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Crystal structure of $RE_{12}Fe_{2+x}Pb_{3-x}$ (RE = Tm, Lu) compounds

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The crystal structures of $Tm_{12}Fe_{2.55}Pb_{2.45}$ and $Lu_{12}Fe_{2.55}Pb_{2.45}$ compounds were refined from X-ray powder diffraction data. The investigated compounds crystallize in the $Er_{12}Fe_2In_3$ structure type (space group *I*4/*mmm*, Pearson code *tI*34) with the lattice parameters $a = 9.6387(5)$, $c = 9.3286(5)$ Å for $Tm_{12}Fe_{2.55}Pb_{2.45}$ and $a = 9.5860(7)$, $c = 9.2428(7)$ Å for $Lu_{12}Fe_{2.55}Pb_{2.45}$.

1. Introduction

A number of compounds with high content of rare-earth element (RE) in the RE-T-In(Pb) systems, where T—transition metal (Fe, Co, Ni), was found recently. For example, compounds crystallizing in the $Sm_{12}Ni_6In$ (space group Im$\bar{3}$, Pearson code *cI*38) [1], Ho_6Co_2Ga (space group *Immm*, Pearson code *oI*36) [2] and $Er_{12}Fe_2In_3$ (space group *I*4/*mmm*, Pearson code *tI*34) [3] structure types form homological series $RE_{3(x+y)}T_{2x}X_y$ (X = In, Pb; *x*—number of RE_3T_2 fragments, *y*—number of RE_3X fragments). The compounds with the $Sm_{12}Ni_6In$ structure type were revealed in some RE–{Co, Ni}–In [1] and RE–{Co, Ni}–Pb [4] systems, the compounds crystallizing in the Ho_6Co_2Ga structure type were found in the RE–Co–In [5–7] and RE–{Co, Ni}–Pb [8,9] systems. The compounds with the $Er_{12}Fe_2In_3$ structure exist only in the systems RE–Fe–In [3]. Considering such similarity of the RE–T–In and RE–T–Pb systems we expected the formation of compounds $RE_{12}Fe_2Pb_3$ with the $Er_{12}Fe_2In_3$ type of structure.

2. Experimental details

Eight samples of the composition $RE_{12}Fe_2Pb_3$ (RE = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were synthesized. The samples, each with a total mass of 1 g, were prepared by arc-melting of pure components (the purity of ingredients is better than 99.9 wt.%) under high-purity argon atmosphere. The ingots were remelted twice to ensure homogeneity. The weight losses after the melting were less than 1%. Homogenizing annealing was carried out at 870 K for 720 h in evacuated quartz tubes. After the thermal treatment, the ampules with samples were quenched in cold water.

X-ray powder diffraction data were collected on automatic diffractometer STOE STADI P with linear PSD detector (transmission mode, $2\theta/\omega$-scan; Cu $K\alpha_1$ radiation, curved germanium [1 1 1] monochromator; 2θ-range $6.0 \le 2\theta \le 124.5^\circ 2\theta$ with step $0.015^\circ 2\theta$; PSD step $0.480^\circ 2\theta$, scan time 300 s/step). The value of linear absorption coefficient was estimated from the logarithmic ratio between the primary beam intensity and its intensity after passing through background and measured samples.

A preliminary data processing, X-ray profile and phase analyses were performed using the STOE WinXPOW (version 2.21) program package [10]. The crystal structure refinement was carried out using the Fullprof software [11].

3. Results and discussion

New compounds were found only in the samples with Tm and Lu as a result of X-ray phase analysis. The presence of additional phases: RE_5Pb_3 [12] was registered for both samples, and besides Lu [13] was observed for the $Lu_{12}Fe_2Pb_3$ sample. The crystal structure of new compounds was refined using Rietveld method. Observed, calculated and difference X-ray diffraction patterns are shown in Fig. 1. The structure was indexed in tetragonal cell. The composition of samples, the reflection intensities and the calculated lattice parameters confirm that compounds crystallize in the $Er_{12}Fe_2In_3$ structure type (space group *I*4/*mmm*, Pearson code *tI*34). Crystal data and details of the structure refinements for the $Tm_{12}Fe_{2.55}Pb_{2.45}$ and $Lu_{12}Fe_{2.55}Pb_{2.45}$ compounds (composition of compounds from structure refinement) are listed in Table 1. During crystal structure refinement of the compounds with $Er_{12}Fe_2In_3$ structure type, Tm (or Lu) atoms were placed in Er atomic positions, namely 16*n* and 8 *h*. Different variants for the location of Fe and Pb atoms were considered. Iron atoms can occupy only 4*e* site (0 0 *z*; *z* ~ 0.38) forming connected Fe2 pairs with acceptable interatomic distances ~2.2 Å, which are, however, unacceptable for Pb atoms. At

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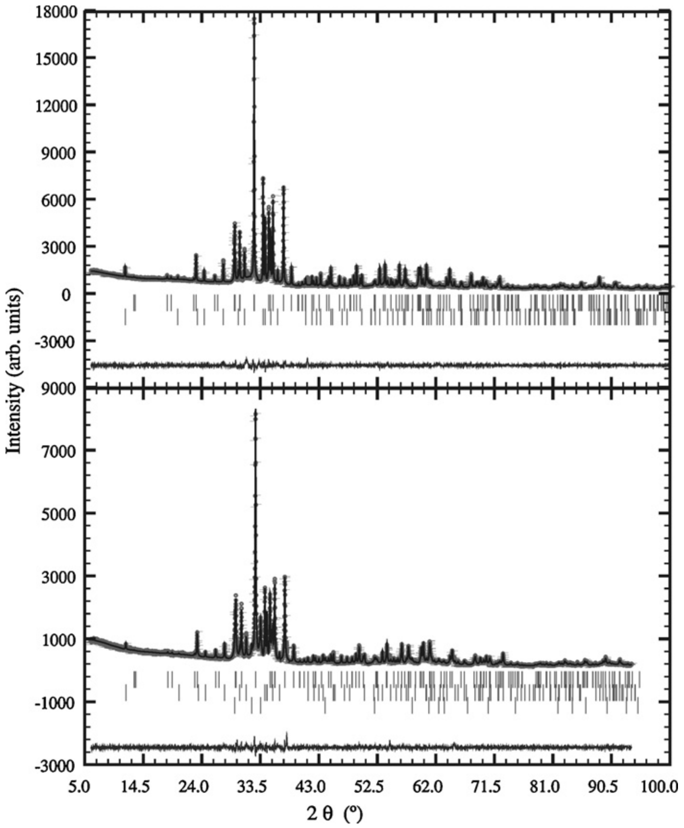

Fig. 1. Observed (●) calculated (—) and difference X-ray diffraction patterns of the plumbides $Tm_{12}Fe_{2.55}Pb_{2.45}$ (tick 1: $Tm_{12}Fe_{2.55}Pb_{2.45}$; tick 2: Tm_5Pb_3) and $Lu_{12}Fe_{2.55}Pb_{2.45}$ (tick 1: $Lu_{12}Fe_{2.55}Pb_{2.45}$; tick 2: Lu_5Pb_3, ticks 3: Lu).

the beginning of refinement Pb atoms were placed in 4*c* and 2*a* sites, taking into account nominal composition of the $RE_{12}Fe_2Pb_3$ alloy and larger coordination numbers of atoms in these positions, comparing to 4*e* position. However, the existence of additional phases R_5Pb_3 (while negligible weight losses during preparation) indicates change of composition of compounds to lower Pb content. Furthermore, inconsistent values of equivalent isotropic displacement parameters in 2*a* Pb site appeared for both samples. The refinement of occupancy parameters at the 2*a* position revealed Pb/Fe mixing. The calculated $Tm_{12}Fe_{2.55}Pb_{2.45}$ and $Lu_{12}Fe_{2.55}Pb_{2.45}$ compositions appeared to be identical for both plumbides. They are very close to the composition of corresponding $Tm_{12}Fe_{2.54}In_{2.46}$ and $Lu_{12}Fe_{2.57}In_{2.43}$ indides [3]. Final positions of the atoms and their thermal parameters for $RE_{12}Fe_{2+x}Pb_{3-x}$ (RE = Tm, Lu) are listed in Table 2.

Projection of the crystal structure of $Tm_{12}Fe_{2.55}Pb_{2.45}$ on the *YZ* plane and the coordination polyhedra of the atoms are shown in Fig. 2. The coordination polyhedra of the thulium atoms are pentagonal prisms with additional atoms (coordination numbers are 13 and 14), for the Fe1 atoms—a square antiprism formed by Tm atoms with the same Fe1 additional atom (CN 9), for the Pb1 atoms—icosahedra [$PbTm_{12}$], and for Fe2/Pb2 statistical mixture—hexahedron [MTm_8]. The coordination sphere of M atoms can also contain 2 atoms of Fe1, located at 3.569(7) Å. Thus, we can assume that coordination number of M atoms is 10. This value is between CN of atoms Pb and Fe what agrees with atomic radii of components.

The interatomic distances (*δ*, Å), the *Δ* values ($\Delta = 100(\delta - \sum r)/\sum r$, where $\sum r$ is the sum of the respective atomic radii) and coordination numbers of the atoms for $Tm_{12}Fe_{2.55}Pb_{2.45}$ compound are listed in Table 3 (values of the atomic radii are taken from [14]: $r(\mathrm{Tm}) = 1.746$ Å, $r(\mathrm{Lu}) = 1.734$ Å, $r(\mathrm{Fe}) = 1.241$ Å, $r(\mathrm{Pb}) = 1.75$ Å. The atomic radii of the mixture of randomly distributed Fe and Pb atoms (M) were calculated using the equations $r(\mathrm{M}) = r(\mathrm{Fe})\cdot\chi(\mathrm{Fe}) + r(\mathrm{Pb})\cdot\chi(\mathrm{Pb})$, $\chi(\mathrm{Fe}) + \chi(\mathrm{Pb}) = 1$, where $\chi(\mathrm{Fe})$ and $\chi(\mathrm{Pb})$ are the iron and lead contents of the statistical mixture ($r(\mathrm{M}) = 1.4955$ Å).

Some Tm–Tm, Tm–M, Tm–Pb interatomic distances are significantly shorter in comparison with the sum of the respective atomic radii. This fact indicates the existence of strong interactions between these atoms. The greatest reduction of the interatomic distances is observed between Fe–Fe atoms ($\Delta = -11.76\%$). Iron atoms form chains of connected pairs. Such pairs of iron atoms are formed in compounds with small content of this element. The rest of interatomic distances in $Tm_{12}Fe_{2.55}Pb_{2.45}$ are equal or larger than the sum of respective atomic radii.

Table 1
Crystal data and structure refinement parameters for the $Tm_{12}Fe_{2.55}Pb_{2.45}$ and $Lu_{12}Fe_{2.55}Pb_{2.45}$ compounds.

Phase	$Tm_{12}Fe_{2.55}Pb_{2.45}$	$Lu_{12}Fe_{2.55}Pb_{2.45}$
Weight fractions of phases, %	$Tm_{12}Fe_{2.55}Pb_{2.45}$, 82.5(10) Tm_5Pb_3,[a] 17.5(4)	$Lu_{12}Fe_{2.55}Pb_{2.45}$, 76.6(10) Lu_5Pb_3,[a] 12.2(4) Lu,[b] 11.2(4)
Structure type	$Er_{12}Fe_2In_3$	$Er_{12}Fe_2In_3$
Space group	*I*4/*mmm*	*I*4/*mmm*
Pearson code	*tI*34	*tI*34
Lattice parameters, Å	*a* = 9.6387(5) *c* = 9.3286(5)	*a* = 9.5860(7) *c* = 9.2428(7)
Volume, Å^3	866.67(8)	849.34(11)
Z	2	2
Density (calc.), g/cm^3	10.261(2)	10.786(3)
Absorption correction, μR_{eff}	1.6	2.5
Profile parameters *U*, *V*, and *W*	0.042(9), 0.009(7), and 0.010(1)	0.03(1), 0.01(1), and 0.014(2)
Asymmetry parameters P_1 and P_2	0.057(8) and 0.014(3)	0.062(5) and 0.003(1)
R_{Bragg}, %	4.27	2.59
R_{F}, %	3.21	1.84
R_{p}, %	4.19	4.87
R_{wp}, %	5.96	6.79

[a] Tm_5Pb_3, Lu_5Pb_3 (Mn_5Si_3 structure type; space group $P6_3/mcm$; $Z = 2$). R1: 6*g* *x* 0 1/4; R2: 4*d* 1/3 2/3 0; Pb: 6*g* *x* 0 1/4 [12]. For Tm_5Pb_3: *a* = 8.8214(5), *c* = 6.4787(4) Å. $x_{R1} = 0.2365(4)$; $x_{Pb} = 0.6041(4)$. $R_{\mathrm{Bragg}} = 7.50\%$, $R_{\mathrm{F}} = 4.47\%$. For Lu_5Pb_3: *a* = 8.7452(7), *c* = 6.4336(6) Å. $x_{R1} = 0.2359(7)$; $x_{Pb} = 0.6045(6)$. $R_{\mathrm{Bragg}} = 5.17\%$, $R_{\mathrm{F}} = 3.54\%$).

[b] Lu (Mg structure type; space group $P6_3/mmc$; $Z = 2$; *a* = 3.5110(4), *c* = 5.5719(3) Å. Lu: 2*c* 1/3 2/3 1/4. $R_{\mathrm{Bragg}} = 3.87\%$, $R_{\mathrm{F}} = 2.46\%$) [13].

Table 2
Atomic and thermal parameters for $RE_{12}Fe_{2+x}Pb_{3-x}$ (RE = Tm, Lu) compounds.

Atom		Occupation	x	y	z	B_{iso}, Å^2
$Tm_{12}Fe_{2.55}Pb_{2.45}$						
Tm1	16*n*	1.00	0	0.2367(2)	0.1939(2)	1.03(8)
Tm2	8*h*	1.00	0.3052(2)	0.3052(2)	0	0.8(1)
Fe1	4*e*	1.00	0	0	0.3826(8)	0.6(2)
Pb1	4*c*	1.00	1/2	0	1/2	1.4(1)
Pb/Fe	2*a*	0.45(1)/0.55(1)	0	0	0	1.2(1)
$Lu_{12}Fe_{2.55}Pb_{2.45}$						
Lu1	16*n*	1.00	0	0.236(3)	0.1936(2)	1.3(1)
Lu2	8*h*	1.00	0.3060(2)	0.3060(2)	0	0.9(1)
Fe1	4*e*	1.00	0	0	0.383(1)	0.2(3)
Pb1	4*c*	1.00	1/2	0	1/2	1.6(1)
Pb/Fe	2*a*	0.45(1)/0.55(1)	0	0	0	2.1(5)

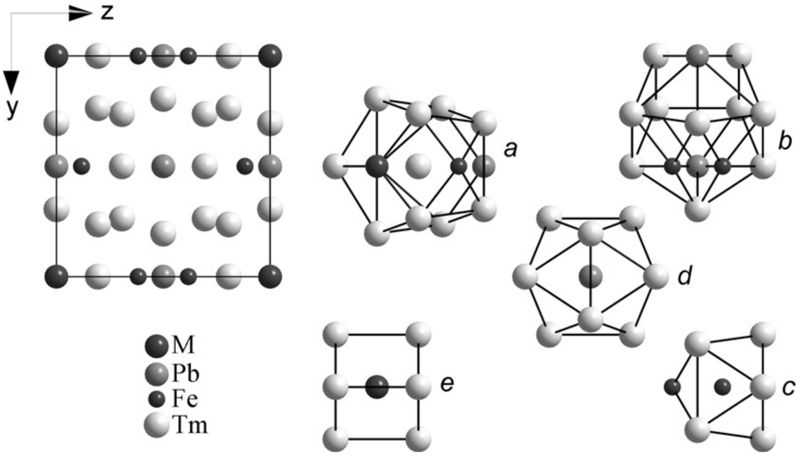

Fig. 2. Projection of the crystal structure of $Tm_{12}Fe_{2.55}Pb_{2.45}$ on the *YZ* plane and the coordination polyhedra of the Tm1 (*a*), Tm2 (*b*), Fe (*c*) atoms, Pb (*d*), *M* (*M* = 0.55Fe + 0.45Pb) (*e*).

Table 3
Interatomic distances (δ, Å), Δ values ($\Delta = 100(\delta - \sum r)/\sum r$), where $\sum r$ is the sum of the respective atomic radii and coordination numbers of the atoms for $Tm_{12}Fe_{2.55}Pb_{2.45}$ compound. *M* = 0.55Fe + 0.45Pb.

Atoms		δ, Å	Δ, %	CN	Atoms		δ, Å	Δ, %	CN
Tm1	1 Fe1	2.882(5)	−11.09	13	Fe1	1 Fe1	2.190(11)	−11.76	9
	1 M	2.912(2)	−10.16			4 Tm2	2.872(3)	−3.85	
	1 Pb1	3.117(2)	−10.84			4 Tm1	2.882(5)	−3.51	
	2 Tm1	3.227(2)	−7.59						
	2 Tm2	3.441(2)	−1.46		Pb1	4 Tm1	3.117(2)	−10.84	12
	2 Tm2	3.516(2)	0.69			4 Tm2	3.490(2)	−0.17	
	Tm1	3.618(3)	3.61			4 Tm1	3.820(2)	9.27	
	2 Tm1	3.739(2)	7.07						
	1 Pb1	3.820(2)	9.27		M	8 Tm1	2.912(2)	−10.16	8 + 2
Tm2	2 Fe1	2.872(3)	−3.85	14		2Fe1	3.569(7)	30.42	
	4 Tm1	3.441(2)	−1.46						
	2 Pb1	3.490(2)	−0.17						
	4 Tm1	3.516(2)	0.69						
	2 Tm2	3.755(3)	7.53						

4. Conclusions

Two new plumbides $RE_{12}Fe_{2+x}Pb_{3-x}$ ($x = 0.55(1)$) with Tm and Lu were synthesized. The compounds crystallize in the $Er_{12}Fe_2In_3$ structure type (space group *I*4/*mmm*, Pearson code *tI*34) with the lattice parameters $a = 9.6387(5)$, $c = 9.3286(5)$ Å for $Tm_{12}Fe_{2.55}Pb_{2.45}$ and $a = 9.5860(7)$, $c = 9.2428(7)$ Å for $Lu_{12}Fe_{2.55}Pb_{2.45}$. These compounds are characterized by partial statistical distribution of Fe and Pb atoms and formation of Fe2 pairs with reduced interatomic distance 2.190 Å.

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