

Rare-earth Metal Substitution in Calcium Germanides with the Tetragonal Cr_5B_3 Type Structure

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Dedicated to Professor Thomas Schleid on the Occasion of His 65th Birthday

Abstract: Calcium germanides with two mid-late rare-earth metals, $\text{Ca}_{5-x}\text{Gd}_x\text{Ge}_3$ and $\text{Ca}_{5-x}\text{Tb}_x\text{Ge}_3$ ($x \approx 0.1\text{--}0.2$), have been synthesized and structurally characterized. Additionally, a lanthanum-rich germanide with calcium substitutions, $\text{La}_{5-x}\text{Ca}_x\text{Ge}_3$ ($x \approx 0.5$) has also been identified. The three structures have been established from single-crystal X-ray diffraction methods and confirmed to crystallize with the Cr_5B_3 -type in the tetragonal space group $I4/mcm$ (no. 140; $Z = 4$; Pearson symbol $tI32$), where part of the germanium atoms are interconnected into Ge_2 -dimers, formally $[\text{Ge}_2]^{6-}$. Rare-earth metal and calcium atoms are arranged in distorted trigonal prisms, square-antiprisms and cubes, centered by Ge or rare-earth/calcium metal atoms. These studies show that amount of trivalent rare-earth metal atoms substituting divalent calcium atoms is in direct correlation with the lengths of the Ge–Ge bond within the Ge_2 -dimers, with distance varying between 2.58 Å in $\text{Ca}_{5-x}\text{Gd}_x\text{Ge}_3$ and 2.75 Å in $\text{La}_{5-x}\text{Ca}_x\text{Ge}_3$. Such an elongation of the Ge–Ge bond is consistent with the notion that the parent Ca_5Ge_3 Zintl phase (e.g. $(\text{Ca}^{2+})_5[\text{Ge}_2]^{6-}[\text{Ge}^{4-}]$) is being driven out of the ideal valence electron count and further reduced. In this context, this work demonstrates the ability of the germanides with the Cr_5B_3 structure type to accommodate substitutions and wider valence electron count while maintaining their global structural integrity.

Introduction

Over the last 10–15 years, we have investigated a number of binary and ternary rare-earth metal germanides.^[1–7] Focus of the prior work has been not only on elements from the p -block (X) that have been introduced, allowing the $RE\text{--}X\text{--}Tt$ systems (RE = rare-earth, Tt = Tetrel, i.e., group 14 elements Si, Ge) to form new structures and bonding patterns,^[2,6] but also on the substitution of rare-earth metals with alkaline-earth metals in different valence state. Good examples of the latter approach and its effects on the electronic structure, site preference, and magnetic properties, respectively, are the extended series $RE_{5-x}\text{Ca}_x\text{Ge}_4$ and $RE_{5-x}\text{Mg}_x\text{Ge}_4$.^[6,7]

The notion that RE^{3+} ions can be aliovalently replaced by Mg^{2+} or Ca^{2+} ones demonstrates that the structure, Gd_5Si_4 -type in the particular cases of $RE_{5-x}\text{Mg}_x\text{Ge}_4$ and $RE_{5-x}\text{Ca}_x\text{Ge}_4$, could be continuously varied based on the amount of valence electrons. Besides exploratory work on the “electronic”-effects

on the structure, we were also intrigued by the possibility to use difference in sizes as a structure-property parameter. In this context, we will note here that Ca^{2+} is about the same size as the early RE^{3+} ions, and larger than the late RE^{3+} ions,^[8] which is the opposite scenario observed with regard to the sizes of the Mg^{2+} and RE^{3+} cations. Employing different size cations presents an opportunity to study the coloring of the metal sites in a given crystal structure. At the same time, we must also note that “electronic”- and “size”-effects clearly become coupled, which was evidenced by the very different homogeneity ranges of the families $RE_{5-x}\text{Mg}_x\text{Ge}_4$ ($1.2 < x < 2.1$; $RE = \text{Gd}\text{--}\text{Lu}$, Y) and $RE_{5-x}\text{Ca}_x\text{Ge}_4$ ($1.5 < x < 3.6$; $RE = \text{La}$, Ce, Nd, Sm, Tb–Lu).

As noted in an earlier contribution on the attempts to make $RE_{5-x}\text{Ca}_x\text{Ge}_4$, a number of Ca-substituted rare-earth germanides crystallizing with the Gd_5Si_4 -type were successfully made.^[6] In addition to the compounds crystallizing with the Gd_5Si_4 -type, in each reaction there were also crystals of $RE_{5-x}\text{Ca}_x\text{Ge}_3$ (both with the hexagonal Mn_5Si_3 type and/or the tetragonal Cr_5B_3 type). Through optimizations of the conditions, high quality samples for magnetization measurements of the hexagonal $RE_{5-x}\text{Ca}_x\text{Ge}_3$ phases (with the early rare-earth metals only) could be synthesized.^[9] However, to date the title tetragonal $RE_{5-x}\text{Ca}_x\text{Ge}_3$ phases (or rather, $\text{Ca}_{5-x}\text{RE}_x\text{Ge}_3$ and $\text{La}_{5-x}\text{Ca}_x\text{Ge}_3$) have not been made as phase-pure samples. Therefore, this paper only discusses the aspects of the synthesis and structural characterization of these compounds.

Results and Discussion

Synthesis

As mentioned in the introduction, the phases $\text{Ca}_{5-x}\text{Gd}_x\text{Ge}_3$ and $\text{Ca}_{5-x}\text{Tb}_x\text{Ge}_3$ ($x \approx 0.1\text{--}0.2$), and $\text{La}_{5-x}\text{Ca}_x\text{Ge}_3$ ($x \approx 0.5$) were discovered over the course of the work on $RE_{5-x}\text{Ca}_x\text{Ge}_4$.^[6] For the full details, the reader is referred to the earlier article describing the full scope of the synthetic work. Here, we will only reiterate that although all rare-earth metals were tried, these are only the members identified so far. Given the very low amounts of rare-earth metals in $\text{Ca}_{5-x}\text{RE}_x\text{Ge}_3$, it is likely that other members exist as well, but have not been properly identified—after all, the yields were low and additional characterization work was not possible. Crystals could not be grown out of Pb or In molten flux either. Only exception is $\text{Eu}_{5-x}\text{Ca}_x\text{Ge}_3$, where a few crystals were grown as a side product to $\text{Eu}_{2-x}\text{Ca}_x\text{PbGe}_2$.^[10] CIF from the refinement for $\text{Eu}_{5-x}\text{Ca}_x\text{Ge}_3$ ($x \approx 0.5$) is provided as supplementary material. Since both Eu_5Ge_3 and Ca_5Ge_3 are known to exist with the same structure,^[11,12] it is possible to suggest that a full range $\text{Eu}_{5-x}\text{Ca}_x\text{Ge}_3$ solid solutions could be prepared.

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Crystal structure

The title compounds crystallize with the well-known tetragonal Cr_5B_3 -type (space group $I4/mcm$ (no. 140); $Z = 4$; Pearson symbol $tI32$).^[13] The structure has received much attention in the past,^[14–17] and will only be briefly discussed. The brief description will be devoted to the structural effects and subtleties associated with the metal-metal substitutions into the structure.

$Ca_{5-x}Gd_xGe_3$ and $Ca_{5-x}Tb_xGe_3$ ($x \approx 0.1–0.2$) are essentially rare-earth metal doped versions of the known binary phase Ca_5Ge_3 ,^[12] and the level of rare-earth metal incorporation is rather small (Table 1). As evident from the metrics of the respective unit cells, there is not much change in the unit cell volumes of $Ca_{5-x}Gd_xGe_3$ and $Ca_{5-x}Tb_xGe_3$ compared to that of Ca_5Ge_3 ($\approx 880 \text{ \AA}^3$), which confirms that conjecture.

$La_{5-x}Ca_xGe_3$ ($x \approx 0.5$), on the other hand, is a rare-earth metal rich phase and can be considered as calcium metal doped version of the binary phase La_5Ge_3 . However, this analogy is somewhat misleading since La_5Ge_3 is dimorphic, with the two known polymorphs being isotypic with Mn_5Si_3 (hexagonal) and with Pu_5Rh_3 (tetragonal).^[4] Following that, the $La_{5-x}Ca_xGe_3$ ($x \approx 0.5$) phase isotypic with Cr_5B_3 cannot be viewed as a simple “alloy”. The unit cell volume for the latter phase is also larger than the rest (Table 1), despite that La and Ca have not too different atomic sizes.^[8] More importantly the very different c/a ratios: $Ca_{5-x}Gd_xGe_3$ and $Ca_{5-x}Tb_xGe_3$ ($c/a \approx 1.92$) vs $La_{5-x}Ca_xGe_3$ ($c/a \approx 1.78$), also paint a picture of unusual relationship between the Ca-rich and Ca-poor variants of the Cr_5B_3 -type structured germanides.

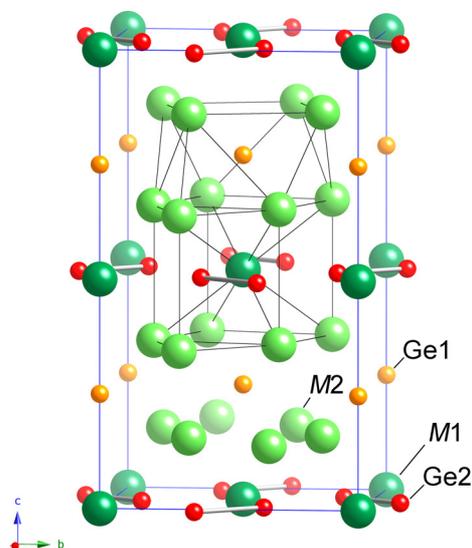


Figure 1. Off [100]-view of the crystal structure of the $Ca_{5-x}RE_xGe_3$ and $La_{5-x}Ca_xGe_3$ ($RE = Gd$ and Tb) compounds, emphasizing the Ge_2 dimers and the packing of the metal-atom polyhedra. The unit cell is outlined.

As it can be gathered from the crystal structure representation in Figure 1, the structure is best seen as an array of fused trigonal prisms and square antiprisms of Ca and RE

atoms that are centered by Ge atoms. Also, as shown in Figure 1, there are cubes made up of metal atoms and centered by predominantly Ca atoms—*vide infra*). The packing of these polyhedra in layers, as shown in Figure 2, leaves behind distorted octahedral of metal atoms (denoted as M1) within the slabs located at $z = 1/4$ and $z = 3/4$, which we have dubbed “2–1” slabs and they host isolated Ge atoms. The slabs located at $z = 0$ and $z = 1/2$ we have dubbed “3–2” slabs and the overall arrangement within this fragment of the structure is reminiscent with the Mo_2FeB_2 -type structure (which is ternary variant of the U_3Si_2 structure.^[18] Within the “3–2” units, there are Ge_2 -dimers present too. Thus, the overall “5–3” structure can be rationalized as an intergrowth of a slab with isolated Ge atoms (“2–1”) and a slab with dimerized Ge atoms (“3–2”). Detailed views of each slab are given in Figure 2. In this regard, the $Ca_{5-x}RE_xGe_3$ structure is very much alike $RE_{5-x}Ca_xGe_4$ which can be also thought to be the intergrowth of a RE_2CaGe_2 slab (also isopointal with Mo_2FeB_2) and a $RE_{2-x}Ca_xGe_2$ slab.^[6] The main difference, besides the global symmetry, is the $RE_{2-x}Ca_xGe_2$ slab in the “5–4” structure, where the Ge atoms are also dimerized. This perhaps is the most succinct way to describe the observed crystal chemistry.

Table 1. Selected single-crystal data collection and structure refinement parameters for $Ca_{5-x}Gd_xGe_3$, $Ca_{5-x}Tb_xGe_3$ and $La_{5-x}Ca_xGe_3$

Empirical formula	$Ca_{4.90(1)}Gd_{0.10}Ge_3$	$Ca_{4.82(1)}Tb_{0.18}Ge_3$	$La_{4.50(1)}Ca_{0.50}Ge_3$
Formula weight	429.9	439.6	776.0
Temperature	200(2) K		
Radiation, λ	Mo K α , 0.71073 Å		
Space group, Z	$I4/mcm$ (No. 140), 4		
a (Å)	7.6978(11)	7.7014(8)	8.0043(10)
c (Å)	14.826(4)	14.811(3)	14.256(4)
c/a	1.93	1.92	1.78
V (Å ³)	878.5(3)	878.4(2)	913.4(3)
ρ_{cal} (g/cm ³)	3.25	3.32	6.28
μ (cm ⁻¹)	137.0	143.4	304.7
Goodness-of-fit on F^2	1.116	1.102	1.053
Unique reflections	317	317	331
Refined parameters	17	17	16
R_1 ($I > 2\sigma$) ^a	0.0161	0.0231	0.0134
wR_2 ($I > 2\sigma$) ^a	0.0377	0.0523	0.0295
Largest diff. peak and hole ($e^-/\text{\AA}^3$)	1.22 & -0.34	3.74 ^b & -0.45	0.81 & -0.57

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

^b The small residual peak is located at $0 \frac{1}{2} \frac{1}{2}$, 2.49 Å away from Ca1. It is possible that there is interstitial chemistry at play here, similar to La_5Pb_3O but attempts to refine light non-metallic elements at that position (H, C, N, O) were not successful.

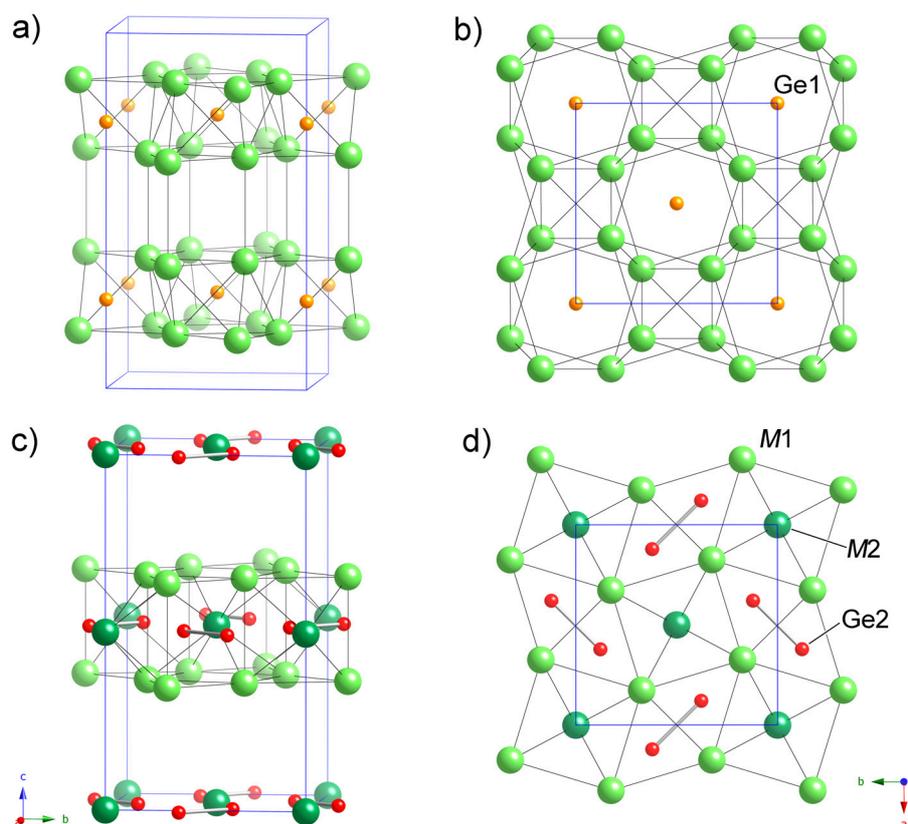


Figure 2. Close-up views in orthogonal directions of the slabs making up the “5–3” structure—the “2–1” slab with isolated Ge atoms is shown in panels (a) and (b); the “3–2” slab with dimerized Ge atoms is depicted in (c) and (d). The square antiprisms around Ge1 are naturally capped by M2 atoms along the c-axis, but clarity, the respective bond are not drawn. These fragments allow the “5–3” structure to be rationalized as their intergrowth.

“5–3” germanides with the Cr_5B_3 structure type contain 4 atoms in the asymmetric unit, 2 of which are for the metal atoms and 2 for the germanium ones (Table 2). Due to the very small amounts of rare-earth element incorporation in $\text{Ca}_{5-x}\text{Gd}_x\text{Ge}_3$ and $\text{Ca}_{5-x}\text{Tb}_x\text{Ge}_3$ ($x \approx 0.1\text{--}0.2$), it is difficult to discern a specific site-preference, although it does appear that one of the metal sites, M2 is exclusively occupied by Ca atoms with the Gd and Tb atoms favoring the other site. In $\text{La}_{5-x}\text{Ca}_x\text{Ge}_3$ ($x \approx 0.5$), the amount Ca is more significant and the preference of Ca for site 4c is clearly observed. This is the position that centers the metal cubes, one of the essential building blocks of the Mo_2FeB_2 -like fragment (Figure 1 and 2). The same site-preference of Ca and RE atoms also exists for the entire series $\text{RE}_{5-x}\text{Ca}_x\text{Ge}_4$.^[6]

According to the refinements, the respective RE/Ca–Ge contacts are in the range 3.05 Å to 3.30 Å (Table 3). The RE–Ge/Ca–Ge in distances are generally slightly longer than the sum of the Pauling (single-bonded) radii of Ca, La (the largest of the RE atoms under consideration), and Ge atoms (e.g., $r_{\text{La}} + r_{\text{Ge}} = 2.93$ Å, $r_{\text{Ca}} + r_{\text{Ge}} = 2.98$ Å); this is suggestive of appreciable directional bonding between these types of atoms. All identified metrics regarding the distances are comparable with those of related RE–Ge systems.^[2,5,19-21]

Table 2. Atomic coordinates of the metal atoms and their equivalent isotropic displacement parameters U_{eq} ^a for $\text{Ca}_{5-x}\text{Gd}_x\text{Ge}_3$, $\text{Ca}_{5-x}\text{Tb}_x\text{Ge}_3$ and $\text{La}_{5-x}\text{Ca}_x\text{Ge}_3$

Atom	Site	x	y	z	U_{eq} (Å ²)
$\text{Ca}_{4.90(1)}\text{Gd}_{0.10}\text{Ge}_3$					
M1 ^a	16l	0.17669(5)	x+1/2	0.14052(4)	0.0131(2)
M2 ^b	4c	0	0	0	0.0156(4)
Ge1	8h	0.38168(4)	x+1/2	0	0.0098(1)
Ge2	4a	0	0	1/4	0.0134(2)
$\text{Ca}_{4.82(1)}\text{Tb}_{0.18}\text{Ge}_3$					
M1 ^a	16l	0.17486(8)	x+1/2	0.14181(6)	0.0155(3)
M2 ^b	4c	0	0	0	0.0180(7)
Ge1	8h	0.38153(6)	x+1/2	0	0.0113(2)
Ge2	4a	0	0	1/4	0.0152(3)
$\text{La}_{4.50(1)}\text{Ca}_{0.50}\text{Ge}_3$					
M1 ^b	16l	0.17398(2)	x+1/2	0.14722(2)	0.0122(1)
M2 ^c	4c	0	0	0	0.0296(3)

Ge1	8h	0.37878(6)	x+1/2	0	0.0121(2)
Ge2	4a	0	0	1/4	0.0124(2)

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

^b Refined occupancies for $M1$: 97.5(1)% Ca and 2.5% Gd in $Ca_{4.90(1)}Gd_{0.10}Ge_3$; 96.0(2)% Ca and 4.0% Tb in $Ca_{4.82(1)}Tb_{0.18}Ge_3$; 100% La in $La_{4.50(1)}Ca_{0.50}Ge_3$.

^c Refined occupancies for $M2$: 99.2(2)% Ca and 0.8% Gd in $Ca_{4.90(1)}Gd_{0.10}Ge_3$; 99.1(4)% Ca and 0.9% Tb in $Ca_{4.82(1)}Tb_{0.18}Ge_3$; 49.1(3)% Ca and 50.9% La in $La_{4.50(1)}Ca_{0.50}Ge_3$.

Metal-metal bonding also appears to be significant with many interactions in the 3.4–3.6 Å range. While, at a first sight, those may seem a bit longer than the $RE/Ca-RE/Ca$ contacts within the $RE_{5-x}Ca_xGe_4$ structures, some of which are on the order of 3.1 Å.^[6,9] This small “discrepancy” is likely an artefact of $RE_{5-x}Ca_xGe_4$ being rare-earth metal richer (and mostly stabilized for the late rare-earth metals which are naturally smaller) compared to discussed $RE_{5-x}Ca_xGe_3$, which are Ca- or La-rich. This speculation is bolstered by the range observed for lengths of $RE/Ca-RE/Ca$ bonds within the $RE_{5-x}Ca_xGe_3$ compounds with the hexagonal Mn_5Si_3 type structure.^[9] Based on the above, such metal-metal interactions are expected to strongly influence the electronic stability of the structure, and indeed, have been shown computationally to contribute to the metallicity of the apparent valence-precise Ca_5Ge_3 phase.^[15]

Table 3. Selected interatomic distances (Å) in $Ca_{5-x}Gd_xGe_3$, $Ca_{5-x}Tb_xGe_3$ and $La_{5-x}Ca_xGe_3$ and their correlations with the unit cell volumes and the number of valence electrons per formula unit

Parameter	$Ca_{4.90(1)}Gd_{0.10}Ge_3$	$Ca_{4.82(1)}Tb_{0.18}Ge_3$	$La_{4.50(1)}Ca_{0.50}Ge_3$
V (Å ³)	878.5(3)	878.4(2)	913.4(3)
# electrons	22.10	22.18	26.50
Ge1–Ge1	2.5762(9)	2.581(1)	2.745(1)
$M1-Ge1$	3.0529(8)	3.079(1)	3.1271(7)
$M1-Ge1$	3.1144(7)	3.1150(9)	3.1885(6)
$M1-Ge2$	3.2678(5)	3.2636(6)	3.3009(4)
$M1-M2$	3.5192(6)	3.5348(7)	3.6268(5)
$M1-M1$	3.618(1)	3.599(2)	3.3986(8)
$M2-Ge1$	3.0760(5)	3.0767(5)	3.1833(5)
$M2-Ge2$	3.707(1)	3.703(1)	3.5640(9)

Speaking of electron counts and the known problems with the application of the Zintl concept to the “5–3” structure as far as alkaline-earth metal tetrelides are concerned, we recall that the rationalizing this relatively simple structure should be straightforward—if one were to ignore all metal-metal bonding and assume the bonding with the Ge_2 -dimers to be a 2-center-2-electron bonds (i.e., $[(Ge_2)^{6-}]$ is isoelectronic with the Br_2 molecule), the structure of the binary Ca_5Ge_3 compound should be rationalized as $(Ca^{2+})_5[(Ge_2)^{6-}](Ge^{4-})$. Notice that the length of the Ge–Ge bond in Ca_5Ge_3 measure on the order of 2.575 Å, in excellent agreement with a number of other binary and ternary

rare-earth germanides such as Eu_5Ge_3 ,^[11] $RE_{5-x}Ca_xGe_3$,^[9] $RE_{5-x}Li_xGe_4$,^[5] the various members of the $[REGe_2]_n[RELi_2Ge]_m$ homologous series,^[22,23] RE_2AGe_2 (RE = rare-earth metal; A = Mg, Cd, In),^[2,20,21] $CaGe_2$,^[24] $CaInGe_4$,^[25] Gd_3Ge_5 ,^[26] and many others.^[27–29] Apparently, this simplified bonding picture of a salt-like solid provides an easy electron balance and leaves no electrons in excess. Yet, as mentioned already, Ca_5Ge_3 is metallic. Mudring and Corbett^[15] have done a comprehensive analysis on this structure and have shown the importance of the overlap of empty Ca 3d states with Ge 4p states, which is not captured by the Zintl formalism. Effectively, this means that what we assigned above as a single bond within the $[Ge_2]^{6-}$ dumbbell is not representative of the actual bonding picture, which is more akin to a (partial) double-bond. This line of thinking is fully supported by the elongation of the Ge–Ge bond in $Ca_{5-x}Gd_xGe_3$ ($x \approx 0.1$), $Ca_{5-x}Tb_xGe_3$ ($x \approx 0.2$), and $La_{5-x}Ca_xGe_3$ ($x \approx 0.5$), where d_{Ge-Ge} increases from 2.58 to 2.75 Å in that order, respectively. The trend is in clear correlation with the number of available valence electrons (Table 3). This situation (reduction of the system by substituting the divalent Ca atoms with the nominally trivalent RE atoms) complements the earlier experimental work on the oxidation of the stable AE_5Tt_3 phases (AE = alkaline-earth metal, Tt = Tetrel, i.e., Si, Ge, Sn, and Pb) to AE_5Tt_3Z (Z = H, F) that has been shown to lead to shortening of the $Tt-Tt$ bonds.^[30]

Prior structural studies on pure binary AE_5Tt_3 phases and the current crystallographic work are in excellent agreement as far as nearly all aspects of the structures are concerned. This includes the somewhat usual elongation of the anisotropic displacement parameter of the metal atom on the 4c site, $M2$ in the notation used throughout this paper. For context—the work by Leon-Escamilla and Corbett on Ca_5Ge_3 shows $U_{11} = U_{22}$ being almost four times smaller than U_{33} ,^[30] the work by Pöttgen *et al* on Eu_5Ge_3 shows $U_{11} = U_{22}$ being almost five times smaller than U_{33} .^[11] As shown in Figure 3 the exact same relationships between the principal U_{ij} tensor components exist for $Ca_{5-x}Gd_xGe_3$, $Ca_{5-x}Tb_xGe_3$, and $La_{5-x}Ca_xGe_3$. The origins of this “effect” are not yet understood and cannot be easily explained with the inherent electronic stability near the 22 valence electrons per formula unit mark (10 from the five alkaline-earth metal atoms and 12 from the 3 germanium atoms). Taking for example $La/Ca2$ in $La_{5-x}Ca_xGe_3$, a phase which is more than 4 electrons richer than $Ca_{5-x}Gd_xGe_3$ and $Ca_{5-x}Tb_xGe_3$, one can see that the distorted germanium octahedron around $La/Ca2$ is actually more uniform and less axially elongated—there are four equatorial Ge atom neighbors at 3.18 Å and two axial ones at 3.56 Å. Yet, the elongation of the thermal ellipsoid for $La/Ca2$ in $La_{5-x}Ca_xGe_3$ is the most extreme. Of course this could be attributed to the nearly statistical 50:50 distribution of atoms with unequal sizes on the said position. At the same time the elongation of the anisotropic displacement parameter of $Gd/Ca2$ and $Tb/Ca2$ along the c -axis is still quite clear (approx. 3 times) while less than 1% rare-earth metal substitutes for Ca on the 4c site (Table 2).

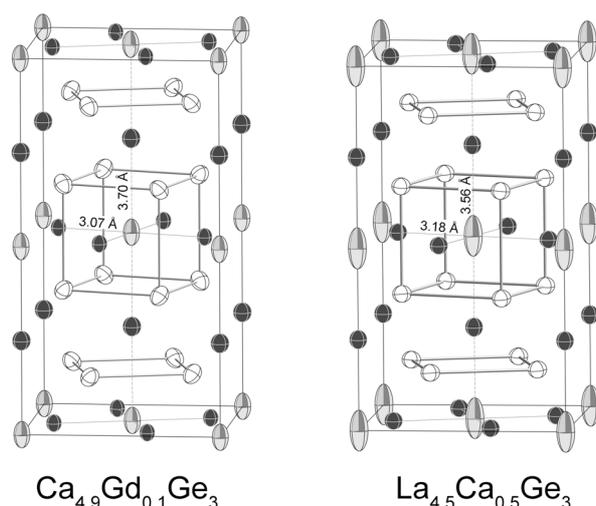


Figure 3. The crystal structures of the $\text{Ca}_{5-x}\text{Gd}_x\text{Ge}_3$ and $\text{La}_{5-x}\text{Ca}_x\text{Ge}_3$ drawn with anisotropic displacement parameters at the 98% probability level. In both refined structures the 4c site ($M2$) has elongated along the c -axis ellipsoid.

Experimental Section

Synthesis. The synthesis followed the established published procedures for $\text{RE}_{5-x}\text{Ca}_x\text{Ge}_4$ and $\text{RE}_{5-x}\text{Ca}_x\text{Ge}_3$.^[6,9] Accordingly, all manipulations were performed inside a glove-box under the inert atmosphere of argon (with oxygen and moisture levels below 1 ppm) or under vacuum. The starting materials were pure elements (> 99.9 % wt.) that were used as received. The reactions were carried out in welded Nb tubes that were then sealed in fused silica ampoules under vacuum. After the heat treatment, the fused silica ampoules were broken, the Nb tubes extracted and brought back into the glove-box and opened. The crystals were small had irregular morphologies. Air stability was not checked.

Powder X-ray Diffraction (PXRD). X-ray powder diffraction patterns were taken at room temperature using a Rigaku Miniflex powder diffractometer with filtered $\text{Cu K}\alpha$ radiation. The scans using were in θ - θ mode ($2\theta_{\text{max}} = 70^\circ$) with a step size of 0.05 and 2 sec/step counting time. The powder pattern data were only used phase analysis, which indicated the presence of multiple products in each reaction batch.

Single-Crystal X-ray Diffraction (SCXRD). Single crystals were selected under dry Paratone-N oil and cut to desired dimensions with a scalpel. Multiple crystals were tried, and for the ones with the best quality, intensity data were collected at 200 K on a Bruker SMART CCD diffractometer. The data collections were carried out at different ω and θ angles with a frame width of 0.8° along with 5–8 sec counting time. The SMART software package^[31] was used to collect the data and was finally integrated using SAINT.^[32] The data was corrected for absorption using SADABS.^[33] The structures were refined on F^2 with the aid of the SHELX package.^[34] The atomic coordinates from the previously reported germanide phases with the Cr_5B_3 type structure served as a suitable starting model for the refinements to take place.^[11,15,30] In the cases of $\text{Ca}_{5-x}\text{Gd}_x\text{Ge}_3$ and $\text{Ca}_{5-x}\text{Tb}_x\text{Ge}_3$ ($x \approx 0.1$ – 0.2), the refinements indicated unphysical site occupation factor (SOF) of almost 110% for the Ca1 site. This was modeled as randomly disordered Ca and RE atoms on that position. Site Ca2 in the structure of $\text{Ca}_{5-x}\text{Tb}_x\text{Ge}_3$ also showed statistically significant deviation from unity, while SOF of Ca2 in the

structure of $\text{Ca}_{5-x}\text{Gd}_x\text{Ge}_3$ deviated from 100% but within 2σ . For consistency though, both refinements are finished with the same constraints on Ca1 and Ca2.

For the structure of $\text{La}_{5-x}\text{Ca}_x\text{Ge}_3$ ($x \approx 0.5$), which is La-rich, an opposite scenario was observed—SOF of site La1 did not show any deviation from unity, while SOF of the La2 site was less than 50%. This was modeled by introducing random La-Ca disorder on that position.

Details of the data collection and selected crystallographic parameters are summarized in Tables 1–3. The corresponding crystallographic information files (CIF) has been deposited with the Cambridge Crystallographic Database Centre (CCDC) and can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk) with the following depository numbers: 2176413–2176416.

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Keywords: Germanides • Crystal structure • Zintl phases • Lanthanides

- 1 S. Bobev, T.-S. You, N.-T. Suen, S. Saha, R. Greene and J. Paglione, *Inorg. Chem.*, 2012, **51**, 620–628.
- 2 N.-T. Suen, P. H. Tobash and S. Bobev, *J. Solid State Chem.*, 2011, **184**, 2941–2947.
- 3 N.-T. Suen and S. Bobev, *Inorg. Chem.*, 2013, **52**, 12731–12740.
- 4 N.-T. Suen and S. Bobev, *Z. Anorg. Allg. Chemie*, 2014, **640**, 805–813.
- 5 N.-T. Suen, T.-S. You and S. Bobev, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.*, 2013, **69**, 1–4.
- 6 N. Suen and S. Bobev, *Z. Anorg. Allg. Chemie*, 2022, e202200016.
- 7 P. H. Tobash, S. Bobev, J. D. Thompson and J. L. Sarrao, *Inorg. Chem.*, 2009, **48**, 6641–6651.
- 8 R. D. Shannon, *Acta Crystallogr. Sect. A*, 1976, **32**, 751–767.
- 9 N.-T. Suen, M. Broda and S. Bobev, *J. Solid State Chem.*, 2014, **217**, 142–149.
- 10 N.-T. Suen, J. Hooper, E. Zurek and S. Bobev, *J. Am. Chem. Soc.*, 2012, **134**, 12708–12716.
- 11 R. Pöttgen and A. Simon, *Z. Anorg. Allg. Chemie*, 1996, **622**, 779–784.
- 12 B. Eisenmann and H. Schäfer, *Z. Naturforsch. B*, 1974, **29**, 460–463.
- 13 C. N. Guy and A. A. Uraz, *J. Less Common Met.*, 1976, **48**, 199–203.
- 14 A. M. Guloy and J. D. Corbett, *Inorg. Chem.*, 1996, **35**, 2616–2622.
- 15 A.-V. Mudring and J. D. Corbett, *J. Am. Chem. Soc.*, 2004, **126**, 5277–5281.
- 16 I. Schewe, P. Böttcher and H.-G. von Schnering, *Z. Krist.*, 1989, **188**, 287–298.
- 17 P. Böttcher, T. Doert, C. Druska and S. Bradtmöller, *J. Alloys Compd.*, 1997, **246**, 209–215.
- 18 F. Hulliger and B. Z. Xue, *J. Alloys Compd.*, 1994, **215**, 267–270.
- 19 G. S. Smith, Q. Johnson and A. G. Tharp, *Acta Crystallogr.*, 1967, **22**, 269–272.
- 20 P. H. Tobash, D. Lins, S. Bobev, A. Lima, M. F. Hundley, J. D. Thompson and J. L. Sarrao, *Chem. Mater.*, 2005, **17**, 5567–5573.
- 21 S.-P. Guo, J. J. Meyers, P. H. Tobash and S. Bobev, *J. Solid State Chem.*, 2012, **192**, 16–22.

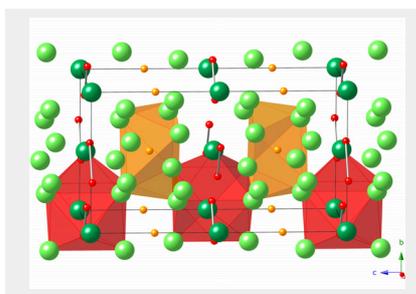
- 22 S.-P. Guo, T.-S. You, Y.-H. Jung and S. Bobev, *Inorg. Chem.*, 2012, **51**, 6821–6829.
- 23 S.-P. Guo, T.-S. You and S. Bobev, *Inorg. Chem.*, 2012, **51**, 3119–3129.
- 24 P. H. Tobash and S. Bobev, *J. Solid State Chem.*, 2007, **180**, 1575–1581.
- 25 T.-S. You, Y. Jung and S. Bobev, *Dalton Trans.*, 2012, **41**, 12446.
- 26 P. H. Tobash, D. Lins, S. Bobev, N. Hur, J. D. Thompson and J. L. Sarrao, *Inorg. Chem.*, 2006, **45**, 7286–7294.
- 27 R. Kraft and R. Pöttgen, *Monatsh. Chemie*, 2004, **135**, 1327–1334.
- 28 J. R. Salvador, J. R. Gour, D. Bilc, S. D. Mahanti and M. G. Kanatzidis, *Inorg. Chem.*, 2004, **43**, 1403–1410.
- 29 U. C. Rodewald and R. Pöttgen, *Solid State Sci.*, 2003, **5**, 487–493.
- 30 E. A. Leon-Escamilla and J. D. Corbett, *J. Solid State Chem.*, 2001, **159**, 149–162.
- 31 SMART, version 5.63; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003.
- 32 SAINT, version 6.45; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003.
- 33 SADABS, version 2.10; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003.
- 34 G. M. Sheldrick, *Acta Crystallogr. Sect. C* 2015, **71**, 3–8.

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The RE–Ca–Ge systems (RE = rare earth element) have been explored. Three new ternary compounds are reported.



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Calcium Germanides with the
Tetragonal Cr₅B₃ Type Structure

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