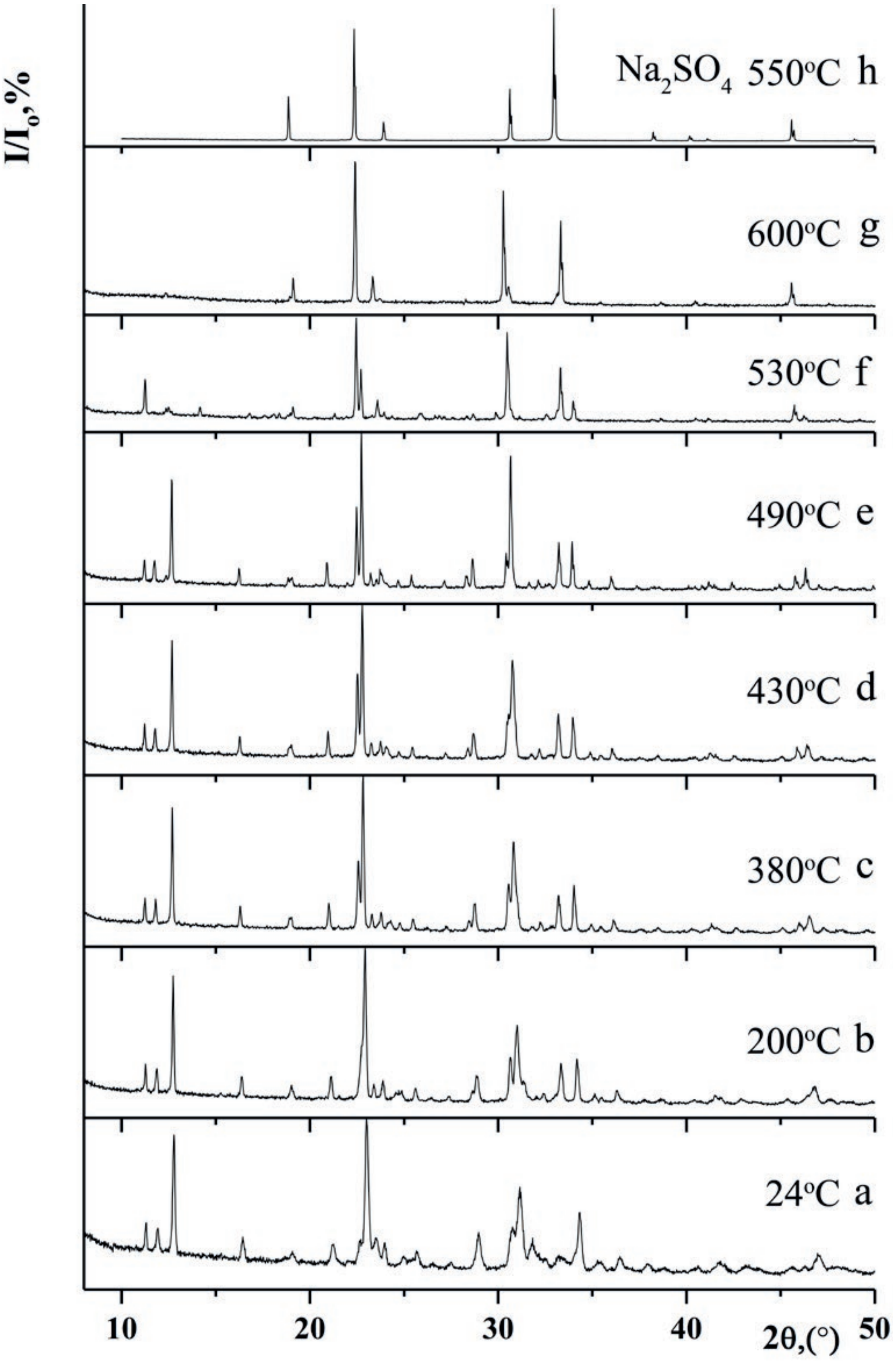

Fig. 2. High-temperature X-ray phase analysis of the sample 93 % Na_2SO_4 - 7 % $In_2(SO_4)_3$: a – 24 °C; b – 200 °C; c – 380 °C; d – 430 °C; e – 490 °C; f – 530 °C; g – 600 °C; h – 550 °C high-temperature modification of Na_2SO_4

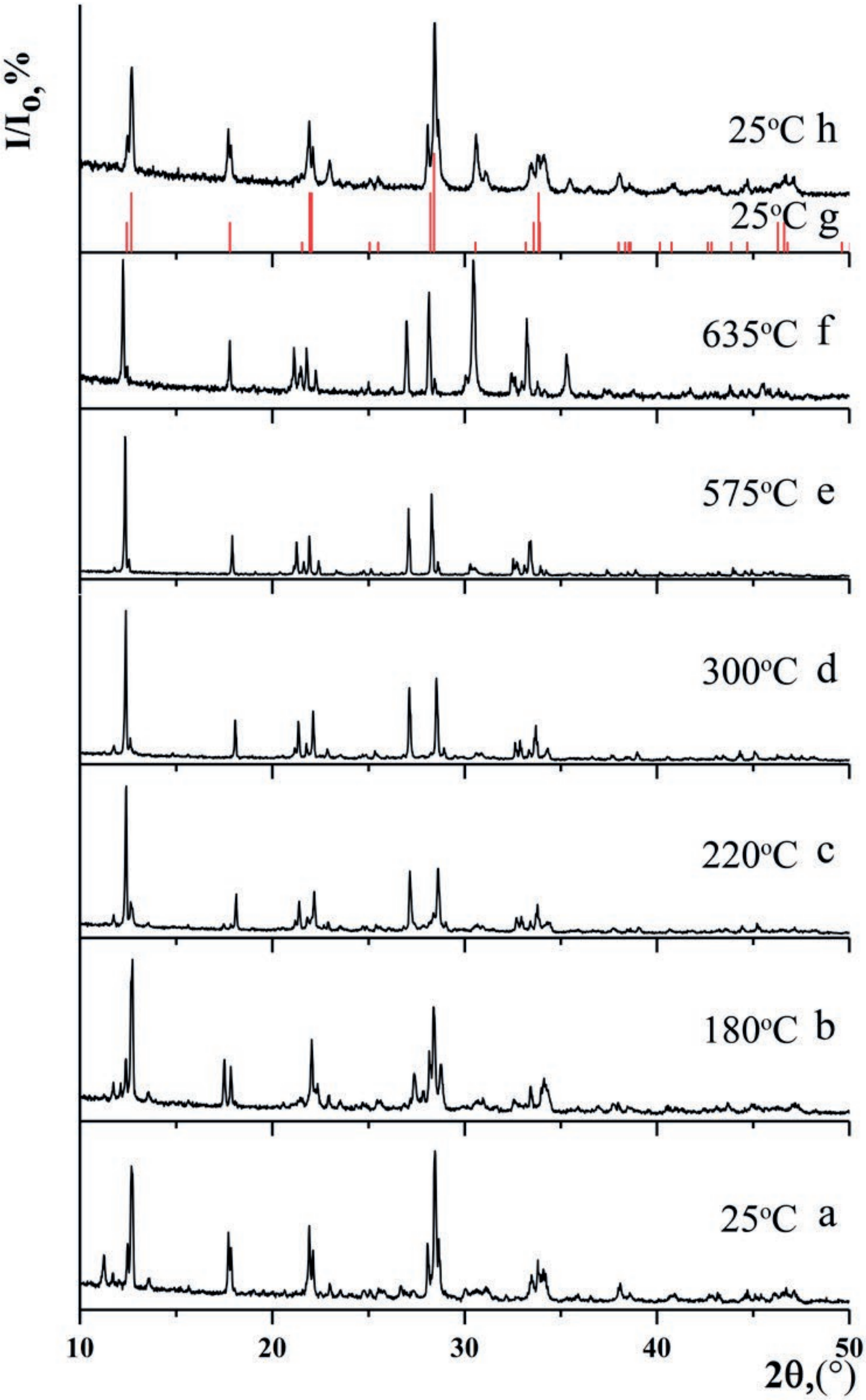

Fig. 3. High-temperature X-ray phase analysis of a sample of 75 % Na_2SO_4 - 25 % $In_2(SO_4)_3$: a – 25 °C; b – 180 °C; c – 220 °C; d – 300 °C; e – 575 °C; f – 635 °C; g – JCPDS 00-027-1414 ($Na_3In(SO_4)_3$) 25 °C; h – 25 °C

According to XRD data $NaInSO_4$ is isostructural to compounds $NaRSO_4$ (R = Al, Ga, V, Fe, Rh, Cr), the so-called “anhydrous alum” [22-24] (structural type of javapaite – $KFe(SO_4)_2$ [25]), see Table 1. According to high-temperature XRD, no polymorphic transitions of $NaInSO_4$ were recorded up to 300 °C. When heated in air it decomposes starting from 600 °C with SO_2 emission.

Table 1. Lattice parameters of $NaR(SO_4)_2$ compounds, monoclinic space group (*C*2/*m*), Z = 2 ("anhydrous alum")

R	*a*, Å	*b*, Å	*c*, Å	β	Ref.
Al	7.9007	5.003	7.1202	92.87	Our data
Al	7.89	5.10	7.10	92.15	[22]
Ga	7.912	5.095	7.143	92.70	Our data
Ga	7.92	5.10	7.13	92.53	[22]
In	8.024	5.069	7.211	90.60	Our data
Fe	8.02	5.14	7.18	92.20	[22]
Cr	7.956	5.112	7.109	92.20	[22]
V	8.020	5.160	7.135	91.870	[24]
V	8.01	5.16	7.14	91.88	[22]
Rh	7.921	5.127	7.134	92.83	[23]

The low-temperature γ-modification $Na_3In(SO_4)_3$ is isostructural to the compounds $Na_3R(SO_4)_3$ (R = Al, Ga, V, Fe, Rh), see Table 2. High-temperature XRD confirmed the polymorphism of $Na_3In(SO_4)_3$ (Fig. 3). X-ray powder diffraction of the mid-temperature β-modification of $Na_3In(SO_4)_3$ is indexed in monoclinic space group (*P*21/*c*) with lattice parameters *a* = 16.187(4) Å, *b* = 13.584(3) Å, *c* = 9.639(2) Å, β = 91.6° (Tab. S2). No analogs were found.

X-ray powder diffraction of the ϕ-phase is indexed in monoclinic space group (*P*21/*c*) with lattice parameters *a* = 7.836 Å, *b* = 14.845 Å, *c* = 4.57 Å, β = 91.14° (Tab. S3). No analogs were also found. The ϕ-phase on heating changes to a solid solution based on high-temperature modification of sodium sulfate at 540 °C. The transition is captured by both thermography and high-temperature XRD data (Fig. 2).

3.1. Na_2SO_4 - $R_2(SO_4)_3$ systems: a comparative analysis

The compounds $Na_3R(SO_4)_3$ and $NaRSO_4$ form extended isomorphic series. We synthesized similar compounds with scandium. Crystallographic data are summarized in Tables 1 and 2. Note that the structural types are preserved despite the change of ionic radii of trivalent cations in wide range. The X-ray diffraction patterns of our synthesized compounds in the systems Na_2SO_4 - $R_2(SO_4)_3$ (R = Al, Ga) are presented in Fig. 5–7 and in the Tables S4-S7. Previous indexing of X-ray radiographs of $Na_3R(SO_4)_3$ (R = Al, Ga) in the tetragonal space group was erroneous [15].

There is a great similarity of phase diagrams of Na_2SO_4 - $R_2(SO_4)_3$ (R = Al, Ga, Fe) and apparently for systems with vanadium, chromium and rhodium. The phase diagrams of systems with rare-earth element (REE) sulfates look different. Compound with cation ratio 3:1 do not exist, while compound with cation ratio 1:1 have different structure. Indium and apparently scandium are intermediate cases.

Solid solutions based on the high-temperature α-modification of sodium sulfate revealed in this work are a typical example of heterovalent isomorphism with a variable number of atoms

Table 2. Lattice parameters of compounds $Na_3R(SO_4)_3$, trigonal space group (*R*-3), Z = 6, and ionic radii of R^{3+} cations according to Shannon [27], coordination number 6

R	*a*, Å	*c*, Å	*r*, Å	Ref.
Al	13.3516	8.9080	0.535	Our data
Ga	13.413	8.980	0.620	Our data
In (γ)	13.970	8.771	0.800	[17]
In (γ)	13.970	8.871	0.800	Our data
Sc	13.881	8.975	0.870	Our data
Fe	13.415	9.0250	0.69-0.785	JCPDS 39-0243
V	13.43	9.091	0.640	[26]
Rh	13.306	8.604	0.665	[23]

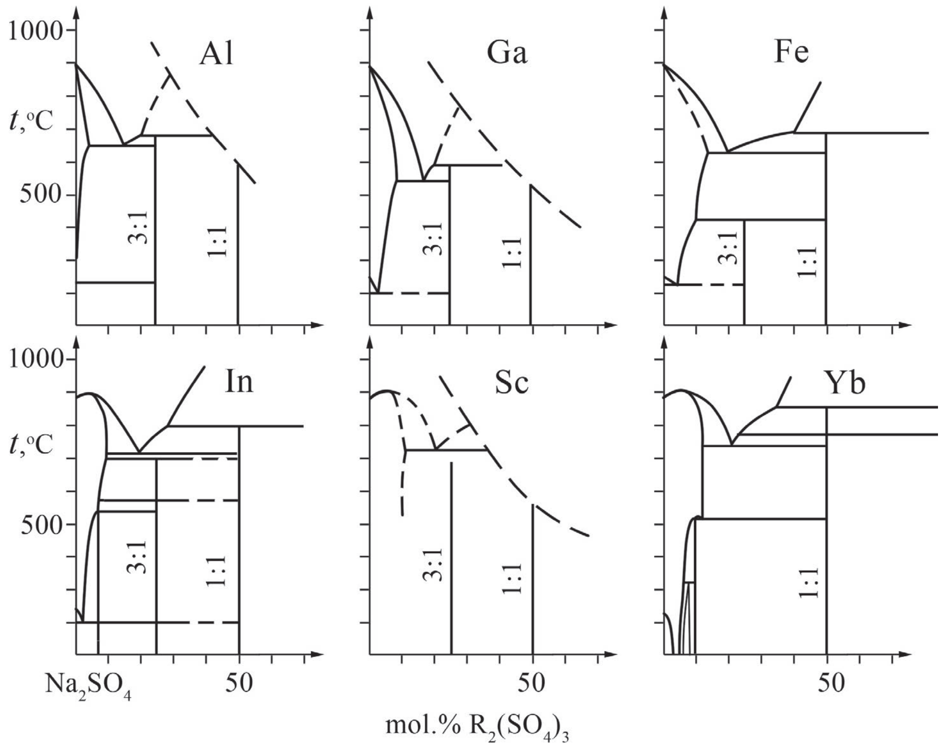

Fig. 4. Scheme of phase equilibria in systems Na_2SO_4 - $R_2(SO_4)_3$

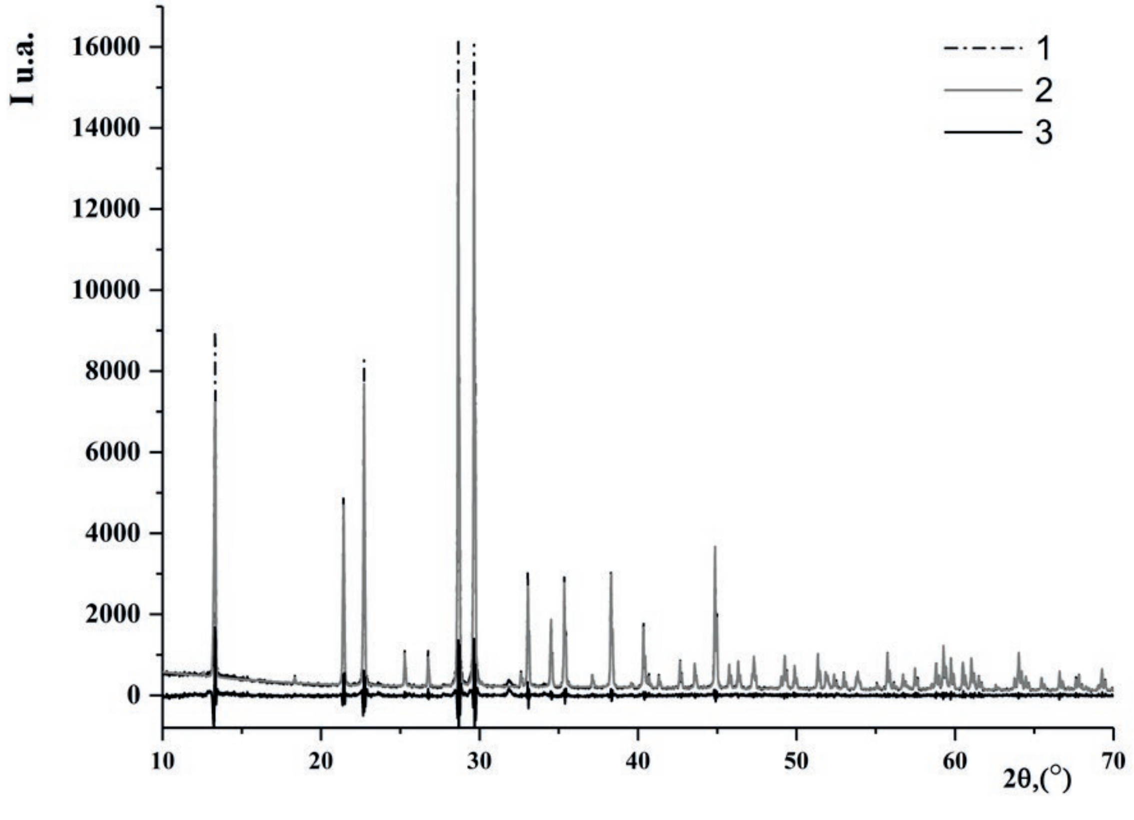

Fig. 5. X-ray diagram of $Na_3Al(SO_4)_3$. *1* – experimental X-ray diagram; *2* – calculated X-ray diagram; *3* – difference curve

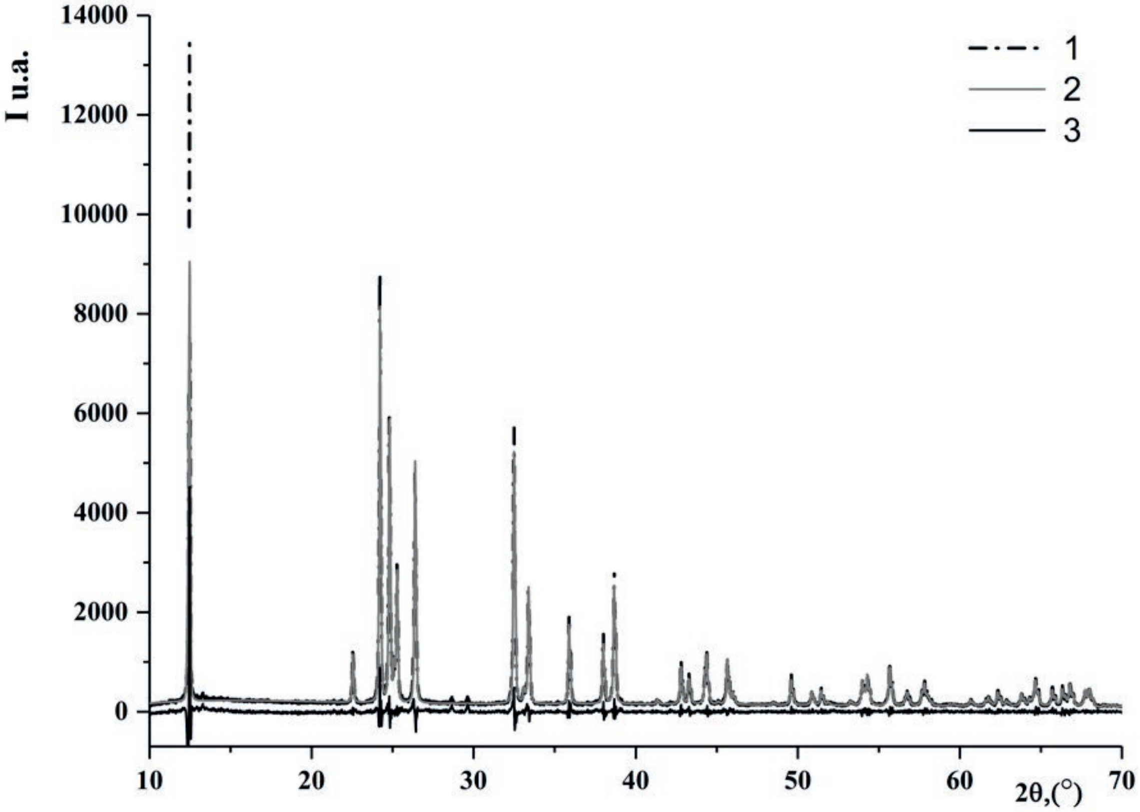

Fig. 6. X-ray diagram of $NaAl(SO_4)_2$. *1* – experimental X-ray diagram; *2* – calculated X-ray diagram; *3* – difference curve

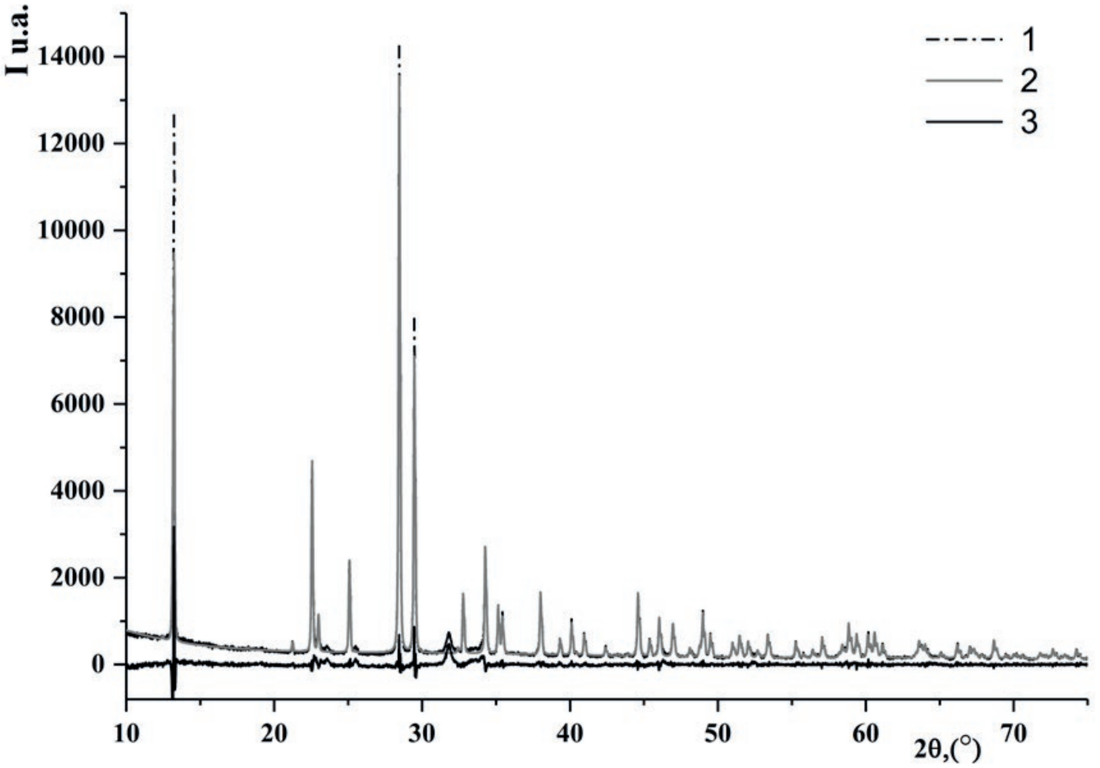

Fig. 7. X-ray diagram $Na_3Ga(SO_4)_3$. *1* – experimental X-ray diagram; *2* – calculated X-ray diagram; *3* – difference curve

in the unit cell [10, 28]. The formation of such solid solutions involves heterovalent cationic substitutions with the formation of vacancies in the cationic sublattice [6]. The formation of solid solutions of this type correlates with maxima on melting curves [29] and high ionic conductivity of the corresponding materials [10]. In Na_2SO_4 - $R_2(SO_4)_3$ systems, in addition to the system with indium sulfate studied in this work, maxima on the melting curves of solid solutions based on Na_2SO_4 with $R_2(SO_4)_3$ are formed in systems with R = Nd, Tb, Yb [13] and are predicted in the system with scandium sulfate, as well as over the entire lanthanide series.

Fig. 8 shows the dependence of the limiting concentration of solid solutions based on Na_2SO_4 with $R_2(SO_4)_3$ on the ionic radius of the trivalent ion for coordination number 6 [27]. For these systems, the coincidence of ionic radii of sodium and isomorphic cations is not an optimal condition for the formation of solid solutions. This is typical for heterovalent solid solutions with a variable number of particles in the unit cell [10]. In the system with bismuth sulfate, where the ionic radii of Na^+ and Bi^{3+} practically coincide, the formation of the corresponding solid solution was not observed at all (the first investigated point corresponds to the content of 5 mol. % $Bi_2(SO_4)_3$ [16]). It is obvious for Na_2SO_4 - $R_2(SO_4)_3$ systems the presence of a two-hump dependence similar to that for solid solutions of divalent metal sulfates in lithium sulfate [30]. Apparently, this character of solubility is associated with the presence of two crystallographic positions in the structure of the high-temperature modification of Na_2SO_4-I [31].

Solid solutions based on high-temperature modification of sodium sulfate are formed in all systems of this group. The thermal effect of the polymorphic transition of sodium sulfate disappears upon addition of gallium sulfate, i.e. stabilization of the structure of hexagonal high-temperature modification of sodium sulfate up to room temperature is observed, which is confirmed by XRD data. The phase diagram of the Na_2SO_4 - $Al_2(SO_4)_3$ system [13] is similar to the Na_2SO_4 - $Ga_2(SO_4)_3$ system, but the Na_2SO_4-based solid solution region is much smaller (~ 2 mol. % at the eutectic temperature), and the introduction of $Al_2(SO_4)_3$ does not lead to stabilization of the α-Na_2SO_4 structure up to room temperature. In the case of indium, the corresponding solid solution is wedged out due to the formation of the ϕ-phase.

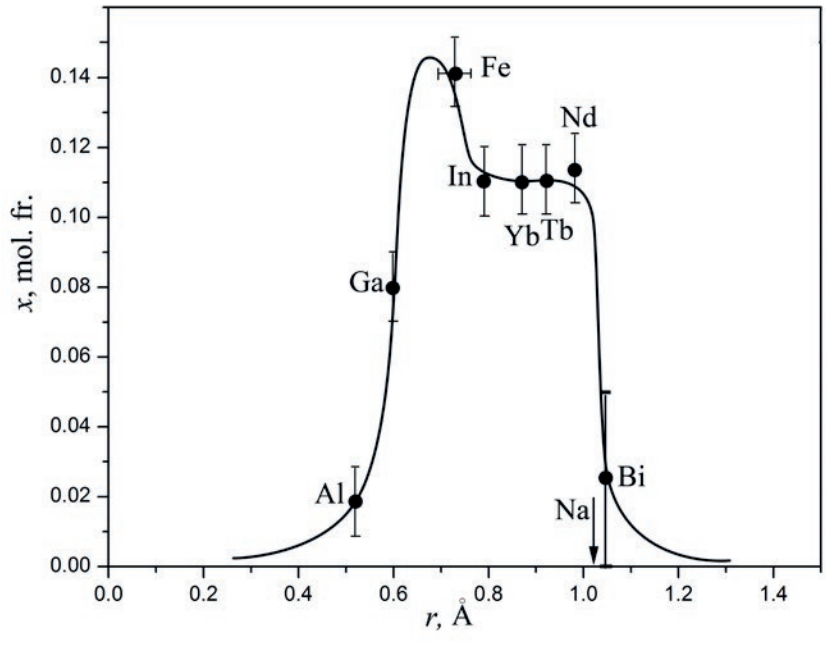

Fig. 8. Dependence of the limiting concentration of solid solutions based on Na_2SO_4 with $R_2(SO_4)_3$ on the ionic radius of the trivalent ion. Data for Al by [11], Ga by [15], Fe by [12], In by this study, Yb, Tb, Nd by [13], Bi by [16]. Ion radii according to [27] for coordination number 6

4. Conclusion

Stabilization to room temperature in the case of REE allowed growing single crystals of stabilized solid solutions doped with neodymium [7] and ytterbium [32]. Solid solution with gallium is the next step.

Indium compounds can be considered as model compounds of corresponding compounds of elements with variable valence (chromium, iron, vanadium) in oxidation degree +3, which can be used as cathode materials in electrochemical devices.

The online version contains supplementary material

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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** Translated by author of the article*

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Received 18.03.2025; approved after reviewing 25.03.2025; accepted for publication 15.04.2025; published online 25.06.2025.