Formation of Multinary Intermetallics from Reduction of Perovskites by Aluminum Flux: $M_3Au_6+$x$Al_{26}Ti$ (M = Ca, Sr, Yb), a Stuffed Variant of the BaHg$_{11}$ Type

Susan E. Latturner and Mercouri G. Kanatzidis*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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New intermetallic phases were synthesized by reacting oxidic perovskites and gold metal in aluminum flux. The combination of MTiO$_3$ (M = Ca, Sr, Ba) and Au metal in excess molten aluminum produces quaternary compounds M$_3$Au$_{6+x}$Al$_{26}$Ti with a stuffed BaHg$_{11}$ structure type. An analogue with M = Yb was also synthesized; it shows mixed valent behavior.

The thermite reaction is a well-known and memorable demonstration of the utility of the reducing ability of aluminum to convert Fe$_2$O$_3$ to molten iron. Preliminary investigations have been carried out on the aluminothermic synthesis of simple borides such as AlB$_{12}$ and LaB$_6$ via reduction of B$_2$O$_3$. The efficacy of aluminum in the reduction of rare earth oxides has been demonstrated in the formation of complex intermetallics such as Sm$_2$Ni(Ni, - Si, - Al)$_{12}$Si$_6$ from the combination of Sm$_2$O$_3$, Ni, and Si in aluminum flux. Less work has been done in exploring the use of aluminum as a reducing agent for more complex oxides, however. In the results described here, perovskites MTiO$_3$ (M = Ca, Sr, and Ba) placed in molten aluminum react to form intermetallic phases. In the presence of gold, cubic BaHg$_{11}$ variant phases M$_3$Au$_{6+x}$Al$_{26}$Ti are produced.

The impetus for this investigation was the isolation of Yb$_3$Au$_4$Al$_{25}$Ti from an aluminum flux reaction intended to produce YbAu$_3$Al$_2$. In addition to this ternary phase, a number of crystals of a cubic phase were isolated. The crystallographic analysis indicated the structure of these crystals was a variant of the BaHg$_{11}$ type. The identity of the atom in the 1b Wyckoff site was unclear; the electron density at this location was too high for aluminum, and not high enough for gold or ytterbium. Careful elemental analysis indicated the presence of a very small amount of Ti in the crystals. The aluminum flux had reduced some unannealed titania cement (a mixture of complex oxides) in the crucible, allowing metallic titanium to be incorporated into the product. It was therefore decided to investigate this reducing behavior further by using complex oxides (perovskites) as reactants.

Perovskites of the type MTiO$_3$ were combined with gold and excess aluminum metal as a reactive, reducing flux in a 1:2:20 MTiO$_3$/Au/Al ratio. M$_3$Au$_{6+x}$Al$_{26}$Ti grows from the flux as large, faceted spheroid chunks. Also formed in the reaction are binary intermetallics such as TiAl$_3$ and BaAl$_4$, recrystallized gold, and oxide powder. The yield of M$_3$Au$_{6+x}$Al$_{26}$Ti is fairly low (ca. 10%); higher yields of around 50% based on the amount of gold used are obtained by using elemental reactants instead of perovskite precursors. The material is fairly stable to 5 M NaOH solution but dissolves in acids.

While the structure of Ba$_3$Au$_4$Al$_{25}$Ti has not been solved yet, the structure of M$_3$Au$_{6+x}$Al$_{26}$Ti (M = Yb, Ca, Sr) is closely related to that of BaHg$_{11}$, as shown in Figure 1. These compounds form in cubic space group $Pm\bar{3}m$, featuring a unit cell centered by titanium coordinated by a cuboctahedron of neighboring aluminum sites. An early transition metal atom (such as Ti) surrounded by a cuboctahedron of 12 Al atoms is a common structural motif in early transition metal aluminides such as TiAl$_3$ and ZrAl$_3$. This suggests that the presence of Ti might template the formation of the cubic M$_3$Au$_{6+x}$Al$_{26}$Ti structure. Our work indicates that all early transition metals in groups 4−7 (from Ti to Re) can be incorporated into this site. One difference between the BaHg$_{11}$ and M$_3$Au$_{6+x}$Al$_{26}$Ti structures is the presence in the latter of an additional atomic

(5) Purposely adding Ti as a reactant increased the yield of Yb$_3$Au$_4$Al$_{25}$Ti.

(6) XRD data for Sr$_3$Au$_4$Al$_{25}$Ti as a representative compound: $Pm\bar{3}m$, $a = 8.7367(6)$ Å; $V = 666.878(8)$ Å$^3$, $Z = 1$, $\rho = 6.165$ g/cm$^3$. Total reflections: 10687; unique reflections, 383; index range $-14 \leq h, k, l \leq 14$. R1/wR2 for I > 2σ(I): 0.0237/0.0435; for all data, 0.0379/0.0465.
position in the center of a cube of eight aluminum atoms. A gold atom occupies this site (the 1a Wyckoff site); M3Au6+x−yAl26Ti can therefore be described as a stuffed variant of BaHg11. The stuffing of the site in the compounds studied here varies from 80% to 100% (Table 1). It is possible that the size of the unit cell controls the filling of this site, with a larger unit cell (such as Sr3Au7Al26Ti) allowing room for full occupancy by gold. Gold-centered Al8 cubes are a feature of the antifluorite structure AuAl2 phase and have also been observed in multinary intermetallics such as Th3Au3Al2Si2 and YbAu4Al3Si7.

Another variation from the parent structure is a splitting of the 12i Wyckoff site to allow for occupancy of this site by a mixture of Al and Au. A possible reason for this splitting is to allow the formation of suitable bond lengths between the aluminum or gold atoms and the neighboring M atom (M = Ca, Sr, Yb). It also allows for Al−Au bonds of an appropriate length between adjacent split sites (see Figure 1). This produces an Au2Al2 rhombus with strong Au−Al bonds (2.57−2.66 Å in length, similar to that found in bulk AuAl2) instead of Al4 or Au4 squares. The disorder in

Table 1. Occupation of the Stuffed Site of M3Au6+xAl26Ti

<table>
<thead>
<tr>
<th>compd</th>
<th>unit cell edge (Å)</th>
<th>Au(1) occupancy x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb3Au6+Al26Ti</td>
<td>8.6509(6)</td>
<td>0.844(7)</td>
</tr>
<tr>
<td>Sr3Au6+Al26Ti</td>
<td>8.7367(6)</td>
<td>0.990(8)</td>
</tr>
<tr>
<td>Ca3Au6+Al26Ti</td>
<td>8.6631(5)</td>
<td>0.80(1)</td>
</tr>
</tbody>
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Figure 1. (a) The structure of M3Au6+xAl26Ti, in the disordered Pn3m subcell. (b) The titanium site, in a cuboctahedron of 12 Al(3) atoms. (c) The stuffed site within a cage of 8 Al atoms, occupied by Au(1). (d) the environment around the M atom includes Al(1) and the Al(2)/Au(2) split site. (e) The Al(2)/Au(2) split site rhombus.

The stuffed site in the compounds studied here did not show any signs of ordering in their X-ray diffraction data, but the calcium analogue did.

The single crystal XRD data for Ca3Au6.8Al26Ti initially indexed as cubic F with an a = 17.3434(9) Å cell; the Fm3m space group of the supercell was indicated. However, the structure could not be solved in this space group, even when the supercell model was put in as a starting point. Powder diffraction data for this compound is shown in Figure 3; data for Sr3Au6.8Al26Ti and theoretical patterns for the disordered subcell and the ordered supercell are also shown for comparison. The X-ray powder pattern of Ca3Au6.8Al26Ti does show the (113), (371), and (795) supercell reflections, but they are weak; other expected supercell reflections such as the (111) and (115) peaks are absent. An attempt was therefore made to solve the single crystal structure in the Pn3m subcell. This proved successful, resulting in an R1 of 0.0357 despite the alarming necessity of ignoring the supercell data (number of unique reflections reduced from 704 to 364). Evidently, even within a “single” crystal of this compound there exist ordered domains and disordered domains. A number of single crystals were screened with similar results.

Figure 2. The Fm3m cell with a* = 2a; the TiAl12 cuboctahedra have been removed to make the AuAl rhombi visible. The light gray cubes are the Al4 cubes containing the stuffed site.


As shown in Figure 1, the ytterbium site is closely coordinated to the Au(2)—Al(2) split site. The disorder in the occupancy and Au(2)Al(2) rhombi orientations in the structure can easily produce local inhomogeneities around the Yb sites in a bulk sample. Similar behavior was observed in YbPd3-Gas, a compound which is also described as a disordered variant of BaHg11.11

As the Yb3Au7Al26Ti sample is cooled below 150 K, the inverse susceptibility begins to show nonlinear behavior, indicating temperature-dependent valence behavior. This likely signals the onset of valence fluctuation. This is often observed in compounds with ytterbium f-bands near or at the Fermi level. As the temperature reaches a certain range, the energetics become favorable for these f-bands to begin to mix with the conduction bands of the sample. This results in a temperature-dependent intermediate valence state. Other ytterbium intermetallics with similar behavior include YbAu7-Al7 and YbAuAl8Si3,7b

In reducing perovskites to form complex intermetallic compounds, molten aluminum metal has proven to be an extremely useful synthetic medium in yet another way. Its reactivity toward highly stable multinary oxides introduces a new field of exploration, with a wide variety of compounds that can potentially be used as reactants in aluminum flux. Advantages of complex oxides as reactants include inherent premixing of elements and finely divided form, less loss of volatile reactants such as alkaline earths,12 and lower price than elemental reagents.

Ongoing experiments indicate that the stuffed BaHg11 structure is a very common result when a late transition metal, an early transition metal, and a rare earth or alkaline earth metal are combined in aluminum flux. We have prepared a wide range of M3Au7Al26T compounds (with M = Ca, Sr, Yb, Eu and T = early transition metals from groups 4—7). Work is in progress to explore the contributing factors to the filling of the stuffed site and the ordering of the split site to form a potential supercell.

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Supporting Information Available: Synthetic procedures and characterization methods; crystallographic data (atomic positions, thermal parameters, bond lengths) for all compounds in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Reactions with Ca metal showed signs of attack of the quartz tube by Ca vapor; this was not apparent in reactions with perovskite CaTiO3. This suggests that while the aluminum flux reduces the titanate species to TiO2, the alkaline earth remains in its divalent state throughout the reaction.