**Chemistry of Metals and Alloys**

*Chem. Met. Alloys* 15 (2022) 12-16
Ivan Franko National University of Lviv
www.chemetal-journal.org

# The ternary system Gd–Ge–Sb at 600°C

Roman DANKEVYCH[1], Yaroslav TOKAYCHUK[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: yaroslav.tokaychuk@lnu.edu.ua*

Received March 13, 2022; accepted June 29, 2022; available on-line September 1, 2022
https://doi.org/10.30970/cma15.0423

**The isothermal section at 600°C of the phase diagram of the ternary system Gd–Ge–Sb was constructed in the whole concentration range, based on X-ray powder diffraction and energy-dispersive X-ray spectroscopy. The formation of a continuous solid solution $Gd_5Ge_{3-x}Sb_x$ ($x$ = 0-3, structure type $Mn_5Si_3$, Pearson symbol *hP*16, space group $P6_3/mcm$, $a$ = 8.5702(8)-8.9745(6), $c$ = 6.4305(5)-6.3431(4) Å) and limited solid solutions based on the binary compounds $Gd_{11}Ge_{10}$ (6 at.% Sb), $Gd_5Ge_4$ (10 at.% Sb), GdSb (6 at.% Ge), and $Gd_4Sb_3$ (28 at.% Ge) was established. Three ternary compounds were found in the system at 600°C: $Gd_6Ge_{4.3}Sb_{11.7}$ (own structure type, *oI*46, *Immm*, $a$ = 4.1420(4), $b$ = 10.4411(9), $c$ = 26.228(2) Å), $Gd_2Ge_{3.28}Sb_{0.65}$ (structure type $Gd_2Ge_{3.38}Bi_{0.42}$, *oS*32, *Cmcm*, $a$ = 4.0198(2), $b$ = 30.3729(18), $c$ = 4.1340(2) Å), and $Gd_5Ge_{2.0\text{-}0.9}Sb_{2.0\text{-}3.1}$ (structure type $Eu_5As_4$, *oS*36, *Cmce*, $a$ = 12.241(7), $b$ = 8.025(3), $c$ = 8.039(3) Å for $Gd_5Ge_{0.90(12)}Sb_{3.10(12)}$).**

**Gadolinium / Germanium / Antimony / X-ray powder diffraction / Energy-dispersive X-ray spectroscopy / Phase diagram / Solid Solution / Ternary compound / Crystal structure**

## Introduction

The determination of the phase equilibria in the ternary system Gd–Ge–Sb is part of a systematic investigation of the interaction between rare-earth metals and *p*-elements of groups IV and V. In parallel with our investigations, the isothermal section of the same phase diagram at 500°C was independently determined [1]. The formation of a $Mn_5Si_3$-type continuous solid solution $Gd_5Ge_{3-x}Sb_x$ ($x$ = 0-1), a $Th_3P_4$-type limited solid solution $Gd_4Ge_xSb_{3-x}$ ($x$ = 0-2), based on the binary compound $Gd_4Sb_3$, and two ternary compounds, $Gd_6Ge_{4.3}Sb_{11.7}$ (own structure type, Pearson symbol *oI*46, space group *Immm*, $a$ = 4.1509, $b$ = 10.4438, $c$ = 26.2400 Å) [2] and $Gd_2Ge_{3.32}Sb_{0.43}$ (structure type $Gd_2Ge_{3.38}Bi_{0.42}$, *oS*32, *Cmcm*, $a$ = 4.02832, $b$ = 30.4101, $c$ = 4.14426 Å), was reported. The existence of the solid solution $Gd_4Ge_xSb_{3-x}$ ($x$ = 0-2) at 1000°C had been reported earlier [3]. In addition, crystal structures have been reported for the ternary compound $Gd_5Ge_{1.84}Sb_{2.16}$ with $Eu_5As_4$-type structure (*oS*36, *Cmce*, $a$ = 15.172, $b$ = 7.982, $c$ = 7.980 Å) [4] and for the $Sm_5Ge_4$-type ternary phase $Gd_5Ge_{3.5}Sb_{0.5}$ (*oP*36, *Pnma*, $a$ = 7.7664, $b$ = 14.8552, $c$ = 7.8255 Å) [5], which probably corresponds to the solid solution based on the binary germanide $Gd_5Ge_4$.

Ternary compounds with $Gd_6Ge_{4.3}Sb_{11.7}$-type structures have also been reported for other ternary *R*–Ge–Sb systems, *R* = Ce, Sm, Tb [2], whereas ternary compounds with $Tm_5Si_2Sb_2$-type structures (*oS*36, *Cmce*, ternary variant of the structure type $Eu_5As_4$) have been reported with *R* = Y, Dy, Ho, Er, Tm [6]. Among the ternary systems *R*–Ge–Sb with other rare-earth metals, isothermal sections of the phase diagram at 400°C have been reported for the system Ce–Ge–Sb, in the whole concentration range [7] and in the range $CeSb_2$–Ge–Sb [8].

The binary systems Gd–Ge, Gd–Sb, and Ge–Sb that delimit the ternary system Gd–Ge–Sn have been studied thoroughly, and the corresponding phase diagrams constructed in the whole concentration range [9,10]. In total, the formation and crystal structures of 12 binary germanides have been reported in the Gd–Ge system and 7 binary antimonides in the system Gd–Sb [11]. Among them, there is one pair of isostructural compounds, $Gd_5Ge_3$ and $Gd_5Sb_3$ (structure type $Mn_5Si_3$, *hP*16, $P6_3/mcm$), which is a prerequisite for the possible formation of a continuous solid solution in the ternary system Gd–Ge–Sb. No stable binary compounds are present in the phase diagram of the system Ge–Sb [10], however, the metastable binary phase GeSb with CoO-type structure (*tI*4, *I*4/*mmm*) was reported in [12].

In this work, we present the results of an experimental investigation of the phase equilibria in the ternary system Gd–Ge–Sb at 600°C in the whole concentration range and crystallographic parameters for two of the ternary compounds, $Gd_2Ge_{3.28}Sb_{0.65}$ and $Gd_5Ge_{0.9}Sb_{3.1}$, determined from X-ray powder diffraction.

## Experimental

63 two- and three-component alloys were synthesized from high-purity metals (Gd ≥ 99.8 mass%, Ge ≥ 99.99 mass%, Sb ≥ 99.97 mass%) by arc-melting under argon atmosphere, using a water-cooled copper hearth, a tungsten electrode and Ti sponges as a getter. To achieve homogeneity, the samples were melted twice. After the synthesis the alloys were wrapped into tantalum foil, sealed in quartz ampoules under vacuum, and annealed at 600°C. After 1 month the ampoules were quenched into cold water. Due to uncontrolled antimony evaporation during the arc-melting, the compositions of the samples were controlled at all stages of the synthesis by using an X-ray fluorescence analyzer ElvaX Pro.

Phase analysis and structure refinements were performed using X-ray powder diffraction data collected at room temperature on diffractometers DRON-2.0M (Fe *K*α-radiation, angular range 10-20° ≤ 2$\theta$ ≤ 120-140°, step 0.05°) and STOE Stadi P (Cu *K*$\alpha_1$-radiation, angular range 6° ≤ 2$\theta$ ≤ 106°, step 0.015°). The profile and structural parameters were refined by the Rietveld method, using the FullProf Suite program package [13]. The boundary compositions of the solid solutions based on the binary compounds, the compositions of the ternary compounds, and some phase equilibria were additionally determined by energy-dispersive X-ray spectroscopy (EDX), performed on a scanning electron microscope TESCAN Vega3 LMU equipped with an energy-dispersive X-ray analyzer Oxford Instruments Aztec ONE with a detector X-Max$^N$20.

## Results and discussion

17 two-component alloys were synthesized to confirm the existence, compositions, and crystal structures of the binary compounds in the Gd–Ge and Gd–Sb systems at 600°C, due to ambiguous literature data on the compositions and crystal structures of some phases. By comparing the experimental X-ray powder diffraction patterns of the synthesized alloys with patterns calculated for the binary compounds, the existence of 11 binaries was confirmed at 600°C: $Gd_3Ge_5$ (structure type $Y_3Ge_5$), $GdGe_{1.5}$ ($AlB_2$), $Gd_3Ge_4$ ($Gd_3Ge_4$), GdGe (TlI), $Gd_{11}Ge_{10}$ ($Ho_{11}Ge_{10}$), $Gd_5Ge_4$ ($Sm_5Ge_4$), $Gd_5Ge_3$ ($Mn_5Si_3$), $Gd_2Sb_5$ ($Dy_2Sb_5$), GdSb (NaCl), $Gd_4Sb_3$ ($Th_3P_4$), and $Gd_5Sb_3$ ($Mn_5Si_3$).

The isothermal section of the phase diagram of the ternary system Gd–Ge–Sb at 600°C was constructed in the whole concentration range (Fig. 1). It consists of 17 single-phase, 33 two-phase, and 17 three-phase fields. The largest number of equilibria (9) are formed by the NaCl-type solid solution based on the binary compound GdSb.

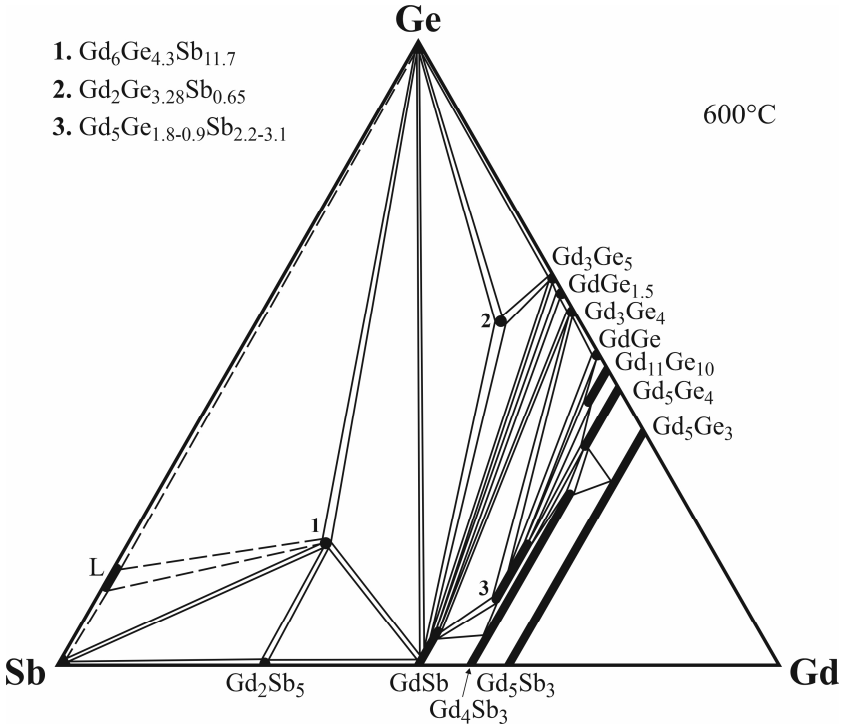



**Fig. 1** Isothermal section of the phase diagram of the ternary system Gd–Ge–Sb at 600°C.

A continuous solid solution forms between the isostructural binary compounds $Gd_5Ge_3$ and $Gd_5Sb_3$ (structure type $Mn_5Si_3$, *hP*16, $P6_3/mcm$). The solid solution retains the structure of the limiting binary compounds throughout the composition range $Gd_3Ge_{3-x}Sb_x$ ($x$ = 0-3). The unit-cell parameter $a$ increases ($a$ = 8.5702(8)-8.9745(6), the unit-cell parameter $c$ decreases ($c$ = 6.4305(5)-6.3431(4) Å), and the cell volume increases ($V$ = 408,97(6)-442.43(5) Å$^3$) with increasing Sb content. Similar composition dependencies of the cell parameters *versus* the Sb content within the continuous solid solution $Gd_3Ge_{3-x}Sb_x$ ($x$ = 0-3) were reported in [1].

The binary gadolinium germanides $Gd_{11}Ge_{10}$ and $Gd_5Ge_4$ dissolve 6 and 10 at.% Sb, respectively, at 600°C and the binary gadolinium antimonides GdSb and $Gd_4Sb_3$ dissolve 6 and 28 at.% Ge, respectively, forming solid solutions of the substitution type characterized by constant Gd concentration. The other binary compounds do not dissolve significant amounts of the third component. Three ternary compounds exist in the system Gd–Ge–Sb at 600°C: $Gd_6Ge_{4.3}Sb_{11.7}$, $Gd_2Ge_{3.28}Sb_{0.65}$, and $Gd_5Ge_{2.0\text{-}0.9}Sb_{2.0\text{-}3.1}$.

The isothermal section of the phase diagram of the ternary system Gd–Ge–Sb at 600°C constructed in this work is similar to the section at 500°C constructed in [1] in the Gd-poor part. A difference appears for the Sb-rich compound in the binary Gd–Sb system: $Gd_2Sb_5$ ($Dy_2Sb_5$, *mP*28, $P2_1/m$) at 600°C, but $Gd_{16}Sb_{39}$ (own type, *mS*124, $C2/m$) at 500°C. In the part of the ternary system with 42-57 at.% Gd the isothermal sections of the phase diagram at 600 and 500°C differ significantly. The binary compound $Gd_3Ge_4$ (own type, *oS*32, *Cmcm*) and the ternary compound of variable composition $Gd_5Ge_{1.8\text{-}0.9}Sb_{2.2\text{-}3.1}$ ($Eu_5As_4$, *oS*36, *Cmce*) exist at 600°C, but were not detected at 500°C. In the Gd-rich part (≥ 57 at.% Gd) the isothermal sections at 500 and 600°C are similar with respect to the formation of the limited solid solution $Gd_4Ge_xSb_{3-x}$ ($x$ = 0-2) and the continuous solid solution $Gd_5Ge_{3-x}Sb_x$ ($x$ = 0-3).

The formation and crystal structure of the ternary compound $Gd_6Ge_{4.3}Sb_{11.7}$ (own structure type, *oI*46, *Immm*) were confirmed at 600°C. The crystallographic parameters refined on X-ray powder data ($a$ = 4.1420(4), $b$ = 10.4411(9), $c$ = 26.228(2) Å) are in good agreement with those determined on X-ray single-crystal data [2].

Crystallographic parameters for the ternary compounds $Gd_2Ge_{3.28}Sb_{0.65}$ and $Gd_5Ge_{2.0\text{-}0.9}Sb_{2.0\text{-}3.1}$ (composition $Gd_5Ge_{0.9}Sb_{3.1}$) were determined by means of X-ray powder diffraction from experimental patterns collected at room temperature on a diffractometer STOE Stadi P from samples of nominal composition $Gd_{37.5}Ge_{52.5}Sb_{10}$ and $Gd_{55.5}Ge_{11.1}Sb_{33.4}$, respectively (Fig. 2). The alloy $Gd_{37.5}Ge_{52.5}Sb_{10}$ contained three phases: the ternary compound $Gd_2Ge_{3.28}Sb_{0.65}$, the binary compound $Gd_3Ge_5$, and the limiting composition of the solid solution $GdGe_xSb_{1-x}$ ($x$ = 0.12) based on the binary compound GdSb, whereas the alloy $Gd_{55.5}Ge_{11.1}Sb_{33.4}$ contained two phases, one corresponding to the Sb-rich limiting composition of the ternary compound $Gd_5Ge_{1.8\text{-}0.9}Sb_{2.2\text{-}3.1}$ and the second one to the limiting composition of the solid solution $GdGe_xSb_{1-x}$ ($x$ = 0.12). Thus, the crystallographic parameters for the ternary compound of variable composition were refined at the Sb-rich limiting composition of its homogeneity range. Experimental details and crystallographic data for the individual phases in the samples $Gd_{37.5}Ge_{52.5}Sb_{10}$ and $Gd_{55.5}Ge_{11.1}Sb_{33.4}$ are listed in Table 1. The compositions of the ternary phases ($Gd_{2.01(3)}Ge_{2.91(5)}Sb_{0.64(3)}$ and $Gd_{5.02(3)}Ge_{0.92(4)}Sb_{3.08(4)}$), determined by energy-dispersive X-ray spectroscopy (Fig. 3), agree with the compositions obtained from the Rietveld refinements.

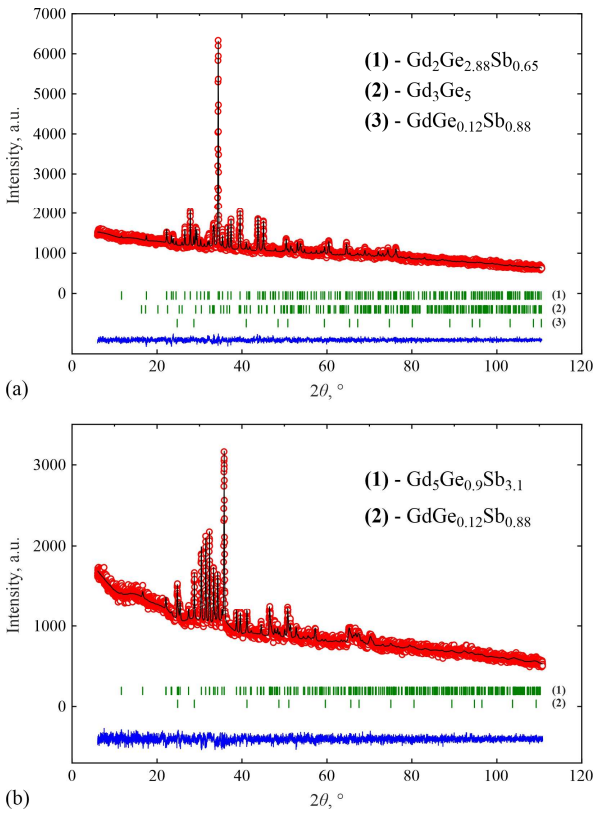
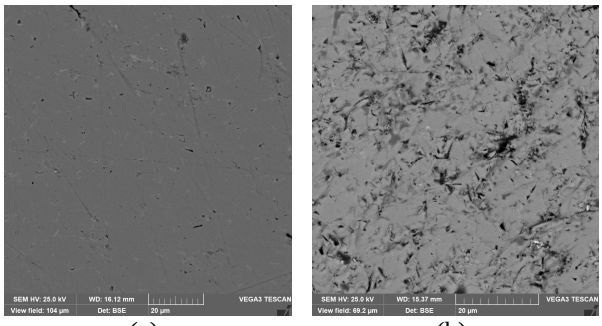



**Fig. 2** Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the samples (a) $Gd_{37.5}Ge_{52.5}Sb_{10}$ and (b) $Gd_{55.5}Ge_{11.1}Sb_{33.4}$ (Cu $K\alpha_1$ radiation). Vertical bars indicate the positions of reflections of the individual phases.

**Table 1** Experimental details and crystallographic data for the individual phases in the samples $Gd_{37.5}Ge_{52.5}Sb_{10}$ and $Gd_{55.5}Ge_{11.1}Sb_{33.4}$.

| Sample | | $Gd_{37.5}Ge_{52.5}Sb_{10}$ | | | $Gd_{55.5}Ge_{11.1}Sb_{33.4}$ | |
|---|---|---|---|---|---|---|
| Chemical formula | | $Gd_2Ge_{3.28(5)}Sb_{0.65(2)}$ | $Gd_3Ge_5$ | $GdGe_{0.12}Sb_{0.88}$ | $Gd_5Ge_{0.90(12)}Sb_{3.10(12)}$ | $GdGe_{0.12}Sb_{0.88}$ |
| Content, mass% | | 82.3(8) | 15.7(3) | 2.0(1) | 92.5(9) | 7.5(2) |
| Structure type | | $Gd_2Ge_{3.38}Bi_{0.42}$ | $Y_3Ge_5$ | NaCl | $Eu_5As_4$ | NaCl |
| Pearson symbol | | *oS*32 | *oF*64 | *cF*8 | *oS*36 | *cF*8 |
| Space group | | *Cmcm* | *Fdd*2 | *Fm*-3*m* | *Cmce* | *Fm*-3*m* |
| Unit-cell parameters: | *a*, Å | 4.0198(2) | 5.7969(15) | 6.1949(8) | 12.241(7) | 6.1952(3) |
| | *b*, Å | 30.3729(18) | 17.396(4) | – | 8.025(3) | – |
| | *c*, Å | 4.1340(2) | 13.791(5) | – | 8.039(3) | – |
| Cell volume *V*, Å$^3$ | | 504.73(5) | 1390.7(6) | 237.74(6) | 938.3(7) | 237.77(3) |
| Formula units per cell *Z* | | 4 | 8 | 4 | 4 | |
| Density $D_X$, g cm$^{-3}$ | | 8.440 | 7.976 | 7.633 | 8.539 | 7.632 |
| Preferred orientation: value / [direction] | | 0.979(6) / [101] | – | – | 0.785(5) / [011] | – |
| Reliability factor: | $R_B$ | 0.0580 | – | – | 0.822 | – |
| Profile parameters | *U* | 0.241(18) | | | 0.553(19) | |
| | *V* | 0.122(15) | | | 0.143(18) | |
| | *W* | 0.041(4) | | | 0.059(11) | |
| Shape parameter | | 0.559(13) | | | 0.670(14) | |
| Asymmetry parameters | $P_1$ | 0.039(10) | | | 0.066(17) | |
| | $P_2$ | 0.014(2) | | | 0.018(3) | |
| Reliability factors: | $R_p$ | 0.0256 | | | 0.0292 | |
| | $R_{wp}$ | 0.0328 | | | 0.0377 | |
| | $\chi^2$ | 1.14 | | | 1.22 | |



(a) (b)

**Fig. 3** Photograph of the polished surface of the samples (a) $Gd_{37.5}Ge_{52.5}Sb_{10}$ (gray phase – $Gd_2Ge_{3.28}Sb_{0.65}$, dark gray phase – $Gd_3Ge_5$, light gray phase – $GdGe_{0.12}Sb_{0.88}$) and (b) $Gd_{55.5}Ge_{11.1}Sb_{33.4}$ (light gray phase – $Gd_5Ge_{0.9}Sb_{3.1}$, gray phase – $GdGe_{0.12}Sb_{0.88}$) in a beam of secondary electrons (TESCAN Vega3 LMU).

The crystal structure of the ternary compound $Gd_2Ge_{3.28}Sb_{0.65}$ belongs to the structure type $Gd_2Ge_{3.38}Bi_{0.42}$ [14]. Atom coordinates, isotropic displacement parameters, and site occupancies are given in Table 2. The main features of the structure are nearly complete ordering of the Ge and Sb atoms, and partial positional disorder of the Ge atoms, which was modeled by partly splitting the site Ge4 in Wyckoff position 4*c* (39 % occupation) into a site in Wyckoff position 8*f* (site Ge3, 27 % occupation). The occupancy of site Ge3 cannot exceed 50 % and the total occupancy of sites Ge3 and Ge4 cannot exceed the sum 2×occ.(Ge3) + 1×occ.(Ge4) = 1, *i.e.* neighboring positions of these sites cannot be occupied simultaneously. The structure type $Gd_2Ge_{3.38}Bi_{0.42}$ belongs to the family of linear intergrowth structures composed by $AlB_2$- (triple layers of trigonal prisms) and $CaF_2$-type slabs (double slabs of “half octahedra”) [15].

**Table 2** Atomic coordinates, site occupancies, and isotropic displacement parameters for $Gd_2Ge_{3.28(5)}Sb_{0.65(2)}$ ($Gd_2Ge_{3.38}Bi_{0.42}$, *oS*32, *Cmcm*, *a* = 4.0198(2), *b* = 30.3729(18), *c* = 4.1340(2) Å).

| Site | Wyckoff position | *x* | *y* | *z* | $B_{iso}$, Å$^2$ |
|---|---|---|---|---|---|
| Gd1 | 4*c* | 0 | 0.44138(19) | ¼ | 0.52(4) |
| Gd2 | 4*c* | 0 | 0.83411(17) | ¼ | 0.45(4) |
| *M* (0.35(2)Ge + 0.65(2)Sb) | 4*c* | 0 | 0.2497(2) | ¼ | 0.81(6) |
| Ge1 | 4*c* | 0 | 0.0907(17) | ¼ | 1.21(15) |
| Ge2 | 4*c* | 0 | 0.6460(3) | ¼ | 1.17(14) |
| Ge3 (Occ. = 0.27(3)) | 8*f* | 0 | 0.0085(9) | 0.088(5) | 1.2(-) |
| Ge4 (Occ. = 0.39(4)) | 4*c* | 0 | 0.014(4) | ¼ | 1.2(-) |

The crystal structure of the ternary compound $Gd_5Ge_{1.8\text{-}0.9}Sb_{2.2\text{-}3.1}$ belongs to the structure type $Eu_5As_4$. Atom coordinates, isotropic displacement parameters, and site occupancies for $Gd_5Ge_{0.90(12)}Sb_{3.10(12)}$ are given in Table 3. At the Sb-rich border of the homogeneity range the position 8*f* is occupied by a statistical mixture of Ge and Sb atoms, while the position 8*d* is occupied by Sb atoms alone. Complete ordering of Ge and Sb atoms (structure type $Tm_5Si_2Sb_2$ [16]) would be possible at the composition $Gd_5Ge_2Sb_2$, which is not included in the homogeneity range of the ternary compound $Gd_5Ge_{1.8\text{-}0.9}Sb_{2.2\text{-}3.1}$ at 600°C. The structure determination of $Gd_5Ge_{1.84}Sb_{2.16}$ revealed statistical mixtures in both Wyckoff positions 8*f* and 8*d*, but with a preference for Ge atoms to occupy the position 8*f* and for Sb atom to occupy the position 8*d* [4].

**Table 3** Atomic coordinates, site occupancies and isotropic displacement parameters for $Gd_5Ge_{0.90(12)}Sb_{3.10(12)}$ ($Eu_5As_4$, *oS*36, *Cmce*, *a* = 12.241(7), *b* = 8.025(3), *c* = 8.039(3) Å).

| Site | Wyckoff position | *x* | *y* | *z* | $B_{iso}$, Å$^2$ |
|---|---|---|---|---|---|
| Gd1 | 16*g* | 0.1320(3) | 0.3315(6) | 0.1621(6) | 0.64(6) |
| Gd2 | 4*a* | 0 | 0 | 0 | 0.56(6) |
| *M* (0.45(6)Ge + 0.55(6)Sb) | 8*f* | 0 | 0.138(2) | 0.3713(19) | 1.0(3) |
| Sb | 8*d* | 0.2058(5) | 0 | 0 | 0.8(2) |

## Conclusions

The isothermal section at 600°C of the phase diagram of the ternary system Gd–Ge–Sb is characterized by the existence of the continuous solid solution $Gd_5Ge_{3\text{-}x}Sb_x$ ($x$ = 0-3, structure type $Mn_5Si_3$), limited solid solutions based on the binary compounds $Gd_{11}Ge_{10}$ (6 at.% Sb), $Gd_5Ge_4$ (10 at.% Sb), GdSb (6 at.% Ge), $Gd_4Sb_3$ (28 at.% Ge), and three ternary compounds, $Gd_6Ge_{4.3}Sb_{11.7}$ (own structure type), $Gd_2Ge_{3.28}Sb_{0.65}$ (structure type $Gd_2Ge_{3.38}Bi_{0.42}$), and $Gd_5Ge_{2.0\text{-}0.9}Sb_{2.0\text{-}3.1}$ (structure type $Eu_5As_4$). The ternary phases are characterized by partial disorder of Ge and Sb atoms.

## Acknowledgment

This work was carried out under the grant of the Ministry of Education and Science of Ukraine No. 0121U109766.

## References

[1] H. Liu, Ch. Liao, W. Zeng, T. Yang, L. Zeng, W. He, *J. Alloys. Compd.* 825 (2020) 153841.
[2] R. Lam, R. McDonald, A. Mar, *Inorg. Chem.* 40 (2001) 952-959.
[3] Y.Y.J. Cheung, V.O. Svitlyk, Y.A. Mozharivskyj, *Inorg. Chem.* 51 (2012) 10169-10175.
[4] J. Yao, Y. Zhang, P.L. Wang, L. Lutz, G.J. Miller, Y.A. Mozharivskyj, *Phys. Rev. Lett.* 110 (2013) 077204.
[5] A.S. Chernyshov, Y.S. Mudryk, D. Paudyal, V.K. Pecharskii, K.A. Gschneidner Jr., D.L. Schlagel, T.A. Lograsso, *Phys. Rev. B* (2009) 80, 184416.
[6] A.Yu. Kozlov, V.V. Pavlyuk, V.M. Davydov, *Intermetallics* 12 (2004) 151-155.
[7] A.O. Stetskiv, V.V. Pavlyuk, O.I. Bodak, *Pol. J. Chem.* 72 (1998) 956-958.
[8] N. Nasir, A.V. Grytsiv, P. Rogl, A. Saccone, G. Giester, *J. Solid State Chem.* 182 (2009) 645-656.
[9] T.B. Massalski (Ed.), *Binary Alloy Phase Diagrams*., ASM International, OH., 1990.
[10] P. Villars, H. Okamoto, K. Cenzual (Eds.), *ASM Alloy Phase Diagram Database. Release 2006/2022*, ASM International.
[11] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park, OH, USA, Release 2021/22.
[12] B.C. Giessen, C. Borromee Gautier, *J. Solid State Chem.* 4 (1972) 447-452.
[13] J. Rodríguez-Carvajal, *Commission on Powder Diffraction (IUCr), Newsletter* 26 (2001) 12-19.
[14] J. Zhang, B. Hmiel, A. Antonelli, P.H. Tobash, S. Bobev, S.R. Saha, K.C. Kirshenbaum, R.L. Greene, J. Paglione, *J. Solid State Chem.* 196 (2012) 586-595.
[15] E. Parthé, Gelato L., Chabot B., Penzo M., Cenzual K., Gladyshevskii R., *TYPIX – Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types*, Springer-Verlag, Berlin, Vol. 1-4 (1993) 1596 p.
[16] A.Yu. Kozlov, V.V. Pavlyuk, V.M. Davydov, *Intermetallics* 12 (2004) 151-155.