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Calcium Substitution in Rare-earth Metal Germanides with the Gd_5Si_4 Type Structure

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Dedicated to Professor Mercouri G. Kanatzidis on the Occasion of His 65th Birthday

Abstract: An extended series of rare-earth metal calcium germanides have been synthesized and structurally characterized. The compounds have the general formula $RE_{5-x}Ca_xGe_4$ ($1.5 < x < 3.6$; RE = rare-earth metal; Ce, Nd, Sm, Tb–Lu) and their structures have been established from single-crystal X-ray diffraction methods. They crystallize with the Gd_5Si_4-type in the orthorhombic space group *Pnma* (no. 62; Z = 4; Pearson symbol *oP*36), where the germanium atoms are interconnected into two kinds of Ge_2-dimers, formally $[Ge_2]^{6-}$. These studies show that Ca can be successfully incorporated into the host RE_5Ge_4 structure, whereby trivalent rare-earth metal atoms can be substituted by divalent calcium atoms. Rare-earth metal and calcium atoms are arranged in distorted trigonal prisms and cubes, centered by either Ge or Ca atoms. On one of the metal sites, the substitution is preferential and in 9 out of then 10 refined structures, the Wyckoff site 4*c* is found almost exclusively occupied by Ca. On the other two metal sites the substitution patterns appear to be governed by the mismatch between the size of the RE^{3+} and Ca^{2+} ions. This work further demonstrates the ability for the Gd_5Si_4 structure type to accommodate the substitution of a non-magnetic element while maintaining the global structural integrity.

Introduction

Following the discovery of giant magnetocaloric effect in $Gd_5Si_2Ge_2$,[1,2] the rare-earth metal silicides and germanides with the RE_5Tt_4 composition (RE = rare-earth, Tt = Tetrel, i.e., group 14 elements Si, Ge) have received much attention.[3-6] Interesting examples of bond making/breaking in RE_5Tt_4 compounds have been reported and thus far have been shown to have dramatic effects on the measured physical properties.[7] Numerous studies have therefore been devoted to compounds crystallizing with the Sm_5Ge_4-type (interslab Tt–Tt bonds broken), Gd_5Si_4-type (interslab Tt–Tt bonds formed), or several monoclinic types, i.e. one being $Gd_5Si_2Ge_2$, that contains a mixture of Tt–Tt dimers and/or monomers. The structural "transformation" between the Sm_5Ge_4-type and the Gd_5Si_4-type (N.B. same global symmetry and number of atoms in the unit cell—orthorhombic space group *Pnma* (no. 62); Pearson symbol *oP*36) has been accomplished through many different ways including temperature, pressure, applied magnetic fields, and variations in the chemical composition.[8-13] The latter has even been extended to elements outside the Tetrel family such as that shown for the phase transformations in $Gd_5Ga_xGe_{4-x}$ where the bonding is highly dependent on the valence electron concentration.[8] Not only have elements from the *p*-block been at the focus, but the substitution of rare-earth metals in the same valence state as shown for $Gd_{5-x}Y_xTt_4$, or substitution of rare-earth metals with alkaline-earth metals in different valence state, as shown for $La_{5-x}Ca_xGe_4$ and $RE_{5-x}Mg_xGe_4$ each report the effects on the electronic structure, site preference, and magnetic properties respectively.[7,14,15]

The approach where RE^{3+} is aliovalently replaced by Mg^{2+} or Ca^{2+} demonstrates that the structure could be continuously varied based on the amount of valence electrons without other structural alterations. The $Yb_{5-x}Mg_xGe_4$ system in particular,[16] is a unique example of a mixed-valent material in which the Yb^{2+}/Yb^{3+} states could be tuned depending on the amount of Mg in the structure. This motivated our further interests towards the exploration for the "size"-effect on the structure through the substitution of Ca^{2+} for a trivalent rare-earth metal, the initial results of which are presented in this article. Here we will note that Ca^{2+} is about the same size as the early RE^{3+} ions, and larger than the late RE^{3+} ions, which is the opposite scenario observed with regard to Mg^{2+} and RE^{3+}.[17] This presents an opportunity to delineate the roles played by the different ions and to study the coloring of the metal sites in the crystal structure.

The attempts to make $RE_{5-x}Ca_xGe_4$ turned out to be successful, and a number of Ca-substituted rare-earth germanides crystallizing with the Gd_5Si_4-type were discovered. They can be described with the general formula $RE_{5-x}Ca_xGe_4$ ($1.5 < x < 3.6$; RE = Ce, Nd, Sm, Tb–Lu). With $La_{5-x}Ca_xGe_4$ having been already reported,[14] only a few members of this extended family remain unknown thus far.

Results and Discussion

Synthesis

As mentioned in the introduction, this study was conceived as a follow-up work on the $RE_{5-x}Mg_xGe_4$ phases.[15] Initially, the loading stoichiometry of the reactions had the 3:2:4 (RE:Ca:Ge) ratio, which previously was used for the synthesis of $RE_{5-x}Mg_xGe_4$ ($x \approx 2$). These reactions were heated to 1373 K (rate 200°/h) where they were left for 20 h and then allowed to cool to 973 K (rate 100°/h) where they were left for 20 days. Although all rare-earth metals were tried, these conditions were not successful for a few of the members of the lanthanide family. Additionally, the first batch of experiments led to the discovery that the amount of Ca in the synthesized phases is typically higher than the amount of Mg on the isotypic $RE_{5-x}Mg_xGe_4$. Therefore, the next set of reactions were loaded according to

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2:3:4 (*RE*:Ca:Ge) ratio, which is more consistent with the refined stoichiometries $RE_{5-x}Ca_xGe_4$ ($x \approx 3$) from the single crystal work. Regardless of the adjusted nominal compositions, not all experiments were successful—for reasons that are not understood yet, $RE_{5-x}Ca_xGe_4$ (*RE* = La, Pr, Eu and Gd) could not be identified. For *RE* = La and Pr, the major products were $RE_{5-x}Ca_xGe_3$; for Eu, the reactions yielded mixtures of binary EuGe (possibly $Eu_{1-x}Ca_xGe$ with the CrB-type) and EuCaGe (Co_2Si-type). In the case of Gd-Ca-Ge, crystals with orthorhombic symmetry but different unit cell parameters ($a \approx 7.7$ Å; $a \approx 8.9$ Å; $c \approx 14.15$ Å; $V \approx 960$ Å^3) were found; the structure of this presumably new ternary (or pseudo-binary) phase remains elusive.

In addition to the compounds crystallizing with the Gd_5Si_4-type, in each reaction there were also crystals of $RE_{5-x}Ca_xGe_3$ (both with the hexagonal Mn_5Si_3 type and/or the tetragonal Cr_5B_3 type).[18,19] Through optimization of the reaction conditions, nearly phase-pure samples of the hexagonal $RE_{5-x}Ca_xGe_3$ phases (with the early rare-earth metals only) could be synthesized and their magnetic response studied;[20] to date the title $RE_{5-x}Ca_xGe_4$ phases, as well as the tetragonal $RE_{5-x}Ca_xGe_3$ have not been made as phase-pure samples. Lowering or raising the reaction temperature was explored, but without success—multiphase products were always present. Reactions in molten metal fluxes were not tried as a part of this study; such experiments with a suitable choice of flux and conditions could lead to the growth of appropriate single-crystals and should be pursued in future works.

Crystal structure

The compounds crystallize with the well-known orthorhombic Gd_5Si_4-type (space group *Pnma* (no. 62); $Z = 4$; Pearson symbol *oP*36).[21-24] 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 of *RE* and Ca atoms that are centered by Ge atoms. Also, as shown in Figure 1, the addition of the cubes made up of metal atoms (and centered by predominantly Ca atoms—*vide infra*) to the above described trigonal prisms results in an overall arrangement (in a slab of the structure) that is reminiscent with the U_3Si_3 structure, or rather its ternary variant, the Mo_2FeB_2-type structure. There are Ge_2-dimers present too, both within the RE_2CaGe_2 slab (Ge1 and Ge2 atoms), as well as between them (Ge3 atoms). Thus, $RE_{5-x}Ca_xGe_4$ can be thought to be the result of an “addition” of two imaginary fragments, namely the RE_2CaGe_2 slab and the $RE_{2-x}Ca_xGe_2$ slab, which are alternatively stacked along the direction of the *b*-crystallographic axis (Figure 1). This perhaps is the most succinct way to describe the observed crystal chemistry. Since this structure has been described in much detail previously,[14,15,16] only a brief description will be devoted to the structural effects associated with the Ca substitution into the structure.

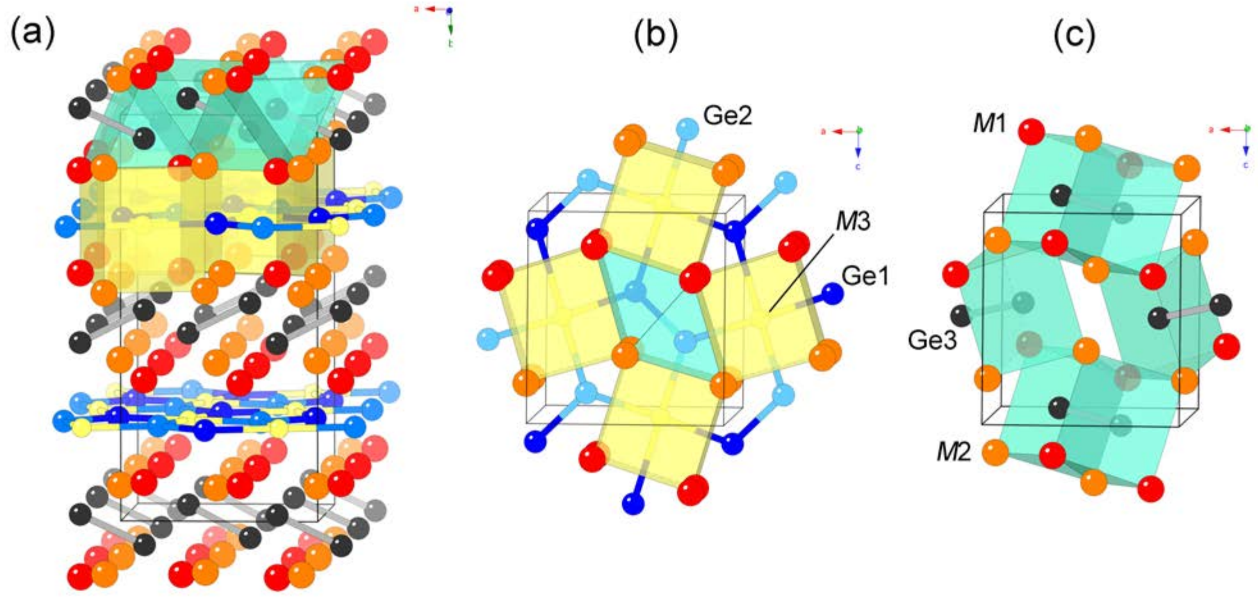

Figure 1. (a) Off [001]-view of the crystal structure of the $RE_{5-x}Ca_xGe_4$ (*RE* = rare-earth metal) compounds, emphasizing the Ge_2 dimers and the packing of the metal-atom polyhedra. The unit cell is outlined. **(b)** Close-up view of the RE_2CaGe_2-like fragments (akin to the Mo_2FeB_2 structure) viewed approximately down the *b*-axis. **(c)** Close-up view of the interslab Ge3–Ge3 fragments and their coordination by *RE*/Ca atoms. The slabs depicted in **(b)** and **(c)** allow the structure to be rationalized as their intergrowth.

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Table 1. Selected single-crystal data collection and structure refinement parameters for $RE_{5-x}Ca_xGe_4$ (*RE* = Ce, Nd, Sm, Tb, and Dy)

Empirical formula	$Ce_{3.22(1)}Ca_{1.88}Ge_4$	$Nd_{2.01(1)}Ca_{2.99}Ge_4$	$Sm_{1.89(1)}Ca_{3.11}Ge_4$	$Tb_{2.40(1)}Ca_{2.60}Ge_4$	$Dy_{1.78(1)}Ca_{3.22}Ge_4$
Formula weight	813.4	698.9	776.0	708.7	914.97
Temperature	200(2) K				
Radiation, λ	Mo Kα, 0.71073 Å				
Space group, Z	*Pnma* (No. 62), 4				
a (Å)	7.693(2)	7.601(2)	7.5654(12)	7.4337(9)	7.4682(9)
b (Å)	15.430(4)	15.361(4)	15.322(2)	15.0951(18)	15.2083(19)
c (Å)	8.092(2)	8.014(2)	7.9623(13)	7.8716(9)	7.8816(10)
V (Å^3)	960.6(5)	935.8(4)	923.0(3)	883.29(18)	895.18(19)
ρ_{cal} (g/cm^3)	5.62	4.96	5.03	5.84	5.26
μ (cm^{-1})	281.5	251.3	263.1	338.0	296.8
Goodness-of-fit on F^2	1.080	1.013	0.976	1.099	1.086
Unique reflections	1235	1202	1186	1141	1156
Refined parameters	49	48	49	49	49
R_1 ($I > 2\sigma_I$)[a]	0.0184	0.0178	0.0236	0.0244	0.0224
wR_2 ($I > 2\sigma_I$)[a]	0.0374	0.0356	0.0457	0.0419	0.0428
Largest diff. peak and hole (e^-/Å^3)	1.04 & −0.72	0.69 & −0.60	1.01 & −0.90	1.23 & −1.12	0.97 & −1.01

[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 $w = 1/[\sigma^2F_o^2 + (AP)^2 + (BP)]$ and $P = (F_o^2 + 2F_c^2)/3$. A and B are the respective weight coefficients (see the CIF data)

Table 2. Selected single-crystal data collection and structure refinement parameters for $RE_{5-x}Ca_xGe_4$ (*RE* = Ho, Er, Tm, Yb, and Lu)

Empirical formula	$Ho_{2.27(1)}Ca_{2.73}Ge_4$	$Er_{2.03(1)}Ca_{2.97}Ge_4$	$Tm_{2.20(1)}Ca_{2.80}Ge_4$	$Yb_{3.47(1)}Ca_{1.52}Ge_4$	$Lu_{2.26(1)}Ca_{2.74}Ge_4$
Formula weight	914.97	748.3	774.2	952.8	795.6
Temperature	200(2) K				
Radiation, λ	Mo Kα, 0.71073 Å				
Space group, Z	*Pnma* (No. 62), 4				
a (Å)	7.4249(6)	7.4095(6)	7.3834(6)	7.3557(5)	7.356(2)
b (Å)	15.1032(12)	15.1211(12)	15.0488(12)	15.0195(11)	14.979(4)
c (Å)	7.8863(6)	7.8894(6)	7.8701(6)	7.8515(6)	7.840(2)
V (Å^3)	884.37(12)	883.93(12)	874.46(12)	867.43(11)	863.9(4)
ρ_{cal} (g/cm^3)	5.81	5.62	5.88	7.30	6.12
μ (cm^{-1})	349.3	340.6	371.9	515.4	408.4
Goodness-of-fit on F^2	0.983	1.039	0.994	1.042	1.027
Unique reflections	1144	1137	1123	1118	1159
Refined parameters	49	49	49	49	49
R_1 ($I > 2\sigma_I$)[a]	0.0211	0.0260	0.0186	0.0291	0.0426
wR_2 ($I > 2\sigma_I$)[a]	0.0387	0.0444	0.0372	0.0598	0.0620
Largest diff. peak and hole (e^-/Å^3)	1.42 & −1.13	1.70 & −1.27	1.20 & −0.85	1.56 & −1.92	2.40 & −2.33

[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 $w = 1/[\sigma^2F_o^2 + (AP)^2 + (BP)]$ and $P = (F_o^2 + 2F_c^2)/3$. A and B are the respective weight coefficients (see the CIF data)

The Gd_5Si_4 structure type contains 6 atoms in the asymmetric unit, 3 of which are the metal atoms. One of these metal sites is almost exclusively occupied by Ca atoms. Only for $Yb_{5-x}Ca_xGe_4$, according to the refinements, there was more Yb than Ca at 4*c* (Table 3); in all other cases, Ca atoms are preferentially found there. This atom (*M*3 in the current notation, Wyckoff site 4*c*) centers the distorted cubes, one of the essential building blocks of the RE_2CaGe_2 fragment (Figure 1(b), the analog of the Mo_2FeB_2-type structure). This position also has six Ge neighbors—using a member in the middle of the series as an example, $Tb_{2.40(1)}Ca_{2.60}Ge_4$, the respective *RE*/Ca–Ge contacts are in the range 2.930 Å to 3.205 Å.

Table 3. Atomic coordinates of the metal atoms and their equivalent isotropic displacement parameters U_{eq}[a] for $RE_{5-x}Ca_xGe_4$ (*RE* = Ce, Nd, Sm, Tb–Lu)

Atom	Site	*x*	*y*	*z*	*RE*:Ca ratio	U_{eq} (Å^2)
$Ce_{3.22(1)}Ca_{1.88}Ge_4$						
*M*1	8*d*	0.18099(3)	0.12255(2)	0.32164(3)	0.767(2):0.233	0.009(1)
*M*2	8*d*	0.02492(3)	0.09765(2)	0.81562(3)	0.832(2):0.168	0.010(1)
*M*3	4*c*	0.35160(1)	1/4	0.9882(1)	0.027(2):0.973	0.010(1)
$Nd_{2.01(1)}Ca_{2.99}Ge_4$						
*M*1	8*d*	0.18337(3)	0.12223(2)	0.32381(3)	0.570(1):0.330	0.009(1)
*M*2	8*d*	0.02839(4)	0.09830(2)	0.81246(4)	0.435(1):0.565	0.011(1)
*M*3	4*c*	0.3539(1)	1/4	0.9882(1)	0:1	0.011(1)
$Sm_{1.89(1)}Ca_{3.11}Ge_4$						
*M*1	8*d*	0.18345(5)	0.12215(2)	0.32510(4)	0.626(2):0.374	0.011(1)
*M*2	8*d*	0.02762(7)	0.09793(3)	0.81309(7)	0.305(2):0.695	0.013(1)
*M*3	4*c*	0.3529(2)	1/4	0.9870(2)	0.022(2):0.978	0.014(1)
$Tb_{2.40(1)}Ca_{2.60}Ge_4$						
*M*1	8*d*	0.18134(4)	0.12229(2)	0.32535(4)	0.856(3):0.144	0.007(1)
*M*2	8*d*	0.02165(7)	0.09609(4)	0.81598(7)	0.320(2):0.680	0.008(1)
*M*3	4*c*	0.3485(2)	1/4	0.9842(2)	0.048(2):0.952	0.007(1)
$Dy_{1.78(1)}Ca_{3.22}Ge_4$						
*M*1	8*d*	0.18222(4)	0.12210(2)	0.32473(4)	0.695(2):0.305	0.009(1)
*M*2	8*d*	0.02215(9)	0.09442(4)	0.81885(8)	0.149(2):0.851	0.011(1)
*M*3	4*c*	0.3496(1)	1/4	0.9834(1)	0.091(2); 0.909	0.008(1)
$Ho_{2.27(1)}Ca_{2.73}Ge_4$						
*M*1	8*d*	0.18114(3)	0.12184(2)	0.32723(3)	0.921(3):0.079	0.008(1)
*M*2	8*d*	0.0189(1)	0.09503(5)	0.8156(1)	0.135(2):0.865	0.012(1)
*M*3	4*c*	0.3458(1)	1/4	0.9827(1)	0.150(1):0.850	0.010(1)
$Er_{2.03(1)}Ca_{2.97}Ge_4$						
*M*1	8*d*	0.18165(4)	0.12171(2)	0.32758(4)	0.849(3):0.151	0.009(1)
*M*2	8*d*	0.0191(1)	0.09441(7)	0.8147(1)	0.072(2):0.928	0.011(1)
*M*3	4*c*	0.3459(2)	1/4	0.9826(1)	0.185(2):0.815	0.010(1)
$Tm_{2.20(1)}Ca_{2.80}Ge_4$						
*M*1	8*d*	0.18129(3)	0.12170(1)	0.32824(3)	0.915(2):0.085	0.008(1)
*M*2	8*d*	0.0166(1)	0.09412(5)	0.8160(1)	0.052(2):0.948	0.010(1)
*M*3	4*c*	0.34478(9)	1/4	0.98245(9)	0.256(2):0.744	0.009(1)
$Yb_{3.47(1)}Ca_{1.52}Ge_4$						
*M*1	8*d*	0.18081(5)	0.12163(3)	0.32809(5)	0.935(4):0.065	0.008(1)
*M*2	8*d*	0.01548(9)	0.09385(5)	0.81681(8)	0.489(3):0.511	0.010(1)
*M*3	4*c*	0.3431(1)	1/4	0.9825(1)	0.616(4):0.384	0.009(1)
$Lu_{2.26(1)}Ca_{2.74}Ge_4$						
*M*1	8*d*	0.18161(9)	0.12134(4)	0.32737(9)	0.824(5):0.176	0.014(1)
*M*2	8*d*	0.0165(3)	0.0930(1)	0.8177(3)	0.104(4):0.896	0.017(1)
*M*3	4*c*	0.3464(2)	1/4	0.9840(2)	0.410(5):0.590	0.013(1)

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From the remaining two metal sites, both Wyckoff 8*d*, one is heavily preferred by the rare-earth metal (*M*1) and the other is preferred (in 8 out of the 10 cases) by the alkaline-earth metal (*M*2). Ce- and Yb- samples show the greatest departure from the described trends (Table 3); for the Nd- sample, this type of coloring of the metal sites is also less pronounced with *M*1 taken by Nd at a level of ca. 57% vs ca. 43% on *M*2. *M*1 and *M*2 in $Ce_{5-x}Ca_xGe_4$ are both Ce-rich, while in $Yb_{5-x}Ca_xGe_4$, *M*1 was still preferred by Yb with *M*2 and *M*3 showing nearly statistical mixtures of Ca and Yb.

The observed site occupation factors are in good agreement with the previous study on $RE_{5-x}Mg_xGe_4$,[15] where the 4*c* site was almost exclusively occupied by Mg, and one of the 8*d* sites was almost exclusively occupied by *RE*. However, one should notice that the level of admixture between Mg/*RE* is different, giving refined chemical formulae $RE_{5-x}Mg_xGe_4$ ($x \approx 2$), while for $RE_{5-x}Ca_xGe_4$ ($x \approx 3$), the incorporation of Ca into the structure tends to be more significant.

As it can be seen from Figure 2, the coloring of the metal sites 8*d* follows a complicated pattern. For the early rare-earths, except Ce, *M*1 and *M*2 can be seen as statistically occupied mixtures, but as one moves from left to right in the lanthanide block, a preference of the rare-earth metal atoms for site *M*1 begins to emerge. The highest amount of rare-earth metal on site *M*1 is attained for the late rare-earth metals Ho–Tm. For *RE* = Yb, there is a clear anomaly, which is most likely associated with a mixed-valent state of Yb in this compound.

The unit cell volumes for the title compounds decrease monotonically across the series, mirroring the lanthanide contraction (Tables 1 and 2). All axes become smaller, although there are small discrepancies, which are clearly due to the variations in the Ca-content. Generally, the unit cell parameters of $RE_{5-x}Ca_xGe_4$ are larger than those in the binary RE_5Ge_4 counterparts due to the larger size of Ca.[17] The amount of Ca appears to be the highest in the samples with Ce and Yb, an observation that can be correlated both with the sizes (closer match between Ca^{2+} and Ce^{3+} and Yb^{2+}) and the melting points (both Ce and Yb have comparable melting points to that of Ca).[17,25]

Within the Gd_5Si_4 structure, there are two types of Ge–Ge bonds, the first being those formed by the Ge1 and Ge2 atoms in the RE_2CaGe_2 fragment (Figure 1(b). They measure on the order of 2.55 Å, in excellent agreement with a number of other binary and ternary rare-earth germanides such as Yb_4MgGe_4,[16] $RE_{5-x}Ca_xGe_3$,[20] $RE_{5-x}Li_xGe_4$,[26] RE_2AGe_2 (*RE* = rare-earth metal; *A* = Mg, Cd, In),[27–29] Ca_4InGe_4,[30] Sm_3Ge_5,[31] Gd_3Ge_4,[32] and many others.[33–38] The second type of Ge_2-dimers are formed by the Ge3 atoms (Figure 1(c), and have slightly longer bonds, which measure *ca*. 2.60–2.66 Å across the entire series. This elongation is not unusual, being that similar disparity is also noticed in a number of isostructural Gd_5Si_4-type compounds. In fact it is the intricate bonding between the *Tt*3–*Tt*3 atoms, which leads to a giant magnetocaloric effect associated with a structural change including the making (Gd_5Si_4-type) and breaking (Sm_5Ge_4-type) of the interslab contacts. Attention should be paid in drawing direct comparisons between various members here, because there are relatively large differences in the refined compositions.

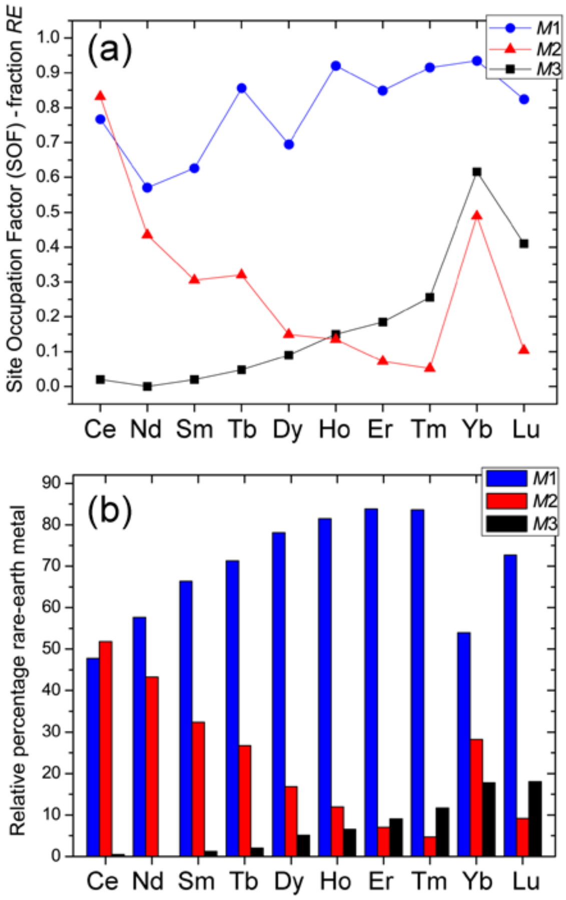

Figure 2. (a) Variations of the site occupation factors (SOF) for sites *M*1, *M*2, and *M*3 in each of the 10 refined $RE_{5-x}Ca_xGe_4$ structures. The scale gives the atomic fraction *RE*-atom at the given position. **(b)** Variations of the relative amounts of rare-earth metal in each of the 10 refined $RE_{5-x}Ca_xGe_4$ structures. For example, in $Ce_{3.22(1)}Ca_{1.88}Ge_4$, nearly 99% of the Ce atoms are distributed over sites *M*1 and *M*2, while for $Er_{2.03(1)}Ca_{2.97}Ge_4$, over 82% of the Er atoms are distributed over site *M*1.

Nonetheless, as shown in (Table 4), the elongation of the Ge3–Ge3 bond is clearly in correlation with the number of available valence electrons. Other factors are also known to affect the bonding between the *Tt*3–*Tt*3 atoms,[39-41] but in the systems under consideration, the valence electron concentrations appear to be the dominant contributor. Exact same relationships can be seen in $Ho_{5-x}Mg_xGe_4$ (and the whole $RE_{5-x}Mg_xGe_4$ family in general), where the *c*/*a* ratio and $d_{Ge3-Ge3}$ have been studied systematically as a function of "*x*". In accordance with those studies, and earlier theoretical considerations, the *Tt*–*Tt* interslab bonds are expected to become shorter/stronger with the removal of "extra" valence electrons.[8,9] The *RE*–Ge/Ca–Ge interatomic distances are generally matching or longer than the sum of the Pauling (single-bonded) radii of Ca, the largest rare-earth metal in the series, Ce, and Ge atoms (e.g., $r_{Ce} + r_{Ge}$ = 2.89 Å, $r_{Ca} + r_{Ge}$ = 2.98 Å); [42] this is suggestive of appreciable directional bonding between those atoms. All distance metrics we identified for $RE_{5-x}Ca_xGe_4$ are comparable with those of related *RE*–Ge systems.[23,26–29,31,32,35,37,38] Metal-metal bonding also appears to be significant as there are *RE*/Ca–*RE*/Ca contacts within the structure that are on the order of 3.1 Å, within the range where such interactions are expected to strongly influence the electronic stability of the structure.

Table 4. Selected interatomic distances (Å) in $RE_{5-x}Ca_xGe_4$ (*RE* = Ce, Nd, Sm, Tb–Lu) and their correlations with the unit cell volumes and the number of valence electrons per formula unit

Parameter	$Ce_{3.22(1)}Ca_{1.88}Ge_4$	$Nd_{2.01(1)}Ca_{2.99}Ge_4$	$Sm_{1.89(1)}Ca_{3.11}Ge_4$	$Tb_{2.40(1)}Ca_{2.60}Ge_4$	$Dy_{1.78(1)}Ca_{3.22}Ge_4$
V (Å^3)	960.6(5)	935.8(4)	923.0(3)	883.29(18)	895.18(19)
Ge3–Ge3	2.663(1)	2.6210(9)	2.6157(11)	2.6236(12)	2.5903(10)
Ge1–Ge2	2.590(1)	2.5626(9)	2.5568(11)	2.5649(12)	2.5540(10)
# electrons	29.23	28	27.89	28.4	27.78
	$Ho_{2.27(1)}Ca_{2.73}Ge_4$	$Er_{2.03(1)}Ca_{2.97}Ge_4$	$Tm_{2.20(1)}Ca_{2.80}Ge_4$	$Yb_{3.47(1)}Ca_{1.52}Ge_4$	$Lu_{2.26(1)}Ca_{2.74}Ge_4$
V (Å3)	884.37(12)	883.93(12)	874.46(12)	867.43(11)	863.9(4)
Ge3–Ge3	2.6432(11)	2.6331(14)	2.6433(10)	2.6356(19)	2.635(3)
Ge1–Ge2	2.5755(12)	2.5676(14)	2.5842(10)	2.564(2)	2.590(3)
# electrons	28.27	28.04	28.2	[a]	28.26

[a] Because of the suspected mixed-valent behavior of Yb in this compound and the uncertain fractions of Yb^{2+}/Yb_{3+}, the number of electrons cannot be calculated

In this work, we did not perform a thorough study to probe the full solubility range of Ca in $RE_{5-x}Ca_xGe_4$, however, based on the Zintl-Klemm concept,[43] one can expect to have a break-point around x = 3, or 28 valence electrons (6 from Ca, 6 from *RE* and 16 from Ge). The reasoning behind this ideal value is simple—if one were to ignore all metal-metal bonding and assume both types of Ge_2-dimers to be representative of 2-center-2-electron bonds, the structure of a binary RE_5Ge_4 should be rationalized as $(RE^{3+})_5([Ge_2]^{6-})_2(3e^-)$. Apparently, this simplified bonding picture of a salt-like solid leaves three electrons in excess. Substituting three of the nominally trivalent *RE* atoms with the divalent Ca atoms will alleviate the "richness" and $(RE^{3+})_2(Ca^{2+})_3([Ge_2]^{6-})_2$ can be considered to be an electron-precise phase. Prior electronic structure calculations have validated this line of thinking,[14] and the inherent electronic stability near the 28 valence electrons mark. Inspections of the refined compositions in Tables 1 and 2 provide a testament that nature does prefer $RE_{\approx 2}Ca_{\approx 3}Ge_3$, as many of the presented structures were actually the result of reactions that had different nominal compositions (*vide supra*). Increasing the Ca amount beyond this level will lead to insufficient number of valence electrons for Ge–Ge bonding, however, for at least two $RE_{5-x}Ca_xGe_4$ samples, x > 3. This is suggestive that the metal-metal bonds, as alluded to earlier, also play an important role. Metal-metal bonding may in fact be seen as even more pronounced for $RE_{\approx 3}Mg_{\approx 2}Ge_3$, since those systems favor higher number of valence electrons, approx. 29 e/f.u., and irrespective of the much smaller unit cell volumes show typically longer Ge3–Ge3 bonds.[15] These observations bolster the notion that for structures having more than the ideal 28 electrons/f.u., the "extra" electrons go on to reduce the Ge atoms even further. Additional evidence for this is on full display if one were to compare the compounds with two neighboring rare-earth elements, Tb and Dy (Table 4). One is with a refined formula $Tb_{2.40(1)}Ca_{2.60}Ge_4$ (i.e., has slightly more than 28 e$^-$/f.u.) and the other has a refined formula $Dy_{1.78(1)}Ca_{3.22}Ge_4$ (i.e., has slightly less than 28 e$^-$/f.u.)—the elongation of the Ge–Ge bonds, particularly the Ge3–Ge3 interslab ones is quite significant—2.624 Å in $Tb_{2.40(1)}Ca_{2.60}Ge_4$ compared to 2.590 Å in $Dy_{1.78(1)}Ca_{3.22}Ge_4$. However, one may also notice that Ge–Ge bonding also weakens as the unit cell volume decreases—$Tm_{2.20(1)}Ca_{2.80}Ge_4$ and $Lu_{2.26(1)}Ca_{2.74}Ge_4$ have intermediate number of valence electrons relative to the Tb and Dy samples but smaller cell volumes, yet, both type of Ge_2-dimers are elongated and measure 2.58-2.59 Å for Ge1–Ge2, and 2.63-2.64 Å for Ge3–Ge3, among the longest in the series. This suggests other factors such as the atomic sizes, metal-metal bonding, also play critical roles for the electronic stability of the structure.

Conclusions

An extended family of rare-earth metal calcium germanides have been synthesized from the corresponding elements in welded Nb tubes. These studies further demonstrate the ability to stabilize new compounds crystallizing with the Gd_5Si_4-type through the substitution of an alkaline-earth metal, in this case Ca, which replaces one of the rare-earth sites in the structure. The site preference observed in the structure shows that the Ca atoms occupy the *M*3 sites which center a distorted cube with its corners composed of rare-earth metal atoms. One of these sites also shows a propensity for admixing with Ca and which from the homogeneity range established, has been shown to influence the observed structural and physical properties. Most notable are the interslab Ge–Ge dimers show a decrease in bond length as more Ca is induced into the structure, but in no case show bond cleavage, each transition to the Sm_5Ge_4-type. Such observations emphasize the ability for the Gd_5Si_4 structure type to accommodate a variety of non-magnetic atoms into the structure all the while maintaining an isostructural system thereby allowing for delicate property tuning. Further studies to gain more effective control over the synthetic conditions could lead to interesting physics in these systems, where through systematic substitution chemistry, one may uncover unusual emergent behavior. The preliminary data presented herein for $Yb_{5-x}Ca_xGe_4$ provide a clear indication for valence state of the rare-earth metal that fluctuates between Yb(II) and Yb(III), making this material a good candidate for additional experimental and theoretical work.

Experimental Section

Synthesis. The synthesis followed the established procedures for $RE_{5-x}Mg_xGe_4$ ($x \approx 2$).[15] 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 of the title $RE_{5-x}Ca_xGe_4$ phases had a shiny and lustrous appearance with irregular morphologies. They remain stable in air and only show signs of surface oxidation over several months

Powder X-ray Diffraction (PXRD). X-ray powder diffraction patterns were taken at room temperature using a Rigaku Miniflex powder diffractometer with filtered Cu Kα radiation. The scans using were in θ–θ mode ($2\theta_{max}$ = 70°) with a step size of 0.05 and 2 sec/step counting time. The powder pattern data were only used to assess the phase purity of the compounds; the JADE 6.5 software package was utilized for this purpose.

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 crystals were mounted on glass fibers. The data collections were carried out at different w and q angles with a frame width of 0.8° along with 5-8 sec counting time. The SMART software package[44] was used to collect the data and was finally integrated using SAINT.[45] The data was corrected for absorption using SADABS.[46] The structures were refined on F^2 with the aid of the SHELX package.[47] The atomic coordinates from the previously reported phases with the Gd_5Si_4 type served as a suitable starting model for the refinements. As was the case for $RE_{5-x}Mg_xGe_4$,[15] the refinements for the title compounds readily confirmed that the 4*c* site in all cases but $Yb_{5-x}Ca_xGe_4$ was preferentially occupied by Ca atoms – for the Ce-, Nd- and Sm-samples, the position was almost exclusively taken by Ca. It was also worthwhile to check for possible deviations from the orthorhombic symmetry in which case, the monoclinic structure of $Gd_{5-x}Y_xGe_4$ system ($U_2Mo_3Si_4$-type structure, space group $P2_1/c$) or even of $Gd_5Si_2Ge_2$ (space group $P2_1/a$) could be probable. The collected single-crystal data were inspected carefully but no reliable indicators that there is a better way to describe the structure than in the orthorhombic space group *Pnma* were found.

Details of the data collection and selected crystallographic parameters are summarized in Tables 1–4. CCDC 2142189-2142198 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Elemental Analysis. The elemental compositions were analyzed with a JEOL 7400F electron microscope equipped with an INCA-OXFORD energy-dispersive spectrometer (EDS). The beam current was 10 μA at 15 kV accelerating potential, and the counting time for each spot was 120 s. Several single crystals were mounted on a conductive carbon tape. For each crystal, at least 3 areas were probed. The averaged totals were in good agreement with the refined compositions. No other heavy elements were detected besides the rare-earth metals, calcium, and germanium.

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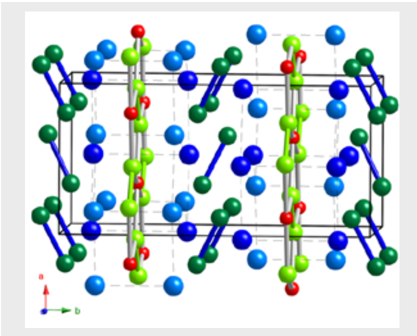
Entry for the Table of Contents

Layout 1:

FULL PAPER

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



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Calcium Substitution in Rare-earth Metal Germanides with the Gd_5Si_4 Type Structure

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