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New polymorph of CaZnGe: Synthesis, crystal structure and thermoelectric properties

Min Zhu, Sheng-Qing Xia*

State Key Laboratory of Crystal Materials, Institute of Crystal Materials, Shandong University, Jinan, Shandong, 250100, People's Republic of China

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ABSTRACT

Intermetallic compounds with layered structures can be potential candidates for thermoelectric applications owing to the excellent electrical and thermal transport properties. Here a new polymorph of CaZnGe, was synthesized and characterized on structures and thermoelectric properties. Different from previously reported isomer, this newly discovered CaZnGe crystallizes in the hexagonal space group *P*-6*m*2 (NO. 187), which can be closely related to the LiZnGe structure type. First principle theoretical calculations were incorporated to investigate the electronic band structure, and the results indicated that this material might be poor metallic, consistent with the measured resistivity behaviour. The thermal conductivity of CaZnGe is rather low at room temperature, but starts to increase dramatically at high temperature region due to the bipolar effect.

1. Introduction

Germanium intermetallics are very interesting for their diverse crystal structures [1–4]. Usually, various cluster ions can be found for the alkali or alkaline-earth analogues, i.e., isolated Ge^{4-} anions in $Li_{18}Na_2Ge_{17}$ [5], $[Ge_2]^{6-}$ dumbbells in $BaMg_2Ge_2$ [6], $[Ge_4]^{4-}$ tetrahedrons in Li_3NaGe_2 [2], and $[Ge_{12}]^{12-}$ in Li_7RbGe_8 [7]. Some phases also feature Ge or MGe (M = another metal) layers as in α-$CaGe_2$ [8], β-$CaGe_2$ [8], $BaZn_2Ge_2$ [9] and Eu_2AuGe_3 [10]. If incorporated with the rare-earth cations, three-dimensional frameworks can also been found for substantial germanium-containing compounds. Such examples include, but not limited to, $RE_2Ru_3Ge_5$ (RE = La, Ce, Nd, Gd, Tb) [11], $Tm_5Zn_4Ge_6$ [12], Sm_4Ge_7 [13], and RE_4TGe_8 (RE = Yb, Gd; T = Cr, Ni, Ag) [14]. The rich structures of these Ge-containing intermetallics also correspond to unusual electronic structures, for which interesting physical properties have been often reported, i.e., thermoelectrics [15–17], superconductivity [18–20], complex magnetic ordering [11,21,22], and potential applications on lithium-ion batteries [23,24]. For Ge-based clathrates, potential thermoelectric applications are often expected since they perfectly fulfill the "PGEC (phonon glass-electron crystal)" criteria [25]. For example, the n-doped type-I clathrate $Ba_8Ga_{16}Ge_{30}$ achieved an optimized figure-of-merit zT 1.35 at 900 K [26].

For the ternary A–Zn–Ge system (A = alkaline-earth or rare-earth metal), the structures can be various originating from the diverse ZnGe anionic layers. Since Ge and Zn atoms are similar in sizes, in many cases they can statistically occupy the same atomic site. Typically, there are three types of patterns observed among these phases: (1) Zn and Ge are both ordered; (2) Zn or Ge is partially occupied or disordered; (3) Zn and Ge are statistically mixed at the same crystallographic sites. For most compounds, the first pattern is valid, however, the rest two were also observed, such as in $RE_5Zn_{4-x}Ge_6$ [22], $R_2Zn_{1-x}Ge_6$ [27], $REGe_{2-x}$ (*RE* = La–Nd, Sm) [13]. Specifically, in the cases of $REGe_{2-x}$ [13] and $Eu(Zn_{1-x}Ge_x)_2$ system [28], more complex structures in combination of several above patterns is usually realized governing by the Ge defect levels or the Zn/Ge contents.

The thermoelectric properties related to the layered Ge-compounds may be very interesting and promising. The two-dimensional anionic structures can exhibit good electrical conductivity owning to the high carriers mobility [29,30], accompanied by low thermal conductivity originating from the scattering of the interlayered cations [31]. In addition, Peierls lattice distortion caused by the layered charge density wave (CDW) may also bring a significant contribution to the decreasing of thermal conductivity [32]. In this work, a new germanium-containing layered intermetallic compound, CaZnGe, was synthesized and systematically characterized. This compound, hereafter β-CaZnGe, is found to be a polymorph of previously reported α-CaZnGe [33], which crystallizes in a different structure closely related to the LiZnGe type [34].

* Corresponding author.
E-mail address: shqxia@sdu.edu.cn (S.-Q. Xia).

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Thermoelectric properties of this new material were explored as well, which were combined by the theoretical calculations to better understand the structure-property-correlations of this novel phase.

2. Experimental

2.1. Synthesis

Single crystals of β-CaZnGe were synthesized by using the Pb-flux reactions. The starting materials were commercially purchased and used as received: Ca (Alfa, 99%), Zn (Alfa, 99.99%), Ge (Alfa, 99.99%), Pb (Alfa 99.99%). All synthetic processes were carried out in an argon-filled glovebox with O_2 level controlled below 0.1 ppm or under vacuum. The reactants were loaded in corundum tubes with a stoichiometric ratio Ca:Zn:Ge:Pb = 2:1:1:15, which were subsequently sealed in fused silica tube by flame seal under a vacuum of 10^{-5} Torr. The reaction mixture was first heated to 950 °C at a rate of 200 °C h^{-1} and then kept at this temperature for 20 h. After this homogeneity process, the furnace was slowly cooled down to 550 °C at a rate of 4 °C h^{-1}. At this temperature, the reaction was terminated and the excess molten Pb-flux was removed by centrifuge. Black crystals of the title compound with layered shapes were obtained. After soaked in a mixed solution containing ~10% H_2O_2 and ~20% CH_3COOH, the surfaces of the crystals were clean and high-purity β-CaZnGe could be prepared. It should be noted that β-CaZnGe seems to form with the reactions in high Ca-contents and a comparing experiment with the stoichiometric ratio of Ca:Zn:Ge:Pb = 1:1:1:15 resulted in the α-CaZnGe instead.

2.2. Single-crystal X-ray diffraction

β-CaZnGe is stable in air, and the single crystal data collections can thus be done at room temperature without further protection of the inert gas. The crystal was first cut into appropriate sizes and then glued to the tip of a glass fiber by using epoxy resin AB glue adhesive. The data collections were carried out by using a Bruker SMART APEX-II CCD area detector on a D8 goniometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with 15 s exposure time and θmax = 28.8°. Data collection, data reduction and integration, together with global unit cell refinements were performed by the INTEGRATE program incorporated in the APEX2 software [35]. Structure refinements were carried out with the aid of the SHELX (version 6.12) program package [36]. Anisotropic atomic displacement parameters were applied for all atoms.

After the structure was solved by direct method, the model was rechecked by refining the structure with freed site occupancies for each atom, which all resulted in reasonable values close to 100%. In addition, if switching the Zn and Ge positions, significantly different temperature parameters were found between Zn and Ge atoms with the ADPs of Ge two or three times higher than those of Zn, and the statistical refinements on Ge sites corresponded to obviously much lower occupancies as 90.4% and 94.5%. With these attempts, the rationality of the reported ordered structure can be verified. Note that for this layered structure, it is reasonable that the Umax/Umin of the atoms in the layers will be a little high due to the anisotropy of the structure, i.e., along the c-axis weaker interatomic interactions and larger ADPs were identified.

Important information on the data collection and structure refinement of β-CaZnGe are summarized in Table 1. Standardized atomic coordinates and isotropic atomic displacement parameters of β-CaZnGe are collected in Table 2. Selected bonding distances are tabulated in Table 3. Further information in the form of CIF has been deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: 49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de); depository CSD-434492 for β-CaZnGe.

Table 1
Selected crystal data and structure refinement parameters for β-CaZnGe.

Formula	β-CaZnGe
fw/g·mol^{-1}	178.04
T/K	296(2)
Radiation, wavelength	Mo-Kα, 0.71073 Å
Space group, No.	*P*-6*m*2 (NO. 187)
Z	3
Cell dimensions	
a/Å	4.237(3)
c/Å	12.760(19)
V/Å^3	198.4(4)
ρ_{calc}/g·cm^{-3}	4.471
$\mu_{Mo\ K\alpha}$/cm^{-1}	2.197
Final *R* indices[a] [$I > 2\sigma_{(I)}$]	$R1 = 0.0465$
	$wR2 = 0.1266$
Final *R* indices[a] [all data]	$R1 = 0.0581$
	$wR2 = 0.1317$
largest diff. peak and hole (e$^-$·Å^3)	1.406/-1.030

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, and $w = 1/[\sigma^2F_o^2+(A\cdot P)^2 + B\cdot P]$, $P = (F_o^2 + 2F_c^2)/3$; A and B are weight coefficients.

Table 2
Refined atomic coordinates and isotropic displacement parameters for β-CaZnGe.

Atoms	*Wyckoff*	*x*	*y*	*z*	U_{eq}[a](Å^2)
Ca1	*2i*	2/3	1/3	0.1653(5)	0.014(2)
Ca2	*1f*	2/3	1/3	0.5	0.017(3)
Zn1	*1a*	0	0	0	0.023(2)
Zn2	2h	1/3	2/3	0.3463(3)	0.020(2)
Ge1	*1c*	1/3	2/3	0	0.018(2)
Ge2	2g	0	0	0.3212(3)	0.017(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

2.3. Elemental analysis

Energy Dispersive X-ray Spectroscopy (EDS) was taken on a picked single crystal of β-CaZnGe with a Hitachi FESEM-4800 field emission microscope equipped with a Horiba EX-450 EDS. The measured composition is in good agreement with the results obtained from the single-crystal X-ray diffraction data (Supporting Information).

2.4. Powder X-ray diffraction

Powder X-ray diffraction patterns was taken at room temperature by a Bruker AXS X-ray powder diffractometer using Cu-Kα radiation to analyze the purity of the β-CaZnGe samples, which were prepared by the spark plasma sintering experiments. Data acquisition was performed with the aid of the Bruker software in a 2θ step size of 0.04°. The experimental patterns were found to

Table 3
Important interatomic distances (Å) in β−CaZnGe.

Atom pairs		Distances (Å)
Ca1 –	Ge1 × 3	3.230(5)
	Ge2 × 3	3.153(5)
	Zn1 × 3	3.230(5)
	Zn2 × 3	3.364(6)
Ca2 –	Ge2 × 6	3.345(3)
	Zn2 × 6	3.135(3)
Zn1 –	Ge1 × 3	2.446(2)
Zn2 –	Ge2 × 3	2.466(2)