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Crystal structures of ErGe₂ and TmGe₂ compounds

Abstract

Crystal structures of ErGe₂ and TmGe₂ compounds were determined by X-ray single crystal diffraction. Both TmGe₂ and ErGe₂ crystallized with the ZrSi₂ structure type (space group *Cmcm*).

Keywords: Rare earths phases, Crystal structure, X-Ray diffraction

Introduction

This paper is a part of systematic study of interaction of erbium and thulium with germanium. Previously, such compounds containing rare earth metals ~33.3 at.% have been investigated: YGe₂ (space group *I4₁/amd*, structure type ThSi₂)¹, LaGe₂ (space group *I4₁/amd*, structure type ThSi₂)², CeGe₂ (space group *I4₁/amd*, structure type ThSi₂)³, PrGe₂ (space group *I4₁/amd*, structure type ThSi₂)⁴, NdGe₂ (space group *I4₁/amd*, structure type ThSi₂)⁵, SmGe₂ (space group *I4₁/amd*, structure type ThSi₂)⁶, EuGe₂ (space group *P-3m1*, structure type EuGe₂)⁷, TbGe₂ (space group *Cmmm*)⁸, TmGe_{1.891}, ErGe_{1.891} (space group *Pmma*)⁹. In this paper, we report our results on synthesis and crystal structure refinement of the ErGe₂ and TmGe₂ binary compounds by X-ray single crystal diffraction.

Experimental details and results

The samples were melted from weighted pieces of initial components of high purity (Er – 99.86 %, Tm – 99.89 %, Ge - 99.999 %) under an argon Ti-gettered atmosphere in an arc furnace with a water-cooled copper hearth and then annealed in an evacuated silica tubes at 873 K for one month.

The samples microstructures were studied using a metallographic microscope (magnification $\times 200 \div 300$). The elemental compositions of some samples were confirmed using the registering scanning electron microscope REMA–102–02 type with 1 μm^2 locality of analysis (Fig.1 and Fig.2).

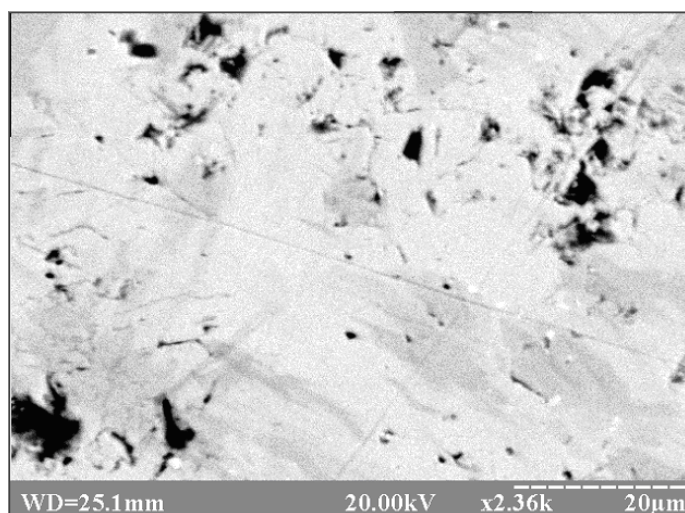


Fig. 1. SEM image for the Er₃₄Ge₆₆(composition of main phase Er(32.998), Ge(67.002))

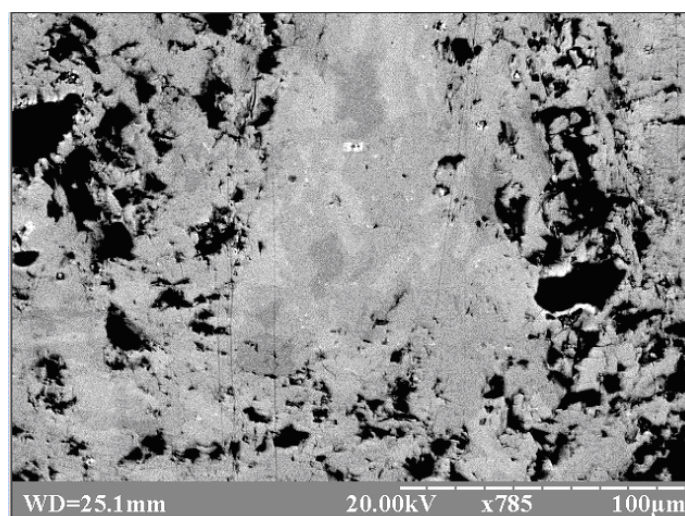


Fig. 2. SEM image for the Tm₃₄Ge₆₆ (composition of main phase Tm(35,359), Ge(64,641))

X-ray patterns of all alloys were taken at room temperature using X-ray powder diffractometer DRON-2.0M with Fe K_{α} radiation ($\theta/2\theta$ scanning, $30^{\circ} \leq 2\theta \leq 150^{\circ}$) and the pure silicon as an internal standard.

The single crystals suitable for X-ray analysis were first checked using Laue and Weissenberg methods (RKV-86 and RGNS-2 chambers, MoK α -

radiation), and afterwards they were studied using automatic single-crystal diffractometer Bruker APEX II (MoK α -radiation, graphite monochromator, ω -scans).

Results and discussion

The single crystals of ErGe_2 and TmGe_2 having prismatic forms were extracted from the samples with the compositions $\text{Er}_{34}\text{Ge}_{66}$ and $\text{Tm}_{34}\text{Ge}_{66}$, respectively. Processing of collection and reduction data were performed using SAINT (Bruker, 2004) programs¹⁰. The solution and refinement of crystal structure were performed using SHELXL-97 programme package¹¹. Standardization procedure was performed using program Structure Tidy¹².

These single crystals were stable in air over the long period of time and had metallic luster. The details of data collection and structure refinement, atomic coordinates and anisotropic thermal displacement parameters for ErGe_2 are given in Table 1. The same data for TmGe_2 are listed in Table 2.

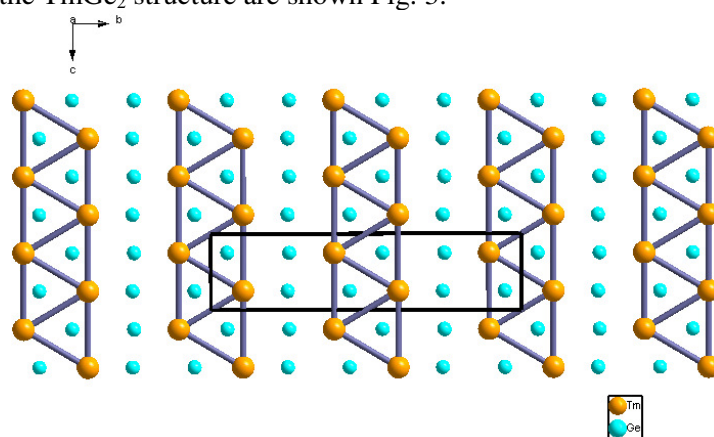
Table 1. Experimental details and crystallographic data for ErGe_2

Compound	ErGe_2
Structure type	ZrSi_2
Space group	Cmcm
Pearson symbol	oC12
Lattice parameters, Å	$a = 4.0190(1)$, $b = 15.8381(7)$, $c = 3.8799(1)$
Absorption coefficient, mm^{-1}	57.436
Theta range for data collection	2.4 to 28.0°
Limiting indices	$-5 \leq h \leq 4$, $-19 \leq k \leq 19$, $-4 \leq l \leq 3$
Reflections collected / unique	168/152
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	152/0/14
Goodness-of-fit on F^2	1.102
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0321$, $wR2 = 0.0956$
R indices (all data)	$R1 = 0.0389$, $wR2 = 0.1004$
Extinction coefficient	0.0008(7)
Largest diff. peak and hole	1.270 and $-1.124 \text{ e} \cdot \text{Å}^{-3}$
Atomic coordinates and displacements: x y z , U_{11} , U_{22} , U_{33} U_{23} U_{13} $U_{12}(\text{Å}^2)$	
Er1 (4c)	0.00000 0.39620 1/4 0.01301 0.01192 0.00943 0.00000 0.00000 0.00000
Ge1 (4c)	-0.50000 0.44545 -1/4 0.01304 0.02073 0.00911 0.00000 0.00000 0.00000
Ge2 (4c)	0.00000 0.24760 -1/4 0.01616 0.01259 0.01322 0.00000 0.00000 0.00000

Table 2. Experimental details and crystallographic data for TmGe₂

Compound	TmGe ₂								
Structure type	ZrSi ₂								
Space group	Cmcm								
Pearson symbol	oC12								
Lattice parameters, Å	$a = 4.020(1), b = 15.768(4), c = 3.8761(5)$								
Absorption coefficient, mm ⁻¹	59.704								
Theta range for data collection	5.10 to 27.00°								
Limiting indices	$-3 \leq h \leq 5, -15 \leq k \leq 19, -4 \leq l \leq 4$								
Reflections collected / unique	162/1468								
Refinement method	Full-matrix least-squares on F ²								
Data / restraints / parameters	162/0/15								
Goodness-of-fit on F ²	1.112								
Final R indices [I > 2σ(I)]	R1 = 0.0307, wR2 = 0.0877								
R indices (all data)	R1 = 0.0354, wR2 = 0.0913								
Largest diff. peak and hole	1.043 and -1.222 e ⁻ Å ⁻³								
Atomic coordinates and displacements:	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12} (Å ²)
Tm1 (4c)	0.00000	0.39650	1/4	0.01339	0.01752	0.01210	0.00000	0.00000	0.00000
Ge1 (4c)	-0.50000	0.55284	-1/4	0.01257	0.02851	0.01015	0.00000	0.00000	0.00000
Ge2 (4c)	-0.50000	0.25249	-1/4	0.01729	0.01832	0.01409	0.00000	0.00000	0.00000

The ErGe₂ and TmGe₂ compounds crystallize in the ZrSi₂ structure type (space group *Cmcm*, Pearson code *oP12*). Both structures were also confirmed by powder diffraction methods. The unit cell projection and packing of trigonal prism in the TmGe₂ structure are shown Fig. 3.

**Fig. 3.** The unit cell projection and packing of trigonal prism in the TmGe₂ structure

A paper concerning the Tm-Ge binary phases has recently been published⁹ and reported on powder X-ray investigation of binary thulium germanides. Three new compounds have been characterized, $\text{TmGe}_{1.83}$ with the $\text{ErGe}_{1.83}$ -type structure (Cmcm; $a=4.050(1)$ Å, $b=29.460(8)$ Å and $c=3.887(1)$ Å), Tm_2Ge_5 with the Er_2Ge_5 -type structure (Pmmn: $a=4.000(1)$ Å; $b=3.875(1)$ Å; $c=18.103(7)$ Å) and $\text{TmGe}_{1.9}$ with a new structural type (Pmma; $a=3.879(1)$ Å, $b=4.034(1)$ Å and $c=22.544(7)$ Å). The structure of $\text{TmGe}_{1.9}$ has been solved by powder X-ray diffraction. This new type may be considered as an intergrowth of ZrSi_2 and $\text{ErGe}_{1.83}$ blocks. This intergrowth structure at the TmGe_2 composition has not been observed.

Conclusions

1. The crystal structures of the ErGe_2 and TmGe_2 compounds were determined by X-ray single crystal diffraction.
2. Both compounds crystallized in the ZrSi_2 structure type (space group Cmcm, Pearson code $oP12$).
3. The intergrowth of ZrSi_2 and $\text{ErGe}_{1.83}$ blocks in the TmGe_2 crystal were not observed.

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