Chemistry of Metals and Alloys

Chem. Met. Alloys 2 (2009) 183-186
Ivan Franko National University of Lviv
www.chemetal-journal.org

Crystal structure of the ternary gallide ErZnGa

Oleg MYKHALICHKO[1]*, Roman GLADYSHEVSKII[1], Viktor HLUKHYY[2], Thomas FÄSSLER[2]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine*
[2] *Department of Inorganic Chemistry with Focus on New Materials, Technical University of Munich, Lichtenbergstrasse 4, 85747 Garching, Germany*
* *Corresponding author. Tel.: +380-32-2394163; e-mail: olegchem@gmail.com*

Received December 4, 2009; accepted December 23, 2009; available on-line April 27, 2010

Single crystals of the ternary compound ErZnGa were synthesized by induction melting. The crystal structure, characterized by an ordered distribution of all atoms, was determined by means of X-ray single-crystal diffraction (diffractometer STOE IPDS IIT, Mo *Kα* radiation): structure type LiGaGe (ordered derivative of the $CaIn_2$ type), Pearson symbol *hP*6, space group $P6_3mc$, a = 4.3928(6), c = 7.0367(14) Å.

Erbium / Zinc / Gallium / Single-crystal X-ray diffraction / Crystal structure / Ordering derivative structure

Introduction

The search for isostructural intermetallic compounds in closely related ternary systems *R*–*T*–*X* (*R* – rare-earth metal, *T* – transition metal, *X* – *p*-element) with the purpose to study the influence of electronic factors on the formation of the crystal structure of compounds with appropriate physical, chemical and mechanical properties is an important task of modern materials science [1]. In the ternary system Er–Cu–Ga the formation of a solid solution of substitution type, based on the binary compound $ErCu_2$ (structure type KHg_2, Pearson symbol *oI*12, space group *Imma*) has been reported [2-5]. In this phase the Ga atoms are able to substitute for half (or even more [6]) of the Cu atoms, achieving the composition ErCuGa. The ternary system Er–Zn–Ga, which is closely related to Er–Cu–Ga, has not yet been studied systematically. In this system the interaction between the components leads to the formation of the ternary compound ErZnGa. For this compound the cell parameters were determined (a = 4.393, c = 7.048 Å) from X-ray powder diffraction [7] and the structure type $CaIn_2$ (Pearson symbol *hP*6, space group $P6_3/mmc$ [8]) was assigned.

The aim of the present work was synthesis of the single crystals of the ErZnGa ternary compound and their precise investigation by means of XRD and EDX analyses.

Experimental

An alloy of nominal composition ErZnGa was synthesized from the pure elements (≥ 99.99 at.% of the main component), which where sealed under argon into a niobium container, and heated in a high-frequency furnace (TIG 2.5/300, Hüttinger Elektronik) at 1300°C for 70 minutes. Then the alloy was slowly cooled to room temperature, which led to the formation of single crystals in the form of hexagonal plates.

A well-faceted single crystal was extracted from the alloy, mounted on a glass fiber and X-ray diffraction data were collected at room temperature on a Stoe IPDS IIT diffractometer (Mo *Kα* radiation, λ = 0.71073 Å) equipped with an Imaging Plate detector. An analytical absorption correction was applied using X-Shape/X-Red software [9,10]. No significant variation of the intensities was observed during the data collection.

The crystal structure of ErZnGa was solved by direct methods and refined by a least-squares method using the program package WinGX [11]. Hexagonal symmetry and the cell parameters a = 4.3928(6), c = 7.0367(14) Å indicated a $CaIn_2$- (space group $P6_3/mmc$) or LiGaGe-type (space group $P6_3mc$) structure [12]. In the former the Zn and Ga atoms statistically occupy a site in Wyckoff position 4*f*, whereas in the latter they occupy two independent

Table 1 Experimental details and crystallographic data for ErZnGa.

Composition	ErZnGa
Formula weight, M_r	302.35
Structure type	LiGaGe
Pearson symbol	*hP*6
Space group	$P6_3mc$
Unit-cell parameters: *a*, Å	4.3928(6)
c, Å	7.0367(14)
Cell volume *V*, Å^3	117.59(3)
Formula units per cell *Z*	2
Density D_X, g cm^{-3}	8.539
Absorption coefficient μ, mm^{-1}	56.398
Crystal size, mm	0.05×0.05×0.02
Color	metallic grey
F(000)	258
Radiation, wavelength λ, Å	Mo $K\alpha$, 0.71073
# of reflections: measured	1764
independent	128
with $I \geq 2\sigma(I)$	117
Reliability factor R_{int}	0.1112
Range of *h*, *k*, *l*	$-5 \leq h \leq 5$, $-5 \leq k \leq 5$, $-8 \leq l \leq 8$
Range θ, °	5.36-27.03
Reliability factors: R ($I \geq 2\sigma(I)$)	0.0521 (0.0482)
wR ($I \geq 2\sigma(I)$)	0.1034 (0.0996)
S	1.366
# of refined parameters	11
Weighting scheme	$1/[(\sigma F_o)^2+(0.0668P)^2]$, $P = (F_o^2 + 2F_c^2)/3$
Residual electron density: $\Delta\rho_{max}$, e Å^{-3}	3.707
$\Delta\rho_{min}$, e Å^{-3}	-3.259
Extinction coefficient [13]	0.041(11)

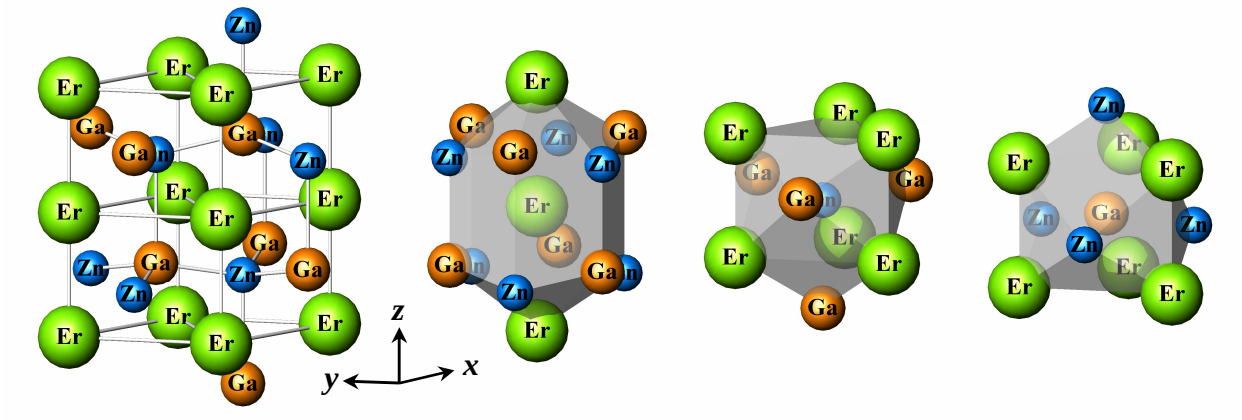

Fig. 1 Atom arrangement and coordination polyhedra in the structure of ErZnGa.

positions 2*b*. It is not possible to state with certainty based on X-ray diffraction data that the Zn and Ga atoms (30 and 31 electrons, respectively) adopt an ordered atom arrangement, however, good interatomic distances (δ(Er-Zn) shorter than δ(Er-Ga)) and displacement parameters were obtained for the refinement in the noncentrosymmetric space group $P6_3mc$. Crystal data and details of the data collection and structure refinement are given in Table 1.

Additionally, the chemical composition of the single crystal was checked by means of energy dispersive X-ray analysis using a scanning electron microscope JEOL SEM 5900LV. The obtained composition agrees well with the nominal composition of the synthesized alloy (Table 2).

Results and discussion

The least-squares refinement confirmed the classification of the ErZnGa structure into the LiGaGe type [12]. The refined atom coordinates and

Table 2 Results of the X-ray spectral analysis of the single crystal ErZnGa.

Element	Content, at. %	Accuracy of analysis, at. %
Er	33.6	± 3.9
Zn	33.8	± 5.1
Ga	32.6	± 5.0

Table 3 Atomic coordinates and displacement parameters ($Å^2$) for ErZnGa (*hP*6, $P6_3mc$, a = 4.3928(6), c = 7.0367(14) Å).

Site	Wyckoff position	x	y	z	U_{eq}
Er	2*a*	0	0	0.000(3)	0.0139(7)
Zn	2*b*	1/3	2/3	0.7140(3)	0.015(3)
Ga	2*b*	1/3	2/3	0.2798(11)	0.015(3)

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Er	0.0089(7)	U_{11}	0.0238(10)	$1/2U_{11}$	0	0
Zn	0.007(4)	U_{11}	0.031(10)	$1/2U_{11}$	0	0
Ga	0.008(3)	U_{11}	0.028(9)	$1/2U_{11}$	0	0

Table 4 Interatomic distances (δ) and coordination numbers (CN) of the atoms in the structure of ErZnGa (*hP*6, $P6_3mc$, a = 4.3928(6), c = 7.0367(14) Å).

Atoms		δ, Å	CN
Er	– 3 Zn	2.949(11)	14
	– 3 Ga	2.972(11)	
	– 3 Ga	3.211(13)	
	– 3 Zn	3.238(13)	
	– 2 Er	3.5184(7)	
Zn	– 3 Ga	2.5782(15)	10
	– 3 Er	2.949(11)	
	– 1 Ga	3.055(8)	
	– 3 Er	3.238(13)	
Ga	– 3 Zn	2.5782(15)	10
	– 3 Er	2.972(11)	
	– 1 Zn	3.055(8)	
	– 3 Er	3.211(13)	

displacement parameters are listed in Table 3. The structure of the ternary compound ErZnGa can be considered as an ordered derivative of the $CaIn_2$ type [8], the realization of which is accompanied by lowering of the hexagonal symmetry ($P6_3/mmc \rightarrow P6_3mc$). The content of the unit cell and the coordination polyhedra of the three independent atom positions in the structure of ErZnGa are shown in Fig. 1. Comparing the unit cells of the structures of $CaIn_2$ (space group $P6_3/mmc$) and ErZnGa ($P6_3mc$) (Fig. 2) one can see that in the structure of ErZnGa the four-fold position of the small-size atoms (4*f*, $P6_3/mmc$), which in the structure type $CaIn_2$ is occupied by In atoms, is split into two two-fold (already not restrained by a mirror plane *m*) positions (2*b*, $P6_3mc$). Each of crystallographically independent positions 2*b* is occupied by Zn and Ga atoms. In the ordered derivative of the $CaIn_2$ type, LiGaGe ($P6_3mc$) [12], the Li atoms occupy the positions of the Er atoms, the Ga and Ge atoms the positions of the Zn and Ga atoms in the structure of ErZnGa.

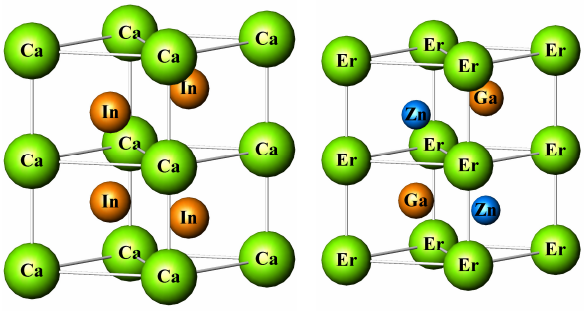

Fig. 2 Unit cells of the structures of $CaIn_2$ and ErZnGa.

The coordination polyhedra of the atoms in the structure of ErZnGa (see Fig. 1) are identical to the polyhedra in the structures of $CaIn_2$ and LiGaGe: distorted hexagonal prisms with centered bases around the Er atoms, and trigonal prisms formed by Er atoms capped by four Ga or Zn atoms forming a tetrahedron around the Zn and Ga atoms. The interatomic distances within the coordination polyhedra are listed in Table 4. Their values show a good correlation with the sum of the atomic radii of the components. A considerable shortening of the interatomic distances in the investigated structure is not observed.

Conclusions

The structure of the ternary compound ErZnGa belongs to the LiGaGe type (Pearson symbol *hP*6, space group $P6_3mc$, a = 4.3928(6), c = 7.0367(14) Å). Its noncentrosymmetric structure is an ordered derivative of $CaIn_2$ type (Pearson symbol *hP*6, space group $P6_3/mmc$). The Er atoms occupy the positions of the Li atoms, the Zn and Ga atoms the positions of the Ga and Ge atoms in the structure of LiGaGe.

Acknowledgements

This work was supported by the Ministry of Ukraine for Education and Science under the grant No. 0109U002070 and by a Leonhard Euler stipendium of DAAD.

References

[1] J.H. Westbrook, R.L. Fleischer (Eds.), *Intermetallic Compounds*, John Wiley & Sons, Chichester, 2008, 276 p.
[2] Yu.N. Grin, R.E. Gladyshevskii, *Gallides*, Metallurgia, Moscow, 1989, 304 p. (in Russian).
[3] P. Villars, M. Berndt, K. Brandenburg, K. Cenzual, J. Daams, F. Hulliger, T. Massalski, H. Okamoto, K. Osaki, A. Prince, H. Putz, S. Iwata (Eds.), *The Pauling File, Binaries Edition*, Crystal Impact, Bonn, 2002.
[4] F. Sommer, J. Schott, B. Predel, *J. Less-Common Met.* 125 (1986) 175-181.
[5] V.Ya. Markiv, N.N. Belyavina, T.I. Zhunkovskaya, *Dopov. Akad. Nauk Ukr. RSR, Ser. A* (2) (1985), 84-88.
[6] M.L. Fornasini, A. Iandelli, F. Merlo, M. Pani, *Intermetallics* 8 (2000) 239-246.
[7] A. Iandelli, *J. Less-Common Met.* 169 (1991) 187-196.
[8] A. Iandelli, *Z. Anorg. Allg. Chem.* 330 (1964) 221-232.
[9] *X-RED (1.26) Data Reduction Program*, Stoe & Cie, Darmstadt, 2004.
[10] *X-SHAPE (2.05) Crystal Optimization for Numerical Absorption Correction*, Stoe & Cie, Darmstadt, 2004.
[11] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837-838.
[12] W. Bockelmann, H. Jacobs, H.U. Schuster, *Z. Anorg. Allg. Chem.* 410 (1974) 233.
[13] G.M. Sheldrick, *Acta Crystallogr. A* 64 (2008) 112-122.