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

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Supporting information

Synthesis and characterization of $M_3Au_{6+x}Al_{26}Ti$ phases

Perovskites MTiO_3 ($\text{M} = \text{Ca}, \text{Sr}$) were synthesized by grinding together MCO_3 and TiO_2 powder (Fisher), pressing into a pellet, and heating at 1000°C for two days. The pellet was ground into powder, then pressed again and reheated at 1000°C for two days. This process was repeated until the X-ray powder patterns of the products indicated homogenous phases which matched the theoretical patterns of CaTiO_3 and SrTiO_3 .

One mmol of MTiO_3 powder was then combined with 2 mmol gold metal (99.99%, from gold coin) and 20 mmol aluminum metal (99.95%, Cerac) in an alumina crucible. This was placed into a fused silica tube which was sealed under vacuum. The mixtures were heated to 1000°C , held there for 1 day, cooled to 860°C in 12 hours, held at 860°C for 2 days, then slowly cooled to room temperature in four days. The crystalline product was separated from the excess aluminum flux by soaking the crucible in 5M NaOH overnight.

The products consist of large spheroid crystals of $\text{M}_3\text{Au}_{6+x}\text{Al}_{26}\text{Ti}$ in 10-20% yield (based on Au), as well as binary intermetallics such as TiAl_3 and SrAl_4 , recrystallized gold, and oxide powder. The $\text{M}_3\text{Au}_{6+x}\text{Al}_{26}\text{Ti}$ phases are often coated with a brownish-gold film which may be the result of slow attack on the product by the NaOH solution. This coating may be the source of the small impurity peaks in the powder XRD patterns (such as the peak at 29° 2-theta).

Reactions using elemental reagents were also carried out to compare the results. In a nitrogen-filled drybox, alkaline earth metal (or ytterbium), gold, aluminum, and titanium were combined in an alumina crucible in a 1:2:15:1 mmol ratio. The crucible was placed in a fused silica tube which was sealed under vacuum. The heating profile and isolation method were the same as described above. The product mixture was also similar, except the yield of $\text{M}_3\text{Au}_{6+x}\text{Al}_{26}\text{Ti}$ was increased to 40-50%.

The elemental composition of the products was characterized using a JEOL JSM-35C scanning electron microscope equipped with a Tracor Northern energy dispersive spectroscopy (EDS) detector. 10-20 sample crystals of each compound were placed on carbon tape and then broken to expose an inner surface for more accurate analysis of bulk composition. Data were acquired using a 20 kV accelerating voltage and a 50 s accumulation time.

Single crystal X-ray diffraction data was collected at room temperature on a Bruker AXS SMART CCD diffractometer. Data processing was performed using the program SAINT; an absorption correction was applied to the data using the SADABS program. The structures were solved using direct methods and refined with the SHELXTL package of programs. Powdered samples for powder XRD and magnetic susceptibility measurements were prepared by crushing crystals which had been analyzed using EDS and confirmed to be the correct phase. Powder diffraction data was collected using an INEL powder diffractometer. Magnetic susceptibility data was collected on powdered samples using a Quantum Design MPMS-5 SQUID magnetometer.