The isothermal section of the Er–Zn–In system was constructed based on X-ray powder data and EDX-analyses at 870 K in the region up to 33.3 at. % Er. Three solid solutions: ErZn1.7In0.30 (CeCu2-type; space group Imma; a = 4.448–4.594(3), b = 6.984–7.176(5), c = 7.610–7.463(5) Å); ErZn17.165In0.046 (ThZn17-type; space group R-3m; a = 8.9465–8.9704(3), c = 13.1199–13.1320(6) Å); ErZn0.68In3.12 (AuCu3-type; space group Pm-3m; a = 4.563–4.504(1) Å) and one ternary compound with homogeneity region ErZn1.36In0.64 (CaIn2-type; space group P63/mmc; a = 6.984(2)–4.662(1), c = 7.023(3)–7.226(2) Å) are formed in the investigated part of this system. The crystal structure of the ErZn0.69In3.28 solid solution was also determined using X-ray single crystal diffraction data on the sample with composition ErZn0.87In2.13.

Keywords: indium, zinc, crystal structure, homogeneity region, phase equilibrium.

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1. Introduction

The interaction of indium with rare earths and 3d-metals has complex character due to different electron structure of interacting components. Much information is available on the crystal structure and the physical properties of ternary compounds in the R–T–In (R = Rare Earth metals, T = Ni, Co or Cu) [1]. Recently, some ternary systems R–Mn–In (R = Gd, Dy) and R–Fe–In (R = Gd, Tb, Dy) [2–5] have been investigated as well. Meanwhile, the research on the ternary systems R–Zn–In is still missing. Only one partial section at 670 K of the phase diagram has been studied for Yb–Zn–In system [6]. This system is characterized by the presence of three extended homogeneity ranges, indium solubility in Yb1.7Zn58 and YbZn2, and of zinc solubility in YbIn2, and the existence of one ternary intermetallic compound, YbZn0.8In1.1 (UHg2 structure type, space group P6/mmm). The few ternary compounds with equiatomic composition with Caln2– (R = La–Gd, Dy–Er, Yb) or KHg2– (R = Eu) types have been found in the systems with zinc [7–9].

Therefore, in the present paper we describe the results of the investigations of the Er–Zn–In ternary system. The isothermal section in the region up to 33.3 at. % of Er at T = 870 K has been constructed, with the focus on the concentration range of phases existence.

2. Experimental

Starting materials for the preparation of the alloys were ingots of the rare earth metals, zinc, and indium, all with nominal purities better than 99.9 %. The 20 samples were synthesized by direct melting inside quartz ampoules under vacuum. The specimens were heated in a box furnace up to 1070 K for 5 hours and annealed at this temperature during 1 hour.

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Then they were cooled to 870 K (at a rate of 20 K/hr) and annealed at this temperature during 168 hours. After that, the cooled ampoules were broken, the alloys were grinded with mortar and pestle and pressed into pellets. The pellets were sealed in evacuated silica tubes and annealed at this temperature during 168 hours. After that, the cooled ampoules were broken, the alloys were grinded with mortar and pestle and pressed into pellets. The pellets were sealed in evacuated silica tubes and annealed for a month at a temperature of 870 K. After annealing no reaction with silica was observed. The X-ray diffraction data for structure refinement were collected on diffractometers Bruker D8, STOE STADI P and Huber Imaging-Plate Guinier camera. The crystal structure refinements were carried out using the Fullprof software [10]. Single crystal X-ray diffraction was performed at room temperature on the Bruker SMART APEX CCD diffractometer with MoKα radiation. The structure was solved by direct methods, and refined by using the SHELXS97 program package [11]. The compositions of some samples were additionally studied by energy dispersive analyses of X-rays (EDX) using a PEMMA-102-02 scanning electron microscope.

3. Result and discussion

The isothermal section of the Er–Zn–In ternary system was built at $T = 870$ K in the region 0–33.3 at. % Er (Fig. 1, Table 1) by means of X-ray powder diffraction data. It was confirmed that at 870 K the following binary compounds exist: ErZn$_2$ (CeCu$_2$-type), ErZn$_3$ (YZn$_3$-type), Er$_2$Zn$_{58}$ (Gd$_2$Zn$_{58}$-type), ErZn$_5$ (ErZn$_5$-type), Er$_{13}$Zn$_58$ (Gd$_{13}$Zn$_{58}$-type), Er$_2$Zn$_{17}$ (Th$_2$Zn$_{17}$-type), ErZn$_{12}$ (ThMn$_{12}$-type), Er$_3$In$_5$ (Pu$_3$Pd$_5$-type), and ErIn$_3$ (AuCu$_3$-type). The binary compounds ErZn$_2$, Er$_2$Zn$_{17}$ and ErIn$_3$ form the substitution type solid solutions across the sections of erbium. The rest binary compounds do not dissolve the third component. According to changes in the lattice parameters and cell volume the homogeneity regions of solid solutions based on ErZn$_2$ and ErIn$_3$ extend to 10.5 at. % In and 22 at. % Zn respectively (Fig. 2) and the composition of solid solutions can be described as ErZn$_{2.17}$In$_{0.30}$ and ErZn$_{1.16}$In$_{0.46}$ respectively.

![Fig. 1. The isothermal section of the Er–Zn–In system at $T = 870$ K](image)

| Phase                  | Structure type | Space group | Lattice parameters, Å | a        | b        | c        |
|-----------------------|----------------|-------------|-----------------------|----------|----------|----------|
| ErZn$_{2.17}$In$_{0.46}$ | CeCu$_2$       | Imma        | 4.448*–4.594(3)       | 6.984*–7.176(5) | 7.610*–7.463(5) |
| ErZn$_{17.16}$In$_{0.46}$ | Th$_2$Zn$_{17}$ | R-3m       | 8.9465*–8.9704(3)     | –        | 13.1199*–13.1320(6) |
| ErZn$_{5.00}$In$_{0.46}$ | AuCu$_3$      | Pm-3m       | 5.463*–5.4904(1)      | –        | –        | –        |
| ErZn$_{2.17}$In$_{0.46}$ | CaIn$_2$      | P6$_3$nmc   | 4.513(2)–4.662(1)     | –        | 7.023(3)–7.226(2) |

* Literature data.
The crystal structure of ErZn$_{0.87}$In$_{2.13}$ solid solution has been investigated by X-ray single crystal method. The single crystal suitable for intensity data collection was selected by mechanical fragmentation from the sample Er$_{0.25}$Zn$_{0.20}$In$_{0.55}$. Single crystal X-ray diffraction was performed on the Bruker diffractometer with MoKα radiation ($\lambda = 0.71073$ Å) in the whole reciprocal sphere at room temperature. All crystallographic data and details of the data collection are listed in the Table 2 and parameters of atoms are shown in Table 3. On the basis of the obtained data, it can be assumed that composition of single crystal is the limited composition of this solid solution.

Table 2

| Experimental details and crystallographic data for ErZn$_{0.87}$In$_{2.13}$ phase |
|---------------------------------|-----------------|
| Molar mass, g/mole                  | 468.7           |
| Structure type                    | AuCu$_3$        |
| Space group, $Z$                  | Pm-3n, 1        |
| Lattice parameters, $a$, Å        | 4.474(4)        |
| $V$, Å$^3$                        | 89.5(3)         |
| Calculated density(g/cm$^3$)      | 8.57            |
| Radiation, wavelength Å           | MoKα $\lambda=0.71073$ |
| Absorption coefficient (mm$^{-1}$)| 30.937          |
| $F(000)$                          | 196             |
| Range $\theta$                   | 4.56–37.60      |
| Temperature (T, K)                | 296(2)          |
| Range hkl                         | $-6 \leq h \leq 6; -7 \leq k \leq 7; -7 \leq l \leq 7$ |
| Total no. of reflections          | 930             |
| Independent reflections           | 73              |
| $R_{ref}$                         | 0.0297          |
| Reflections with $I>2\sigma(I)$  | 73              |
| Refinement method                 | Full-matrix least-squares on $F^2$ |
| Goodness-of-fit on $F^2$          | 1.315           |
| Extinction coefficient            | 0.027(4)        |
| $R$[$I>2\sigma(I)$] ($R_1=\ldots$) | 0.0159; 0.0364  |
| $R$[all] ($R_1=\ldots$)           | 0.0159          |
| Largest diff. peak/hole, e/Å$^3$  | 1.768/-1.817   |
Table 3
Atomic coordinates and thermal displacement parameters (Å²) for ErZn0.87In0.13 phase

| Atom | Wyckoff site | Occupation | x   | y   | z   | $U_{eq}$ | $U_{11}$ | $U_{22}$ | $U_{33}$ |
|------|--------------|------------|-----|-----|-----|---------|---------|---------|---------|
| Er   | 1a           | 1          | 0   | 0   | 0.0661(2) 0.0661(2) 0.0661(2) 0.0061(2) 0.0661(2) 0.0061(2) | 0.0061(2) | 0.0061(2) | 0.0061(2) |
| X    | 3c           | 0.71(2)In+0.29Zn 1/2 1/2 0.0123(4) 0.0090(4) 0.0190(5) 0.0090(4) | 0.0123(4) | 0.0090(4) | 0.0190(5) | 0.0090(4) |

* $U_{eq}$ is defined as one third of the trace of orthogonalized $U_{ij}$ tensor; $U_{12}=U_{13}=U_{23}=0$ Å²

The crystal structure of ErZn$_{2.17}$In$_{0.30}$ solid solutions has been investigated by X-ray powder diffraction on the Er$_{0.33}$Zn$_{0.67}$In$_{0.00}$ sample. Fig. 3, a shows the X-ray diffraction patterns of the respective sample. The results of the crystal structure investigation (Table 4, 5) revealed the occupancies of the smaller atomic positions by statistic mixtures (Zn/In).

The phase and EDX analyses of a sample (Fig. 4, b) in the region near the Er$_2$Zn$_{17}$ binary compound established the formation of the Er$_2$Zn$_{17.16}$In$_{0.46}$ solid solution up to ~3 at. % In. The crystal structures of this solid solutions was investigated by X-ray powder diffraction on the Er$_2$Zn$_{17.16}$In$_{0.46}$ sample (Fig. 4, a), which contained an additional In phase (weight fractions of phases = 5 %). The crystal structure data and details of structure refinements are given in Table 4 and 5. The one crystallographic position (6c) in the structure of this phase is occupied of by the mixtures of Zn and In atoms.

Fig. 3. Observed, calculated and difference X-ray diffraction patterns of the ErZn$_{1.18}$In$_{0.13}$ (a) and ErZn$_{1.08}$In$_{0.92}$ (b) phases

Fig. 4. Observed, calculated and difference X-ray diffraction patterns of the Er$_2$Zn$_{17.16}$In$_{0.46}$ sample (1 – phase Er$_2$Zn$_{16.54}$In$_{0.46}$; 2 – In) (a) and EDX microphotographs of this sample (b) (1 – phase Er$_2$Zn$_{16.54}$In$_{0.46}$; 2 – Er; 3 – In)
The existence of earlier known ternary compound with CaIn$_2$-type was confirmed. The homogeneity region was determined for this compound across the section 33.3 at. % Er (Fig. 5), and the composition of compound can be described by formula ErZn$_{1.28}$-$0.80$In$_{0.72}$-$1.20$.

Additionally, the investigation of crystal structure of this compound was performed by X-ray powder diffraction on the Er$_{0.333}$Zn$_{0.367}$In$_{0.30}$ sample. Fig. 3b shows the X-ray diffraction patterns. According to the results of the crystal structure investigation (Table 4, 5) the crystallographic position (4f) is occupied by mixtures (Zn/In).

![Graph showing the dependence of lattice parameters and the unit cell volume of ErZn$_{1.28}$-$0.80$In$_{0.72}$-$1.20$ vs. the concentration of In](image)

**Table 4** Experimental details and crystallographic data for ErZn$_{1.13}$In$_{0.13}$, ErZn$_{1.54}$In$_{0.46}$, ErZn$_{1.68}$In$_{0.32}$ phases

| Refined composition | ErZn$_{1.13}$In$_{0.13}$ | ErZn$_{1.54}$In$_{0.46}$ | ErZn$_{1.68}$In$_{0.32}$ |
|---------------------|-------------------------|--------------------------|-------------------------|
| $D_{oib}$, g/cm$^3$  | 8.41                    | 7.94                     | 8.50                    |
| $Mr$, g/mole         | 390.5                   | 1462                     | 342.08                  |
| Structure type       | CeCu$_2$                | Th$_2$Zn$_{17}$          | CaIn$_2$                |
| Space group, Z       | Imam, 4                 | R-3m, 19                 | P6/mmc, 2               |
| Lattice parameters   |                         |                          |                         |
| $a$, Å               | 4.4532(1)               | 8.9704(3)                | 4.6070(8)               |
| $b$, Å               | 7.1263(3)               | –                        | –                       |
| $c$, Å               | 7.5801(3)               | 13.1320(6)               | 7.162(1)                |
| $V$, Å$^3$           | 240.55(2)               | 915.14(6)                | 131.16(6)               |
| Equipment            | STOE STADI P            | Guinier Camera           | Guinier Camera          |
| Wavelength           | CuK$_{\alpha}$          | CuK$_{\alpha}$          | CuK$_{\alpha}$         |
| 20 range             | 6.00–110.00°            | 10.00–102.00°           | 10.00–102.00°          |
| Step size in 20°     | 0.015                   | 0.005                    | 0.005                   |
| $R_B$, $R_F$, %      | 3.00; 2.61              | 3.33, 4.09               | 6.51; 6.34              |
| $R_p$, $R_{wp}$, %   | 6.36; 9.51              | 3.96, 5.65               | 5.83; 8.49              |

Therefore, the ternary system Er–Zn–In is characterized by formation of one ternary compound and three solid solutions based on ErZn$_2$, Er$_2$Zn$_{17}$ and ErIn$_3$ binary compounds. The variations of lattice parameters in the homogeneity regions of mentioned above solid solutions and the ternary compound are due to the substitution of the larger In atoms ($r = 1.626$ Å) by the smaller Zn atoms ($r = 1.332$ Å) [12] or vice versa. It should be noted that for the solid solutions the variation of lattice parameters is slightly deviated from Vegard’s rule.
Comparing the Er–{Mn, Fe, Co, Ni, Cu Zn}–In systems with each other, it should be underlined that the ternary system with zinc has some similarity only with the Er–Mn–In system. In both systems, the ternary compounds exist on cross-section 33.3 at. % R and form the homogeneity regions. The main difference between Er–Zn–In and related systems is the formation of several solids solutions based on binary compounds. On the other hand, this feature is characteristic for the Yb–Zn–In [6] and the Yb–Zn–Ga [13] systems. Furthermore, small number of compounds is another similar feature of these systems. Regarding to the structural types of phases, it should be mentioned that the phases exist on cross-section 33.3 at. % R in the Er–{Mn, Cu}–In, {Er, Yb}–Zn–In systems and the Yb–Zn–Ga system as well as are crystallised in the hexagonal structure types; moreover the majority of them are related to Al(B2-type).

4. Conclusion
The phase equilibria of Er–Zn–In system at 870 K are characterized by the formation of one ternary compound, namely ErZn16.54In0.46 (CaIn2-type). The some of the binary compounds, namely ErZn2 (CeCu2-type), Er2Zn17 (ThZn17-type) and ErIn3 (AuCu3-type) reveal homogeneity ranges by Zn/In or In/Zn substitutions.

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ВЗАЄМОДІЯ КОМПОНЕНТІВ У СИСТЕМІ Er–Zn–In
В ОБЛАСТІ 0–0,333 АТ. % Er ПРИ 870 K

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За результатами рентгенографії та частково ЕДРС аналізів побудовано ізотермічний переріз діаграми стану потрійної системи Er–Zn–In при 870 K в області до 0,333 ат. % Еr. Зразки для дослідження виготовляли методом безпосередньої взаємодії компонентів у вакуумованих кварцових ампулах з використанням програмованої термічної обробки.
У дослідженні області системи Er–Zn–In утворюється три тверді розчини та одна тернарна сполука з областю гомогенності. Межі області гомогенності тернарної фази зі структурою типу CaIn$_2$ простягаються від 0,24 до 0,40 ат. частки Індію, а її склад описують формуллою ErZn$_{0,28}$In$_{0,72}$ (просторова група P6$_3$/mmc; a = 4,513(2)–4,662(1), c = 7,023(3)–7,226(2) Å). В межах області гомогенності відбувається збільшення параметрів комірки внаслідок заміщення менших атомів цинку на більші атоми індію. Твердий розчин на основі бінарної сполуки ErZn$_2$ також утворюється вздовж ізоконцентрати Ербію 0,333 ат. частки, а склад фази може бути описаний формулою: ErZn$_{2,17}$In$_{0,30}$ (структурний тип CeCu$_2$, просторова група Ima$^2$; a = 4,448–4,594(3), b = 6,984–7,176(5), c = 7,610–7,463(5) Å ). Розчинність Індію в бінарній сполуці ErZn$_{17}$ (структурний тип TbZn$_{17}$, просторова група R-3m; a = 8,9465–8,9704(3), c = 13,1199–13,1320(6) Å) становить до 0,03 ат. часток. Твердий розчин на основі бінарної сполуки ErIn$_3$ (структурний тип AuCu$_3$, просторова група Pm-3m; a = 4,562–4,504(1) Å) існує вздовж ізоконцентрати ербію 0,25 ат. часток до 0,22 ат. часток цинку. В межах цього твердого розчину відбувається заміщення атомів In на атоми Zn. Кристалічну структуру цього твердого розчину вивчали рентгеноструктурним методом моноокристала на прикладі фази складу ErZn$_{0,87}$In$_{2,13}$.

Ключові слова: ербій, цинк, індій, фазові рівноваги, кристалічна структура, твердий розчин.

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