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Crystal Structure of New Compounds in the *RE*–Ag–Al Systems

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The crystal structure of new ternary aluminides $Ce_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$ with $x = 0.39$, $y = 0.18$ ($Dy_{2-x}(Ag_{0.46}Al_{0.54})_{17}Ag_y$ ($x = 0.25$, $y = 0.23$)-type structure), $a = 9.3742(2)$, $c = 9.1525(3)$ Å, $R = 0.059$), and $Ce(Ag_{0.58}Al_{0.42})_{11}$ ($BaCd_{11}$-type structure, $a = 11.0466(3)$, $c = 7.1101(5)$ Å, $R = 0.066$) have been determined using X-ray powder diffraction data and Rietveld least squares refinement. Isotypic compounds $RE_{1.6}(Ag, Al)_{17}$ ($Dy_{2-x}(Ag_{0.46}Al_{0.54})_{17}Ag_y$-type structure) with *RE* = La, Pr, Nd, and Sm and *RE*(Ag, Al)$_{11}$ ($BaCd_{11}$-type structure) with *RE* = La and Eu have been synthesized and their lattice constants have been determined.

INTRODUCTION

During the investigation of the Ce–Ag–Al system phase diagram we found two new ternary compounds with approximate compositions: $Ce_8Ag_{42}Al_{50}$ and $Ce_8Ag_{52}Al_{40}$. This paper presents the results of crystal structure determination of the above compounds and search for isotypic compounds with other light rare-earths (*RE*).

EXPERIMENTAL

Samples for investigation were prepared by direct arc melting of constituent elements, namely: *RE* metals with a purity of 99.5 wt%, Ag (99.9 wt%) and Al (99.99 wt%) under purified argon atmosphere. Ingots were then annealed at 870 K during 1200 hr in evacuated quartz ampules and quenched in cold water. Phase analysis was carried out using X-ray powder diffraction patterns obtained by Debye–Scherrer technique with nonfiltered Cr*K* radiation. The full profile diffraction data were collected on automated powder diffractometer DRON-3M using filtered Cu*K*α radiation (θ–2θ scan technique with the step of 0.05° and exposition time of 20–30 sec in every point) and refined using Rietveld full profile method. X-Ray powder diffraction patterns of the isotypic compounds were recorded on powder diffractometer in continuous mode using germanium as standard (stated purity 99.99 wt%, $a = 5.6573(2)$ Å). The lattice parameters (Table 1) were refined by full matrix least-squares. All calculations were performed using the CSD program package created by Aksel'rud *et al.* (1).

STRUCTURE REFINEMENT

The powder diffraction pattern of compound with approximate composition $Ce_8Ag_{42}Al_{50}$ was indexed on the basis of hexagonal unit cell with lattice parameters listed in Table 1. Previously we have reported the crystal structure of the compound $Dy_{2-x}(Ag_{0.46}Al_{0.54})_{17}Ag_y$ ($x = 0.25$, $y = 0.23$) (own-type structure, derivative of the Th_2Ni_{17}-type structure) with similar composition and lattice parameters (2). Calculation of theoretical intensities for the compound $Ce_8Ag_{42}Al_{50}$ assuming atomic parameters as found for $Dy_{2-x}(Ag_{0.46}Al_{0.54})_{17}Ag_y$ proved the same structure. Refinement of the occupancy parameters revealed the statistical distribution of silver and aluminum atoms in the following positions 4(*f*), 6(*g*), 12(*j*), and 12(*k*) and partial occupancy of the position 2(*b*) by cerium atoms. Differential Fourier synthesis showed a significant maximum in the site position 4(*e*) which corresponds to a partially occupied position (9.1(8)%) by silver atoms as it was in the structure of $Dy_{2-x}(Ag_{0.46}Al_{0.54})_{17}Ag_y$. Therefore we found that the compound composition could be described by the formula $Ce_{3.22(2)}Ag_{14.4(2)}Al_{19.6(2)}Ag_{0.36(3)}$ or $Ce_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$ with $x = 0.39$, $y = 0.18$.

Final atomic positional and thermal parameters (corresponding residual values are: $R_p = 0.123$, $R_i = 0.059$) are listed in Table 2. Table 3 illustrates the agreement between observed and calculated intensities of the reflections for $Ce_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$ structure. The coordination numbers and coordination polyhedra of atoms in this structure are the same as in the $Dy_{2-x}(Ag_{0.46}Al_{0.54})_{17}Ag_y$ structure (2). Ternary aluminides $RE_{1.6}Ag_{7.5}Al_{9.5}$ with *RE* = La, Pr, Nd, Sm have the same structure as $Ce_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$ and their lattice parameters are listed in Table 1.

X-Ray powder diffraction pattern of compound with approximate composition $Ce_8Ag_{52}Al_{40}$ was indexed assuming tetragonal unit cell with the lattice parameters $a = 11.04(1)$, $c = 7.11(2)$ Å. Analysis of the literature data about crystal structures of related compounds (3, 4) allows us to assume the $BaCd_{11}$-type structure for this com-

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TABLE 1

Lattice Parameters and Unit Cell Volumes of the Compounds $RE_{2-x}(Ag, Al)_{17}Ag_y$ and $RE(Ag, Al)_{11}$

Compound	*a*, Å	*c*, Å	V, Å^3
$La_{1.6}Ag_{7.5}Al_{9.5}$[a]	9.408(3)	9.144(5)	700.9
$Ce_{1.61}Ag_{7.38}Al_{9.8}$[a]	9.3742(2)	9.1525(3)	698.08
$Pr_{1.6}Ag_{7.5}Al_{9.5}$[a]	9.357(2)	9.102(4)	690.1
$Nd_{1.6}Ag_{7.5}Al_{9.5}$[a]	9.344(3)	9.130(5)	690.3
$Sm_{1.6}Ag_{7.5}Al_{9.5}$[a]	9.318(4)	9.111(9)	685.1
$LaAg_6Al_5$[b]	11.065(2)	7.123(2)	872.1
$CeAg_{6.39}Al_{4.61}$[b]	11.0466(3)	7.1101(5)	867.63
$EuAg_5Al_6$[b]	11.080(5)	7.110(4)	872.9

[a] Compounds with $Dy_{2-x}(Ag_{0.46}Al_{0.54})_{17}Ag_y$-type structure.

[b] Compounds with $BaCd_{11}$-type structure.

TABLE 2

Crystal Data and Results of the Structures Refinements for $Ce_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$ ($x = 0.39$, $y = 0.18$) and $Ce(Ag_{0.58}Al_{0.42})_{11}$

Compound	$Ce_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$	$Ce(Ag_{0.58}Al_{0.42})_{11}$
Structure type	$Dy_{2-x}(Ag_{0.46}Al_{0.54})_{17}Ag_y$	$BaCd_{11}$
Space group	$P6_3/mmc$	$I4_1/amd$
Diffractometer	Powder, DRON-3M, Cu$K\alpha$, graphite monochromator	
2θ limits	18–120°	14–120°
Mode of refinement	Full profile	
Number of variables	20	11
Number of possible reflections	227	179
R_i, R_p	0.059, 0.123	0.066, 0.132

Positional and thermal parameters

$Ce_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$	$Ce(Ag_{0.58}Al_{0.42})_{11}$
1.22(2)Ce : 2(*b*) 0 0 $\frac{1}{4}$, $B = 0.24(12)$ Å^2; 2Ce : 2(*d*) $\frac{1}{3}$ $\frac{2}{3}$ $\frac{3}{4}$, $B = 0.23(6)$ Å^2; 0.36(3)Ag : 4(*e*) 0 0 *z*, $z = 0.581(4)$, $B = 0.50(4)$ Å^2; 4T1(1.71(4)Ag + 2.29(4)Al) : 4(*f*) $\frac{1}{3}$ $\frac{2}{3}$ *z*, $z = 0.1053(4)$, $B = 0.40(9)$ Å^2; 6T2(2.49(5)Ag + 3.51(5)Al) : 6(*g*) $\frac{1}{2}$ 0 0, $B = 0.20(10)$ Å^2; 12T3(4.38(7)Ag + 7.62(7)Al) : 12(*j*) *x y* $\frac{1}{4}$, $x = 0.3307(5)$, $y = 0.3677(4)$, $B = 0.64(6)$ Å^2; 12T4(5.86(8)Ag + 6.14(8)Al) : 12(*k*) *x* 2*x* *z*, $x = 0.1630(2)$, $z = 0.9784(2)$, $B = 0.59(6)$ Å^2	4Ce : 4(*a*) 0 $\frac{3}{4}$ $\frac{1}{8}$, $B = 0.40(8)$ Å^2; 4Ag : 4(*b*) 0 $\frac{1}{4}$ $\frac{3}{8}$, $B = 0.94(10)$ Å^2 8T1(4.33(6)Ag + 3.67(6)Al) : 8(*d*) 0 0 $\frac{1}{2}$, $B = 1.5(2)$ Å^2; 32T2(17.2(2)Ag + 14.8(2)Al) : 32(*i*) *x y z*, $x = 0.1197(3)$, $y = 0.4550(2)$, $z = 0.1735(4)$, $B = 1.12(8)$ Å^2

TABLE 3

List of Observed (I_o) and Calculated (I_c) Intensities for the Compounds $Ce_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$ ($x = 0.39$, $y = 0.18$) and $Ce(Ag_{0.58}Al_{0.42})_{11}$

$Ce_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$							$Ce(Ag_{0.58}Al_{0.42})_{11}$					
h	*k*	*i*	*l*	d_c	I_c	I_o	*h*	*k*	*l*	d_c	I_c	I_o
1				2	3	4	5			6	7	8
0	1	$\bar{1}$	0	8.128	31	30	0	1	1	5.979	30	38
0	2	$\bar{2}$	1	3.711	37	35	1	1	2	3.236	123	116
1	1	$\bar{2}$	2	3.274	240	235	2	3	1	2.814	239	240
1	2	$\bar{3}$	1	2.909	83	80	0	4	0	2.762	100	99
0	1	$\bar{1}$	3	2.855	68	70	1	3	2	2.492	999	1000
0	3	$\bar{3}$	0	2.706	369	371	2	4	0	2.470	657	654
0	2	$\bar{2}$	3	2.439	471	472	0	1	3	2.317	216	215
2	2	$\bar{4}$	0	2.344	758	750	0	4	2	2.181	107	112
0	3	$\bar{3}$	2	2.329	1000	999	0	5	1	2.110	292	291
0	0	0	4	2.288	343	349	3	4	1	2.110	260	259
1	2	$\bar{3}$	3	2.163	142	144	2	4	2	2.028	228	230
2	2	$\bar{4}$	2	2.086	499	502	2	5	1	1.971	71	77
1	1	$\bar{2}$	4	2.056	96	100	1	5	2	1.850	36	37
0	4	$\bar{4}$	1	1.981	41	40	0	6	0	1.841	30	25
2	3	$\bar{5}$	1	1.825	59	60	0	0	4	1.778	22	22
0	3	$\bar{3}$	4	1.747	39	41	1	4	3	1.778	53	53
1	4	$\bar{5}$	2	1.652	101	98	4	5	1	1.676	36	37
2	2	$\bar{4}$	4	1.637	167	167	3	5	2	1.672	90	92
2	3	$\bar{5}$	3	1.590	107	110	2	2	4	1.618	89	92
1	2	$\bar{3}$	5	1.572	76	78	2	5	3	1.551	23	30
3	3	$\bar{6}$	0	1.562	42	45	0	7	1	1.541	32	42
3	3	$\bar{6}$	2	1.478	158	160	2	4	4	1.443	95	104
1	1	$\bar{2}$	6	1.451	47	50	5	5	2	1.430	161	166
0	5	$\bar{5}$	3	1.433	31	32	1	7	2	1.430	120	123
2	4	$\bar{6}$	3	1.371	103	106	0	8	0	1.381	39	42
0	6	$\bar{6}$	0	1.353	221	225	1	5	4	1.374	44	44
0	3	$\bar{3}$	6	1.329	198	190	1	8	1	1.345	17	19
1	5	$\bar{6}$	3	1.316	48	50	4	7	1	1.345	38	41
2	3	$\bar{5}$	5	1.306	56	53	3	7	2	1.343	26	28
2	5	$\bar{7}$	2	1.250	39	42	0	3	5	1.326	46	44
0	2	$\bar{2}$	7	1.244	33	30	3	5	4	1.296	63	63
4	8	$\overline{12}$	0	1.235	107	105	2	6	4	1.246	84	83

pound. Intensity calculations were performed using positional parameters as follows: Ce in 4(*a*) and the smaller Ag and Al atoms in all other occupied positions in $BaCd_{11}$ structure. Calculated intensities agreed with the observed powder patterns. Finally we have established atomic distribution in this structure as shown in Table 2. Thus the compound has the composition $CeAg_{6.39(5)}Al_{4.61(5)}$ or $Ce(Ag_{0.58}Al_{0.42})_{11}$ which agrees quite well with the initial sample composition. Refinement of atomic positional and thermal parameters taking into account texture (texture parameter along [0 0 1] axis is equal to 0.85(1)) resulted in residuals: $R_p = 0.132$, $R_i = 0.066$. The list of observed and calculated intensities for $Ce(Ag_{0.58}Al_{0.42})_{11}$ is given in Table 3.

Composition and lattice parameters of isotypic compounds formed with other rare-earth metals are listed in Table 1.

DISCUSSION

We have analyzed the interatomic distances in structures of the compounds investigated. The shortest interatomic distances are 2.649(2) Å (T1–T1) and 2.645(6) Å (T2–T2) for $Ce_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$ and $Ce(Ag_{0.58}Al_{0.42})_{11}$ respectively. They are shorter than the corresponding sum of classical metallic radii of Ag and Al by as much as 8%. Such a shortening of interatomic distances is normal for intermetallic compounds with metallic-type bonding.

Linear decreasing of the cell volumes of $Dy_{2-x}(Ag_{0.42}Al_{0.58})_{17}Ag_y$-type compounds from La to Sm (Table 1) indicates the same valent state of *RE* atoms in these compounds. From other investigated compounds with $BaCd_{11}$-type structure the $Eu(Ag, Al)_{11}$ has the largest unit cell volume. It may indicate that Eu is partially divalent in this compound.

Present investigation permits us to compare *RE*–Ag–Al systems with studied earlier *RE*–Cu–Al ones. Ternary compounds with Th_2Ni_{17}- and Th_2Zn_{17}-type structures and/or related ones are formed in both *RE*–Cu–Al and *RE*–Ag–Al systems. In all investigated systems the copper (or silver) content in Th_2Zn_{17}-type compounds is higher than the correspondent content in Th_2Ni_{17}-type ones. It may be a reason, that such phenomenon is caused by the electron concentration change resulted from the substitution of Cu (or Ag) atoms by Al ones.

Compounds with $BaCd_{11}$-type structure are forming in *RE*–{Cu, Ag}–Al systems only with light rare-earths.

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