**On the ternary $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ ($\text{RE} = \text{Gd} - \text{Tm}$), $\text{RE}_3\text{Ag}_{5\pm x}\text{Mg}_{11\pm x}$,
 $\text{REAg}_{4+x}\text{Mg}_{2-x}$, $\text{RE}_4\text{Ag}_{10.3}\text{Mg}_{12}$ and $\text{RE}_4\text{Ag}_{10+x}\text{Mg}_{3-x}$ ($\text{RE} = \text{Ce} - \text{Nd}, \text{Sm}$)
phases**

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Abstract

Twenty ternary magnesium based phases (fourteen of them for the first time) have been prepared by reacting the elements at high temperature. Their crystal structures were studied by means of powder X-ray diffraction. $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ ($\text{RE} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$ and Tm) crystallize with the MgNi_2 structure type, $\text{RE}_3\text{Ag}_{5\pm x}\text{Mg}_{11\pm x}$ ($\text{RE} = \text{Ce}, \text{Pr}, \text{Nd}$ and Sm) with the $\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ structure type, $\text{REAg}_{4+x}\text{Mg}_{2-x}$ ($\text{RE} = \text{Ce}$ and Pr) with the YbMo_2Al_4 structure type, $\text{RE}_4\text{Ag}_{10.3}\text{Mg}_{12}$ ($\text{RE} = \text{Ce}, \text{Pr}$ and Nd) with the $\text{La}_4\text{Ag}_{10.3}\text{Mg}_{12}$ structure type and $\text{RE}_4\text{Ag}_{10+x}\text{Mg}_{3-x}$ ($\text{RE} = \text{Ce}, \text{Pr}, \text{Nd}$ and Sm) with the $\text{Ca}_4\text{Au}_{10}\text{In}_3$ structure type. Description of the structures in terms of interatomic relations and coordination are briefly discussed.

Keywords: Magnesium; Rare-earth intermetallics; Structure analysis; X-ray diffraction.

1. Introduction

Over the past years, the magnesium based ternary systems, alloys and compounds have intensively been studied with respect to phase analyses, crystal chemistry, physical properties, and hydrogenation behaviour due to their scientific and potential technological interest. An overview on the rare earth – transition metal – magnesium compounds was recently given [1]. Information on the rare earth – magnesium – p-metal systems can be found in [2, 3].

Among the RE–Ag–Mg systems, the isothermal section was constructed only for the La–Ag–Mg system at 400°C [4], and eight ternary phases have been identified [4–6]: $\text{LaAg}_{1-1.15}\text{Mg}_{1-0.85}$ (ZrNiAl type), $\text{La}_4\text{Ag}_{9.85-10.30}\text{Mg}_{3.15-2.70}$ ($\text{Ca}_4\text{Au}_{10}\text{In}_3$ type), $\text{LaAg}_{2-2.45}\text{Mg}_{2-1.55}$ (own type), $\text{LaAg}_{3.85-4.88}\text{Mg}_{2.15-1.12}$ (YbMo_2Al_4 type), $\text{LaAg}_{4.90-5.05}\text{Mg}_{1.10-0.95}$ (own type), $\text{La}_4\text{Ag}_{9.1-11.0}\text{Mg}_{12.4-11.3}$ (related to the $\text{Sc}_4\text{Cu}_{14.76}\text{Ga}_{7.51}$ type), $\text{La}_3\text{Ag}_{2.4-5.0}\text{Mg}_{13.6-11.0}$ ($\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ type) and $\text{LaAg}_{1.32-2.52}\text{Mg}_{10.68-9.48}$ (related to the ThMn_{12} type). Intermetallic $\text{REAg}_x\text{Mg}_{3-x}$ (RE = La, Ce, Pr, Nd and Sm) phases (BiF_3 and MnCu_2Al types) in the range $0 \leq x \leq 2$ were studied in [7]. Investigations on ternary phases with equiatomic composition REAgMg (RE = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb) (ZrNiAl and TiNiSi types) is given in [8–12].

The RE–Mg–Al systems are well explored [13–25]. So far, the isothermal sections were built in the whole concentration region for RE = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Ho [13–23] or partial by for RE = Tb [24]. The $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ (RE = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Yb) phases with the assigned structure types MgZn_2 or MgNi_2 are usually formed in the above mentioned systems [13–25]. Single crystal structural investigations of $\text{Eu}_{1.83}\text{Mg}_{11.34}\text{Al}_6$ (related to the $\text{Th}_2\text{Ni}_{17}$ type), $\text{EuMg}_{0.38}\text{Al}_{3.62}$ (BaAl_4 type), $\text{EuMg}_{0.86}\text{Al}_{1.14}$ (MgCu_2 type) and $\text{Eu}_2\text{Mg}_3\text{Al}$ ($\text{Mg}_2\text{Cu}_3\text{Si}$ type), were also performed [26].

The present work is a part of a systematic investigation of the magnesium based ternary alloy systems and compounds. Herein, we report on the synthesis and structure determination of new RE–Ag–Mg (RE = Ce, Pr, Nd and Sm) and previously described RE–Mg–Al (RE = Gd, Tb, Dy, Ho, Er, Tm and Yb) ternary phases. A brief description of the structures in the term of interatomic relations and coordination is also given.

2. Experimental details

Metals with nominal purities >99.95 wt.% (rare earth ingots, silver plate, aluminium and magnesium wires) were used as starting materials. At the beginning all components were

defragmented into small pieces ($\Phi < 1$ mm), mixed with the desired compositions, pressed into pellets ($\Phi = 10$ mm) and stored under inert atmosphere. Each sample was further synthesized by direct melting of pellets inside alumina or graphite containers under flowing argon at high temperature (850–900 °C), followed by slowly cooling to room temperature. Finally, fragments of the as-prepared ingots were wrapped with tantalum foil, sealed in evacuated small quartz tubes and annealed at 400 °C for 20 days. After the heat treatments, the samples were quenched by submerging the quartz tubes into cold water and analysed. The very exothermic reactions and magnesium evaporation frequently lead to significant composition changes and to multiphase samples after the synthesis. Therefore, the final composition of the samples were analysed by X-ray phase diffraction and chemical analysis. Obtained results of selected samples can be found in Table S1 (Supplementary data).

A PANalytical X'Pert Pro diffractometer (Cu $K\alpha$ -radiation) was used for the X-ray phase and structural analyses of the powdered polycrystalline samples. The scans were taken in the $\theta/2\theta$ mode with the following parameters: 2θ region, 15–120°; step scan, 0.03°; counting time per step, 15–20 s. Theoretical powder patterns were calculated with the help of the PowderCell program [27] and used for the identification of the phases. The lattice parameters were obtained by least-squares fitting using the Latcon program [28]. The FullProf [29] program was used for Rietveld refinements. A JEOL Scanning Microscope JSM-T330A, coupled with an energy dispersive X-ray spectroscopy (EDS) device, was used to obtain chemical data for the composition of the selected synthesized samples.

3. Results and discussion

Six earlier reported $RE_xMg_{1-x}Al_2$ (RE = Gd, Tb, Dy, Ho, Er and Yb) and one new (RE = Tm) phases have been obtained after annealing of the samples at 400 °C and their crystal structures have been studied for the first time. Thirteen new ternary $RE_3Ag_{5\pm x}Mg_{11\pm x}$ (RE = Ce, Pr, Nd and Sm), $REAg_{4+x}Mg_{2-x}$ (RE = Ce and Pr), $RE_4Ag_{10.3}Mg_{12}$ (RE = Ce, Pr and Nd) and $RE_4Ag_{10+x}Mg_{3-x}$ (RE = Ce, Pr, Nd and Sm) phases have been found in the RE–Ag–Mg systems; crystal structure determination for some of them has been performed using the Rietveld method.

X-ray diffraction patterns of selected phases are shown in Fig. 1. Calculated lattice parameters are summarized in Table 1. Atomic coordinates, isotropic displacement parameters, and interatomic distances for the atoms of above mentioned compounds can be found in Tables 2–3 and in the Supplementary data (Tables S2-S5).

Structural peculiarities, coordination and interactions of the atoms in the $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ (MgNi_2 structure type), $\text{RE}_3\text{Ag}_{5\pm x}\text{Mg}_{11\pm x}$ ($\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ structure type), $\text{REAg}_{4+x}\text{Mg}_{2-x}$ (YbMo_2Al_4 structure type) and $\text{RE}_4\text{Ag}_{10+x}\text{Mg}_{3-x}$ ($\text{Ca}_4\text{Au}_{10}\text{In}_3$ structure type) compounds are given below.

3.1. The $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ phases ($\text{RE} = \text{Gd} - \text{Yb}$)

Point $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ ($\text{RE} = \text{Gd} - \text{Yb}$, Table 1) composition phases with the structure of the hexagonal Laves phase MgNi_2 (space group $P6_3/mmc$) (Table 2) were found in the annealed Al-rich samples. Taking into account the early reported data on $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ phases [13-25], which show that they are only formed along cross-section of 66.7 at.% Al and indicate a RE/Mg mixing, the following distribution on the atoms in the structures of the $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ phases was suggested: The aluminium atoms occupy three crystallographically independent positions (Ni, 4*f*, 6*g* and 6*h*), while the rare earth and magnesium atoms are distributed over the Mg sites (the Mg-rich mixture positioned the 4*e* site, and the 4*f* site are in favour for the RE-rich mixture).

The Al atoms built up rows of face- and corner-sharing $[\text{Al}_4]$ tetrahedra along the *c* axis, forming a three-dimensional network (Fig. 2a). The Al-Al distances within the tetrahedral network range from 2.631 to 2.832 Å. These Al-Al distances are all shorter than in *fcc* aluminium [30], where each aluminium atom has twelve aluminium neighbours at 2.86 Å. The RE/Mg-Al distances (3.153 – 3.258 Å) are usually longer than the sum of the metallic radii of ~3.10 Å for rare earth metals, magnesium and aluminium [30]. Each RE/Mg atoms have four nearest RE/Mg neighbours at distances between 3.166 and 3.444 Å, and these compare well with the average RE/Mg-RE/Mg distances of ~3.36 Å in *hcp* metals [30].

The coordination polyhedra of the $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ structure are shown in Fig. 2b. The RE atoms have 16 neighbours $[\text{RE}_4\text{Al}_{12}]$, while the smaller aluminium atoms have 12 $[\text{RE}_6\text{Al}_6]$. The 12 neighbours around the Al sites have slightly distorted icosahedral arrangements. These different coordination polyhedra in the $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ structure are slightly distorted Frank-Kasper polyhedra.

The $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ is the only series of individual phases which were described among the RE-Mg-Al systems. Comparing RE-Mg-Al systems with the RE-Mg-Ga and RE-Mg-In related ones, a few remarks can be given. The RE-Mg-{Ga, In} are poorly studied systems. Systematic investigation were performed only for the {La, Ce, Yb}-Mg-Ga systems [31, 32]. Up to our best knowledge, information on the formation of the Laves phases in the

RE–Mg–{Ga, In} systems does not exist. However, the crystal structure of the equiatomic REMgGa (RE = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu, ZrNiAl structure type; RE = Eu, TiNiSi structure type), REMgIn (RE = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu, ZrNiAl structure type; RE = Eu, MgNi₂ structure type) and RE₂MgGa₂ (RE = Sc and Y) compounds are described in [33–35]. The existence of YbMgGa₄, Yb₅Mg₃Ga₇ and Yb₂Mg₄Ga₃ phases, with own structure types, are claimed in [32, 36].

3.2. The RE₃Ag_{5±x}Mg_{11±x} phases (RE = Ce – Nd, Sm)

The RE₃Ag_{5±x}Mg_{11±x} (RE = Ce, Pr, Nd and Sm) phases with the Gd₃Ru₄Al₁₂ structure type (space group *P6₃/mmc*) have been found in the as-cast and annealed samples (Table 3). Here, rare earth atoms occupy one independent position (Gd, 6*h*). Silver and magnesium atoms usually form a statistical mixture M. However, silver atoms have a tendency to fill the Ru sites (2*a* and 6*g*), and the magnesium rich mixtures are positioned in further four locations (Al, 2*b*, 4*f*, 6*h* and 12*k*).

In the crystal structure of the RE₃Ag_{5±x}Mg_{11±x} phases distorted cubes and rhombic prisms [Ag_{1+x}Mg_{4-x}] can be outlined, the last ones being connected by common edges and corners. A three-dimensional [Ag_{5±x}Mg_{11±x}] network is obtained, the larger voids being filled by the rare earth atoms (Fig. 3*a*). The Ag–Mg distances within the [Ag_{1+x}Mg_{4-x}] units vary between 2.595 and 3.035 Å, which are shorter than the sum of the metallic radii of the pure metals (*r*_{Ag} + *r*_{Mg} = 3.04 Å) [30]. The Mg–Mg contacts range from 3.033 to 3.231 Å, and they are close to the shortest distances of 3.20 Å in pure magnesium metal [30]. A large variety of contacts between rare earth and magnesium or silver atoms can be seen in the RE₃Ag_{5±x}Mg_{11±x} structures. However, the shortest ones, indicating strong bonding, can be considered only for RE–Mg (3.366 – 3.376 Å).

The near-neighbour coordination of the atoms in the RE₃Ag_{5±x}Mg_{11±x} phases are presented in Fig. 3*b*. The RE atoms are located inside septa-capped pentagonal prisms [RE₂M₁₅]. The coordination polyhedra of the M1 atoms are deformed cubes [M₈]. The neighbours of the M2 and M6 atoms form 11– [RE₃M₈] and 13–vertex [RE₃M₁₀] pseudo Frank–Kasper polyhedra, respectively. Slightly distorted icosahedra [RE₃M₉], [RE₄M₈] and [RE₂M₁₀] are the coordination spheres of the M3–M5 atoms.

Since the discovery of Gd₃Ru₄Al₁₂ [37], a number of isostructural Ru– and Os–based aluminides had been synthesized [37, 38]. Further investigation among the phases with the Gd₃Ru₄Al₁₂ type were focused on the Fe– and Co– aluminides and extended from lanthanides

to actinides [40–47]. Recently, two representatives ($\text{U}_3\text{Co}_{12-x}\text{Si}_4$ and $\text{U}_3\text{Co}_{12-x}\text{Ge}_4$) of the slightly deformed and defected $\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ type were reported in [48]. It should be underlined that among the rare earth – transition metal – magnesium systems only one phase, i.e. $\text{La}_3\text{Ag}_{4+x}\text{Mg}_{12-x}$, of this type was studied [4].

3.3. The $\text{REAg}_{4+x}\text{Mg}_{2-x}$ phases ($\text{RE} = \text{Ce}, \text{Pr}$)

The $\text{REAg}_{4+x}\text{Mg}_{2-x}$ ($\text{RE} = \text{Ce}$ and Pr) compounds have been found to crystallize with the YbMo_2Al_4 structure type (space group $I4/mmm$) (Table 4). Here, the Ce and Pr atoms are situated in the positions of the Yb (2a); mixture of 9/10Ag + 1/10Mg ($\text{RE} = \text{Ce}$) or pure silver ($\text{RE} = \text{Pr}$) are located in the Al sites (8h); the Mo positions (4d) are occupied by the 1/4Ag + 3/4Mg ($\text{RE} = \text{Ce}$) or 2/5Ag + 3/5Mg ($\text{RE} = \text{Pr}$) mixtures.

The structure of these phases with outlined three-dimensional network $[\text{Ag}_{4+x}\text{Mg}_{2-x}]$ is shown in Fig. 4a. Here, infinite magnesium (magnesium rich mixture M1) chains can be seen along the z axis. The M1–M1 distances of 2.743–2.770 Å are distinctly shorter than the shortest distances (3.20 Mg–Mg Å and 2.88 Ag–Ag Å) in the pure metals [30]. The M1 chains are coordinated by condensed $[\text{Ag}_4]$ ($\text{RE} = \text{Pr}$) or $[\text{M}_2\text{Ag}_2]$ ($\text{RE} = \text{Ce}$) squares at distances of 2.738–2.777 Å. These distances are significantly shorter than in *fcc* silver (2.88 Å) [30], which is in contrast to the weaker inter-square M2–M2 touches (2.991–2.998 Å). The M1–M2 distances of 2.940–2.948 Å are close to the sum of the metallic radii for silver and magnesium. Within the $[\text{Ag}_{4+x}\text{Mg}_{2-x}]$ network cerium and praseodymium atoms fill the voids between two $[\text{M}_2\text{Ag}_2]$ and $[\text{Ag}_4]$ squares, respectively. Calculated distances of 3.112–3.127 Å between the RE and M2/Ag are noticeably short pointing to strong interactions between these atoms.

The rare earth atoms have a 20-vertex coordination polyhedra $[\text{M}_{20}]$, while the Mg and Ag atoms are located inside 14-vertex $[\text{RE}_4\text{M}_{10}]$ and 11-vertex $[\text{RE}_3\text{M}_8]$ pseudo Frank–Kasper polyhedra, respectively (Fig. 4b).

Besides the above mentioned $\text{REAg}_{4+x}\text{Mg}_{2-x}$ ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}$) phases, the aluminides YbMo_2Al_4 , GdMo_2Al_4 , ErMo_2Al_4 and $\text{YbCu}_{5.15}\text{Al}_{0.88}$ [49, 50], the gallides RETi_2Ga_4 ($\text{RE} = \text{Zr}, \text{Sc}, \text{Y}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$ and Lu) and REV_2Ga_4 ($\text{RE} = \text{Zr}, \text{Sc}, \text{Y}$ and Er) [51–59], the indide $\text{SrAu}_{4.76}\text{In}_{1.24}$ [60], and some transition metal-based $\text{CeCu}_{4.7}\text{Mn}_{1.3}$ and REAu_4Cd_2 ($\text{RE} = \text{Ca}, \text{Sr}$ and Eu) [61, 62] compounds have been reported to have the YbMo_2Al_4 structure type.

3.4. The $RE_4Ag_{10+x}Mg_{3-x}$ phases ($RE = Ce - Nd, Sm$)

The $RE_4Ag_{10+x}Mg_{3-x}$ ($RE = Ce, Pr, Nd$ and Sm) phases (Fig. 5a) crystallize isotypically to the $Ca_4Au_{10}In_3$ (or partially ordered Zr_7Ni_{10}) structure type (space group $Cmca$). The atomic parameters were refined from powder X-ray diffraction data for $RE = Ce, Pr$ and Nd (Table 5). Among the seven crystallographically independent positions in this structure, two of them (Ca, 8d and 8f) are occupied by the rare earth atoms. Silver, magnesium or their mixtures are positioned in the other five sites. The three, 8f, 16g and 16g, locations (Au) are predominantly filled by the silver atoms. The magnesium atoms have the tendency to be situated the 4a and 8e (In) sites.

In the structure of the $RE_4Ag_{10+x}Mg_{3-x}$ phases a complex three-dimensional $[Ag_{10+x}Mg_{3-x}]$ network can be considered (Fig. 5a). The Ag–Mg distances within this network range from 2.774 to 3.191 Å. Most of these distances are shorter than the sum of the metallic radii [29] of 3.04 Å ($r_{Ag} + r_{Mg}$), indicating a substantial degree of the Ag–Mg bonding. Besides the strong Ag–Mg bonds, a wide variety of the Ag–Ag interaction due to the high silver content can be also observed. The Ag–Ag distances cover the broad range from 2.757 to 3.400 Å, which are close or even smaller than the sum of the metallic radii [29]. The $[Ag_{10+x}Mg_{3-x}]$ network leaves large cavities which are filled by the rare earth atoms. The bonding of the rare earth atoms to the network proceeds via the RE–Ag as well as RE–Mg contacts. However, a shortest one of 2.962–2.999 Å can be seen only for RE–Ag pairs. The RE–RE distances are significantly large than sum of metallic radii of 3.64 Å in pure rare earth metals.

The coordination polyhedra of the $RE_4Ag_{10+x}Mg_{3-x}$ structure are given in Fig. 5b. The rare earth atoms (RE1 and RE2) are located inside tetra- and septa-capped deformed pentagonal prisms, $[RE_2M_{15}]$ and $[RE_2M_{15}]$. Deformed cubooctahedra $[RE_4M_8]$ and icosahedra $[RE_4M_8]$ are the coordination spheres for the magnesium (M1 and M2) atoms, respectively. Nearest neighbours of the silver (M3) atoms form bicapped square antiprisms $[RE_5M_5]$. Penta-capped deformed trigonal prisms $[RE_4M_7]$ surround the silver (M4 and M5) atoms.

Taking the presented results into account and data on the $La_4Ag_{10}Mg_3$ [5] and $Ca_4Au_{10}In_3$ [63] compounds it should be noted that only six ternary ordered (or partially ordered) representatives with the Zr_7Ni_{10} structure type are reported until to now.

4. Conclusion

Crystallographic data on twenty ternary phases, namely, $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ (MgNi_2 structure type), $\text{RE}_3\text{Ag}_{5\pm x}\text{Mg}_{11\pm x}$ ($\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ structure type), $\text{REAg}_{4+x}\text{Mg}_{2-x}$ (YbMo_2Al_4 structure type), $\text{RE}_4\text{Ag}_{10.3}\text{Mg}_{12}$ ($\text{La}_4\text{Ag}_{10.3}\text{Mg}_{12}$ structure type) and $\text{RE}_4\text{Ag}_{10+x}\text{Mg}_{3-x}$ ($\text{Ca}_4\text{Au}_{10}\text{In}_3$ structure type), have been given. The crystal structure of some of them was fully investigated by means of powder X-ray diffraction. RE/Mg substitutions were revealed in the RE–Mg–Al phases, while the Ag/Mg statistical mixtures were found in the RE–Ag–Al phases. A brief discussion of the crystal structures was also performed. Taking into account the available information on the RE–Mg–Al and RE–Ag–Mg phase diagrams, the formation of compounds with isostructural or deformed structures in other systems related to the investigated ones cannot be excluded.

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Tables:

Table 1 Crystallographic data of the ternary RE–Mg–Al and RE–Ag–Mg phases

Table 2 Atomic and displacement parameters in the structure of the $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ compounds

Table 3 Atomic and displacement parameters in the structure of the $\text{RE}_3\text{Ag}_{5\pm x}\text{Mg}_{11\pm x}$ compounds

Table 4 Atomic and displacement parameters in the structure of the $\text{REAg}_{4+x}\text{Mg}_{2-x}$ compounds

Table 5 Atomic and displacement parameters in the structure of the $\text{RE}_4\text{Ag}_{10+x}\text{Mg}_{3-x}$ compounds

Figure captures:

Fig.1. Rietveld refinement of the samples (a) $\text{Er}_{11}\text{Mg}_{22}\text{Al}_{67}$ (1 – $\text{Er}_{0.31}\text{Mg}_{0.69}\text{Al}_2$, 2 – ErAl_3) ($R_p = 4.95\%$, $R_{wp} = 6.33\%$); (b) $\text{Ce}_{19}\text{Ag}_{24}\text{Mg}_{57}$ (1 – $\text{Ce}_3\text{Ag}_{4.7}\text{Mg}_{11.3}$, 2 – $\text{CeAg}_{0.9}\text{Mg}_{2.1}$) ($R_p = 7.79\%$, $R_{wp} = 10.4\%$); (c) $\text{Pr}_{23}\text{Ag}_{60}\text{Mg}_{17}$ (1 – $\text{Pr}_4\text{Ag}_{10}\text{Mg}_3$, 2 – $\text{Pr}_{14}\text{Ag}_{51}$) ($R_p = 9.33\%$, $R_{wp} = 12.1\%$).

Fig. 2. Unit cell, three-dimensional network of the connected $[\text{Al}_4]$ tetrahedra (a) and coordination polyhedra of the atoms in the $\text{RE}_x\text{Mg}_{1-x}\text{Al}_2$ structure (b).

Fig. 3. Crystal structure of the $\text{RE}_3\text{Ag}_{5\pm x}\text{Mg}_{11\pm x}$ phases: three-dimensional network (a) and coordination polyhedra of the atoms (b). Rare earth atoms, Mg/Mg-rich mixtures and Ag/Ag-rich mixtures are shown by blue, green and cyan filled circles.

Fig. 4. Three-dimensional network $[\text{Ag}_{4+x}\text{Mg}_{2-x}]$ (a) and coordination polyhedra of the atoms (b) in the $\text{REAg}_{4+x}\text{Mg}_{2-x}$ structure. Rare earth atoms, Mg-rich mixtures and Ag/Ag-rich mixtures are shown by blue, green and cyan filled balls.

Fig. 5. Three-dimensional network $[\text{Ag}_{10+x}\text{Mg}_{3-x}]$ (a) and coordination polyhedra of the atoms (b) in the $\text{RE}_4\text{Ag}_{10+x}\text{Mg}_{3-x}$ structure. Rare earth atoms, Mg-rich mixtures and Ag/Ag-rich mixtures are shown by blue, green and cyan filled spheres.

Table 1

Crystallographic data of the ternary RE–Mg–Al and RE–Ag–Mg phases

No	Phase	Structure type	Lattice parameters			
			<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
1	Gd _{0.45} Mg _{0.55} Al ₂	MgNi ₂	5.5317(4)	–	17.7993(14)	471.7
2	Tb _{0.45} Mg _{0.55} Al ₂	MgNi ₂	5.5143(3)	–	17.7450(10)	467.3
3	Dy _{0.38} Mg _{0.62} Al ₂	MgNi ₂	5.4938(3)	–	17.6876(10)	462.3
4	Ho _{0.34} Mg _{0.66} Al ₂	MgNi ₂	5.4842(13)	–	17.6701(5)	460.3
5	Er _{0.31} Mg _{0.69} Al ₂	MgNi ₂	5.4710(14)	–	17.6687(6)	458.0
6	Tm _{0.23} Mg _{0.77} Al ₂	MgNi ₂	5.4576(19)	–	17.6795(8)	456.0
7	Yb _{0.36} Mg _{0.64} Al ₂	MgNi ₂	5.4879(2)	–	17.7947(9)	464.1
8	Ce ₃ Ag _{4.7} Mg _{11.3}	Gd ₃ Ru ₄ Al ₁₂	9.8088(5)	–	10.4477(6)	870.5
9	Pr ₃ Ag _{5.2} Mg _{10.8}	Gd ₃ Ru ₄ Al ₁₂	9.7843(6)	–	10.4254(8)	864.3
10	Nd ₃ Ag _{5.1} Mg _{10.9}	Gd ₃ Ru ₄ Al ₁₂	9.7620(6)	–	10.4073(7)	858.9
11	Sm ₃ Ag _{5.3} Mg _{10.7}	Gd ₃ Ru ₄ Al ₁₂	9.7318(7)	–	10.3798(9)	851.3
12	CeAg _{4.1} Mg _{1.9}	YbMo ₂ Al ₄	7.1783(12)	–	5.5390(12)	285.4
13	PrAg _{4.86} Mg _{1.14}	YbMo ₂ Al ₄	7.1605(13)	–	5.4866(13)	281.3
14	Ce ₄ Ag _{10.1} Mg _{2.9}	Ca ₄ Au ₁₀ In ₃	14.1140(15)	10.2779(11)	10.3731(12)	1504.7
15	Pr ₄ Ag _{10.0} Mg _{3.0}	Ca ₄ Au ₁₀ In ₃	14.0344(14)	10.2324(11)	10.3318(11)	1483.7
16	Nd ₄ Ag _{10.5} Mg _{2.5}	Ca ₄ Au ₁₀ In ₃	13.993(2)	10.2069(15)	10.3095(15)	1472.5
17	Sm ₄ Ag _{9.9} Mg _{3.1}	Ca ₄ Au ₁₀ In ₃	13.849(3)	10.134(2)	10.246(3)	1438.1
18	Ce ₄ Ag _{10.3} Mg ₁₂	La ₄ Ag _{10.3} Mg ₁₂	9.563(2)	24.920(5)	9.5871(19)	2284.9
19	Pr ₄ Ag _{10.3} Mg ₁₂	La ₄ Ag _{10.3} Mg ₁₂	9.579(3)	24.779(7)	9.610(2)	2281.1
20	Nd ₄ Ag _{10.3} Mg ₁₂	La ₄ Ag _{10.3} Mg ₁₂	9.542(2)	24.769(5)	9.568(2)	2261.4

Table 2 Atomic and displacement parameters in the structure of the RE_xMg_{1-x}Al₂ compounds

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occupation G
Gd_{0.45}Mg_{0.55}Al₂ (Gd_{0.450(5)}Mg_{0.550(5)}Al₂)					
RE1	4e	0	0	0.0895(4)	0.068(3)Gd + 0.932(3)Mg
RE2	4f	1/3	2/3	0.65326(11)	0.831(8)Gd + 0.169(8)Mg
Al1	4f	1/3	2/3	0.1250(4)	1Al
Al2	6g	1/2	0	0	1Al
Al3	6h	0.1632(15)	2x	1/4	1Al
Displacement parameter: $B_{\text{All}} = 1.01(5) \text{ \AA}^2$. Reliability factors: $R_B = 6.68 \%$, $R_F = 4.70 \%$.					
Tb_{0.45}Mg_{0.55}Al₂ (Tb_{0.452(4)}Mg_{0.548(4)}Al₂)					
RE1	4e	0	0	0.0892(3)	0.083(3)Tb + 0.917(3)Mg
RE2	4f	1/3	2/3	0.65364(9)	0.820(6)Tb + 0.180(6)Mg
Al1	4f	1/3	2/3	0.1260(3)	1Al
Al2	6g	1/2	0	0	1Al
Al3	6h	0.1626(12)	2x	1/4	1Al
Displacement parameter: $B_{\text{All}} = 0.91(5) \text{ \AA}^2$. Reliability factors: $R_B = 5.47 \%$, $R_F = 4.34 \%$.					
Dy_{0.38}Mg_{0.62}Al₂ (Dy_{0.378(4)}Mg_{0.622(4)}Al₂)					
RE1	4e	0	0	0.0916(4)	0.041(3)Dy + 0.959(3)Mg
RE2	4f	1/3	2/3	0.65408(11)	0.716(5)Dy + 0.284(5)Mg
Al1	4f	1/3	2/3	0.1264(3)	1Al
Al2	6g	1/2	0	0	1Al
Al3	6h	0.1615(12)	2x	1/4	1Al
Displacement parameter: $B_{\text{All}} = 0.93(5) \text{ \AA}^2$. Reliability factors: $R_B = 5.43 \%$, $R_F = 3.43 \%$.					
Ho_{0.34}Mg_{0.66}Al₂ (Ho_{0.340(2)}Mg_{0.660(2)}Al₂)					
RE1	4e	0	0	0.0914(3)	0.045(2)Ho + 0.955(2)Mg
RE2	4f	1/3	2/3	0.65460(8)	0.636(3)Ho + 0.364(3)Mg
Al1	4f	1/3	2/3	0.1260(2)	1Al
Al2	6g	1/2	0	0	1Al
Al3	6h	0.1621(8)	2x	1/4	1Al
Displacement parameter: $B_{\text{All}} = 1.11(4) \text{ \AA}^2$. Reliability factors: $R_B = 2.98 \%$, $R_F = 2.26 \%$.					
Er_{0.31}Mg_{0.69}Al₂ (Er_{0.307(2)}Mg_{0.693(2)}Al₂)					
RE1	4e	0	0	0.0924(3)	0.050(2)Er + 0.950(2)Mg
RE2	4f	1/3	2/3	0.65513(9)	0.564(3)Er + 0.436(3)Mg
Al1	4f	1/3	2/3	0.1262(2)	1Al
Al2	6g	1/2	0	0	1Al
Al3	6h	0.1609(9)	2x	1/4	1Al
Displacement parameter: $B_{\text{All}} = 1.16(4) \text{ \AA}^2$. Reliability factors: $R_B = 3.69 \%$, $R_F = 2.93 \%$.					

Table 2 (continued)

Atom	Site	x	y	z	Occupation G
Tm _{0.23} Mg _{0.77} Al ₂ (Tm _{0.227(2)} Mg _{0.773(2)} Al ₂)					
RE1	4e	0	0	0.0926(4)	0.051(2)Tm + 0.949(2)Mg
RE2	4f	1/3	2/3	0.65566(14)	0.404(3)Tm + 0.596(3)Mg
Al1	4f	1/3	2/3	0.1260(3)	1Al
Al2	6g	1/2	0	0	1Al
Al3	6h	0.1607(11)	2x	1/4	1Al
Displacement parameter: $B_{\text{All}} = 1.55(5) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 3.69 \%$, $R_{\text{F}} = 3.14 \%$.					
Yb _{0.36} Mg _{0.64} Al ₂ (Yb _{0.362(3)} Mg _{0.638(3)} Al ₂)					
RE1	4e	0	0	0.0916(3)	0.093(2)Yb + 0.907(2)Mg
RE2	4f	1/3	2/3	0.65491(9)	0.630(4)Yb + 0.370(4)Mg
Al1	4f	1/3	2/3	0.1265(3)	1Al
Al2	6g	1/2	0	0	1Al
Al3	6h	0.1624(10)	2x	1/4	1Al
Displacement parameter: $B_{\text{All}} = 0.65(4) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 3.61 \%$, $R_{\text{F}} = 2.39 \%$.					

Table 3 Atomic and displacement parameters in the structure of the $\text{RE}_3\text{Ag}_{5\pm x}\text{Mg}_{11\pm x}$ compounds

Atom	Site	x	y	z	Occupation G
$\text{Ce}_3\text{Ag}_{4.7}\text{Mg}_{11.3}$ ($\text{Ce}_3\text{Ag}_{4.75(9)}\text{Mg}_{11.25(9)}$)					
Ce	6h	0.1981(2)	2x	1/4	1Ce
M1	2a	0	0	0	1Ag
M2	2b	0	0	1/2	0.049(11)Ag + 0.951(11)Mg
M3	4f	1/3	2/3	0.0113(16)	0.052(7)Ag + 0.948(7)Mg
M4	6g	1/2	0	0	0.967(6)Ag + 0.033(6)Mg
M5	6h	0.5667(9)	2x	1/4	0.112(7)Ag + 0.888(7)Mg
M6	12k	0.1587(8)	2x	0.5852(7)	0.060(5)Ag + 0.940(5)Mg
Displacement parameter: $B_{\text{All}} = 0.96(6) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 4.77 \%$, $R_{\text{F}} = 3.04 \%$.					
$\text{Pr}_3\text{Ag}_{5.2}\text{Mg}_{10.8}$ ($\text{Pr}_3\text{Ag}_{5.23(8)}\text{Mg}_{10.77(8)}$)					
Pr	6h	0.1987(3)	2x	1/4	1Pr
M1	2a	0	0	0	1Ag
M2	2b	0	0	1/2	0.050(13)Ag + 0.950(13)Mg
M3	4f	1/3	2/3	-0.0023(17)	0.081(9)Ag + 0.919(9)Mg
M4	6g	1/2	0	0	1Ag
M5	6h	0.5671(10)	2x	1/4	0.151(8)Ag + 0.849(8)Mg
M6	12k	0.1583(9)	2x	0.5814(8)	0.094(4)Ag + 0.906(4)Mg
Displacement parameter: $B_{\text{All}} = 0.84(7) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 6.15 \%$, $R_{\text{F}} = 3.56 \%$.					
$\text{Nd}_3\text{Ag}_{5.1}\text{Mg}_{10.9}$ ($\text{Nd}_3\text{Ag}_{5.09(10)}\text{Mg}_{10.91(10)}$)					
Nd	6h	0.1996(3)	2x	1/4	1Nd
M1	2a	0	0	0	1Ag
M2	2b	0	0	1/2	1Mg
M3	4f	1/3	2/3	0.0073(20)	0.043(10)Ag + 0.957(10)Mg
M4	6g	1/2	0	0	0.978(8)Ag + 0.022(8)Mg
M5	6h	0.5643(12)	2x	1/4	0.163(9)Ag + 0.837(9)Mg
M6	12k	0.1588(10)	2x	0.5812(8)	0.097(5)Ag + 0.903(5)Mg
Displacement parameter: $B_{\text{All}} = 0.71(7) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 6.45 \%$, $R_{\text{F}} = 3.81 \%$.					
$\text{Sm}_3\text{Ag}_{5.3}\text{Mg}_{10.7}$ ($\text{Sm}_3\text{Ag}_{5.33(9)}\text{Mg}_{10.67(9)}$)					
Sm	6h	0.2003(3)	2x	1/4	1Sm
M1	2a	0	0	0	1Ag
M2	2b	0	0	1/2	1Mg
M3	4f	1/3	2/3	-0.0024(20)	0.115(12)Ag + 0.885(12)Mg
M4	6g	1/2	0	0	1Ag
M5	6h	0.5623(14)	2x	1/4	0.194(10)Ag + 0.806(10)Mg
M6	12k	0.1593(13)	2x	0.5768(10)	0.087(6)Ag + 0.913(6)Mg
Displacement parameter: $B_{\text{All}} = 1.5(1) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 10.9 \%$, $R_{\text{F}} = 8.01 \%$.					

Table 4 Atomic and displacement parameters in the structure of the REAg_{4+x}Mg_{2-x} compounds

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occupation G
CeAg _{4.1} Mg _{1.9} (CeAg _{4.10(8)} Mg _{1.90(8)})					
Ce	2 <i>a</i>	0	0	0	1Ce
M1	4 <i>d</i>	0	1/2	1/4	0.250(11)Ag + 0.750(11)Mg
M2	8 <i>h</i>	0.3066(4)	<i>x</i>	0	0.899(15)Ag + 0.101(15)Mg
Displacement parameter: $B_{\text{All}} = 0.8(1) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 4.92 \%$, $R_{\text{F}} = 2.85 \%$.					
PrAg _{4.86} Mg _{1.14} (PrAg _{4.86(3)} Mg _{1.14(3)})					
Pr	2 <i>a</i>	0	0	0	1Pr
M1	4 <i>d</i>	0	1/2	1/4	0.430(16)Ag + 0.570(16)Mg
M2	8 <i>h</i>	0.3088(5)	<i>x</i>	0	1Ag
Displacement parameter: $B_{\text{All}} = 1.1(1) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 5.58 \%$, $R_{\text{F}} = 3.49 \%$.					

Table 5 Atomic and displacement parameters in the structure of the $\text{RE}_4\text{Ag}_{10+x}\text{Mg}_{3-x}$ compounds

Atom	Site	x	y	z	Occupation G
$\text{Ce}_4\text{Ag}_{10.1}\text{Mg}_{2.9}$ ($\text{Ce}_4\text{Ag}_{10.10(11)}\text{Mg}_{2.90(11)}$)					
Ce1	8d	0.2991(4)	0	0	1Ce
Ce2	8f	0	0.2996(8)	0.2001(8)	1Ce
M1	4a	0	0	0	0.172(19)Ag + 0.828(19)Mg
M2	8e	1/4	0.2754(32)	1/4	0.097(16)Ag + 0.903(16)Mg
M3	8f	0	0.0920(9)	0.4033(10)	1Ag
M4	16g	0.1405(6)	0.0333(7)	0.2070(7)	0.934(15)Ag + 0.066(15)Mg
M5	16g	0.3644(5)	0.2941(7)	0.0268(6)	1Ag
Displacement parameter: $B_{\text{All}} = 0.5(1) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 4.84 \%$, $R_{\text{F}} = 3.21 \%$.					
$\text{Pr}_4\text{Ag}_{10}\text{Mg}_3$ ($\text{Pr}_4\text{Ag}_{9.99(17)}\text{Mg}_{3.01(17)}$)					
Pr1	8d	0.3028(4)	0	0	1Pr
Pr2	8f	0	0.3044(8)	0.2004(8)	1Pr
M1	4a	0	0	0	0.196(19)Ag + 0.804(19)Mg
M2	8e	1/4	0.3025(33)	1/4	0.059(15)Ag + 0.941(15)Mg
M3	8f	0	0.0970(9)	0.4033(9)	1Ag
M4	16g	0.1391(7)	0.0334(7)	0.2088(7)	0.945(15)Ag + 0.055(15)Mg
M5	16g	0.3618(6)	0.2956(7)	0.0287(6)	0.975(15)Ag + 0.025(15)Mg
Displacement parameter: $B_{\text{All}} = 1.1(1) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 7.56 \%$, $R_{\text{F}} = 5.62 \%$.					
$\text{Nd}_4\text{Ag}_{10.5}\text{Mg}_{2.5}$ ($\text{Nd}_4\text{Ag}_{10.52(5)}\text{Mg}_{2.48(5)}$)					
Nd1	8d	0.3009(4)	0	0	1Nd
Nd2	8f	0	0.3028(8)	0.2016(8)	1Nd
M1	4a	0	0	0	0.23(2)Ag + 0.77(2)Mg
M2	8e	1/4	0.2889(28)	1/4	0.145(16)Ag + 0.855(16)Mg
M3	8f	0	0.0965(10)	0.4036(10)	1Ag
M4	16g	0.1406(7)	0.0318(7)	0.2064(7)	1Ag
M5	16g	0.3626(6)	0.2934(7)	0.0257(6)	1Ag
Displacement parameter: $B_{\text{All}} = 0.6(1) \text{ \AA}^2$. Reliability factors: $R_{\text{B}} = 6.83 \%$, $R_{\text{F}} = 4.33 \%$.					

$b \leftarrow \rightarrow a$
 $\downarrow$
 c

● R1
● R2
● A1

R

M1

M2

M3

M4

M5

M6

R

M1

M2

R1

R2

M1

M2

M3

M4

M5

- 1) Ternary samples from the RE–Mg–Al and RE–Ag–Mg systems were synthesized at high temperature.
- 2) Twenty ternary magnesium based phases were identified.
- 3) The crystal structures of selected intermetallics were studied and discussed.