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$Al_{7+x}Fe_{23}Ge_{14-x}$ and $Al_{7+x}Fe_9Ge_{5-x}$: Two new ternary compounds related to Fe_6Ge_5

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ABSTRACT

The title compounds were synthesised from the pure elements by arc melting and subsequent heat treatment at 800 °C. They were characterised by powder- and single-crystal XRD, their homogeneity ranges were investigated by scanning electron microscopy and EDX from a series of samples with distinct overall compositions. $Al_{7+x}Fe_{23}Ge_{14-x}$ ($-0.8 \leq x \leq 1.8$, orthorhombic, space group $Cmc2_1$, Pearson symbol $oC176$; $a = 7.912\ (2)$, $b = 19.786(6)$, $c = 14.769(5)$ Å) adopts a new crystal structure type, while $Al_{7+x}Fe_9Ge_{5-x}$, ($-0.7 \leq x \leq 3.5$, monoclinic, space group $C2/m$, Pearson symbol $mC42$; $a = 10.147(2)$, $b = 7.5394(12)$, $c = 7.8744(12)$ Å, $\beta = 108.396(15)°$) was found to be isotypic with Fe_3Ga_4. Within the accuracy of structure refinements the Fe atoms build an ordered and fully occupied *sub*lattice, whereas extensive mixed occupation between aluminium and germanium atoms is evident. Both compounds exhibit noticeable homogeneity ranges based on extensive (Al,Ge) substitutions. Their crystal structures are related to the Fe_6Ge_5-structure type (monoclinic, space group $C2/m$, Pearson symbol $mC44$). Structural features and relations are discussed; homogeneity ranges as well as the corresponding lattice parameters are given.

1. Introduction

Intermetallic compounds of transition metals in combination with triels and tetrels are of fundamental as well as of practical interest. Due to their superior properties with respect to temperature, stress and corrosion resistance, iron aluminides are interesting for various applications, and many ternary systems including aluminium and iron have been investigated in this context. In particular the Al–Fe–Si system has been intensively studied in the past, due to its additional importance for aluminium-based alloys. The addition of silicon to Al–Fe alloys leads to a large number of ternary intermetallic phases, especially, in the aluminium-rich corner of the phase diagram [1,2]. This gives rise to the question, whether the related Al–Fe–Ge phase diagram is of comparable complexity.

Up to now, few data is reported in the Al–Fe–Ge ternary phase diagram. Most of the investigations concern the phase equilibria of the *B*2- and *D*0$_3$-type compounds in the iron-rich part of the phase diagram [3–8] or the amorphous phases determined by rapid quenching in the aluminium-rich part [9–13]. Publications related to the crystal structures of possible compounds in this system are not available, apart from a reported metastable phase $Al_2Fe_6Ge_3$, which is related to Fe_6Ge_5 [14,15]. This metastable phase was discovered by ball milling of the pure elements and investigated by Mössbauer spectroscopy and powder XRD.

The current work is part of a systematic explorative investigation of the system Al–Fe–Ge and reports on the synthesis and characterization of the two new compounds $Al_{7+x}Fe_{23}Ge_{14-x}$ and $Al_{7+x}Fe_9Ge_{5-x}$.

2. Experimental

The title compounds were found as stable phases in more than 10 samples of different composition within the Al–Fe–Ge system. These samples are predominantly located in vertical sections of constant iron (38–43 at.%Fe) and varying aluminium and germanium contents (whole range). They were prepared by melting the pure elements, aluminium slug (99.999%, Alfa Aesar), iron sheet (99.9%, vacuum cast) and germanium pieces (99.999%, Alfa Aesar) in an arc furnace under inert gas atmosphere (argon). Zirconium was used as getter material; the samples were turned upside down

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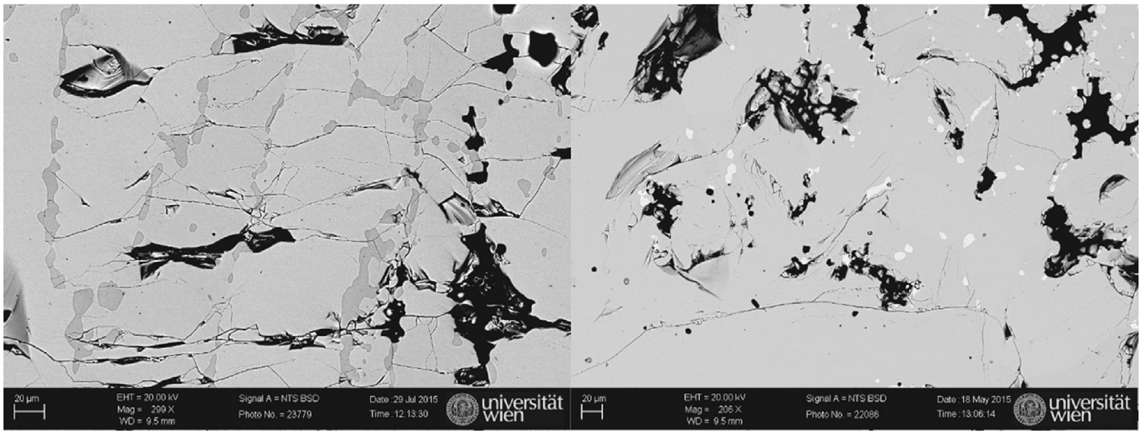

Fig. 1. BSE images of samples $Al_{15}Fe_{50}Ge_{35}$ (at.%) with the major phase $Al_{7+x}Fe_{23}Ge_{14-x}$ (left) and $Al_{33}Fe_{43}Ge_{24}$ (at.%) with the major phase $Al_{7+x}Fe_{9}Ge_{5-x}$ (right). The minor phases present are AlFeGe (will be published elsewhere) and $Al_{7+x}Fe_{23}Ge_{14-x}$, respectively. Single crystals for structure analyses were picked from these samples.

Table 1
Data Collection and Structure refinement parameters.

Compound	$Al_{7+x}Fe_9Ge_{5-x}$ ($-0.7 \le x \le 3.5$)	$Al_{7+x}Fe_{23}Ge_{14-x}$ ($-0.8 \le x \le 1.8$)
Structure type	Fe_3Ga_4	$Al_{7+x}Fe_{23}Ge_{14-x}$
Pearson symbol	m*C*42	*oC*176
a [Å]	10.147(2)	7.912(2)
b [Å]	7.5394(12)	19.786(6)
c [Å]	7.8744(12)	14.769(5)
ß [°]	108.396(15)	–
Space group	*C*2/*m* (no. 12)	*Cmc*2_1 (no. 36)
V [Å^3]/*Z*	571.6/2	2312.0/4
ρcalc [g cm^{-3}]/μ(MoKα) [mm^{-1}]	6.13/24.5	7.29/33.3
Crystal dimensions (μm)	50 × 60 × 90	35 × 40 × 45
Range of data collection ($\pm h \pm k \pm l$) [°]	$3 < 2\theta < 70$	$3 < 2\theta < 70$
Number of images/scan time [s/°]	639/120	773/270
Rotation angle per image	2°	1.5°
Distinct ω-angles for φ-scans mode	11	11
Measured reflections	4,350	18,508
Unique reflections (n)/reflections with $F_o > 4\sigma(F_o)$	1332/1235	5328/3343
$R_{int} = \Sigma \vert F_o^2\text{-}F_o^2(\text{mean})\vert / \Sigma F_o^2$	0.026	0.046
Extinction parameter k:		
$F_c^* = F_c \cdot k[1 + 0.001 \cdot F_c^2 \lambda^3/\sin(2\theta)]^{-1/4}$	0.00368(17)	0.00010(1)
$R1 = \Sigma(\vert\vert F_o\vert\text{-}\vert F_c\vert\vert)/\Sigma F_o$ (observed/all reflections)	0.017/0.019	0.037/0.077
$wR2 = [\Sigma w(F_o^2\text{-}F_c^2)^2/\Sigma\vert wF_o^4]^{1/2}$	0.037	0.085
$\text{GooF} = \{\Sigma[w(F_o^2\text{-}F_c^2)^2]/(n\text{-}p)\}^5$	1.06	1.05
Weighting parameters *a*/*b*	0.015/0.87	0.022/39.7
Max Δ/σ/number of variable parameters (p)	<0.001/21	<0.001/180
Final difference Fourier map [eÅ^{-3}]	−0.97 to +0.66	−2.56 to +3.01

and re-melted for homogenisation two times. The resulting sample pills were placed in alumina crucibles and sealed into quartz glass phials under dynamic vacuum at 10^{-3} mbar. After annealing the samples at 800 °C for two weeks, the phials were quenched in water. Any mass losses during the arc melting as well as the annealing process were found to be negligible (>1%).

The samples were initially characterised by X-ray powder diffraction measurements using a Bruker D8 advance diffractometer in Bragg-Brentano *pseudo*focussing geometry (CuK_α radiation, $\lambda = 1.54056$ Å, Lynxeye silicon strip detector and SolX energy dispersive detector, variable slit aperture with 12 mm, scan of $10° \le 2\theta \le 120°$). Rietveld-refinements of the observed powder patterns (Topas software [16]) were utilised to determine the overall sample composition by a semi-quantitative approach. Unknown patterns were indexed and checked for isotypic or at least structurally related phases; the ICSD database [17] served for searching of compounds exhibiting crystal structures with similar lattice parameters, symmetry and/or composition. Scanning electron microscopy (Zeiss Supra 55 VP ESEM, acceleration voltage 20 kV and beam current 10 nA) was used for microstructure investigations. The composition of the phases was obtained by energy dispersive X-ray spectroscopy (EDX). Energy calibration of the EDX signal was performed with a cobalt-standard; pure element standards aluminium, iron and germanium were used for the calibration of quantitative analysis. Evidence for any oxygen contamination could be found neither on the surface, nor in the bulk of the samples, during the elemental analyses. Single crystals of uniform dimensions were isolated for single-crystal X-ray diffractometry (NONIUS four-circle diffractometer, CCD detector with frame size 621 × 576 pixels in binned mode, 300 μm capillary-optics collimator, MoK_α radiation, graphite monochromator, rotation angle per image 2°; detector-to-sample distance 30 mm, Collect software [18,19]). The measured intensities were corrected for Lorentz, polarization and absorption effects (multi-scan method). The unit-cell metrics (least-squares refinements of reflection positions of all measured Bragg reflections) were in good