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Crystal structures of $ErGe_2$ and $TmGe_2$ compounds

Abstract

Crystal structures of $ErGe_2$ and $TmGe_2$ compounds were determined by X-ray single crystal diffraction. Both $TmGe_2$ and $ErGe_2$ crystallized with the $ZrSi_2$ 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: YGe_2 (space group $I4_1/amd$, structure type $ThSi_2$)[1] $LaGe_2$ (space group $I4_1/amd$, structure type $ThSi_2$)[2], $CeGe_2$ (space group $I4_1/amd$, structure type $ThSi_2$)[3], $PrGe_2$ (space group $I4_1/amd$, structure type $ThSi_2$)[4], $NdGe_2$ (space group $I4_1/amd$, structure type $ThSi_2$)[5], $SmGe_2$ (space group $I4_1/amd$, structure type $ThSi_2$)[6], $EuGe_2$ (space group *P-3m1*, structure type $EuGe_2$)[7], $TbGe_2$(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 $ErGe_2$ and $TmGe_2$ 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 ×200 ÷ 300). The elemental compositions of some samples were confirmed using the registering scanning electron microscope REM-MA–102–02 type with $1\mu m^2$ locality of analysis (Fig.1 and Fig.2).

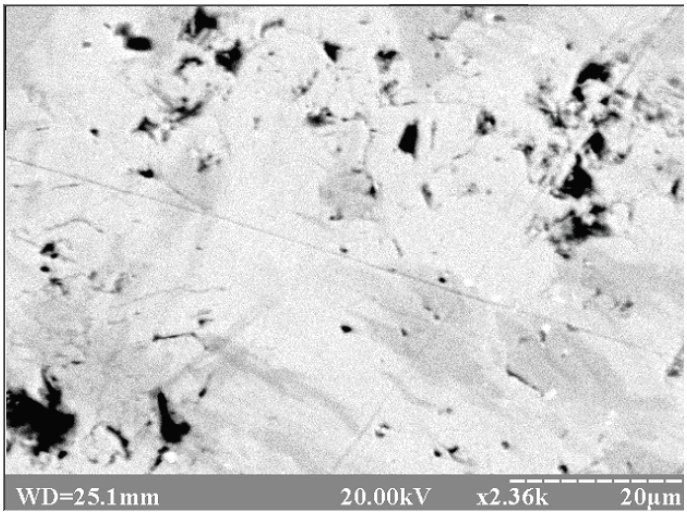

Fig. 1. SEM image for the $Er_{34}Ge_{66}$(composition of main phase Er(32.998), Ge(67.002))

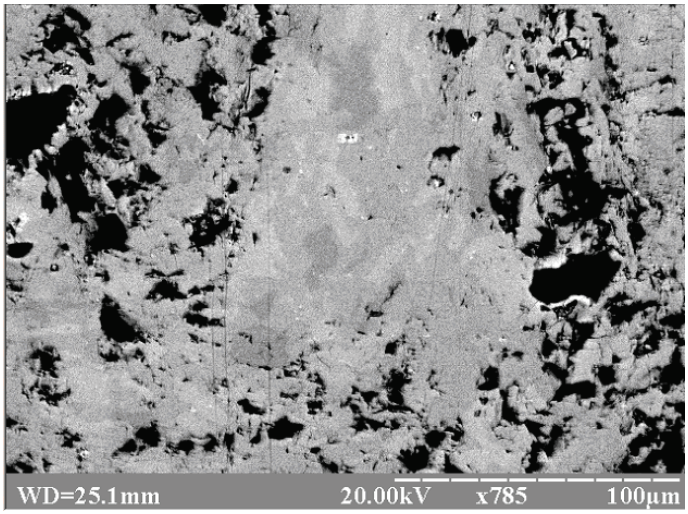

Fig. 2. SEM image for the $Tm_{34}Ge_{66}$ (composition of main phase Tm(35,359), Ge(64,641))

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, $30^o \leq 2\theta \leq 150^o$) 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, MoKα-

radiation), and afterwards they were studied using automatic single-crystal diffractometer Bruker APEX II (MoKα-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 $Er_{34}Ge_{66}$ and $Tm_{34}Ge_{66}$, respectively. Processing of collection and reduction data were performed using SAINT (Bruker, 2004) programs[10]. The solution and refinement of crystal structure were performed using SHELXL-97 programme package[11]. Standardization procedure was performed using program Structure Tidy[12].

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 =< h =< 4, -19 =< k =< 19, -4 =< l =< 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>2sigma(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 e· $Å^{-3}$
Atomic coordinates and displacements: x y z, U_{11}, U_{22}, U_{33} U_{23} U_{13} U_{12}($Å^2$)				
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 $TmGe_2$

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 =< h =< 5, -15 =< k =< 19, -4 =< l =< 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>2sigma(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 $e \cdot Å^{-3}$				
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 $ErGe_2$ and $TmGe_2$ compounds crystallize in the $ZrSi_2$ structure type (space group *Cmcm*, Pearson code *oP*12). Both structures were also confirmed by powder diffraction methods. The unit cell projection and packing of trigonal prism in the $TmGe_2$ structure are shown Fig. 3.

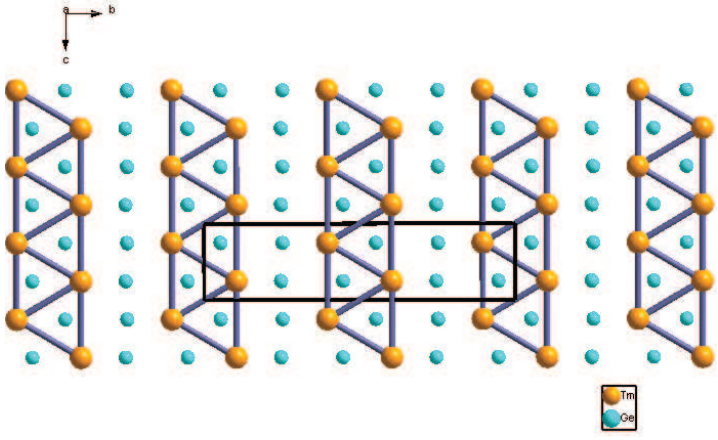

Fig. 3. The unit cell projection and packing of trigonal prism in the $TmGe_2$ structure

A paper concerning the Tm-Ge binary phases has recently been published[9] and reported on powder X-ray investigation of binary thulium germanides. Three new compounds have been characterized, $TmGe_{1.83}$ with the $ErGe_{1.83}$-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 $TmGe_{1.9}$ 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 $TmGe_{1.9}$ has been solved by powder X-ray diffraction. This new type may be considered as an intergrowth of $ZrSi_2$ and $ErGe_{1.83}$ 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 *oP*12).
3. The intergrowth of $ZrSi_2$ and $ErGe_{1.83}$ blocks in the $TmGe_2$ crystal were not observed.

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