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Abstract
Three ordered structures of the tetragonal BaAl_4 type were identified in the Ba–Au–Sn system, from which a unified view of the interplay between the valence electron counts (VECs) and phase stabilities of these three types of derivatives can be developed. The BaNiSn_3 (I4mm), ThCr_2Si_2 (I4/mmm), and CaBe_2Ge_2 (P4/nmm) type BaAu_{x}Sn_{4-x} phases occurred respectively at \( x = 0.78(1)–1, 1.38(1)–1.47(1), \) and 1.52(1)–2.17(1), consistent with theoretical atomic “coloring” analyses that reveal an optimal VEC of \( \sim 14 \) for the ThCr_2Si_2 type but larger and smaller values respectively for the BaNiSn_3- and CaBe_2Ge_2-type structures.

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Ordered BaAl₄-Type Variants in the BaAuₓSn₄₋ₓ System: A Unified View on Their Phase Stabilities versus Valence Electron Counts

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Supporting Information

ABSTRACT: Three ordered structures of the tetragonal BaAl₄ type were identified in the Ba–Au–Sn system, from which a unified view of the interplay between the valence electron counts (VECs) and phase stabilities of these three types of derivatives can be developed. The BaNiSn₃ (I₄/mmm), ThCr₂Si₂ (I₄/mmm), and CaBe₂Ge₂ (P₄/nmm) type BaAuₓSn₄₋ₓ phases occurred respectively at \( x = 0.78(1) - 1 \), 1.38(1)–1.47(1), and 1.52(1)–2.17(1), consistent with theoretical atomic “coloring” analyses that reveal an optimal VEC of \( \approx 14 \) for the ThCr₂Si₂ type but larger and smaller values respectively for the BaNiSn₃- and CaBe₂Ge₂-type structures.

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horough exploration of potentially new superconductors is bedrock for understanding the fundamental nature of superconductivity and for any potential applications in energy-related fields. Recently, nonconventional superconductivity has been observed in several precious metal-based, tetragonal BaAl₄-type phases [e.g., BaPd₃Sn₄₋ₓPd₃As₂ (A = Ca, Sr) \textsuperscript{5}, SrPd₃Ge₇ \textsuperscript{5}, SrPt₃As₉ \textsuperscript{3} and LaPd₂Sb₂ \textsuperscript{4} ], suggesting that neither Fe nor As in similar phases, which have attracted much enthusiasm in the past 5 years, is necessary to yield superconducting phenomena. Furthermore, superconductivity can apparently occur in any of the three ordered ternary variants of BaAl₄, i.e., noncentrosymmetric BaNiSn₃ (I₄/mmm, abbreviated as the “113” phase) and centrosymmetric ThCr₂Si₂ (I₄/mmm) and CaBe₂Ge₂ (P₄/nmm) types, both “122” phases. Because Pd and Pt show structural and electronic roles similar to those of their noble metal analogues Ag and Au in some intermetallics \textsuperscript{6–9} we are investigating Au-containing ternary “122” crystalline analogues to examine whether they could also exhibit superconductivity. Superconductivity has been reported for the Au-containing binary compounds CaAu₄, BaAu₄, AuZn₃, Au₅Al, AuGa, AuGa₂, and AuTi \textsuperscript{10} and, very recently, the ternary compounds SrAuSi₁₂ \textsuperscript{11}.

The initial target BaAuₓSn₃ was first prepared by melting the stoichiometric mixture of elements at 950 °C for 2 h and annealing at 600 °C for 1 week. This reaction yielded a single-phase product with the CaBe₂Ge₂-type structure, with \( a = 4.7935(6) \) Å and \( c = 11.213(3) \) Å. Then, reactions of BaAuₓSn₄₋ₓ (\( y = 0.75–2.25 \)) were completed under the same conditions from which the ThCr₂Si₂- and BaNiSn₃-type BaAuₓSn₄₋ₓ neighbors were also confirmed by single-crystal X-ray diffraction; see detailed experimental procedures and crystallographic data in the Supporting Information (SI). Herein, the structural properties of these BaAuₓSn₄₋ₓ phases and their relationship to valence electron counts (VECs) will be discussed; the results of doping experiments and property measurements will be published elsewhere.

Variations of the lattice parameters and unit cell volumes as a function of the refined composition \( x \) (or VEC) in BaAuₓSn₄₋ₓ are shown in Figure 1. The data points within each homogeneous composition range, i.e., \( x = 0.78(1) – 1 \) for BaNiSn₃, \( x = 1.38(1) – 1.47(1) \) for ThCr₂Si₂, and \( x = 1.52(1) – 2.17(1) \) for CaBe₂Ge₂, can each be linearly fitted according to Vegard’s law. Extensions of the fitted lines meet at \( x \approx 1.0 \) and 1.5, where kinks denoting discontinuous phase transitions are observed. However, variations of the lattice parameters or volumes do not always follow atomic size (Au, 1.439 Å; Sn, 1.623 Å) expectations; the chemical bonding factor might prevail whenever unexpected trends appear, e.g., in the region of \( x \approx 1 \). In this work, the homogeneity ranges were established by refined compositions from single-crystal data. The lower and upper limits of these ranges for each phase were determined from multiphase products, except that the lower limit of 1.52(1) of the CaBe₂Ge₂-type phases is from the \( y = 1.50 \) reaction but not from the \( y = 1.45 \) reaction, which yielded too little (5–10%) of the CaBe₂Ge₂-type phase in its product (cf. Figure S1 in the SI). Considering the small differences between the refined compositions for products of and the loaded compositions of...
these two reactions, 1.52(1) versus 1.47(1), and the small gap in composition between these two products \( (S_{1/2}) \), it is difficult to obtain more accurate values. Interested readers shall refer to the SI for details on determination of the phase widths.

The most striking variations among these three structures, shown in Figure 2, are the different atomic orderings on the basal (connected by black, dashed lines) and apical (or pyramidal) sites.\(^\text{(12)}\) As a result, the two square-pyramidal layers in the BaNiSn\(_3\)-type structure are symmetrically equivalent and polar along \( c \). In contrast, the two layers in the ThCr\(_2\)Si\(_2\)-type phase are nonpolar, although they remain symmetrically equivalent. In the CaBe\(_2\)Ge\(_2\)-type phase, the two layers are nonpolar and no longer symmetrically equivalent. These subtle structural variations lead to very small differences among their powder X-ray diffraction patterns (Figures S1 and S2 in the SI). In particular, the BaNiSn\(_3\)- and ThCr\(_2\)Si\(_2\)-type phases are essentially indistinguishable from each other, whereas the two space groups \( I4/mmm \) and \( I4/mmm \) have the same systematic absence conditions. Therefore, assignments of the BaNiSn\(_3\)- and ThCr\(_2\)Si\(_2\)-type structures often demand single-crystal data, which have accurate intensity statistics. In this work, the electron densities determined from the observed Fourier maps give significant clues for centric versus acentric symmetries, as shown in Figure S3 in the SI.

The occurrence of these three structural types as a function of the composition (or VEC) in the same system is unprecedented, and the results obtained from this system are far-reaching. In some BaAl\(_2\)-related systems, only one of the two “122” structural types occurs, either with or without the “113” phase, and a small number of systems contain both ThCr\(_2\)Si\(_2\)- and CaBe\(_2\)Ge\(_2\)-type phases.\(^\text{(13)}\) Also, if the two “122” types occur in the same system, they are often found as low- and high-temperature polymorphs, including the \((Y, La, Nd, Ga, Dy, Ho)-Ir-Si\) systems that contain all three BaAl\(_2\)-type variants.\(^\text{(13)}\) Perhaps some other BaAl\(_2\)-related systems showing similar behavior should be reexamined, in particular those involving single-point exploration, a small phase width, a narrow phase gap to neighbors, or the absence of single-crystal data. Systems with lattice parameters not following Vegard’s law also need careful scrutiny. In addition, two words of caution are (1) a “113” reaction does not always result in formation of the BaNiSn\(_3\)-type phase \( \text{e.g., BaAuT}_3 \) \( (T=In, TI) \) \(^\text{(12)}\) and BaPtIn\(_3\) \(^\text{(15)}\) form the ThCr\(_2\)Si\(_2\)-type structure) and (2) the CaBe\(_2\)Ge\(_2\)-type phase if low-intensity peaks at small \( 2\theta \) angles allowed by the P lattice \( (\text{cf. Figures S1 and S2 in the SI}) \) were misinterpreted as a second phase, especially if a pure phase product has not been attained.

The Ba–Au–Sn system serves as a model platform to study the “coloring problem”,\(^\text{(12)}\) i.e., the chemical ordering between Au and Sn in these three structures. The observed coloring of a structural network by two or more elements involves minimization of either the “site energy” or “bond energy” or their combination.\(^\text{(16)}\) In fact, important observations and explanations regarding the coloring problem for BaAl\(_2\)-related structures have been reported before,\(^\text{(12,17–22)}\) but conclusions are usually generalized from different systems, in which additional factors, like cation sizes, may be influential. The present system simplifies examination to the refined \( x \) parameter only. Figure 3 shows variations of the Au and Sn occupations at the basal and apical sites as a function of the refined \( x \). Au atoms only occupy apical sites in the BaNiSn\(_3\)-type phases, a result consistent with an earlier assessment that the more electronegative element should occupy the apical sites in BaAl\(_2\)-type structures to minimize the site energy.\(^\text{(16)}\) Following this trend, any additional Au \( (>2\text{ atoms/}} \) cell) in \( x > 1 \) structures should go to the other set of apical sites, but this would necessarily create close interactions between formally reduced Au atoms. As a result, these Au atoms are directed toward the basal sites while allowing Au/Sn mixed occupations at both basal and apical sites, as in the ThCr\(_2\)Si\(_2\)-type structures (Figure 2). The same trend continues in the CaBe\(_2\)Ge\(_2\)-type structures until one basal square is fully occupied by Au for \( x > 2 \) structures. Here discontinuous variations of the Au and Sn occupations at \( x = 1.0 \) and 1.5 afford additional evidence for structural changes.

Why do the BaNiSn\(_3\)-, ThCr\(_2\)Si\(_2\)-, and CaBe\(_2\)Ge\(_2\)-type BaAu\(_{1-x}\)Sn\(_x\) phases occur for specific compositions or VEC values? There are discussions in the literature on the phase stability of a single type \(^\text{(17,20–22)}\) or different systems,\(^\text{(16)}\) but no clear boundaries have been proposed for all three closely related structure types. Now, from the Ba–Au–Sn system, a unified view of the interplay between VECs and their corresponding phase stabilities can be developed. Figure 4 shows the relative energies of the BaNiSn\(_3\)- and ThCr\(_2\)Si\(_2\)-type \( \text{“Sn}_x\text{Au}_{1-x}\) \( \text{hypothetical models (compared to that of the CaBe\(_2\)Ge\(_2\)-type) as a function of VEC based on the extended Hückel tight-binding (EHTB) method. This method has been shown to give useful information on the relative stabilities of different structures without demanding accurate total energies.\(^\text{(16)}\) As shown in Figure 4, the CaBe\(_2\)Ge\(_2\)-type phase has the lowest energy for VEC \( < 13.7 \), whereas the

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**Figure 2.** (100) perspectives of the unit cells of BaNiSn\(_3\)-type Ba\(_{1-x}\)Au\(_x\)Sn\(_3\) \( (I4/mmm) \), ThCr\(_2\)Si\(_2\)-type Ba\(_{1-x}\)Au\(_x\)Sn\(_{1-x}\) \( (I4/mmm) \), and CaBe\(_2\)Ge\(_2\)-type Ba\(_{1-x}\)Au\(_x\)Sn\(_3\) \( (Pn/mnm) \). The origin of Ba\(_{1-x}\)Au\(_x\)Sn\(_3\) is shifted to the Ba site for a direct comparison.

**Figure 3.** Variations in the unit cell occupations of the basal and apical sites by Au and Sn atoms versus refined \( x \) (bottom) or VEC (top) in Ba\(_{1-x}\)Au\(_x\)Sn\(_3\).
ThCr$_2$Si$_2$-type phase has the lowest energy in the VEC range of 13.6 < VEC < 14.3 and the BaNiSn$_3$-type phase for x > 14.3. These computational results are consistent with the present experimental observations (shaded) and other calculations.\(^{21}\) This outcome could be a guide for future explorations of the BaNiSn$_3$- and CaBe$_2$Ge$_2$-type competitors relative to the ThCr$_2$Si$_2$-type phase, if they all exist.

The phase stabilities were also evaluated from a structure-bonding perspective by using the TB-LMTO-ASA method. The Fermi levels of BaNiSn$_3$-type structures exist in a shallow valley in the DOS in the BaAuSn$_3$ model and those for the ThCr$_2$Si$_2$-type model, under rigid band assumption, upon decreasing slope of another valley, as shown in Figure S4(a) in the SI. Meanwhile, Au–Sn and Sn–Sn interactions show essentially nonbonding character at ca. –2.0 to 0.5 eV, indicating optimized orbital interactions. However, a lump exists between the two foregoing valleys in the DOS, a possible clue for the occurrence of a phase transition. Similar bonding and DOS features are seen in the CaBe$_2$Ge$_2$-type BaAuSn$_3$ model (Figure S4(b) in the SI). In addition, a ThCr$_2$Si$_2$-type “122” model was ~28.5 meV/cell higher in total energy than the CaBe$_2$Ge$_2$-type model, suggesting that the latter is more stable at the “122” proportion, consistent with experimental observation. Further analysis of the electronic structures of BaAu$_x$Sn$_{4−x}$ phases is underway to extract electronic influences on their structural behavior.

In conclusion, the BaNiSn$_{3−x}$, ThCr$_2$Si$_{2−x}$, and CaBe$_2$Ge$_2$-type BaAu$_x$Sn$_{4−x}$ phases were structurally and electronically characterized as a function of x. This system offers, for the first time, the opportunity to demonstrate and verify how phase widths and phase stabilities of these three prolific structure types are related to the VECs. It turns out that the ThCr$_2$Si$_2$-type phase is optimized at VEC ~ 14, whereas the BaNiSn$_3$- and CaBe$_2$Ge$_2$-type structures are stabilized, respectively, at larger and smaller VECs. Because these “122” and “113” structures have small differences in their powder X-ray diffraction patterns, it is important to be attentive to possible phase widths and composition gaps between them.

## ASSOCIATED CONTENT

* Supporting Information
  
  Detailed information on the synthesis and theoretical calculations, Tables S1–S6, Figures S1–S4, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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