

Crystallochemistry of the novel two-layer $RECuMg_4$ ($RE = La, Tb$) ternary compounds

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Abstract

The crystal structures of the new ternary compounds $LaCuMg_4$ and $TbCuMg_4$ were studied by X-ray powder diffraction and single-crystal methods, respectively. Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDXS) was used for examining microstructure and phase composition. $LaCuMg_4$ crystallizes in the $UCoAl_4$ structure type (space group $P\bar{6}2m$, Pearson code $hP18$, $a = 1.03911(1)$, $c = 0.45126(1)$ nm, $Z = 3$, $R_F = 0.0654$), while $TbCuMg_4$ exhibits a new structure (space group $Cmmm$, Pearson code $oS48$, $a = 1.35797(6)$, $b = 2.03333(9)$, $c = 0.39149(2)$ nm, $Z = 8$, $wR_2 = 0.0426$). Both structures represent a family of two-layer compounds. All interatomic distances indicate metallic type bonding. The structural peculiarities of these compounds and their relations are discussed.

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1. Introduction

The $RE-T-Mg$ intermetallic systems (RE , rare earth metal, T , transition metal) have recently attracted great attention due to the interesting properties and applications of their alloys. The research work in this field is particularly focused on the investigation of series of novel compounds, which are studied both from the fundamental (crystal structure, chemical bonding) and the applicative (physical properties, hydrogen absorption and storage) point of view. The crystal chemistry and main features of a number of such ternary phases are summarized in an overview by Rodewald et al. [1].

Our research groups have been involved since long time in the investigation of constitutional properties of both binary and ternary Mg alloys and some $RE-T-Mg$ systems have been recently studied [2–4]. The interaction of the components in such systems is complicate enough, numerous ternary phases being detected in them.

During the investigation of the $La-Cu-Mg$ isothermal section at 400 °C [4] in the whole concentration range several ternary phases were found on the composition line characterized by a ratio 1:1 between La and Cu (e.g. La_2Cu_2Mg , $LaCuMg$, $LaCuMg_3$, $LaCuMg_4$). A first indexation of the X-ray powder pattern of $LaCuMg_4$ indicated a tetragonal crystal structure [4]. A more detailed crystal structure analysis revealed for this phase a hexagonal symmetry.

The $Tb-Cu-Mg$ system was chosen to make a comparison between constitutional properties of $RE-Cu-Mg$ systems containing light and heavy rare earth metals, and a phase with the same stoichiometry ($TbCuMg_4$) was found

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to exist. Its crystal structure was determined by single-crystal X-ray measurement and analysis: it represents a new structure type in the orthorhombic crystal system.

The results of the metallographic and crystallographic characterization of the intermetallics LaCuMg₄ and TbCuMg₄ are reported in this work.

One of the objectives of studies of crystal chemistry is to classify and arrange the various observed structure types so as to show relationships which may exist between them. Such classifications provide a greatly condensed description of crystal structures details, thus permitting much structural information to be comprehended and kept in mind. Here, we present a part of a systematic analysis of two-layer compounds related to those investigated in this work. The main aspects discussed are comparison of the packing of centered pentagonal, tetragonal and trigonal prisms, search of interstructural relations and comparison of coordination polyhedra typical for the atoms.

2. Experimental Section

2.1. Synthesis and phase analysis

Lanthanum, terbium, nickel and magnesium, all with nominal purities >99.9 wt%, were used as starting elements.

A few alloys of nominal composition La_{16.7}Cu_{16.6}Mg_{66.7} were prepared by induction melting the stoichiometric amounts of the constituent metals placed together into an outgassed tantalum crucible sealed by arc-welding under a flow of pure argon. Samples were then sealed in silica ampoules under vacuum and annealed in a resistance furnace at different temperatures (400, 600, 700 or 950 °C) in order to obtain a single-phase alloy.

An alloy of nominal composition Tb₁₅Cu₁₇Mg₆₈ was prepared by placing stoichiometric amounts of the metals, protected in a Nb-container, arc-welded in pure argon atmosphere, in an evacuated quartz ampoule (pressure inside 10⁻⁵–10⁻⁶ Pa). This was then located in a resistance furnace with a thermal cycle controller. Heating was carried out at a rate of 5 °C/min up to $T = 1200$ °C and this temperature was held for 20 min. The sample was then slowly cooled (0.25 °C/min) down to 400 °C and this temperature was held for 2 h. Finally, irregularly shaped single crystals, exhibiting metallic luster, were isolated from the alloy by mechanical fragmentation.

Both La- and Tb-containing alloys could readily be separated from the crucible. No side reaction of the samples with the crucible was detected.

Before X-ray measurements samples were analyzed by means of light optical microscopy (LOM), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS). Quantitative analyses were performed with an acceleration voltage of 20 kV for 50 s. Cobalt standard was used for calibration. X-ray spectra were processed by the software package INCA Energy (Oxford Instruments, Analytical Ltd., Bucks, UK).

2.2. X-ray structure determination

The crystal structure of LaCuMg₄ was solved *ab initio*. As mentioned above, the LaCuMg₄ was published to have tetragonal symmetry [4] (TREOR program was used for indexing). For the further crystal structure solution with subsequent Rietveld refinement, a better quality XRPD was collected. The powder data were obtained with an X'Pert MPD (Philips, Almelo, the Netherlands) diffractometer, with the Bragg–Brentano optics, using monochromatic CuK α 1 radiation ($\lambda = 0.15406$ nm) at room conditions. Here, powder pattern indexing was performed with the DICVOL04 program [5] indicating a hexagonal cell with $a = 1.03945(1)$ nm, $c = 0.45148(1)$ nm. Special reflection conditions were not detected in the measured 2θ range suggesting seven possible space groups: $P6$ (No. 168), $\bar{P}6$ (No. 174), $P6/m$ (No. 175), $P622$ (No. 177), $P6mm$ (No. 183), $\bar{P}62m$ (No. 189) and $P6/mmm$ (No. 191). Profile parameters were derived from the Le Bail fit (FULLPROF program [6]) and the structure was solved in the space group $\bar{P}62m$ by global optimization in direct space by FOX program [7] (attempts to find a solution in the other six space groups were unsuccessful). The structure was refined by the Rietveld method. In the final refinement cycles, 22 parameters were allowed to vary: sample shift, scale factor, two cell parameters, six profile parameters (Pseudo-Voigt peak shape function), five positional parameters, six isotropic thermal displacement parameters for all atom positions and texture parameter (the preferred orientation corresponds to [001] direction). Background was refined with a polynomial function.

Single-crystal data of TbCuMg₄ were collected at room temperature by using a four-circle diffractometer (Xcalibur Oxford Diffraction diffractometer) with CCD detector (graphite monochromatized MoK α radiation, $\lambda = 0.071073$ nm). Scans were taken in the ω mode, the analytical absorption corrections were made by CrysAlisRed [8]. The crystal structure of TbCuMg₄ was successfully solved by direct methods and refined using SHELX-97 package programs [9]. Systematic absences indicated as possible space groups $C222$ (No. 21), $Cmm2$ (No. 35), $Amm2$ (No. 38) and the centrosymmetric $Cmmm$ (No. 65). The statistical test of the distribution of the E values [10] suggested that the structure is centrosymmetric with probability 85.20%. However, following the advice of Marsh [11], the structure solution and refinement were also performed in the non-centrosymmetric groups. The results clearly indicate that TbCuMg₄ crystallizes in the centrosymmetric space group $Cmmm$, since the solution and refinement in the non-centrosymmetric variants were not satisfactory. The occupancy parameters were refined for this structure in order to check for deviations from the ideal composition. Whereas no significant deviations were found, the ideal occupancy parameters were retained in the final refinement cycles of this structure. Data were then refined with anisotropic displacement parameters for all atoms. The final difference Fourier syntheses revealed no

significant residual peaks—the highest maximum residual electron density is $1.64 \text{ e } \text{\AA}^{-3}$ from Tb and the deepest hole is $1.02 \text{ e } \text{\AA}^{-3}$ from Mg.

The atomic positions for both structures were standardized with the *STRUCTURE TIDY* program [12]. Listings of the observed and calculated structure factors are available.¹

3. Results and discussion

3.1. SEM–EDXS characterization

Global compositions of $\text{La}_{16.7}\text{Cu}_{16.6}\text{Mg}_{66.7}$ samples generally correspond to the nominal one. However, the alloys annealed at 600, 700 or 950 °C show only a small amount of LaCuMg_4 , located at the grain borders of a phase whose composition (about 25 at% La, 5 at% Cu, 70 at% Mg) corresponds to a solid solution based on the binary LaMg_3 compound.

The thermal treatment at 400 °C for 1 month was instead successful to obtain an almost LaCuMg_4 single-phase alloy. Since good quality single crystals were not detected in this sample, it was analyzed by X-ray powder diffraction.

The $\text{Tb}_{15}\text{Cu}_{17}\text{Mg}_{68}$ sample prepared as reported in Section 2 shows a large amount of TbCuMg_4 : the quality of its crystals allowed in this case a single-crystal selection and analysis.

3.2. Crystal structure of LaCuMg_4

Crystal data, details of data collection and structure refinement for LaCuMg_4 are listed in Table 1. Observed, calculated and differential X-ray powder diffraction patterns of the LaCuMg_4 sample are shown in Fig. 1. The standardized atomic positions and isotropic atomic displacement parameters of this compound are collected in Table 2.

The title compound crystallizes in the hexagonal UCoAl_4 -type [13] structure. No binary phases with analogous structure were found to exist. The LaCuMg_4 structure contains six crystallographically independent atomic positions: one La and two Mg atoms occupy sites of symmetry $m2m$, two Cu atoms occupy sites of symmetry $-6..$ and $-62m$, respectively, another Mg occupies a $m..$ site. Equatorially, five-capped pentagonal prisms $[\text{La}_1\text{Cu}_2\text{Mg}_{13}]$ (CN 15) from adjacent atoms enclose La atoms. Two different polyhedra are characteristic for Mg atoms: distorted cubooctahedron $[\text{Mg}_6\text{Cu}_2\text{Mg}_8\text{La}_2]$ or $[\text{Mg}_4\text{Cu}_2\text{Mg}_6\text{La}_4]$ (CN 12) and bi-capped cubooctahedron $[\text{Mg}_5\text{Cu}_3\text{Mg}_8\text{La}_3]$ (CN 14). Equatorially, tri-capped trigo-

Table 1

Crystallographic data and details of experimental conditions and structure refinement for the LaCuMg_4 compound

| | |
|---|--|
| Empirical formula | LaCuMg_4 |
| Structure type | UCoAl_4 |
| Crystal system | Hexagonal |
| Space group | $P\bar{6}2m$ (No. 189) |
| Pearson symbol, Z | $hP18, 3$ |
| Sample composition (EDXS) | $\text{La}_{16.7}\text{Cu}_{16.6}\text{Mg}_{66.7}$ |
| 2θ range (deg); number of points | 7.07–130.07; 4101 |
| Step size (deg); counting time (s) | 0.03; 40 |
| Number of unique reflections | 194 |
| Unit-cell parameters | |
| a (nm) | 1.03911(1) |
| c (nm) | 0.45126(1) |
| V (nm ³) | 0.42198(3) |
| Number of refined structural parameters | 13 |
| Preferred orientation: direction, value | [00 1], 1.0048(4) |
| Reliability factors | |
| R_F | 6.54 |
| R_B | 12.3 |
| R_P | 6.29 |
| R_{wp} | 8.45 |
| χ^2 | 11.8 |

nal prisms $[\text{Cu}_2\text{Mg}_6\text{La}_3]$ and $[\text{Cu}_3\text{Mg}_9]$ (CN 9) surround the smallest Cu atoms in the structure. The unit cell projection of LaCuMg_4 onto the x – y plane is shown in Fig. 2 together with outlined coordination polyhedra of all atoms.

The shortest Mg–Cu distance in the structure is 0.2624 nm, which corresponds to 91.1% of the sum of the atomic radii; the remaining Mg–Cu contacts are close to the sum of the metallic single-bond radii. Mg–Mg contacts vary from 0.3053 to 0.3238 nm (3.200 nm is the shortest distance in *hcp* magnesium); as a consequence we can assume a strong Mg–Mg bonding. The La–Cu bond length, 0.3153 nm, is only slightly longer than the sum of the metallic single-bond radii (0.315 nm). The La–Mg contacts cover a wider range of distances: 0.3339–0.3693 nm. However, the majority of these contacts match well the sum of the metallic single-bond radii (0.3470 nm). The list of interatomic distances is reported in Table 3.

3.3. Crystal structure of TbCuMg_4

Table 4 contains the crystal data information, details of data collection and structure refinement. Standardized atomic positions and anisotropic thermal displacement parameters are listed in Table 5.

TbCuMg_4 is the first representative of a new structure type of intermetallic compounds (IMC). Each crystallographic position of the unit cell is fully occupied by only one sort of atoms: two $m2m$ site symmetry positions are occupied by Tb and Mg, respectively, two mmm positions—by two Mg atoms, four $..m$ positions—by a Cu

¹Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD CSD-418214 (LaCuMg_4), CSD-418215 (TbCuMg_4).

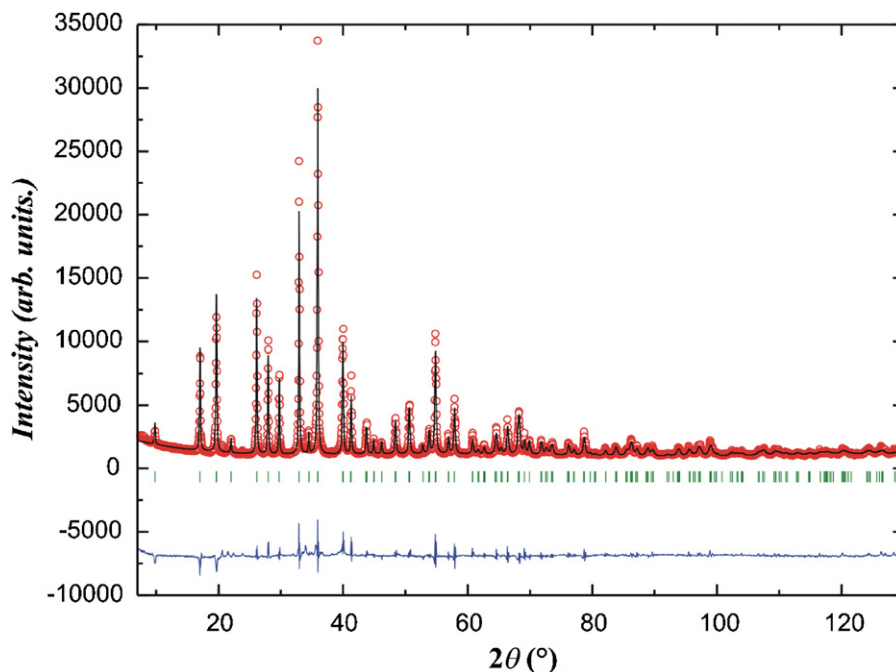


Fig. 1. Observed (circles), calculated (line) and difference (bottom line) X-ray powder diffraction patterns for the LaCuMg₄ compound. Vertical bars indicate the Bragg positions of the corresponding phase.

Table 2
Atomic coordinates and isotropic thermal displacement parameters ($\times 10^3 \text{ \AA}^2$) for the LaCuMg₄ compound

| Atom | Wyckoff position | x/a | y/b | z/c | U_{eq} |
|------|------------------|------------|------------|-------|-----------------|
| La1 | 3 <i>f</i> | 0.4064(3) | 0 | 0 | 14.8(7) |
| Cu2 | 2 <i>c</i> | 1/3 | 2/3 | 0 | 23.0(2) |
| Cu3 | 1 <i>a</i> | 0 | 0 | 0 | 22.0(3) |
| Mg4 | 6 <i>k</i> | 0.2935(13) | 0.4746(12) | 1/2 | 21.1(2) |
| Mg5 | 3 <i>f</i> | 0.7475(12) | 0 | 0 | 20.0(5) |
| Mg6 | 3 <i>g</i> | 0.1696(13) | | 1/2 | 19.2(6) |

Table 3
Interatomic distances δ (nm) with estimated standard deviations in parentheses and coordination numbers (CN) of the atoms in the LaCuMg₄ compound

| LaCuMg ₄ | | |
|---|------|------------|
| δ (nm) | | |
| Equatorially tri-capped trigonal prism (CN 9) | | |
| Cu2 | 6Mg4 | 0.2902(1) |
| | 3La1 | 0.3153(3) |
| Equatorially tri-capped trigonal prism (CN 9) | | |
| Cu3 | 3Mg5 | 0.2624(6) |
| | 6Mg6 | 0.2863(8) |
| Distorted cubooctahedron (CN 12) | | |
| Mg4 | 2Cu2 | 0.2902(9) |
| | 2Mg5 | 0.3101(10) |
| | Mg6 | 0.3111(11) |
| | 2Mg4 | 0.3160(14) |
| | Mg4 | 0.3259(23) |
| | 2La1 | 0.3534(10) |
| | 2La1 | 0.3568(11) |
| Distorted cubooctahedron (CN 12) | | |
| Mg6 | 2Cu3 | 0.2863(8) |
| | 2Mg6 | 0.3053(17) |
| | 2Mg4 | 0.3111(12) |
| | 4Mg5 | 0.3234(3) |
| | 2La1 | 0.3339(10) |
| Bi-capped cubooctahedron (CN 14) | | |
| Mg5 | Cu3 | 0.2624(13) |
| | 4Mg4 | 0.3101(9) |
| | 4Mg6 | 0.3238(10) |
| | La1 | 0.3544(13) |
| | 2La1 | 0.3693(2) |
| | 2Cu2 | 0.3951(8) |

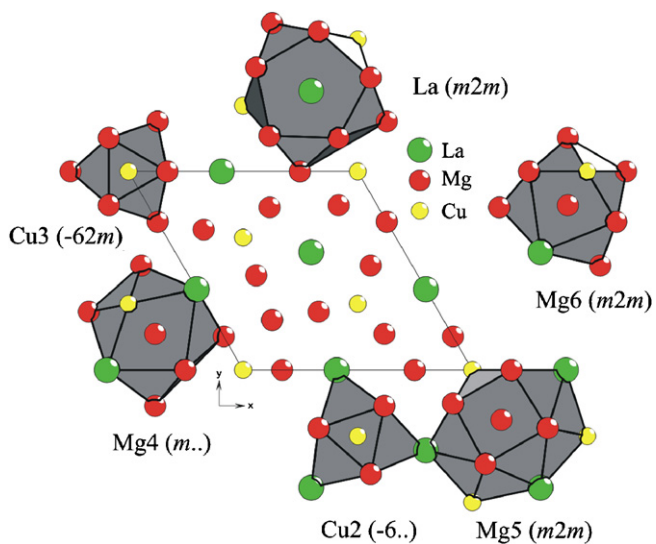


Fig. 2. Unit cell projection of the LaCuMg₄ structure onto x - y plane. The coordination polyhedra of the atoms are shown; symmetries of the central atoms are indicated in parentheses.

Table 3 (continued)

| LaCuMg ₄ | | |
|---|------|------------|
| δ (nm) | | |
| Equatorially five-capped pentagonal prism (CN 15) | | |
| La1 | 2Cu2 | 0.3153(1) |
| | 2Mg6 | 0.3339(10) |
| | 4Mg4 | 0.3534(9) |
| | Mg5 | 0.3544(13) |
| | 4Mg4 | 0.3568(7) |
| | 2Mg5 | 0.3693(10) |

Table 4

Crystallographic data for the TbCuMg₄ single crystal and experimental details of the structure determination

| | |
|---|--|
| Empirical formula | TbCuMg ₄ |
| Structure type | TbCuMg ₄ |
| Formula weight, M_r | 319.70 |
| Crystal system | Orthorhombic |
| Space group | $Cmnm$ (No. 65) |
| Pearson symbol, Z | $oS48$, 8 |
| Crystal dimensions (mm ³) | $0.24 \times 0.08 \times 0.07$ |
| Unit cell dimensions | |
| a (nm) | 1.35797(6) |
| b (nm) | 2.03333(9) |
| c (nm) | 0.39149(2) |
| V (nm ³) | 1.08098(9) |
| Calculated density, D_{calc} (g cm ⁻³) | 3.929 |
| Absorption coefficient, μ (mm ⁻¹) | 17.20 |
| Scan mode | ω |
| Theta range for data collection (deg) | 3.0–26.4 |
| $F(000)$ | 1136 |
| Range in hkl | $-16 \leq h \leq 16$, $-24 \leq k \leq 25$, $-2 \leq l \leq 4$ |
| Absorption correction: analytical | $T_{\text{min}} = 0.207$; $T_{\text{max}} = 0.302$ |
| Total no. of reflections | 3316 |
| Independent reflections | 661 ($R_{\text{int}} = 0.0333$) |
| Reflections with $I > 2\sigma(I)$ | 634 ($R_{\text{sigma}} = 0.0210$) |
| Weighting scheme | $1/[\sigma(F_0)^2 + (0.0221 \times P)^2 + 2.7785 \times P]$ |
| Data/parameters | 661/44 |
| Goodness-of-fit on F^2 | 1.219 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0211$; $wR_2 = 0.0417$ |
| R indices (all data) | $R_1 = 0.0223$; $wR_2 = 0.0426$ |
| Extinction coefficient | 0.00057(8) |
| $\Delta\rho_{\text{fin}}$ (max/min) (e Å ⁻³) | 1.64 and -1.03 e/Å ³ |

Table 5

Atomic coordinates and anisotropic thermal displacement parameters ($\times 10^{\text{nm}^2}$) for the TbCuMg₄ single crystal

| Atom | Wyckoff position | x/a | y/b | z/c | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} | U_{eq} |
|------|------------------|-------------|-------------|-------|----------|----------|----------|-----------|----------|----------|-----------------|
| Tb1 | $4i$ | 0 | 0.36821(1) | 0 | 15.0(2) | 18.3(2) | 14.4(2) | 0 | 0 | 0 | 15.9(1) |
| Tb2 | $4g$ | 0.30234(2) | 0 | 0 | 18.1(2) | 13.8(2) | 14.8(2) | 0 | 0 | 0 | 15.6(1) |
| Cu3 | $8q$ | 0.34089(5) | 0.10533(3) | 1/2 | 19.4(3) | 17.5(3) | 17.0(3) | $-1.0(2)$ | 0 | 0 | 18.0(2) |
| Mg4 | $8q$ | 0.11775(13) | 0.25641(8) | 1/2 | 19.4(9) | 17.6(3) | 26.2(8) | $-0.4(6)$ | 0 | 0 | 21.1(4) |
| Mg5 | $2a$ | 0 | 0 | 0 | 29.0(20) | 21.5(17) | 23.5(17) | 0 | 0 | 0 | 24.6(8) |
| Mg6 | $2c$ | 1/2 | 0 | 1/2 | 18.5(17) | 16.5(16) | 20.6(16) | 0 | 0 | 0 | 18.5(7) |
| Mg7 | $8p$ | 0.24488(12) | 0.16892(8) | 0 | 19.6(8) | 18.7(8) | 22.7(8) | 0.4(6) | 0 | 0 | 20.3(4) |
| Mg8 | $8q$ | 0.13229(13) | 0.07945(8) | 1/2 | 20.1(8) | 20.1(8) | 27.1(9) | $-0.9(7)$ | 0 | 0 | 22.4(4) |
| Mg9 | $4i$ | 0 | 0.16468(12) | 0 | 21.3(12) | 21.2(12) | 27.7(12) | 0 | 0 | 0 | 23.4(5) |

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $U_{ij} = -2\pi^2[(h^2 a^*)^2 U_{11} + \dots + 2hka^* b^* U_{12}]$.

atom and three Mg atoms, respectively, finally a $2mm$ position corresponds to a Tb atom.

Both Tb atoms are surrounded by 17 adjacent atoms forming the distorted pseudo Frank-Kasper polyhedra [Tb1Cu₄Mg₉Tb₄] and [Tb2Cu₄Mg₉Tb₄]. The characteristic polyhedra of Mg atoms in this structure are a distorted rhombic dodecahedron (CN 14) of different compositions ([Mg4CuMg₁₁Tb₂], [Mg5Mg₁₂Tb₂], [Mg6Mg₂Tb₁₂], [Mg8CuMg₁₁Tb₂], [Mg9Mg₁₃Tb]) and a distorted cubooctahedron [Mg7Cu₂Mg₈Tb₂] (CN 12). The smallest Cu atoms in the structure are enclosed by equatorially tri-capped trigonal prisms [Cu3Mg₅Tb₄]. The unit cell projection of TbCuMg₄ onto x - y plane is shown in Fig. 3 together with the coordination polyhedra of all atoms.

The shortest distance in the structure is 0.2684 nm between Mg and Cu, corresponding to 93.2% of the sum of the atomic radii. Tb–Mg and Tb–Cu distances do not deviate noticeably from the sum of covalent radii, being generally a little longer. Majority of Mg–Mg distances have a negative deviation from the sum of the metallic single-bond radii (the whole range is 0.3079–0.3915 nm) assuming a strong Mg–Mg bonding to the atoms from the nearest environment. Interatomic distances in the TbCuMg₄ structure are collected in Table 6.

3.4. Crystallographic relations with other structure types

The LaCuMg₄ and TbCuMg₄ compounds belong to the family of two-layer compounds, which includes more than 70 other inorganic structure types according to *TYPIX* [14]. After a detailed study of the crystal structure of LaCuMg₄, it was noticed that it can be represented as a packing of centered pentagonal, tetragonal and trigonal prisms. Among the variety of two-layer structure types, a number of structures was found, whose crystal space could be filled by similar centered pentagonal, tetragonal and trigonal prisms arranged in different ways. A selection of such structures is reported in Fig. 4, together with the corresponding Schläfli symbols. These symbols are useful to describe networks of atoms, giving size and number of polygons surrounding each non-equivalent node in the network.

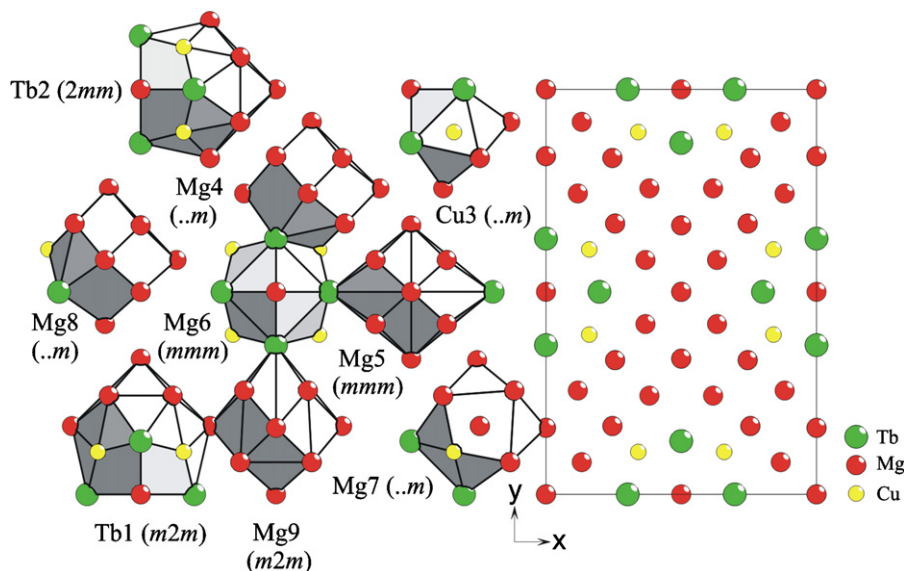


Fig. 3. Unit cell projection of the TbCuMg_4 structure onto x - y plane. The coordination polyhedra of the atoms are shown; symmetries of the central atoms are indicated in parentheses.

Table 6

Interatomic distances δ (nm) with estimated standard deviations in parentheses and coordination numbers (CN) of the atoms in TbCuMg_4 compound

| TbCuMg_4 | | |
|---|------|-----------|
| δ (nm) | | |
| Equatorially tri-capped trigonal prism (CN 9) | | |
| Cu3 | 2Mg7 | 0.2684(1) |
| | Mg4 | 0.2867(2) |
| | Mg8 | 0.2881(2) |
| | 2Tb2 | 0.2948(1) |
| | 2Tb1 | 0.2965(1) |
| | Mg6 | 0.3042(1) |
| Distorted rhombic dodecahedron (CN 14) | | |
| Mg5 | 8Mg8 | 0.3109(1) |
| | 2Mg9 | 0.3349(2) |
| | 2Mg5 | 0.3915(1) |
| | 2Tb2 | 0.4106(1) |
| Distorted rhombic dodecahedron (CN 14) | | |
| Mg6 | 4Cu3 | 0.3042(1) |
| | 4Tb1 | 0.3319(1) |
| | 4Tb2 | 0.3322(1) |
| | 2Mg6 | 0.3915(1) |
| Distorted rhombic dodecahedron (CN 14) | | |
| Mg4 | Cu3 | 0.2867(2) |
| | 2Mg7 | 0.3101(2) |
| | 2Mg9 | 0.3141(2) |
| | 2Mg7 | 0.3159(2) |
| | Mg4 | 0.3198(3) |
| | 2Tb1 | 0.3399(1) |
| | Mg4 | 0.3601(3) |
| | Mg8 | 0.3604(2) |
| | 2Mg4 | 0.3915(2) |
| Distorted rhombic dodecahedron (CN 14) | | |
| Mg8 | Cu3 | 0.2881(2) |
| | 2Mg7 | 0.3079(2) |
| | 2Mg5 | 0.3109(1) |
| | 2Mg9 | 0.3172(2) |
| | Mg8 | 0.3231(2) |

Table 6 (continued)

| TbCuMg_4 | | |
|--|------|-----------|
| δ (nm) | | |
| | 2Tb2 | 0.3431(1) |
| | Mg8 | 0.3593(3) |
| | Mg4 | 0.3604(2) |
| | 2Mg8 | 0.3915(1) |
| Distorted rhombic dodecahedron (CN 14) | | |
| Mg9 | 4Mg4 | 0.3141(2) |
| | 4Mg8 | 0.3172(2) |
| | 2Mg7 | 0.3327(2) |
| | Mg5 | 0.3349(2) |
| | 2Mg9 | 0.3915(1) |
| | Tb1 | 0.4138(3) |
| Distorted pseudo Frank-Kasper (CN 17) | | |
| Tb1 | 4Cu3 | 0.2965(1) |
| | 2Mg6 | 0.3319(1) |
| | 4Mg4 | 0.3399(1) |
| | 2Mg7 | 0.3546(2) |
| | 2Tb2 | 0.3793(1) |
| | 2Tb1 | 0.3915(1) |
| | Mg9 | 0.4139(3) |
| Distorted pseudo Frank-Kasper (CN 17) | | |
| Tb2 | 4Cu3 | 0.2948(1) |
| | 2Mg6 | 0.3322(1) |
| | 4Mg8 | 0.3431(1) |
| | 2Mg7 | 0.3522(2) |
| | 2Tb1 | 0.3793(1) |
| | 2Tb2 | 0.3915(1) |
| | Mg5 | 0.4106(1) |
| Distorted cubooctahedron (CN 12) | | |
| Mg7 | 2Cu3 | 0.2684(1) |
| | 2Mg8 | 0.3079(2) |
| | 2Mg4 | 0.3101(2) |
| | 2Mg4 | 0.3159(2) |
| | Mg7 | 0.3300(2) |
| | Mg9 | 0.3327(2) |
| | Tb2 | 0.3522(2) |
| | Tb1 | 0.3546(2) |

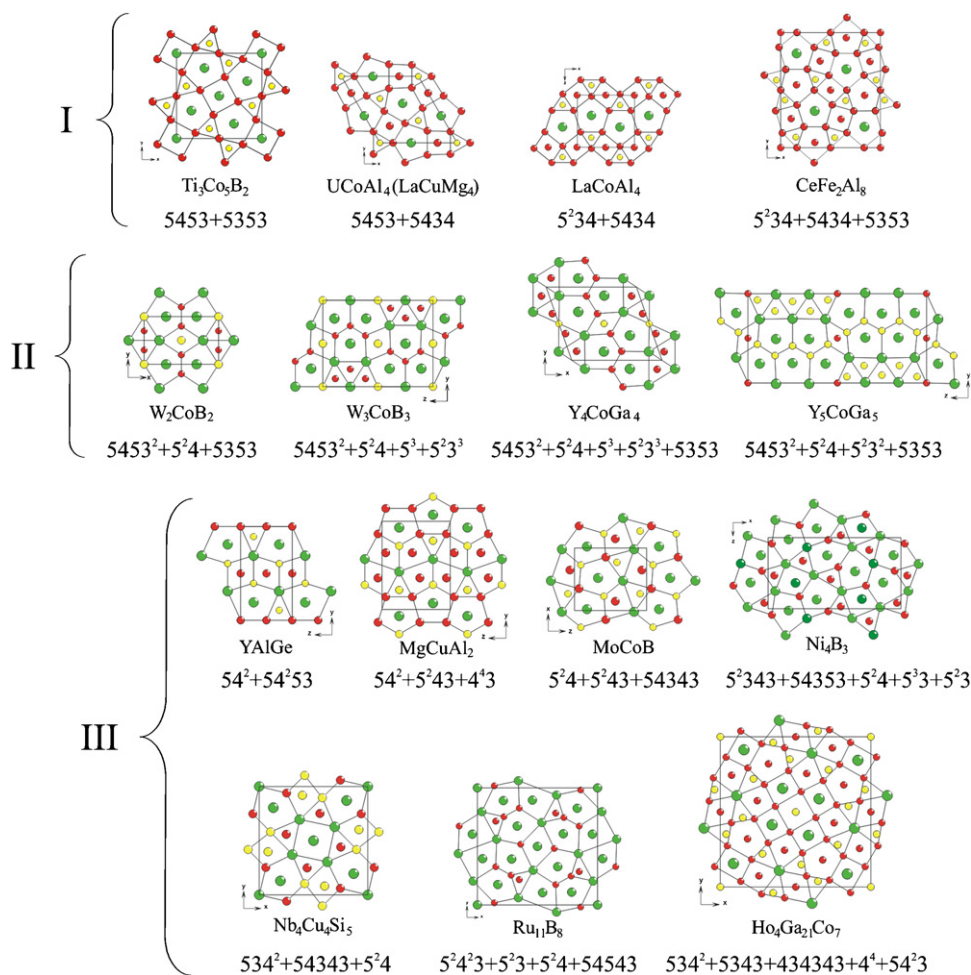


Fig. 4. Two-layer structures with centered pentagonal, tetragonal and trigonal prisms. Schläfli symbols for the corresponding planar networks are indicated below. Structures are divided into three groups marked by roman numerals.

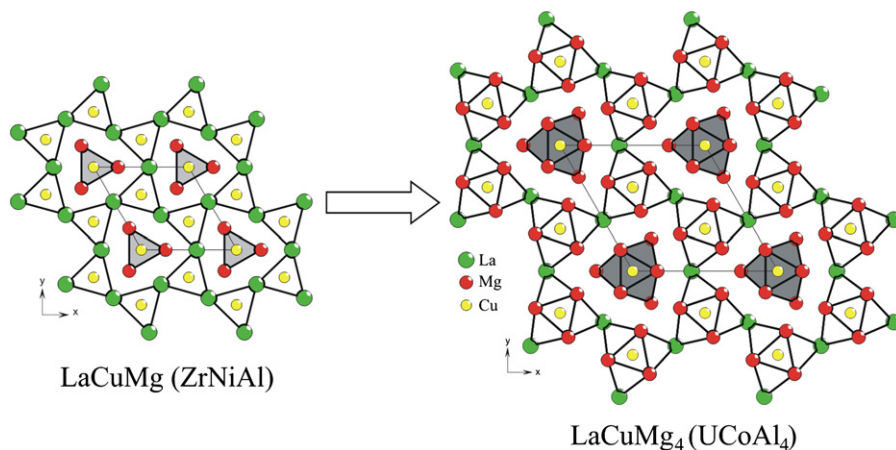


Fig. 5. The LaCuMg_4 structure as an interstitial variant of LaCuMg .

Crystal structures shown in Fig. 4 can be conveniently divided into three groups. The UCoAl_4 structure type (which LaCuMg_4 crystallizes in) belongs to the first group; it has two non-equivalent nodes surrounded by 5453 and 5434 fragments. The presence of 5453 motifs makes it related to the $\text{Ti}_3\text{Co}_5\text{B}_2$ type [15] (5453 + 5353). From the other side, the

5434 fragment makes it similar to LaCoAl_4 [16] ($5^234 + 5434$) and CeFe_2Al_8 [17] ($5^234 + 5434 + 5353$), both characterized by zigzag chains of centered pentagonal prisms separated by the chains of centered trigonal and tetragonal prisms.

We have attributed to the second group four structure types with the same ratio of biggest and smallest atoms:

W_2CoB_2 [18] ($5453^2 + 5^24 + 5353$), W_3CoB_3 [19] ($5453^2 + 5^24 + 5^3 + 5^23^3$), Y_4Co_4Ga [20] ($5453^2 + 5^24 + 5^3 + 5^23^3 + 5353$) and Y_5Co_5Ga [21] ($5453^2 + 5^24 + 5^3 + 5^23^3 + 5353$). In this series, the number of non-equivalent nodes smoothly increases, for all structures the presence of similar prisms packed fragments is distinctive. Moreover, corresponding layers in the Y_4Co_4Ga and Y_5Co_5Ga structures are characterized by identical Schläfli symbols.

The third group includes structures without resembling prisms arrangement fragments: $YAlGe$ [22] ($54^2 + 54^253$), $MgCuAl_2$ [23] ($54^2 + 5^243 + 4^43$), $MoCoB$ [24] ($5^24 + 5^243 + 54343$), Ni_4B_3 [25] ($5^2343 + 54353 + 5^24 + 5^33 + 5^23$), $Nb_5Cu_4Si_5$ [26] ($534^2 + 54343 + 5^24$), $Ru_{11}B_8$ [27] ($5^24^23 + 5^23 + 5^24 + 54543$) and $Ho_6Ga_{21}Co_7$ [28] ($534^2 + 5343 + 434343 + 4^4 + 54^23$).

The $LaCuMg_4$ compound can be also regarded as an interstitial variant of the common $ZrNiAl$ -type. As the ternary $LaCuMg$ compound belongs to the latter structure type [4,29], hereinafter we shall refer to it for simplicity. The trigonal prisms $[CuLa_6]$ and $[CuMg_6]$ (shifted one relative to another at $z = 1/2$), which can be considered the

fundamental motifs of $LaCuMg$, are similar to the corresponding equatorially tri-capped motifs $[CuMg_6La_3]$ and $[CuMg_6Mg_3]$ (situated at the same height) in $LaCuMg_4$ (see Fig. 5). As well the formation of $LaCuMg_4$ may be interpreted as an inclusion of Mg_6 and Mg_3 blocks in the form of trigonal prisms and planar triangles into $LaCuMg$ structure (see Table 7). This leads the unit cell volume to increase three times as much. Taking into account that both compounds lie on the composition line that links the $LaMg$ binary to Mg in the phase diagram it becomes reasonable an empirical formula as $3LaCuMg + 9Mg = 3LaCuMg_4$ (indexes correspond to formula units).

Although the $TbCuMg_4$ compound has the same stoichiometry as the discussed $LaCuMg_4$, their crystal structures are different. The following fragments, occurring with the ratio 2:16, can be considered the constructive elements of the crystal structure of $TbCuMg_4$:

- I. CsCl-type cubes with four centered trigonal prisms which share tetragonal faces (like in Mo_2FeB_2 type [30]; it should be mentioned that Tb_2Cu_2Mg is isostructural to the latter [31]).
- II. Distorted α -Fe type fragments (with the difference that it consists of two atom sorts).

Structure types showing similar structure fragments are shown in Fig. 6, where those fragments are outlined. The crystal structure of $Nb_5Cu_4Si_5$ can be viewed as stacking of layers of identical (I) motifs which are shifted relative to each other at $z = 1/2$. The Nb_4P_7 structure [32] is composed of (I) fragments and others similar to them (with the difference that half of trigonal prisms are differently oriented with axes in (1 0 1) plane) as shown in the picture. Jung and Schweitzer [33] determined the crystal

Table 7

The atoms distribution in the $LaCuMg$ ($ZrNiAl$) type and its interstitial variant $LaCuMg_4$ ($UCoAl_4$)

| LaCuMg ($ZrNiAl$) \rightarrow + Mg_6, Mg_3 blocks \rightarrow | | | | | LaCuMg ₄ ($UCoAl_4$) | | | | |
|---|------|-------|-----|-----|-----------------------------------|------|--------|--------|-----|
| Atom | Site | x/a | y/b | z/c | Atom | Site | x/a | y/b | z/c |
| La1 | 3f | 0.582 | 0 | 0 | La1 | 3f | 0.4064 | 0 | 0 |
| Cu2 | 2d | 1/3 | 2/3 | 1/2 | Cu2 | 2c | 1/3 | 2/3 | 0 |
| Cu3 | 1a | 0 | 0 | 0 | Cu3 | 1a | 0 | 0 | 0 |
| Mg4 | 3g | 0.256 | 0 | 1/2 | Mg6 | 3g | 0.1696 | 0 | 1/2 |
| Inclusion | | | | | Mg4 | 6k | 0.2935 | 0.4746 | 1/2 |
| Inclusion | | | | | Mg5 | 3f | 0.7475 | 0 | 0 |

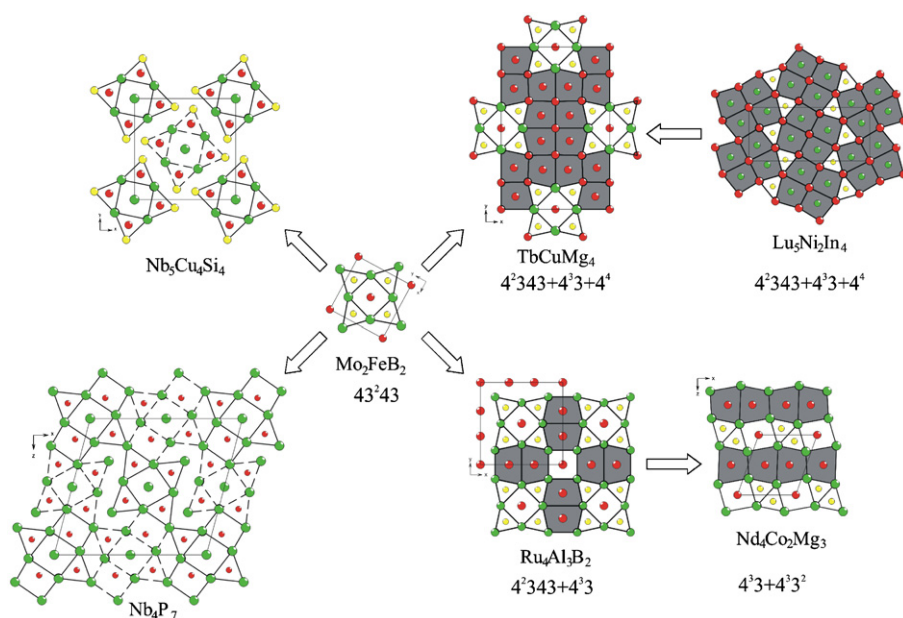


Fig. 6. Interstructural relations of two-layer structure types with specific tetragonal and trigonal prisms packing as distinguishing features. Distorted α -Fe and CsCl fragments are colored in gray. Fragments at different heights are illustrated by solid and dotted lines.

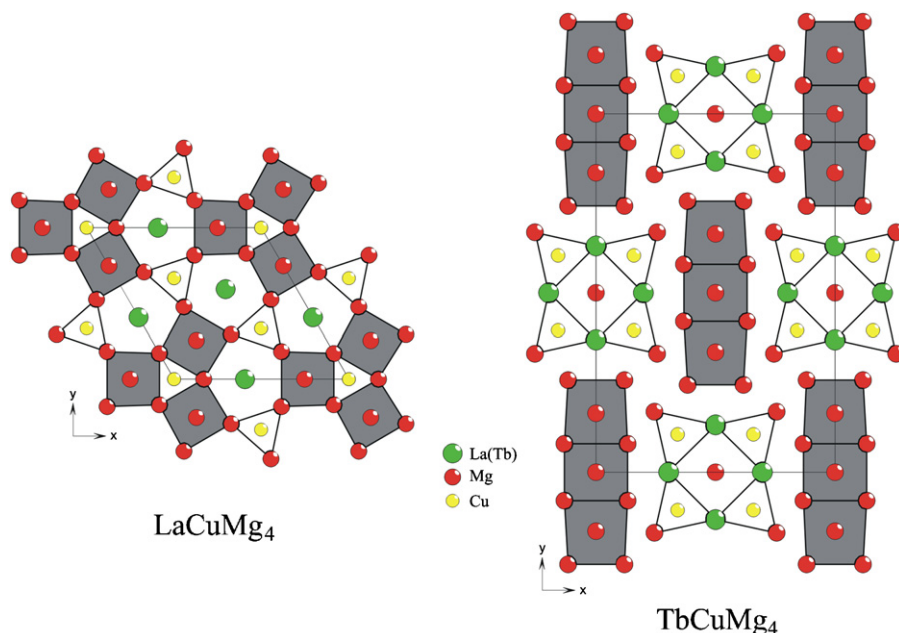


Fig. 7. Slightly distorted body centered Mg blocks as structural motifs in the LaCuMg_4 and TbCuMg_4 compounds.

structure of $\text{Ru}_4\text{Al}_3\text{B}_2$ which in addition to (I) motifs includes distorted CsCl-type cubes. The recently reported $\text{Nd}_4\text{Co}_2\text{Mg}_3$ -type [34] has similar chains of distorted body centered cubes parted by corrugated chains of stacked AlB_2 and CsCl fragments.

The Schläfli symbols for the planar atoms networks reflect well the similarity between TbCuMg_4 ($4^2343 + 4^33 + 4^4$) and $\text{Ru}_4\text{Al}_3\text{B}_2$ ($4^2343 + 4^33$). The ternary IMC $\text{Lu}_5\text{Ni}_2\text{In}_4$ [35], characterized by the presence of AlB_2 and distorted CsCl fragments (ratio 2:8), has the same combination of pentagonal, tetragonal and trigonal prisms around nonequivalent nodes as TbCuMg_4 .

The LaCuMg_4 and TbCuMg_4 compounds are also related between themselves. According to the classification scheme of IMC by Kryp'yakevitch [36], based on the coordination polyhedra of atoms of the smallest size, the crystal structures of the LaCuMg_4 and TbCuMg_4 compounds belong to the same class of compounds with trigonal-prismatic coordination and its derivatives (class no. 10, coordination number $6 + n$, where $n = 0-5$). As the title compounds form in the Mg-rich regions of the corresponding phase diagrams, similar body centered Mg blocks were singled out. In the LaCuMg_4 structure such three blocks share in pairs their edges forming trigonal prisms inside. In TbCuMg_4 , three body centered Mg motifs connect linearly sharing their faces to give separate fragments (see Fig. 7).

4. Conclusions

(1) The crystal structures of the LaCuMg_4 and TbCuMg_4 compounds were studied by X-ray powder diffraction and single crystal methods, respectively.

- (2) LaCuMg_4 crystallizes in the UCoAl_4 -type and represents an interstitial variant of LaCuMg (ZrNiAl-type) by inclusion of Mg_6 blocks; TbCuMg_4 is a new structure type of IMC.
- (3) The structure peculiarities of title compounds as two-layer structures were discussed and their relations with other structure types were described in the way of similar structure fragments packing.
- (4) The same slightly distorted body centered Mg blocks were found in LaCuMg_4 and TbCuMg_4 indicating that a relation exists also between these two structures.
- (5) The results obtained in this work in terms of crystal structures determination and comparison permit us to predict similar crystallochemical features for other RE–T–Mg ternary phases whose crystal structures are still unknown, especially for those with composition close to the line that links the RET (T = 3d metal) binary compound to Mg in the corresponding phase diagrams. The confirmation of such predictions will be the object of our future investigations.

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