Chemistry of
Metals and Alloys

Chem. Met. Alloys 11 (2018) 1-5
Ivan Franko National University of Lviv
www.chemetal-journal.org

Interaction of the components in the system Lu–Ag–Ge at 500°C

Bohdana BELAN[1]*, Mykola MANYAKO[1], Roman GLADYSHEVSKII[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
* *Corresponding author. Tel.: +380-32-2394506; e-mail: bohdanabelan@gmail.com*

Received May 1, 2018; accepted June 27, 2018; available on-line January 1, 2019

The isothermal section of the phase diagram of the Lu–Ag–Ge system at 500°C was investigated based on X-ray diffraction and microstructure analysis. The binary compound $LuAg_2$ (structure type $MoSi_2$, Pearson symbol *tI*6, space group *I*4/*mmm*) was found to dissolve up to 20 at.% Ge: *a* = 3.6297(6)-3.6292(6), *c* = 9.191(7)-9.2341(7) Å. The other binary compounds of the Lu–Ag and Lu–Ge systems dissolve not more than 5 at.% of the third component. The ternary compound LuAgGe (structure type ZrNiAl, Pearson symbol *hP*9, space group *P*-62*m*, *a* = 7.0677(4), *c* = 4.1665(3) Å) was confirmed. An additional, new phase with unknown structure was observed in an alloy of nominal composition $Lu_{52}Ag_9Ge_{39}$.

Lutetium / Silver / Germanium / Phase diagram / Crystal structure / Ternary compound

Introduction

The results presented in this paper are part of a systematic study of *R*–Ag–Ge systems, where *R* is a rare-earth metal, carried out at the Department of Inorganic Chemistry of the Ivan Franko National University of Lviv. Among the ternary systems with rare-earth metals of the yttrium subgroup, only the Y–Ag–Ge and Ho–Ag–Ge systems have so far been studied in the full concentration range [1,2]. Two compounds were found in the system with yttrium: one of them, $YAg_{1.4\text{-}1.0}Ge_{0.6\text{-}1.0}$, crystallizes in the structure type ZrNiAl (Fe_2P) [3] and the other one, $Y_3Ag_4Ge_4$, in the structure type $Gd_3Cu_4Ge_4$ [1]. Only one compound, HoAgGe (structure type ZrNiAl), was found in the Ho–Ag–Ge system [2]. No significant solubility of the third component was observed in any of the binary compounds. Preliminary data on our investigation of the Lu–Ag–Ge system were presented at a conference [4].

Among the binary systems that delimit the Lu–Ag–Ge ternary system, the Lu–Ge and Ag–Ge systems have been studied in the full concentration range, whereas the Lu–Ag system has only been investigated in the Ag-rich part [5]. Compounds do not form in the Ag–Ge system. The information available on the binary compounds in the Lu–Ge and Lu–Ag systems [6,7] may be summarized as follows: $LuGe_2$ (structure type $ZrSi_2$, Pearson symbol *oS*12, space group *Cmcm*), Lu_2Ge_3 ht (AlB_2, *hP*3, *P*6/*mmm*), Lu_2Ge_3 rt (vacancy derivative of the AlB_2 type), Lu_3Ge_4 (Er_3Ge_4, *oS*28, *Cmcm*), $Lu_{11}Ge_{10}$ ($Ho_{11}Ge_{10}$, *tI*84, *I*4/*mmm*), Lu_5Ge_4 ht (Sm_5Ge_4, *oP*36, *Pnma*), Lu_5Ge_3 (Mn_5Si_3, *hP*16, *P*6_3/*mcm*), $LuAg_4$ ($MoNi_4$, *tI*10, *I*4/*m*), $LuAg_2$ ($MoSi_2$, *tI*6, *I*4/*mmm*), LuAg (CsCl, *cP*2, *Pm*-3*m*).

In this paper we present the results of an investigation of the Lu–Ag–Ge ternary system at 500°C. The structure of the compound LuAgGe (structure type ZrNiAl, space group *P*-62*m*) [3], was confirmed by a complete refinement.

Experimental

The samples were synthesized from high-purity metals (Lu ≥ 99.98 wt.%, Ag ≥ 99.9 wt.%, Ge ≥ 99.99 wt.%) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. To achieve high efficiency of the interaction between the components, the samples were melted twice. The alloys were then annealed at 500°C in evacuated quartz ampoules for three weeks, and subsequently quenched in cold water. Phase analysis of 65 samples was performed by X-ray powder diffraction (RKD-57.3 camera, Cr *K* radiation). The lattice parameters were refined from diffractometer data (diffractometer DRON-3.0, Cu *Kα* radiation) and complete crystal structure refinements (diffractometer STOE Stadi P, Cu $K\alpha_1$ radiation;

program DBWS-9807 [8]) were carried out applying the Rietveld method. The microstructures were studied visually using a Neophot-30 microscope.

Results

Fig. 1 shows the result of the investigation of the interaction of the components in the Lu–Ag–Ge system by X-ray diffraction and microstructural analysis in the whole concentration range at 500°C.

The existence of three binary compounds in the Lu–Ag system ($LuAg_4$, $LuAg_2$, LuAg) and of four of the seven compounds reported in the Lu–Ge system [6] was confirmed at 500°C: Lu_5Ge_3 (structure type Mn_5Si_3), $Lu_{11}Ge_{10}$ ($Ho_{11}Ge_{10}$), Lu_3Ge_4 (Er_3Ge_4), and $LuGe_2$ ($ZrSi_2$). The compound Lu_5Ge_4 (Sm_5Ge_4) only exists at high temperature and the α-modification of the compound Lu_2Ge_3 (derivative of AlB_2) was not observed.

The investigation showed that the binary compound $LuAg_2$ (structure type $MoSi_2$, space group *I*4/*mmm*) dissolves up to 20 at.% Ge: $a = 3.6297(6)$-$3.6292(6)$, $c = 9.191(7)$-$9.2341(7)$ Å. The cell parameters of the Mn_5Si_3-type phase in the alloy of composition $Lu_{62.5}Ag_5Ge_{32.5}$ were $a = 8.262(2)$, $c = 6.201(4)$ Å, in good agreement with literature data for the binary compound Lu_5Ge_3 [7], which seems to exclude significant solubility of silver. The change of the cell parameters ($a = 3.991(1)$-$3.996(2)$, $b = 15.571(3)$-$15.603(1)$, $c = 3.850(1)$-$3.556(2)$ Å) within the homogeneity range of the solid solution based on the compound $LuGe_2$ (structure type $ZrSi_2$) indicates slight solubility of silver. The other binary compounds of the Lu–Ag and Lu–Ge systems do also not dissolve more than 5 at.% of the third component.

The phase equilibria were confirmed by visual microstructure analysis. The $Lu_{33.3}Ag_{26.7}Ge_{40}$ and $Lu_{33.3}Ag_{21.7}Ge_{45}$ alloys were two-phase, which indicates that a two-phase region exists between the binary compound $LuGe_2$ and the ternary compound LuAgGe. The microstructure of the alloy $Lu_{31}Ag_9Ge_{60}$ confirmed the existence of a three-phase region defined by these two compounds and elementary Ge. The three-phase region between the binary compounds LuAg and Lu_5Ge_3 and elementary Lu was established by microstructural analysis of the alloys $Lu_{62.5}Ag_{25}Ge_{12.5}$, $Lu_{62.5}Ag_{20}Ge_{17.5}$, and $Lu_{62.5}Ag_{15}Ge_{22.5}$. In total, the isothermal section of the phase diagram of the Lu–Ag–Ge system at 500°C consists of 12 single-phase, 23 two-phase and 12 three-phase regions.

The existence of the ternary compound LuAgGe with ZrNiAl structure type [3] was confirmed in the Lu–Ag–Ge system at the temperature of the investigation. In addition, a new phase with unknown structure was observed in the alloy of composition $Lu_{52}Ag_9Ge_{39}$.

Gibson *et al.* [3] determined the cell parameters of the ternary compound LuAgGe ($a = 7.0125$, $c = 4.1337$ Å) and identified the structure as belonging to the structure type ZrNiAl (space group *P*-62*m*). A complete structure determination was carried out here, using powder diffraction data collected at room temperature. The cell parameters, $a = 7.0677(4)$, $c = 4.1665(3)$ Å, are in good agreement with the literature data. The atomic coordinates and isotropic displacement parameters are given in Table 1. No deviations from a stoichiometric ZrNiAl-type structure were observed.

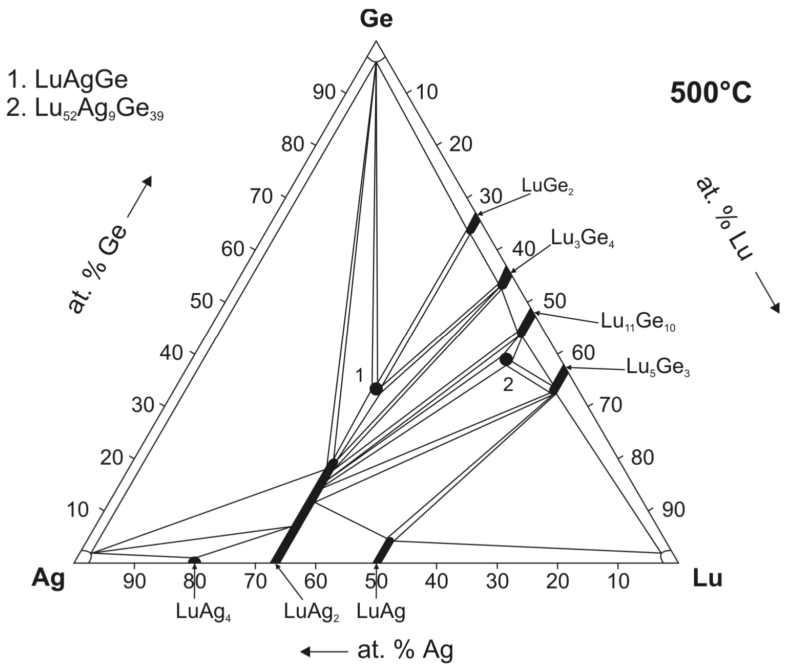

Fig. 1 Isothermal section of the phase diagram of the Lu–Ag–Ge system at 500°C.

Table 1 Atomic coordinates and isotropic displacement parameters for LuAgGe: structure type ZrNiAl, Pearson symbol *hP*9, space group *P*-62*m*, $R_p = 0.0508$, $R_{wp} = 0.0815$, $R_B = 0.1113$.

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Lu	3*f*	0.5813(5)	0	0	0.7(1)
Ag	3*g*	0.2542(9)	0	½	1.5(2)
Ge1	2*d*	⅓	⅔	0	0.7(2)
Ge2	1*a*	0	0	0	0.7(2)

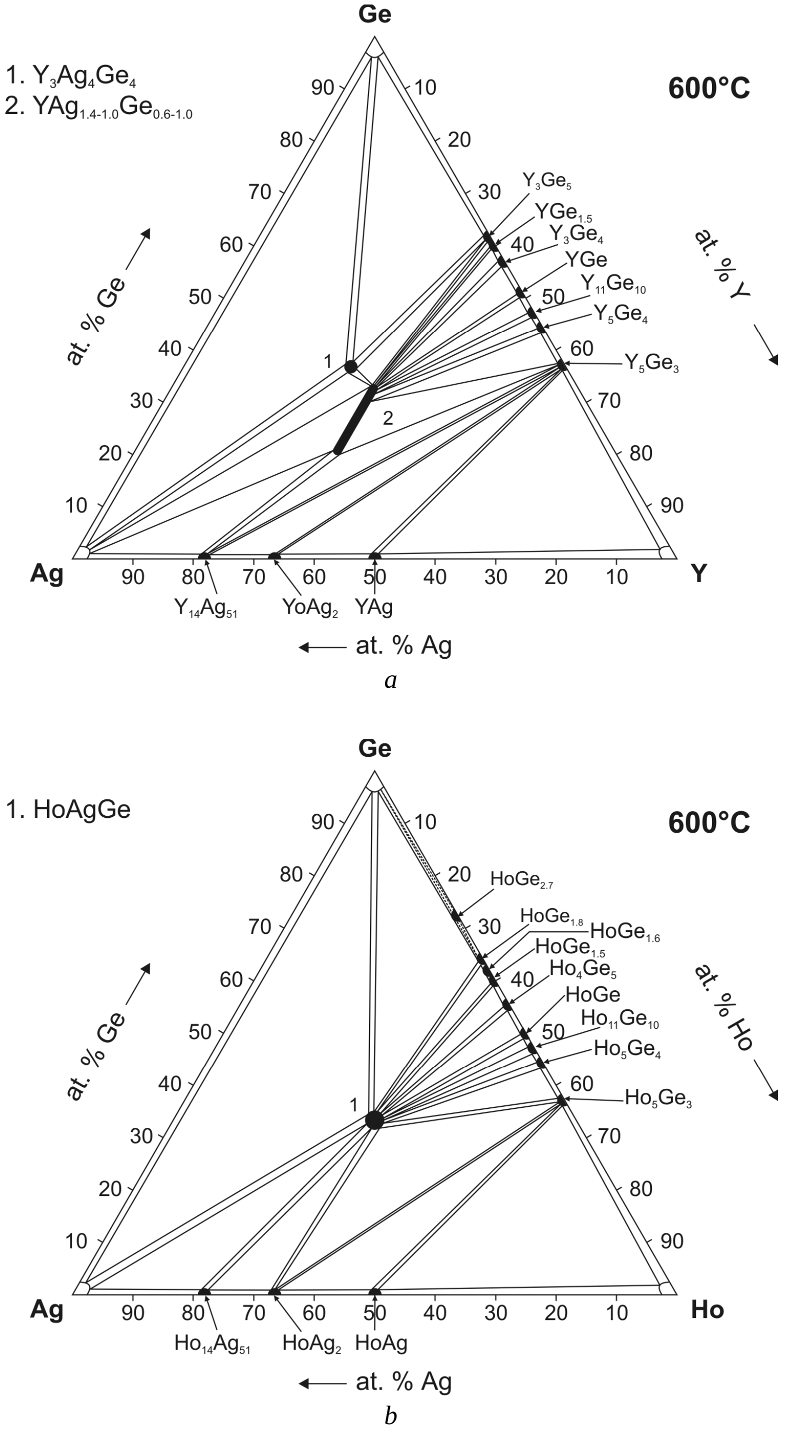

Fig. 2 Isothermal sections of the phase diagrams of the Y–Ag–Ge [1] (*a*) and Ho–Ag–Ge [2] (*b*) systems at 600°C.

Discussion

Among the *R*–Ag–Ge systems with rare-earth metals of the yttrium subgroup isothermal sections (at 600°C) of phase diagrams have been built only for the systems with yttrium and holmium [1,2] (Fig. 2).

The Lu–Ag–Ge system, investigated here, has in common with the systems {Y,Ho}–Ag–Ge the formation of a compound of equiatomic composition with the structure type ZrNiAl (ternary ordered variant of the binary type Fe_2P). YAgGe is the limiting point of the homogeneity region of $YAg_{1.4-1.0}Ge_{0.6-1.0}$ with ZrNiAl-type structure in the system with yttrium and HoAgGe is the only ternary compound in the system with holmium. One more compound was observed in the systems with yttrium and lutetium, but the compositions are different: $Y_3Ag_4Ge_4$ and ~$Lu_{52}Ag_9Ge_{39}$. Significant solubility of the third component in binary compounds was only observed in the Lu–Ag–Ge system, where the binary compound $LuAg_2$ dissolves up to 20 at.% Ge.

Other *R*–Ag–Ge systems (*R* = Gd, Tb, Dy, Er, Tm, Yb) have been studied only for the formation of particular compounds. Compounds with the structure type ZrNiAl were found to exist in all of these systems [3,9]. The compound $Yb_2Ag_{0.5}Ge_4$ forms in the Yb–Ag–Ge system [10] and three additional compounds were reported in the Gd–Ag–Ge system: Gd_2AgGe_6, $GdAgGe_3$, and $GdAg_{0.6}Ge_{1.4}$ [11].

The formation of compounds at the equiatomic composition is also characteristic for the corresponding systems with light rare-earth metals, {La,Ce,Pr,Nd,Sm,Eu}–Ag–Ge [3,11], however, these compounds adopt a larger variety of structure types. Hence, in the systems {La,Ce,Pr}–Ag–Ge the equiatomic compounds crystallize in the structure type NdPtSb, which is a branch of the type LiGaGe and a superstructure of the $CaIn_2$-type structure, characterized by ordered distribution of the smaller atoms (here silver and germanium) [1,12,13]. A disordered $CaIn_2$-type structure was refined on as-cast samples with cerium [14]. Compounds with ZrNiAl-type structures were found in the {Nd,Sm}–Ag–Ge systems [15,16] and a compound with AlB_2-type structure in the Eu–Ag–Ge system [17]. An equiatomic compound with orthorhombic KHg_2-type structure was also reported in the Eu–Ag–Ge system [18], but later claimed to be off-stoichiometric [17,19].

It may be noted that the interaction of silver and germanium with rare-earth elements of the cerium subgroup has been more investigated than the interaction with elements of the yttrium subgroup. Isothermal sections of the phase diagrams have been constructed for the La–Ag–Ge system at 500°C [20], the Ce–Ag–Ge system at 850°C [14], the Pr–Ag–Ge system at 600°C [1], and the Eu–Ag–Ge system at 400°C [17]. According to the Handbook on Inorganic Substances [11], 34 different compounds have been reported in the {La,Ce,Pr,Nd,Sm,Eu}–Ag–Ge systems.

In the rare-earth–silver–germanium systems with elements of the cerium subgroup more relationships are observed than in the corresponding systems with rare-earth metals of the yttrium subgroup, where only the formation of ternary compounds with ZrNiAl (Fe_2P)-type structures is in common. Not only compounds with equiatomic compositions and different structure types are formed in the {La,Ce,Pr,Nd,Sm}–Ag–Ge systems but also compounds adopting the structure types Ce_2CuGe_6, $CeGa_2Al_2$, and $Gd_3Cu_4Ge_4$ [11]. The Eu–Ag–Ge system differs from the others, obviously because, as shown for $EuAg_{2.2}Ge_{1.8}$ and EuAgGe [17], the effective valence of europium is equal to II. Four compounds are known in the Gd–Ag–Ge system according to [11], including one adopting the structure type Ce_2CuGe_6. This indicates that gadolinium behaves more like an element of the cerium subgroup when it interacts with silver and germanium. The existence of a 3:4:4 compound (structure type $Gd_3Cu_4Ge_4$) in the Y–Ag–Ge system, but in no other system with a rare-earth metal of the yttrium subgroup, can be explained either by the not yet complete investigation of systems with silver, germanium and light rare-earth metals, or by peculiarities of the electronic structure.

References

[1] I. Savysyuk, E. Gladyshevskii, N. Tsytsyk, *Visn. Lviv. Univ., Ser. Khim.* 39 (2000) 8-12 (in Ukrainian).

[2] O.L. Sologub, O.S. Protsyk, *Visn. Lviv. Univ., Ser. Khim.* 31 (1991) 31-34 (in Ukrainian).

[3] B. Gibson, R. Pöttgen, R.K. Kremer, A. Simon, K.R.A. Ziebeck, *J. Alloys Compd.* 239 (1996) 34-40.

[4] B. Belan, M. Manyako, S. Pukas, R. Gladyshevskii, *Coll. Abstr. XIII Int. Conf. Crystal Chemistry of Intermetallic Compounds*, Lviv (Ukraine), 2016, p. 72.

[5] K.A. Gschneidner Jr., O.D. McMasters, D.G. Alexander, R.F. Venteicher, *Metall. Trans.* 1 (1970) 1961-1971.

[6] E.I. Gladyshevskii, O.I. Bodak, *Crystal Chemistry of Intermetallic Compounds of Rare-Earth Metals*, Vyshcha Shkola, Lviv, 1982, 255 p. (in Russian).

[7] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, Release 2017/18, ASM International, Materials Park (OH), 2017.

[8] R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paiva-Santos, *J. Appl. Crystallogr.* 28 (1995) 366-367.

[9] G. Zanicchi, D. Mazzone, V. Contardi, R. Marazza, G. Rambaldi, D. Rossi, *Gazz. Chim. It.* 113 (1983) 257-259.

[10] S.C. Peter, M. Chondroudi, C.D. Malliakas, M. Balasubramanian, M.G. Kanatzidis, *J. Am. Chem. Soc.* 133 (2011) 13840-13843.

[11] P. Villars, K. Cenzual, R. Gladyshevskii, *Handbook of Inorganic Substances 2017*, De Gruyter, Berlin, 2017, 1955 p.

[12] V.K. Pecharsky, K.A. Gschneidner Jr., O.I. Bodak, A.S. Protsyk, *J. Less-Common Met.* 168 (1991) 257-267.

[13] M.M. Dz’oba, I.A. Savysyuk, O.O. Shcherban, E.I. Gladyshevskii, *Visn. Lviv. Univ., Ser. Khim.* 36 (1996) 59-65 (in Ukrainian).

[14] E. Cordruwisch, D. Kaczorowski, A. Saccone, P. Rogl, R. Ferro, *J. Phase Equilib.* 20 (1999) 407-422.

[15] O.V. Zaplatynsky, P.S. Salamakha, O.I. Sologub, O.S. Procyk, O.I. Bodak, *Pol. J. Chem.* 70 (1996) 267-269.

[16] I.A. Savysyuk, E.I. Gladyshevskii, R.E. Gladyshevskii, *J. Alloys Compd.* 214 (2001) 167-169.

[17] B.D. Belan, I.N. Soroka, L.V. Kryvulya, O.I. Bodak, O.S. Protsyk, *Visn. Lviv. Univ., Ser. Khim.* 38 (1999) 54-57 (in Ukrainian).

[18] R. Pöttgen, *Z. Naturforsch. B* 50 (1995) 1071-1074.

[19] F. Merlo, M. Pani, M.L. Fornasini, *J. Alloys Compd.* 232 (1996) 289-295.

[20] O.I. Bardin, O.I. Bodak, B.D. Belan, L.V. Kryvulya, O.S. Protsyk, *Visn. Lviv. Univ., Ser. Khim.* 38 (1999) 58-63 (in Ukrainian).