JOURNAL OF SOLID STATE CHEMISTRY 114, 342–345 (1995)

Crystal Structure of $CaCu_{0.15}Ga_{3.85}$—A New Variant of the $BaAl_4$ Structure Type: Structure Analysis from X-Ray Powder Diffraction Data

Yu. Grin,[1] M. Ellner, and B. Predel

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Seestrasse 92, D-70174 Stuttgart, Germany

and

B. Baumgartner

STOE Application Laboratory, Hilpertstrasse 10, D-64295 Darmstadt, Germany

Received November 10, 1993; in revised form April 19, 1994; accepted April 20, 1994

The new intermetallic compound $CaCu_{0.15}Ga_{3.85}$ was found during the investigation of the stability of the $BaAl_4$ structure type in ternary gallium-containing systems. The crystal structure has been investigated by means of a powder diffraction technique. The experimental diffraction data set has been obtained by the use of a Ge(111) primary monochromator and a linear position sensitive detector. The sample was measured in transmission mode using $CuK\alpha_1$ radiation in the range from 10° to 130° in 2θ with a step width of 0.02°. Unit cell parameters have been determined by means of automatic indexing and refined from the diffraction angles of 45 reflections: monoclinic system, $a = 11.5741(2)$ Å, $b = 4.2264(1)$ Å, $c = 4.3573(1)$ Å, $\beta = 110.499(1)°$, $V = 199.65(1)$ Å^3, space group $C2/m$. Full profile refinement of coordinate and anisotropic thermal displacement parameters led to the residual values $R(I) = 0.058$ and $R(P) = 0.155$ for all 193 reflections possible in the range measured. The final values of the atomic coordinates are as follows: 2Ca in 2(a) 0 0 0, $B_{eq} = 1.0(2)$ Å^2; 4$(Ga_{0.962}Cu_{0.038})$1 in 4(i) $x0z$, $x = 0.3858(1)$, $z = 0.4099(5)$, $B_{eq} = 0.50(7)$ Å^2; 4$(Ga_{0.962}Cu_{0.038})$2 in 4(i), $x = 0.2524(2)$, $z = 0.7764(4)$, $B_{eq} = 0.66(7)$ Å^2. Atomic coordination numbers are 20 for Ca, 9 for $(Ga_{0.962}Cu_{0.038})$1, and 12 for $(Ga_{0.962}Cu_{0.038})$2. The shortest interatomic distances are observed between gallium (copper) atoms: 2.485, 2.568, 2.605, and 2.655 Å. The structure of $CaCu_{0.15}Ga_{3.85}$ is the first representative of a new structure type and is described as a distorted variant of the $BaAl_4$ structure type: $(a, b, c)_{CaCu_{0.15}Ga_{3.85}} = (a, b, c)_{BaAl_4} \times (1, 0, 1; 1, 0, 0; 0, 1, 0)$. Isotypic compounds were found in the ternary systems {Ca, Yb}–{Ni, Pd, Pt, Cu, Ag, Au}–Ga.

INTRODUCTION

The $BaAl_4$ type of structure is very significant among the ternary gallides of rare earth (alkaline earth) and transition metals. A large group of ternary phases in the systems *RE*–{Co, Ni, Cu, Pd, Ag, Pt, Au}–Ga (see, for example, (1)) and {Ca, Sr, Ba}–{Ag, Au}–Ga (2) has been found to have this type of structure. The binary gallides rarely have the 1 : 4 stoichiometry and this structure type; exceptions are $EuGa_4$ (3), $SrGa_4$ (4), and $BaGa_4$ (4). The structure of the compounds $CaGa_4$ (5) and $YbGa_4$ (6) can be described as the monoclinically distorted variant of the $BaAl_4$ type. Another way to stabilize this structural motive in the systems mentioned above is the building of the defect derivatives: for example, the $RE_3Ag_xGa_{11-x}$ phases with the La_3Al_{11} structure type (7) or the new compound $Yb_3Au_{5.5}Ga_{5.5}$ with its own structure type (8). During the investigation of the stability of the $BaAl_4$ structure type in the ternary gallium-containing systems, we found new phases with a constant content of 20 at.% of Yb or Ca and a very small amount of the transition metal. The aim of this work was the structural analysis of the new compounds found.

EXPERIMENTAL

The samples, each with a total mass of about 2.5 g, were prepared from stoichiometric amounts of ingots of the elements with a minimum purity of 99.9 mass% in tantalum crucibles in a high-frequency furnace under argon (5*N* purity grade, Messer–Griesheim). Weight losses were found to be within 0.5 mass%. Homogenization heat treatment was performed for 300 hr at 600°C

[1] To whom correspondence should be addressed at Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70506 Stuttgart, Germany.

0022-4596/95 $6.00

on samples wrapped in protective molybdenum foil and sealed in evacuated silica tubes, and was followed by quenching in cold water.

For the crystallographic characterization of the phases found, Enraf–Nonius Guinier FR552 cameras with monochromatized Cu$K\alpha_1$ or Fe$K\alpha_1$ radiation were used.

The experimental diffraction data set was obtained on a STOE STADI P focusing monochromatic beam diffractometer (9) equipped with a curved Ge(111) primary monochromator and a linear position sensitive detector. The samples were measured in transmission mode using Cu$K\alpha_1$ radiation in the range from 10° to 130° in 2θ with a step width of 0.02°.

Data treatment, structure solution, and presentation were performed using the CSD (crystal structure determination) program package (10).

RESULTS AND DISCUSSION

Phase Formation

Ternary phases with the composition RM_xGa_{4-x} have been found in the 11 systems {Ca, Yb}–{Ni, Cu, Pd, Ag, Pt, Au}–Ga. Some of them exist in a narrow temperature range: the characteristic powder pattern of $YbPd_{0.1}Ga_{3.9}$ and $YbPt_{0.125}Ga_{3.875}$ can be recorded only immediately after heat treatment at 600°C, as the material is unstable with time. The as-cast samples and the samples heat treated at the lower temperature (400°C) reveal mainly the original $BaAl_4$ structure type. No ternary compound with the new structure type was found in the Ca–Pt–Ga system. The solid solution of Pt in $CaGa_4$ was found at 600°C in the sample $Ca_{20}Pt_2Ga_{78}$, and the sample $Ca_{20}Pt_3Ga_{77}$ always had the original $BaAl_4$ structure after heat treatment at 600°C.

The new phases found are probably formed by chemical reaction with a small amount of liquid or without a liquid phase. No single crystals suitable for structure determination were obtained. Therefore, the crystal structure of the $CaCu_{0.15}Ga_{3.85}$ and $CaAg_{0.15}Ga_{3.85}$ samples has been investigated by the powder diffraction method.

Structure Solution

Diffraction angles and peak intensities for the $CaCu_{0.15}Ga_{3.85}$ compound have been evaluated from the total diffraction profile. Unit cell parameters have been determined by means of automatic indexing and refined from the diffraction angles of 45 reflections: monoclinic system, $a = 11.5741(2)$ Å, $b = 4.2264(1)$ Å, $c = 4.3573(1)$ Å, $\beta = 110.499(1)°$, $V = 199.65(1)$ Å^3, with possible space groups $C2/m$, $C2$, and Cm. The structure solution was determined in the space group $C2/m$ by means of direct methods. The atomic coordinates of all three independent atoms in the unit cell were evaluated using the reflections with $E > 1.0$. Full profile refinement of coordinate and anisotropic thermal displacement parameters led to the residual values $R(I) = 0.058$ and $R(P) = 0.155$ for all 193

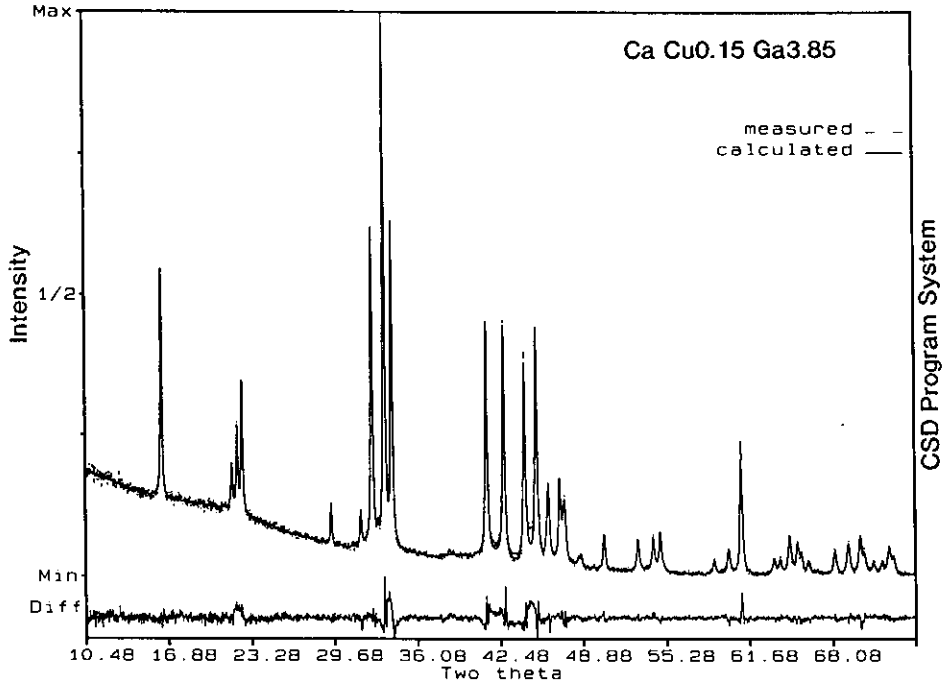

FIG. 1. Measured (---) and calculated (—) diffraction profiles for $CaCu_{0.15}Ga_{3.85}$ are shown in the upper graph. The lower graph depicts differences in the same scale.

TABLE 1
Structural Data of Ca(Cu, Ag,)$_{0.15}$Ga$_{3.85}$ Compounds
($CaCu_{0.15}Ga_{3.85}$ Structure Type, Space Group $C2/m$)

Composition	$Ca_{20}Cu_3Ga_{77}$	$Ca_{20}Ag_3Ga_{77}$
a (Å)	11.5741(2)	11.5749(2)
b (Å)	4.2264(1)	4.2654(1)
c (Å)	4.3573(1)	4.3670(1)
β (°)	110.499(1)	110.753(1)
Ca in 2(a) 000		
B	1.0(2)	0.20(1)
$X1$ in 4(i) $x0z$		
$X1$	0.962Ga + 0.038 Cu	0.962Ga + 0.038Ag
x	0.3858(1)	0.3868(2)
z	0.4099(5)	0.4076(6)
B	0.50(7)	0.69(5)
$X2$ in 4(i) $x0z$		
$X2$	0.962Ga + 0.038Cu	0.962Ga + 0.038Ag
x	0.2524(2)	0.2531(3)
z	0.7764(2)	0.7725(6)
B	0.66(7)	0.62(5)
Type of data	Powder, full profile	Powder, full profile
Number of reflections	193	195
R(I)	0.0577	0.0959
R(P)	0.1550	0.2124
d(Ca–$X1$) (Å)	3.235(1)	3.248(2)
	3.314(1)	3.330(2)
d(Ca–$X2$) (Å)	3.377(2)	3.410(3)
	3.421(2)	3.418(3)
d(Ca–Ca) (Å)	4.2264(1)	4.2654(1)
	4.3573(1)	4.3670(1)
d($X1$–$X1$) (Å)	2.485(2)	2.452(3)
d($X1$–$X2$) (Å)	2.568(2)	2.585(4)
	2.605(2)	2.624(2)
	2.655(3)	2.653(4)
d($X2$–$X2$) (Å)	2.883(2)	2.933(3)
	3.184(2)	3.177(3)

reflections possible in the range measured. The experimental and calculated diffraction profiles for the Ca $Cu_{0.15}Ga_{3.85}$ compound are shown in Fig. 1.

The final values of the atomic coordinates are listed in Table 1. In view of the small difference between the scattering factors of Cu and Ga and the very small amount of copper in the structure, no refinement of the occupation coefficients for the $X1$ and $X2$ site positions was performed. No significant preferences in the distribution of the transition metal atoms between the two possible sites could be detected during the refinement of the structure of the isotypic $CaAg_{0.15}Ga_{3.85}$ compound. Refinement was performed with isotropic thermal displacement coefficients. The structural data are given in Table 1.

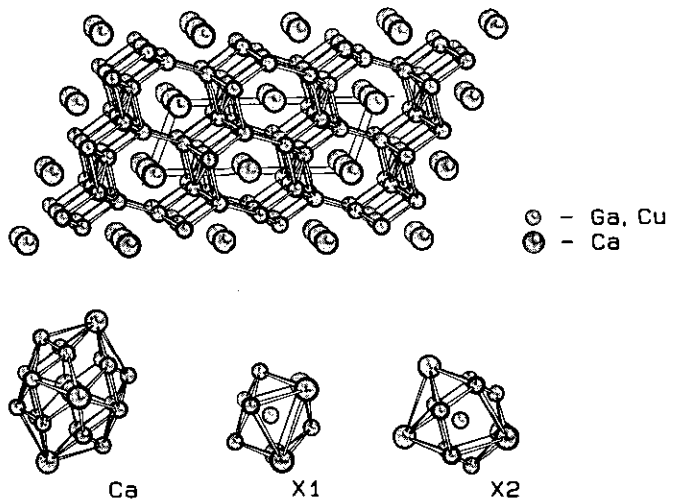

FIG. 2. The structure view of $CaCu_{0.15}Ga_{3.85}$ along the y axis and the coordination polyhedra of the atoms.

Crystal Chemistry

The crystal structure of the $CaCu_{0.15}Ga_{3.85}$ compound is the first representative of a new structure type. The space view of the structure and the coordination polyhedra of all atoms are presented in Fig. 2. The coordination number of the Ca atoms is 20; they are located in the large holes of the gallium (copper) atom framework outlined in Fig. 2. Gallium (copper) atoms have coordination numbers of 9 for the $X1$ site (the coordination polyhedron is a tetragonal antiprism with an additional vertex in front of the basic face) and 12 for the $X2$ site (the coordination polyhedron is a strongly distorted cubooctahedron). The interatomic distances observed between gallium (copper) atoms (see Table 1) are significantly shorter than the sum of the atomic radii (r_{Ga} = 1.39, r_{Cu} = 1.28, and r_{Ca} = 1.97 Å).

All atomic environments are very similar to those in the $BaAl_4$ type of structure, which confirms the close relationship between these two structure types. In fact, all phases having the $CaCu_{0.15}Ga_{3.85}$ structure are located on the isothermal section (600°C) of the ternary phase diagrams between the binary compounds $CaGa_4$ (or $YbGa_4$) and are ternary phases with the $BaAl_4$ type of structure. Therefore, the structure of $CaCu_{0.15}Ga_{3.85}$ can be described as a distorted variant of the $BaAl_4$ structure type with the unit cell relationship $(a, b, c)_{CaCu_{0.15}Ga_{3.85}}$ =

TABLE 2
Crystallographic Data of the RT_xGa_{4-x} Compounds ($CaCu_{0.15}Ga_{3.85}$ Structure Type, Space Group $C2/m$)

Composition	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
$Ca_{20}Cu_3Ga_{77}$	11.5741(2)	4.2264(1)	4.3573(1)	110.499(1)	199.65(1)
$Ca_{20}Ag_3Ga_{77}$	11.5749(2)	4.2654(1)	4.3670(1)	110.753(1)	201.62(1)
$Ca_{20}Au_3Ga_{77}$	11.6495(8)	4.2572(3)	4.3519(4)	110.632(5)	201.99(8)
$Ca_{20}Ni_2Ga_{78}$	11.5481(9)	4.2460(8)	4.3548(6)	110.65(1)	199.81(10)
$Ca_{20}Pd_2Ga_{78}$	11.5414(2)	4.2750(9)	4.3626(2)	110.70(2)	201.35(8)
$Yb_{20}Cu_3Ga_{77}$	11.4816(5)	4.2204(4)	4.3382(2)	110.594(6)	196.79(7)
$Yb_{20}Ag_{2.5}Ga_{77.5}$	11.5189(6)	4.2613(6)	4.3404(3)	110.857(8)	199.09(8)
$Yb_{20}Au_3Ga_{77}$	11.5574(4)	4.2519(4)	4.3364(2)	110.666(4)	199.38(6)
$Yb_{20}Ni_2Ga_{78}$	11.4839(9)	4.2482(8)	4.3326(3)	110.760(10)	197.65(12)
$Yb_{20}Pd_2Ga_{78}$	11.4818(4)	4.2397(3)	4.3442(2)	110.626(5)	197.91(6)
$Yb_{20}Pt_{2.5}Ga_{77.5}$	11.5435(7)	4.2540(6)	4.3214(4)	110.913(7)	198.03(11)

$(a, b, c)_{BaAl_4} \times (1, 0, 1; 1, 0, 0; 0, 1, 0)$. The structure of the $CaGa_4$ type shows the next step of the distortion: $(a, b, c)_{CaGa_4} = (a, b, c)_{BaAl_4} \times (1, -1, 0; 0.5, -0.5, 0.5; 1, 1, 0)$. The deformation stage is remarkably dependent on the concentration: small amounts of transition metal replacing gallium in the binary $CaGa_4$ (or $YbGa_4$) compounds again restore the original $BaAl_4$ type of structure.

Isotypic Compounds

The compounds isotypic to $CaCu_{0.15}Ga_{3.85}$ and $CaAg_{0.15}Ga_{3.85}$ have been found in chemically related ternary systems of ytterbium or calcium with gallium and transition metals of nickel or copper groups. The unit cell parameters were refined from the X-ray Guinier powder patterns and are shown in Table 2. A contraction of the unit cell volume of the ternary phases compared to binary $CaGa_4$ (or $YbGa_4$) compounds has been observed in all cases ($V_{CaGa_4} = 202.8$ Å^3 (5), $V_{YbGa_4} = 200.0$ Å^3 (11)). The unit cell volume contraction for YbM_xGa_{4-x} compounds in all cases is larger than that for the isotypic calcium phases (Fig. 3).

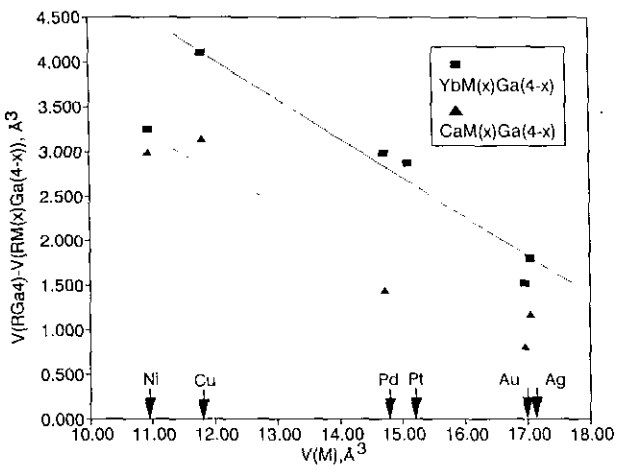

FIG. 3. Unit cell volume contraction $V_{RGa_4} - V_{RM_xGa_{4-x}}$ versus effective atomic volume of the transition metal (V_M) for the ternary compounds with the $CaCu_{0.15}Ga_{3.85}$ type of structure.

ACKNOWLEDGMENT

This work was supported by the Deutsche Forschungsgemeinschaft.

REFERENCES

1. Yu. N. Grin, P. Rogl, K. Hiebl, F. E. Wagner, and H. Noël, *J. Solid State Chem.* **70,** 168 (1987).
2. G. Cordier, G. Dörsam, and C. Rohr, *J. Less-Common Met.* **166,** 115 (1990).
3. P. I. Kripyakevich, E. I. Gladyshevsky, and D. I. Dzyana, *Kristallografiya* **10,** 471 (1965).
4. G. Bruzzone, *Acta Crystallogr.* **18,** 1081 (1965).
5. G. Bruzzone, M. L. Fornasini, and F. Merlo, *J. Less-Common Met.* **154,** 67 (1989).
6. S. Cirafici and M. L. Fornasini, *J. Less-Common Met.* **163,** 331 (1990).
7. Yu. N. Grin, M. Ellner, K. Hiebl, P. Rogl, O. M. Myakush, and O. M. Sichevich, *J. Solid State Chem.* **105,** 399 (1993).
8. Yu. Grin, M. Ellner, B. Predel, and K. Peters, *J. Alloys Compounds* **201,** 209 (1993).
9. "STOE Automatic X-Ray Powder Diffractometer Systems." STOE&Cie, Darmstadt, 1992.
10. L. G. Akselrud, Yu. N. Grin, P. Yu. Zavalii, V. K. Pecharski, and V. S. Fundamentski, *in* "Twelfth European Crystallogr. Meeting, Collected Abstracts, Moscow," Vol. **3,** p. 155. 1989.
11. Yu. N. Grin, M. Ellner, K. Hiebl, and P. Rogl, *J. Alloys Compounds* **196,** 207 (1993).