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New rare-earth metal germanides with bismuth substitution. Synthesis, structural variations, and magnetism of the $RE[Bi_xGe_{1-x}]_2$ (RE=Y, Pr, Nd, Sm, Gd–Tm, Lu) compounds

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ABSTRACT

Single-crystals of the novel rare-earth metal-bismuth digermanides with idealized formula $RE[Bi_xGe_{1-x}]_2$ (RE=Y, Pr, Nd, Sm, Gd–Tm, Lu; $x<0.16(1)$) have been obtained using the Bi-flux technique. Their structures have been established by single-crystal X-ray diffraction; they can be divided into three classes, closely related to the $ZrSi_2$ structure with the space group *Cmcm* (no. 63). The structural relationship and the variations with the type of the rare-earth metal have been explored and discussed. Temperature-dependent magnetization measurements on the single-crystals reveal magnetic behavior, which have been rationalized based on the mean-field theory. At cryogenic temperatures, the localized 4*f* electrons in most of the compounds exhibit antiferromagnetic ordering, mediated by the conduction electrons via Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interactions.

1. Introduction

Rare-earth metal (RE) containing compounds offer a wealth of structures and intriguing properties [1]. They are also excellent candidates for fundamental studies on the factors determining a bonding arrangement of a specific kind, the evolution of the properties within a given structure, and ultimately the structure–property relationships. RE–silicides and RE–germanides are well suited for these types of investigations, and in recent years, such compounds have attracted considerable attention [2]. For instance, in the Dy–Ge binary phase diagram alone [3,4], it has been reported that there are at least eight distinct phases in the narrow compositional range from DyGe to $DyGe_2$. Such structural diversity suggests that the realization of the multitude of structures is a consequence of multiple cooperating factors, among which topological or electronic considerations are the primary ones [5].

In our previous work, we have demonstrated that one can extend the $ZrSi_2$ structure type (known only for $REGe_2$ when RE=Tm and Lu) to the mid-to-late rare-earth metals by the addition of Sn, forming the series $RE[Sn_xGe_{1-x}]_2$ (RE=Y, Gd–Tm) [6]. These orthorhombic structures afforded an unusual result—Ge and Sn showed a tendency to order on two polyanionic sub-lattices, effectively rendering the compounds in question as nearly stoichiometric (referred to as RESnGe hereafter). The synthesis in these cases was greatly facilitated by the use of the flux techniques [7], which can depress thermal strain (and to some degrees the heterogeneous nucleation) compared with the traditional arc-melting route. However, when we attempted to synthesize analogous compounds with In (notice the small difference in atomic sizes and electronegativity between indium and tin [8]), the RE_2InGe_2 (RE=Sm, Gd–Ho, Yb) with the tetragonal U_3Si_2 type structure formed instead [9]. We reasoned that indium is one electron-poorer than Sn, thereby leading to electronic deficiency, which is likely the reason the chemistry did not work. In the next set of experiments, we attempted to determine if the size of the dopant element is a critical factor and considered the existence of $RE[Pb_xGe_{1-x}]_2$ (isoelectronic substitution of Ge with a much heavier element, Pb). These experiments were also unsuccessful and led to the identification of a number of binary germanides, including RE_3Ge_4 (RE=Y, Gd–Tm) [4b,10]. At this point, we decided to also explore the electron-richer Bi, which surprisingly produced a very large family of bismuth-substituted digermanides with general formulas $RE[Bi_xGe_{1-x}]_2$ (RE=Y, Pr, Nd, Sm, Gd–Tm, Lu). Depending on the nature of the rare-earth metal, they form in three very similar structures, which for the sake of simplicity, are hereafter referred to as REBiGe.

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With the paper, we report the synthesis and the flux-growth of single-crystals of these compounds. Their structures, established from single-crystal X-ray diffraction, and the basic magnetic properties – determined by means of bulk magnetometry – are also discussed.

2. Experimental

2.1. Synthesis

Most of the synthetic work was performed inside an argon-filled glove box or under vacuum. All elements used for synthesis were purchased from Alfa or Aldrich with stated purity greater than 99.9 wt.%. In a typical experiment, a reaction mixture containing the starting materials in the molar ratio *RE*:Ge:Bi=1:2:8 (*RE*=La–Sm, Gd–Lu) was loaded into 2 cm^3 alumina crucibles. The crucibles were subsequently encapsulated in fused silica tubes, which were flame-sealed under vacuum and heated for reaction in a box furnace. The heating program included a quick ramping to 1273 K at a rate 200 K/h, homogenization for 20 h, and cooling down to 873 K at a rate of 10 K/h. At this temperature the excess molten flux was easily removed by decanting it and the grown crystals were isolated. Details of the metal flux method can be found elsewhere [7].

The Bi-flux technique produced the best results in terms of yield and crystal quality. Due to the very different melting temperatures of the constituent elements and the evaporative loss of bismuth, the *RE*BiGe phase could not be reliably made via arc-melting. Induction melting in sealed tubes worked, but the method was unsuccessful in producing phase-pure material—even after a long time (1–2 weeks) annealing, the induction melted products were multi-phase mixtures and the size/quality of the single-crystals from induction melting was inferior compared to the flux-produced samples.

2.2. X-ray diffraction

Single-crystal X-ray diffraction data were collected on a Bruker SMART CCD-based diffractometer (3-circle goniometer, monochromated MoKα sealed source with λ=0.71073 Å). The data acquisitions were performed in batch runs at different ω and φ angles with the SMART software [11a]. The raw data were integrated using SAINT [11b] and semiempirical absorption correction was applied using SADABS [12]. The unit cell parameters were refined using all measured reflections. The structure solution and refinement were done using the SHELXTL package [13]. Refined parameters included the scale factor, the atomic positions with anisotropic displacement parameters (excluding the disordered Ge4 is structures **I** and **II**—see below), extinction coefficients (where applicable). Tables 1–3 give further details of the data collection and structure refinement parameters for all structures; final positional and equivalent isotropic displacement parameters for selected ones are listed in Tables 4–6, respectively [14]. Important interatomic distances are provided in Table 7.

X-ray powder diffraction patterns were collected using a Rigaku MiniFlex powder diffractometer (filtered CuKα radiation with λ=1.5418 Å). The collected powder patterns were primarily used for phase identification of the reaction products, carried out with the aid of the JADE 6.5 software package. The experimental powder X-ray diffraction patterns matched well with those calculated from the single-crystal work.

2.3. Magnetic susceptibility measurements

Field-cooled dc magnetization (M) measurements were conducted using a quantum design magnetic property measurement system (MPMS) SQUID. The measurements were done on single-crystal samples in the direction parallel to the basal plane under an applied field (H) of 500 Oe. The temperature range of the measurements was from 5 K to 300 K. Measurement in the direction normal to the basal plane was also performed on a single-crystal of HoBiGe to examine the effects of crystal anisotropy. Superconductivity has been reported for $LuGe_2$ [15], thus magnetization measurements (in a SQUID magnetometer down to 1.8 K) and resistivity measurements (in a dilution refrigerator down to 50 mK) of $Lu[Bi_xGe_{1-x}]_2$ were also carried out.

2.4. Energy-dispersive X-ray spectroscopy (EDX) analysis

EDX analysis was conducted using a JEOL 7400 F electron microscope equipped with an INCA-Oxford energy-dispersive spectrometer. Data were acquired for several areas on the same sample and then averaged. The obtained results (provided as supporting information) are in good agreement with the refined compositions and the elemental-mapping confirms the homogeneity of the samples.

Table 1
Selected single-crystal data collection and structure refinement parameters for $RE[Bi_xGe_{1-x}]_2$ (*RE*=Pr, Nd, Sm, Gd, Tb).

	Structure **I**				
Empirical formula	$PrBi_{0.31(1)}Ge_{1.63(1)}$	$NdBi_{0.28(1)}Ge_{1.62(1)}$	$SmBi_{0.26(1)}Ge_{1.64(2)}$	$GdBi_{0.21(1)}Ge_{1.69(2)}$	$TbBi_{0.14(1)}Ge_{1.74(2)}$
Formula weight	323.75	321.21	322.86	324.45	315.01
Space group, Z			*Cmcm* (no. 63), *Z*=8		
Radiation, λ			MoKα, 0.71073 Å		
Temperature			−153 °C		
Unit cell parameters					
a/Å	4.147(2)	4.1204(4)	4.0733(7)	4.0404(12)	4.0052(14)
b/Å	31.279(14)	31.070(3)	30.715(5)	30.444(9)	30.213(10)
c/Å	4.303(2)	4.2592(4)	4.2047(7)	4.1629(12)	4.1210(14)
V/Å^3	558.1(4)	545.27(9)	526.03(15)	512.1(3)	498.7(3)
ρ_{calc}/g cm^{-3}	7.721	7.833	8.153	8.416	8.391
μ/cm^{-1}	538.9	544.6	573.6	595.5	485.9
Data: parameters ratio	477: 30	433: 30	423: 29	421: 29	402: 29
Final *R*1[a] ($I>2\sigma_I$)	*R*1=0.0317, *wR*2=0.0642	*R*1=0.0258, *wR*2=0.0589	*R*1=0.0214, *wR*2=0.0484	*R*1=0.0276, *wR*2=0.0525	*R*1=0.0233, *wR*2=0.0535
Largest diff. peak and hole/ e$^-$ Å^{-3}	1.40 and −1.50	1.71 and −1.40	1.40 and −1.57	3.04 and −3.01	1.90 and −2.33

[a] $R1=\sum||F_o|-|F_c||/\sum|F_o|$; $wR2=[\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w=1/[\sigma^2F_o^2+(A\cdot P)^2+(B\cdot P)]$, and $P=(F_o^2+2F_c^2)/3$; *A* and *B* weight coefficients.