Journal of Alloys and Compounds 647 (2015) 707–710

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Letter

Novel aluminide $CePt_{3-x}Al_x$ of the $CeNi_3$ type structure, with $0.61 < x < 0.81$

Keywords:
Rare-earth intermetallics
Crystal structure
X-ray diffraction

ABSTRACT

This article reports on the synthesis and crystal structure of $CePt_{3-x}Al_x$ ($x = 0.73$). According to single crystal diffraction data, $CePt_{2.27(1)}Al_{0.73(1)}$ compound crystallizes with the $CeNi_3$ – type, space group *P*6_3/*mmc*, lattice parameters: $a = 5.5634(5)$ Å, $c = 16.6658(13)$ Å, Z = 6, $R_1 = 0.033$ for 385 reflections ($I > 2\sigma(I)$). The $CePt_{3-x}Al_x$ compound possesses homogeneity range extends a $0.61 < x < 0.81$, as two crystallographic positions occupied with a mixture of Pt and Al atoms.

1. Introduction

An investigation of the formation and crystal structure of the intermetallic phases existing in the Ce–Pt–Al system was undertaken few years ago. The results of the synthesis, crystal structure and some properties of the twelve obtained ternary phases – CePtAl, $CePtAl_2$, $CePtAl_3$, $CePt_3Al_2$, $Ce_{0.67}Pt_2Al_5$, $Ce_{1.33}Pt_3Al_8$, $CePt_3Al_5$, $Ce_3Pt_4Al_6$, Ce_3Pt_5Al, $Ce_3Pt_5Al_2$, $CePt_2Al_2$ and $Ce_2Pt_9Al_{16}$ – have been reported in papers [1–7]. Three of them – $Ce_3Pt_5Al_2$, Ce_3Pt_5Al, $CePt_3Al_2$ – are located in the Pt-rich region of the Ce–Pt–Al system. All three compounds do not have a homogeneity region. In this part of the system, we have revealed one new intermetallic – $CePt_{3-x}Al_x$ of $CeNi_3$ structure type with an extended homogeneity range. In other Al-containing systems, for example Dy–Fe–Al and Yb–Zn–Al, the compounds with such structure type and homogeneity ranges of various width were found. There is a $DyFe_{3-x}Al_x$ compound with homogeneity range of $0.40 < x < 1.20$ [8] and $YbZn_{3-x}Al_x$ compound with homogeneity range of $0.40 < x < 0.88$ [9]. Herein, we report on synthesis and features of the crystal structure of new intermetallic in the Ce–Pt–Al system.

2. Experimental

The synthesis was performed by the reaction of elemental Ce (99.85%), Pt (99.99%), and Al (99.999%) by arc melting under an argon atmosphere on a water-cooled copper hearth. To ensure homogeneity, the ingots were turned over and remelted several times. The alloys were homogenized in evacuated quartz ampoules by annealing in muffle furnace at 700 °C for 30 days. Then the ampoules were quenched in cold water.

Chemical composition of the $CePt_{3-x}Al_x$ samples with $x = 0.61–0.81$ were investigated by energy-dispersive X-ray spectroscopy carried out using a Carl Zeiss LEO EVO 50XVP electron microscope equipped with an Oxford Instruments EDX INCA Energy 450 analyser. The uncertainty of measurements for each element did not exceed 0.6 at.%.

X-ray analysis was carried out by powder and single-crystal methods. Powder patterns were obtained using an STOE STADI P transmission diffractometer, $CuK_{\alpha1}$ (1.54056 Å), a curved Ge(111) primary beam monochromator and linear position densitive detector. The experimental conditions were $10° < 2\theta < 90°$, step scan 0.01° and counting time 10 s per point. The powder patterns were indexed with the help of the STOE WinXpow v.2.24 program [10]. The refinements of $CePt_{3-x}Al_x$ structures on X-ray powder diffraction data were carried out with FULLPROF [11] and WinPLOTR [12], using pseudo-Voigt functions for peak shape and the Chebyshev's polynomial for the background.

Single crystal of the $CePt_{2.27(1)}Al_{0.73(1)}$ phase was found in the sample of $Ce_{27}Pt_{55}Al_{18}$ composition. Data of single crystal was collected at room temperature on a Bruker–AXS SMART 1000 CCD (MoK_α radiation, $\lambda = 0.71073$ Å). Absorption was considered with the help of SADABS [13]. The structure was solved by direct methods (SHELXS – 97 program [14]) and refined by full-matrix least-squares procedures in the anisotropic approximation (SHELXL – 97 program [14]). Atomic coordinates were standardized with STRUCTURE TIDY [15] and structure was drawn with DIAMOND [16]. The main crystal data and structure refinement parameters for the intermetallic compound $CePt_{3-x}Al_x$ ($x = 0.73$) are summarized in Table 1. The atomic coordinates and equivalent isotropic displacement parameters of the structure are listed in Table 2. Selected interatomic distances are provided in Table 3.

3. Results and discussion

The compound of the fixed composition $CePt_3$ does not exist in the Ce–Pt system. However, the addition of aluminum stabilizes a phase of composition ranging from $CePt_{2.39}Al_{0.61}$ (15.3 at.% Al) to

http://dx.doi.org/10.1016/j.jallcom.2015.06.061
0925-8388/

Table 1
The main crystal data and structure-refinement parameters for the intermetallic compound $CePt_{3-x}Al_x$ (x = 0.73).

Crystal system	Hexagonal
Lattice parameters (Å)	a = 5.5634(5) c = 16.6658(13)
Cell volume (Å^3)	446.72(7)
Space group	$P6_3/mmc$
Formula per unit cell	6
Calculated density (g/cm^3)	13.45
Radiation	MoKα
Linear absorption coefficient (mm^{-1})	121.39
Single crystal sizes (mm)	0.07 × 0.05 × 0.01
Scan range (degrees)	2.44–37.49
Range in *hkl*	$-9 \le h \le 5$ $-8 \le k \le 9$ $-28 \le l \le 27$
Total number of reflection	5529
Independent reflections, R_{int} (F^2)	505, 0.0537
Number of reflections with $I > 2\sigma$	385
Number of the parameters refined	18
Goodness of fit	1.034
R1/wR2 ($I > 2\sigma(I)$)	0.033/0.069
R1/wR2 (all data)	0.051/0.077

Table 2
The atomic coordinates and equivalent isotropic displacement parameters of the structure $CePt_{3-x}Al_x$ (x = 0.73).

Atom	Wyckoff position	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2
Ce1	2*c*	1/3	2/3	3/4	0.0149(3)
Ce2	4*f*	1/3	2/3	0.53878(8)	0.0141(2)
Q*	2*c*	1/3	2/3	1/4	0.0225(16)
E**	2*a*	0	0	0	0.0138(3)
Pt1	12*k*	0.16687(6)	0.33375(12)	0.13153(3)	0.01192(12)
Al1	2*b*	0	0	1/4	0.017(2)

Q* = 0.06(1)Pt + 0.94(1)Al.
E** = 0.76(1)Pt + 0.24(1)Al.

$CePt_{2.19}Al_{0.81}$ (20.3 at.% Al) with hexagonal $CeNi_3$ type of structure.

The new hexagonal phase was found in all eleven prepared samples as a majority phase. The lattice parameters varied for different samples, suggesting the existence of homogeneity range $CePt_{3-x}Al_x$. The EDX data confirmed suggestion about the existence of homogeneity range and allowed to establish the dependence between the x values and the lattice parameters. For most samples, the composition observed from EDX is close to the one of the initial mixture (Table 4). The differences in several cases are mainly caused by the presence of impurities, for example $CePt_2$. X-ray pattern of $CePt_{3-x}Al_x$ (x = 0.66) is shown in Fig. 1.

Table 3
Selected interatomic distances (Å) in the structure of $CePt_{3-x}Al_x$ (x = 0.73).

Atoms	*d*
Ce1–3Q	3.2120(4)
Ce1–3Al1	3.2120(4)
Ce1–12Pt1	3.4112(4)
Ce2–6Pt1	3.1823(7)
Ce2–3Pt1	3.2601(13)
Ce2–3E	3.2764(5)
Ce2–3Ce2	3.4634(4)
Q–6Pt1	2.5439(6)
Q–3Ce1	3.2120(4)
Q–3Al1	3.2120(4)
E–6Pt1	2.7185(6)
E–6Ce2	3.2764(5)
Pt1–Q	2.5439(6)
Pt1–Al1	2.5464(6)
Pt1–E	2.7185(6)
Pt1–2Pt1	2.7783(11)
Pt1–2Pt1	2.7851(11)
Pt1–2Ce2	3.1823(7)
Pt1–Ce2	3.2601(13)
Pt1–Ce1	3.4112(4)
Al1–6Pt1	2.5464(6)
Al1–3Ce1	3.2120(4)
Al1–3Q	3.2120(3)

According to the single crystal determination, in the $CePt_{2.27}Al_{0.73}$ structure the two atomic positions 2a (E) and 2c (Q) of six crystallographically independent ones have mixed occupation of Pt and Al atoms in different proportions. In general, the structure of $CePt_{2.24}Al_{0.76}$ can be presented as a three-dimensional framework of Pt and Al atoms and atoms in mixed positions E (0.76 Pt + 0.24 Al) and Q (0.06 Pt + 0.94 Al). Cerium atoms are located in the voids of the framework (Fig. 2). The structure can be also described as built of three types of layers perpendicular to the direction [001]. The first corrugated layer is formed by cerium atoms and atoms in the E positions (A), as in $MgZn_2$ structure type. Platinum atoms form the Kagome nets (B). Cerium atoms, aluminum atoms and atoms in the Q sites form a planar layer (C). Two last-mentioned layers are observed in the structures of $CePt_5$ and $CePt_3Al_2$ ($CaCu_5$ – type). These three types of layers are packed in the unit cell in a sequence … B′[ABCBA′B′C′B′A]B….

The coordination polyhedron of Q [$Pt_6Ce_3Al_3$] and of Al1 [$Pt_6Ce_3Q_3$] is a distorted hexagonal analogue of cuboctahedron, in which the both bases consist of platinum atoms. Cerium and aluminum (or Q) atoms are alternated by each other in an equatorial plane. The environment of atom in the mixed position E [Pt_6Ce_6] is a distorted icosahedron consisting of six platinum and six cerium atoms. The environment of the Pt1 [$Pt_4Ce_4Al_1Q_1E_1$] atom is also a distorted icosahedron, including one aluminum, four platinum and three cerium atoms and two atoms in the mixed position E and Q. The coordination polyhedron of the Ce1 [$Pt_{12}Al_3Q_3$] atom is a hexagonal prism formed of platinum atoms with the aligned lateral sides of alternating aluminum atoms and atoms in the Q. The Ce2 [$Pt_9Ce_3E_3$] polyhedron can be described as a distorted hexagonal antiprism, in which a bottom basis consists of platinum atoms and a top one consists of alternating cerium atoms and atoms in the E. There are three platinum atoms over the top basis.

The lattice parameter “*a*” of different samples monotonically increases in the range of 5.5016(14)–5.5607(13) Å with the increasing aluminum content, as its atomic radius (1.43 Å) is larger than atomic radius of platinum atom (1.38 Å). In contrast, parameter “*c*” decreases from 16.959(6) to 16.572(4) Å with the increasing aluminum content, because the “*c*” parameter is affected by the interaction of Pt and Al atoms in the mixed position, resulting in the reduction of interatomic distances between the mixed positions from 2.78 Å to 2.54 Å.

Table 4
Cell parameters of $CePt_{3-x}Al_x$ structure and EDX results.

Initial mixture	EDX	Lattice parameters (Å)	
		a	*c*
$CePt_{2.50}Al_{0.50}$	$Ce_{0.98}Pt_{2.40}Al_{0.62}$	5.5016(14)	16.959(6)
$CePt_{2.44}Al_{0.56}$	$Ce_{1.01}Pt_{2.40}Al_{0.59}$	5.5075(15)	16.951(5)
$CePt_{2.36}Al_{0.64}$	$Ce_{0.99}Pt_{2.36}Al_{0.65}$	5.5126(3)	16.909(1)
$CePt_{2.36}Al_{0.64}$	$Ce_{1.00}Pt_{2.30}Al_{0.70}$	5.5168(14)	16.878(4)
$CePt_{2.33}Al_{0.67}$	$Ce_{0.99}Pt_{2.27}Al_{0.74}$	5.5187(15)	16.856(4)
$CePt_{2.28}Al_{0.72}$	$Ce_{0.99}Pt_{2.26}Al_{0.75}$	5.525(6)	16.857(15)
$CePt_{2.25}Al_{0.75}$	$Ce_{0.98}Pt_{2.23}Al_{0.79}$	5.542(5)	16.698(16)
$CePt_{2.24}Al_{0.76}$	$Ce_{1.00}Pt_{2.22}Al_{0.78}$	5.546(5)	16.684(16)
$CePt_{2.20}Al_{0.80}$	$Ce_{1.00}Pt_{2.21}Al_{0.79}$	5.5490(6)	16.6595(14)
$CePt_{2.17}Al_{0.83}$	$Ce_{1.00}Pt_{2.21}Al_{0.79}$	5.5598(13)	16.603(4)
$CePt_{2.16}Al_{0.84}$	$Ce_{1.00}Pt_{2.17}Al_{0.83}$	5.5607(13)	16.572(4)

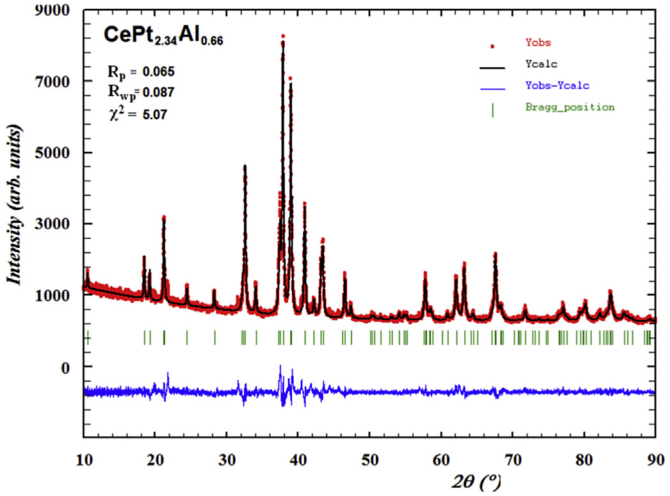

Fig. 1. Observed X-ray powder pattern (crosses) and Rietveld refinement profile (solid line) for the $CePt_{3-x}Al_x$ phase. The Bragg angle positions are indicated by vertical bars. The lower profile gives the difference between observed and calculated data.

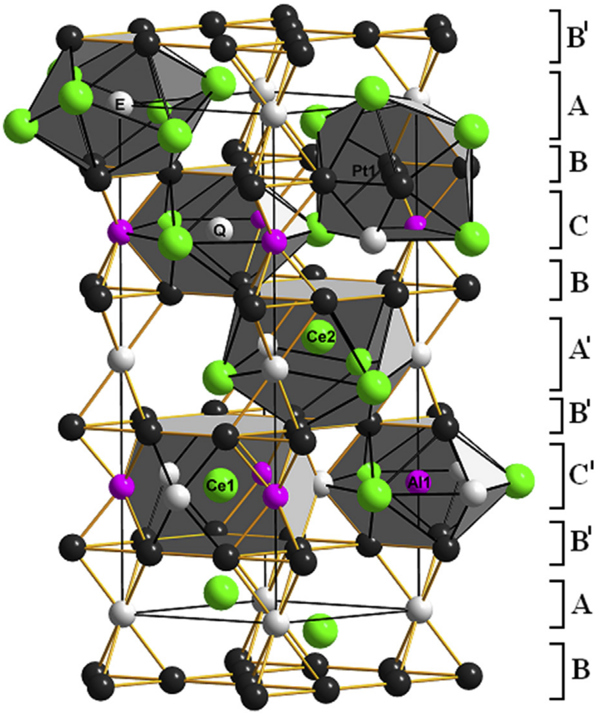

Fig. 2. View of the structure of $CePt_{3-x}Al_x$ and coordination polyhedra for Ce1, Ce2, E, Q, Al1 and Pt1 atoms. The unit cell is outlined.

The variations of the lattice parameters "a" and "c" deviate from the linear dependence which is typical for solid solutions obeying the Vegard's rule. Possibly, this was caused by the irregular distribution of defects in the samples, or covalent interactions that occur between atoms Pt and Al in mixed position.

The change of the lattice parameters "*a*" and "*c*" which occurs in the structure $CePt_{3-x}Al_x$ during the substitution of aluminum for platinum atoms is associated with the interaction between these atoms. A similar increasing of the lattice parameter "*a*" and decreasing of the lattice parameter "*c*" is observed in the structure $CePt_3Al_2$ (a = 5.581 Å; c = 3.949 Å) compared to the structure $CePt_5$ (a = 5.366 Å; c = 4.377 Å). Aluminum atoms in the intermetallic $CePt_3Al_2$ are located in the similar layers with cerium atoms. Platinum atoms form the Kagome nets. The interaction of aluminum atoms and platinum atoms from different layers leads to the reduction of the distance between the layers: Pt–Al interatomic distance 2.548 Å in the structure $CePt_3Al_2$ and analogous Pt–Pt interatomic distance 2.681 Å in the structure CePt5. Resulting in reduction of the lattice parameter "*c*". On the other hand, the reduction of the distance between the layers leads to the "extrusion" of cerium atoms from the layer thereby increasing the parameter "*a*".

The shortest interatomic distances in $CePt_{2.27}Al_{0.73}$ structure occur for Pt1–Al1 (2.5464 Å), Pt1 – Q (2.5439 Å) and Pt1 – E (2.7185 Å). As the mixed Q position consists essentially of aluminum atoms, the Pt1 – Q distance is close to the sum of the covalent radii of platinum (1.29 Å) and aluminum (1.25 Å) atoms [17]. Analogous Pt–Al distance in the $CePt_3Al_2$ structure is 2.548 Å. The Pt1 – E interatomic distance increases to 2.7185 Å, because platinum atoms are larger than aluminum atoms and their content is more in the mixed position E. The Al1 – Q distance is equal to 3.2120 Å that corresponds to a typical metallic bonding. This is in a good agreement with the distance between aluminum atoms (3.220 Å) in the $CePt_3Al_2$ structure. In the Kagome nets, the interatomic distances between platinum atoms in $CePt_{2.27}Al_{0.73}$ and in $CePt_3Al_2$ are close and equal to 2.7783–2.7851 Å and 2.790 Å, respectively [1].

The substitution of aluminum for platinum atoms in $CePt_{3-x}Al_x$ compound occurs in two crystallographic positions – 2(a) and 2(c). It was determined that aluminum atoms statistically replace platinum atoms only in the layers containing cerium atoms. Other sites are fully occupied by cerium 2(c), 4(f); platinum 12(k) and aluminum 2(b) atoms. On the other hand, substitution of aluminum atoms for atoms of transition metal is observed in the different sites in the $YbZn_{3-x}Al_x$ and the $DyFe_{3-x}Al_x$ compounds. In the $YbZn_{3-x}Al_x$ compound, aluminum and zinc atoms statistically occupy two crystallographic position 2(a) and 12(k). Zinc atoms occupy two crystallographic positions 2(c) and 2(b). In the $DyFe_{3-x}Al_x$ compound iron atoms occupy three crystallographic position 2(a), 2(b) and 2(c). The crystallographic position 12(k) is statistically occupied by aluminum and iron atoms.

4. Conclusions

The crystal structure of the $CePt_{2.27}Al_{0.73}$ compound of the Ce–Pt–Al system has been determined. This is the first compound with so large homogeneity range found in the Ce–Pt–Al system.

Acknowledgment

The work was performed at User Facilities Center of M.V.Lomonosov Moscow State University under support of Ministry of Education and Science of Russia, Contract N16.552.11.7081 and RFBR (research Grant No. 15-03-04434).

References

[1] C. Schank, F. Jahrling, L. Luo, A. Grauel, C. Wassilew, R. Borth, G. Olesch, C.D. Bredl, C. Geibel, F. Steglich, 4f-conduction electron hybridization in ternary Ce-TM-Al compounds, J. Alloys Comp. 207 (1994) 329–332.
[2] E.V. Murashova, A.I. Tursina, N.G. Bukhanko, A.V. Gribanov, I.V. Chernyshev, Yu D. Seropegin, Ternary compounds $Ce_{0.67}Pt_2Al_5$ and $Ce_{1.33}Pt_3Al_8$, J. Alloys Compd. 398 (2005) 100–105.
[3] A.I. Tursina, N.G. Bukhanko, A.V. Gribanov, V.A. Shchelkunov, Y.V. Nelyubina, A new ternary aluminide, $CePt_3Al_5$, J. Acta Crystallogr. E61 (2005) 285–286.
[4] A.I. Tursina, A.V. Gribanov, N.G. Bukhanko, P. Rogl, Y.D. Seropegin, Crystal structure of the novel compound $Ce_3Pt_4Al_6$, J. Chem. Met. Alloys 1 (2008) 62–66.
[5] A. Tursina, H. Noël, E. Murashova, Y. Morozova, Y. Seropegin, Crystal structures of the new intermetallics Ce_3Pt_5Al and $Ce_3Pt_5Al_2$, J. Chem. Met. Alloys

7 (2014) 15–19.

[6] N.G. Bukhanko, A.V. Gribanov, H. Kaldarar, Novel $CePt_2Al_2$: crystal structure and physical properties, in: Book of Abstracts of 16th International Conference on Solid Compounds of Transition Elements, Dresden, Germany, July 26-31, 2008, p. 162.

[7] A.I. Tursina, E.V. Murashova, H. Noël, N.G. Bukhanko, Y.D. Seropegin, Crystal structure and magnetic properties of the new intermetallic $Ce_2Pt_9Al_{16}$, J. Intermet. 17 (2009) 780–783.

[8] H. Österreicher, D. McNeely, Studies on compounds $DyFe_3$, Dy_6Fe_{23} and Dy_2Fe_{17} with Al substitution for Fe, J. Less Common Met. 53 (1977) 235–243.

[9] D. Mazzone, P. Manfrinetti, M.L. Fornasini, Phases in the Al-Yb-Zn system between 25 and 50 at% ytterbium, J. Solid State Chem. 182 (2009) 2344–2349.

[10] STOE WINXPOW, Program Package for the Operation of Powder Diffractometers and Analysis of Powder Diffractograms, Version 2.24.

[11] J. Rodriguez-Carvajal, FULLPROF: a program for rietveld refinement and pattern matching analysis, in: Book of Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr., Toulouse, France, July 16-19, 1990, p. 127.

[12] T. Roisnel, J. Rodriguez-Carvajal, WinPLOTR: a Windows tool for powder diffraction patterns analysis, in: Materials Science Forum (EPDIC 7), Barcelona, Spain, May 20-23, 2000, p. 118.

[13] G.M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.

[14] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr. A64 (2008) 112–122.

[15] L.M. Gelato, E. Parthe, STRUCTURE TIDY - a computer program to standardize crystal structure data, J. Appl. Crystallogr. 20 (1987) 139–143.

[16] G. Bergerhoff, DIAMOND, Gerhard – DomagkStrab, 1.53121 Bonn, Germany, 1996.

[17] J. Emsley, The Elements, Clarendon Press, Oxford, 1989.

Yu Morozova*, Zh Kurenbaeva, S. Dunaev, E. Murashova
Department of Chemistry, Lomonosov Moscow State University,
119991 Leninskie Gory 1/3, Moscow, Russia

* Corresponding author.
E-mail address: yu.s.morozova@gmail.com (Y. Morozova).

29 April 2015