Ternary Alkaline-Earth Gold Nitrides

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A series of intermetallic phases formed by the alkaline-earth metals Ca, Sr, Ba with the noble metal Au have been studied in detail for a long time. A modification of these intermetallic systems can be approached by the insertion of non-metals into the systems, e. g., formation of nitrides. In the field of alkaline-earth gold nitrides, two compounds are well characterized: Ca_3AuN [1] and Ca_2AuN [2]. Ca_3AuN was synthesized at 1 bar N_2 reaction pressure, whereas Ca_2AuN could only be prepared above 150 bar starting from a mixture of Ca_3N_2 and Au. After the successful work on the high pressure syntheses of new binary alkaline-earth metal nitride diazenides [3, 4] (see "***[N_2^{2-}] Dumb-Bells Trapped within a Cage of Alkaline-Earth Metals***") we went on with the investigation of the preparation of ternary gold nitrides with the heavier alkaline-earth metals.

In the system Sr-Au-N the synthesis of Sr_2AuN succeeded starting from the diazenide SrN_2 [3] and gold powder at 1070 K above 200 bar N_2 - reaction pressure. The investigations show that the reaction is strongly affected by molar Sr:Au ratio. Smallest deviations from the ideal value 2:1 lead to the thermodynamically more stable intermetallic phases SrAu and $SrAu_2$ as main products without fail. Additionally, the studies show that for the optimization of the reaction conditions not only pressure and temperature are of importance but also the starting components such as Sr_2N, SrN or SrN_2. The best results are achieved by using the pure diazenide. The dark brown microcrystalline powder Sr_2AuN is very sensitive to moisture and air [5].

The structure determination succeeded by a combination of X-ray and neutron diffraction experiments. The latter were carried out to obtain reliable nitrogen positions. Additionally, chemical analyses were performed with the carrier gas hot extraction or combustion method. These results confirmed the nitrogen content determined by the structural investigations and showed that the contents of the impurities H, C, O are below the detection limits. Moreover, speciation led – in comparison to the binary strontium-nitrogen compounds (see "***Chemical Analysis – Quantitative Speciation of Nitrogen***") – to the verification that excusively [N^{3-}]-species are existent in Sr_2AuN.

The orthorhombic structure of Sr_2AuN (***Cmcm***, ***Z*** = 4) which is isotypic to Ca_2AuN contains undulated layers of edge-sharing, slightly distorted strontium octahedra that are centered by nitrogen. The most distinctive feature of the refined structure are infinite nearly planar zig-zag chains of gold lying inbetween these layers (Fig. 1). The Au–Au bonding angle is 119.5° (Ca_2AuN 118.3°). The Au–Au distances of 3.038(1) Å are larger than in elemental gold (2.884 Å) and in Ca_2AuN (2.884 Å). For molecular systems with gold-gold interactions the energetically most favorable distance has been calculated to be around 3.0 Å [6].

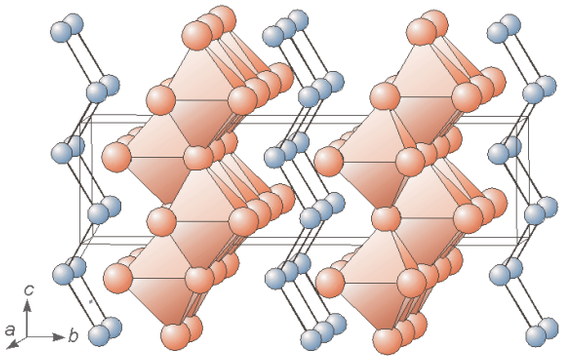

Fig. 1: Crystal structure of Sr_2AuN: Sr: red; Au: blue. The parallel orientated zig-zag chains of gold and layers of edge-sharing SrN_6-octahedra are visualized.

References

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