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Communication

Electron-Precise/Deficient LaCaGe (3.4 □ *x* □ 3.8) and CeCaGe (3.0 □ *x* □ 3.3): Probing Low-Valence Electron Concentrations in Metal-Rich GdSi-type Germanides

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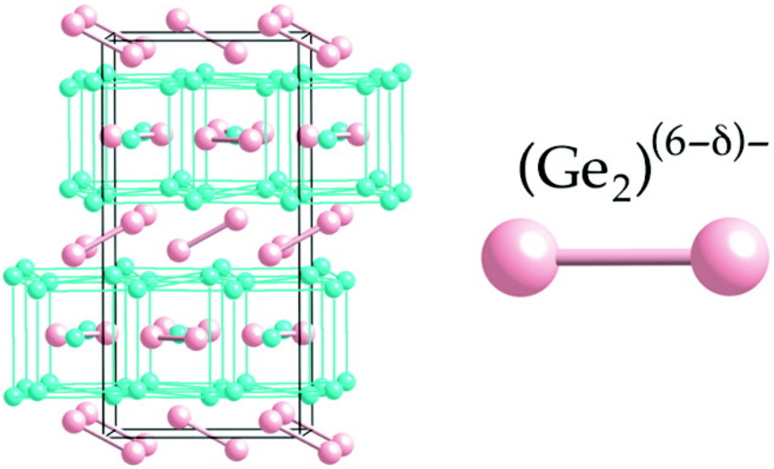

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COMMUNICATIONS

Electron-Precise/Deficient $La_{5-x}Ca_xGe_4$ ($3.4 \leq x \leq 3.8$) and $Ce_{5-x}Ca_xGe_4$ ($3.0 \leq x \leq 3.3$): Probing Low-Valence Electron Concentrations in Metal-Rich Gd_5Si_4-type Germanides

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While Zintl−Klemm concept is a good starting point for understanding structures of Zintl phases and polar intermetallics, recent progress in the area has recognized the significant role of active cations in determining structure formations through close-packing, cation−anion interactions, and cation−cation metallic bond formation.[1] For instance, open-shell configuration of (poly)anions is often possible when other factors strongly contribute, particularly in polar intermetallics of triels. However, questions still remain both experimentally and theoretically as to how substantial the competing structure-forming factors can be against the closed/open-shell anion−anion bond formation.[2] In this communication, we report for the first time the syntheses of electron-precise/deficient alloys, $Ln_{5-x}Ca_xGe_4$ ($x = 3.37$, 3.66, 3.82 for Ln = La; $x = 3.00$, 3.20, 3.26 for Ln = Ce), in the metal-rich R_5Tt_4 Zintl system (R = rare earth metal; Tt = Si, Ge).[3] The new alloys extend the electronic phase width from electron-rich to open-shell electron-deficient region in the metal-rich Zintl system and demonstrate possible occurrence of *varied* electron deficiencies in Zintl phases without structural changes, as a result of other existing structure-forming factors.[4]

R_5Tt_4 compounds exhibit both cation−cation and anion−anion bonding in their closely related structural variations, α-, β-, and γ-types.[5] The alkaline-earth analogues are not known in the literature. All of the structures contain two different kinds of Tt atoms based on their bonding behavior: two Tt1 and two Tt2 atoms (Figure 1) in a formula unit. While all Tt2 atoms are dimerized in the structures (d(Tt−Tt) = 2.5−2.7 Å), the proportions of dimerized Tt1 atoms are different: all Tt1 atoms in the α-type (Gd_5Si_4-type), only a half in the β-type (the monoclinic modification of $Gd_5Si_2Ge_2$), and none in the γ-type (Sm_5Ge_4-type).

Following the Zintl−Klemm concept,[6] the α-, β-, and γ-type structures are all *electron-rich* with chemical formulas $(R^{3+})_5(Tt_2^{6-})_2(3e^-)$, $(R^{3+})_5(Tt_2^{6-})_{1.5}(Tt^{4-})(2e^-)$, and $(R^{3+})_5(Tt_2^{6-})(Tt^{4-})_2(e^-)$, respectively. The bottom of the conduction bands consists of R−R and R−Tt bonding and Tt−Tt antibonding states.[5d] The suggested electron counting scheme of the R_5Tt_4 structures implies that the structure formations may also be affected by changes in VEC. Indeed, it has been demonstrated that the bond formation between the Tt1 atoms can be induced when a γ-type compound is deprived of some of the excess electrons by partial substitutions of Ge atoms with size-equivalent triel Ga in $Gd_5Ga_xGe_{4-x}$ ($x = 0-2.2$; $31 \geq \mathrm{VEC} \geq 28.8$)[5d] and in $La_5Ga_xGe_{4-x}$ ($x = 1$). When $x \geq 1$ ($30 \geq \mathrm{VEC}$), the alloys formed in a α-type structure, and the highest Ga content ($x = 2.2$; VEC = 28.8) was still electron-rich.

In our design of synthesis to explore the low VEC region for the R_5Tt_4-type structures, divalent Ca was chosen to partially substitute the trivalent atoms, and La and Ce were selected for a trivalent element because of their ionic size[7] ($r_{La^{3+}} = 1.50$ Å; $r_{Ce^{3+}} = 1.48$ Å) close to that of Ca^{2+} ($r_{Ca^{2+}} = 1.48$ Å) and their plausible formal +3 oxidation state in intermetallics. The syntheses and characterization are described in Supporting Information. From single-crystal and powder X-ray diffraction studies of the products, we have identified as major phases the electron-precise or deficient $Ln_{5-x}Ca_xGe_4$ alloys ($28 \geq \mathrm{VEC} \geq 27.2$), which exhibit the lowest VECs ever observed in the R_5Tt_4 system. The results from elemental analysis were consistent with the compositions estimated from the single-crystal X-ray diffraction analysis and generally with the loaded compositions. With the observed VEC values, all the alloys are found to exhibit the α-type structure, and this is in line with the behavior of the $Gd_5Ga_xGe_{4-x}$.

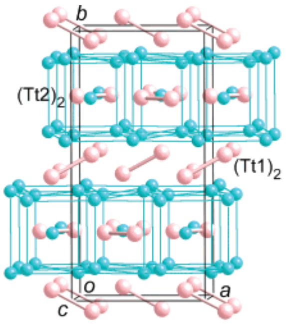

Figure 1. Off [001] perspective view of the α-type orthorhombic structure of R_5Tt_4. Blue: R. Pink: Tt. The β- and γ-type structures also have similar atomic arrangements but with different Tt−Tt bonding behaviors (see the text).

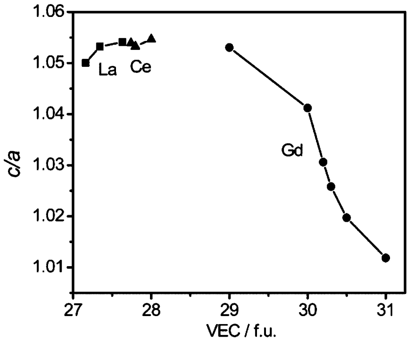

Figure 2. The c/a ratio plotted as a function of VEC for $Ln_{5-x}Ca_xGe_4$ and $Gd_5Ga_xGe_{4-x}$[5d] alloys.

The new alloys exhibit larger unit cell parameters than the $Gd_5Ga_xGe_{4-x}$ (Figure S1). This is reasonable because La (La^{3+}) and Ce (Ce^{3+}) are larger than Gd (Gd^{3+}). The c/a ratio has been suggested previously as an indicator of the Tt1−Tt1 dimer bonding,[5c] as it increases upon the decrease in the closest Tt1−Tt1 distance due to the dimer bond formation (Figure 2). In comparison to the $Gd_5Ga_xGe_{4-x}$,[5d] however, the ratios are almost constant at 1.05 for all the $Ln_{5-x}Ca_xGe_4$, indicating that there is no drastic differences in the structures among the new alloys. This is reasonable because all the Tt1 atoms become dimerized in the α-type structure of the $Ln_{5-x}Ca_xGe_4$. A similar behavior is noticed

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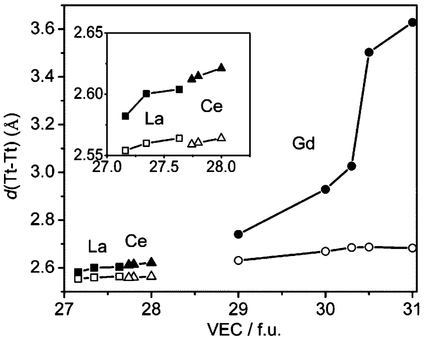

Figure 3. The dimer bond distances in $Ln_{5-x}Ca_xGe_4$ and $Gd_5Ga_xGe_{4-x}$[5d] alloys plotted as a function of VEC. The solid and open circles correspond to Tt1−Tt1 and Tt2−Tt2 distances, respectively, in the text.

among R_5Si_4 (R = Gd, Tb, Dy, Er)[8] and $Gd_5(Si_xGe_{1-x})_4$ ($0.58 < x \leq 1$),[9] in which all of the Tt atoms exist as dimers.

In Figure 3, the dimer bond distances are shown with different VECs. Overall, the bond distances are less in electron-precise or deficient alloys than the electron-rich ones ($Gd_5Ga_xGe_{4-x}$), while the opposite is expected when only the unit cell sizes are concerned. The dramatic decrease in Tt1−Tt1 in $Gd_5Ga_xGe_{4-x}$ is caused by the dimer bond formation, while the gradual decrease in Tt2−Tt2 can be understood by the previous theoretical results that the bottom of the conduction bands contain σ_p* antibonding character of the Ge dimers.[5d] From VEC = 29 to 28, the bond shortening is likely due to the complete removal of the conduction electrons. Interestingly, further gradual decreases in the dimer bonds are apparent in the $Ln_{5-x}Ca_xGe_4$. This is understandable when we consider the filled π* states present in the electron-precise Ge_2^{6-} dimers ($\sigma_s^2\sigma_s^{*2}\sigma_p^2\pi^4\pi^{*4}\sigma_p^{*0}$) in a simplistic bonding scheme. The electron deficiency in the new alloys should occur in the π* states that will be located largely in the top region of the valence bands. Therefore, the alloys can be described as $(Ln^{3+})_{5-x}(Ca^{2+})_x(Ge_2^{6-})_2(yh^+)$, where h^+ represents a hole in the valence bands and $y = x - 3$ ($0 \leq y \leq 0.8$).

The LMTO−ASA calculations[10] were carried out on an electron-precise $La_2Ca_3Ge_4$, whose structure was modeled from the $La_{1.63}Ca_{3.37}Ge_4$ by having La and Ca atoms ordered according to the observed site preference (Table S2). In Figure 4, the band structure shows an energy gap at the Fermi level for the electron-precise model alloy, predicting a semiconducting behavior. The Ge atoms contribute much less compared to the La/Ca in the conduction bands, and the COHP curves[11] indicate that the Ge−Ge antibonding character is well spread out over the conduction bands as well as at the top of the valence bands. This is consistent with the electron configuration of the Ge_2 dimers adopted in our previous discussions for the explanation of the trend in the bond distance changes.

The existence of the band gap should be taken cautiously because the calculations were carried out on a model structure. Although not shown here, however, we consistently observed the energy gap in the band structures calculated for all the model structures with $x \geq 3$ even when the La and Ca atom positions were exchanged. This band gap formation may be due to the smaller electronegativity of Ca and the shortened Ge−Ge distances.

In summary, the new $Ln_{5-x}Ca_xGe_4$ alloys show that the formation of the metal-rich Zintl compounds R_5Tt_4 can be extended to an electron-deficient region, and precise satisfaction of the Zintl−Klemm concept is found to be inessential in the structure formation. It is suspected that the existence of cation−cation bonding is not required for the stabilization of the R_5Tt_4-type structures either. The robust nature of the structures is likely due to the strong cation−anion bonding of the rare earth ions both covalently and electrostatically. In practice, our work suggests an interesting possibility of substantial modification of the magnetic and electrical properties in R_5Tt_4, especially the Gd-analogues, through systematic (Ca^{2+}) cation substitutions. Furthermore, we anticipate more of such stimulating examples when they are *purposely* sought through designed syntheses, and it may provide a viable route in modifying physical properties of Zintl phases and polar intermetallics in general.

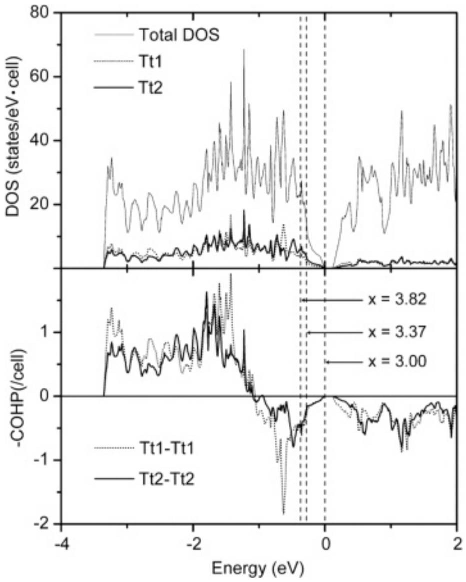

Figure 4. DOSs (upper panel) and COHPs (lower panel) for a model compound, $La_2Ca_3Ge_4$. The vertical lines are the Fermi levels for the corresponding *x* values within a rigid band approximation.

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Supporting Information Available: Experimental, single-crystal X-ray crystallographic files in CIF format, Tables of crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) Regardless of their possible metallic properties, "metal-rich" Zintl systems or phases are defined here as cation-rich compounds exhibiting anionic moieties of metal or metalloid elements whose structures can be generally understood by applying classical or modern electron counting rules of molecules.
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