

# NEW TYPE-I CLATHRATES $A_8Hg_3Ge_{43}$ ( $A = K, Rb$ )

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## Abstract

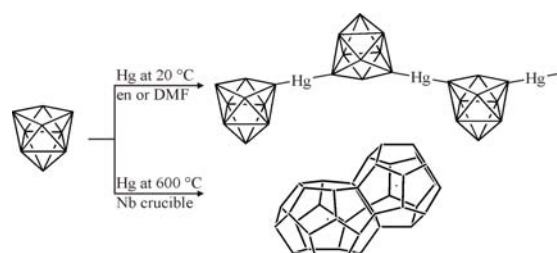
The Hg-substituted type-I clathrates  $A_8Hg_{3+x}Ge_{43-x}$  ( $A = K, Rb$ ) were obtained by solid-state reactions from the corresponding Zintl phases  $A_4Ge_9$  and Hg or HgO. The crystal structure of the compounds was determined by single-crystal and powder X-ray diffraction methods. They crystallize in the space group  $Pm\bar{3}n$ , with  $a = 10.849(1)$  Å and  $x = 0.19(5)$  for  $K_8Hg_{3+x}Ge_{43-x}$  as well as  $a = 10.875(1)$  Å and  $x = 0.03(7)$  for  $Rb_8Hg_{3+x}Ge_{43-x}$ . Specific atom positions (6c site) of the Ge framework are partially substituted by Hg atoms, whereas the alkali-metal atoms reside in the center of the cavities. Both compounds exceed the electron-counting rule for Zintl phases.

## Introduction

Polyanionic clathrates of the elements Si, Ge and Sn have been studied for over 40 years.<sup>1</sup> The interest however rose rapidly in the last decade, since some ternary compounds, such as  $Sr_8Ga_{16}Ge_{30}$ <sup>2</sup> exhibit considerable thermoelectric efficiency. This perspective becomes even more intriguing for certain doped clathrates that may act as Kondo insulators.<sup>3</sup> In this light, the synthesis of chemically well defined materials are necessary. Different synthetic approaches have been applied, depending mostly on the properties of the tetrel element.<sup>4,5</sup> Sn-based clathrates are predominantly obtained by fusion of the elements at temperatures below 700 °C.<sup>1,5</sup> Due to the much higher melting points of the elements, the synthesis of Si and Ge clathrates requires reaction temperatures around 1000 °C or even higher as well as application of external pressure.<sup>5</sup> Alternatively, thermal decomposition of

$A_4Tt_4$  phases ( $Tt = Si, Ge$ ) under dynamic vacuum in order to remove the excess alkali metal has been implemented for the synthesis of the type-I  $A_8Tt_{46}$  and type-II  $A_{24-x}Tt_{136}$  clathrates ( $A = Na, K, Rb, Cs$ ).<sup>6</sup> Recently, high yields of crystalline  $A_{8-x}Si_{46}$  ( $A = Na, K$ ) were achieved by the oxidation of  $A_4Si_4$  with gaseous HCl or  $H_2O$ ,<sup>7</sup> whereas the guest-free type-II  $\square_{24}Ge_{136}$  clathrate ( $\square$  denotes here vacant cationic positions) was synthesized by heating  $Na_4Ge_9$  to 300 °C in a 1:1 mixture of  $AlCl_3$  and n-dodecyltrimethyl-ammonium-chloride.<sup>8</sup> Moreover, the type-IX clathrate  $Ba_6Ge_{25}$  was found to produce type-I  $Ba_8Cu_{6-x}Ge_{40+x}$  in rather high purity when reacted with stoichiometric amounts of Cu and Ge.<sup>9</sup>

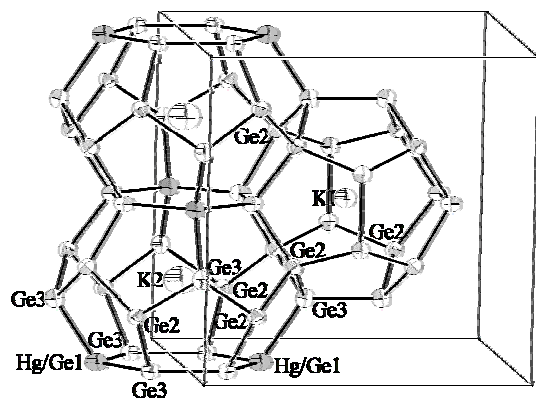
Recently we reported on the synthesis of Hg-substituted clathrates  $A_8Hg_4Sn_{42}$  ( $A = K, Rb, Cs$ ).<sup>10</sup> All attempts to prepare the homologue Ge clathrates as pure phases failed mainly due to the high melting temperature of Ge. Initiated by our successful reaction of  $[Ge_9]^{4-}$  clusters with Hg in ethylenediamine or dimethylformamide solutions leading to the isolation of the polymer  ${}^1[HgGe_9]^{2-}$ ,<sup>11</sup> we performed the synthesis of the Hg-substituted type-I clathrates  $A_8Hg_{3+x}Ge_{43-x}$  using the neat solid  $A_4Ge_9$  ( $A = K, Rb$ ) as precursor.



**Scheme 1.** Reaction of  $[Ge_9]^{4-}$  with Hg towards formation of the polymer  ${}^1[HgGe_9]^{2-}$  or the clathrate-I  $A_8Hg_3Ge_{43}$  ( $A = K, Rb$ ).

## Results and Discussion

The starting materials were stored in an Ar-filled glove box: K (Merck, 99%), Rb (Riedel de Haën, 99.9%), Ge (Chempur, 99.9999%+), Hg (Aldrich, 99.99%+), HgO (Alfa Aesar, 99%) and WO<sub>3</sub> (Aldrich, 20 μm powder, 99%+). Initially, the binary phases A<sub>4</sub>Ge<sub>9</sub> were obtained in corundum crucibles.<sup>12</sup> Two different routes were then followed for the synthesis of the clathrates. Equimolar amounts of A<sub>4</sub>Ge<sub>9</sub> and Hg were loaded in niobium ampoules. These were weld sealed, enclosed in quartz tubes, heated to 600 °C for 24 hours, annealed at 400 °C for 72 hours and subsequently cooled down to room temperature at a rate of 4 K min<sup>-1</sup>.



**Figure 1.** Partial view of the clathrate-I structure for K<sub>8</sub>Hg<sub>3.19</sub>Ge<sub>42.81</sub>: two types of framework cages in the unit cell centered by the guest metal (K1@Ge<sub>20</sub> and K2@(Ge/Hg)<sub>24</sub>). All thermal ellipsoids are presented at 90% probability level.

The phase analysis of the homogenized reaction products was performed on a Stoe STADI P2 diffractometer (Ge(111) monochromator for Cu-K $\alpha$  radiation) equipped with a linear position sensitive detector. The powder patterns were refined with the Rietveld method (*FULLPROF*, Version 3.20). The products consisted of microcrystalline powder of A<sub>8</sub>Hg<sub>3+x</sub>Ge<sub>43-x</sub> and a secondary phase whose powder pattern remains unindexed. This admixture proved to be air sensitive and reacted exothermally with distilled water and acetone. Some Hg drops were also observed and were removed under dynamic vacuum

(12 hours at 100 °C and 2 10<sup>-2</sup> mbar). The powder diagrams of the resulting pure phases of A<sub>8</sub>Hg<sub>3+x</sub>Ge<sub>43-x</sub> were analyzed with the Rietveld method. It seemed crucial to use A<sub>4</sub>Ge<sub>9</sub> in deficiency, since  $\alpha$ -Ge as byproduct would be very difficult to remove.

In search for a method to obtain also single crystals various flux methods and reaction mixtures were checked. Finally, a mixture of A<sub>4</sub>Ge<sub>9</sub>:WO<sub>3</sub>:HgO was successful. This mixture was loaded at a molar ratio of 5:6:3 in a niobium ampoule and treated thermally exactly as used for the first method. The reaction products consisted of grey, good quality single crystals of A<sub>8</sub>Hg<sub>3+x</sub>Ge<sub>43-x</sub> as well as significant amounts of A<sub>2</sub>WO<sub>4</sub> and  $\alpha$ -Ge. HgO decomposes already at 400–450 °C,<sup>13</sup> allowing Hg to react with Ge, in its “activated” A<sub>4</sub>Ge<sub>9</sub> form. The presence of WO<sub>3</sub> or eventually A<sub>2</sub>WO<sub>4</sub> presumably favours the crystal growth of the clathrate, as recently found for K<sub>4</sub>Ge<sub>9</sub> as well.<sup>14</sup> The EDX analyses (JEOL 5900LV scanning electron microscope system operating at 20 kV and equipped with a LINK AN 10000 detector system) on the single crystals confirmed the presence of A, Hg and Ge.

Noteworthy, attempts to synthesize the title compounds by fusion of the pure elements were rather unsuccessful. The very strong vapor pressure of Hg at high temperatures triggered the swelling of the ampoule till it cleaved, leading to the escape of Hg and alkali metals from the ampoule. Only the reaction of A and Ge (or A<sub>8</sub>Ge<sub>44</sub>□<sub>2</sub>)<sup>15</sup> with excess of Hg at 700 °C for 15 days did result in A<sub>8</sub>Hg<sub>3+x</sub>Ge<sub>43-x</sub> but in yields below 10%, as indicated by the quantitative analysis of the corresponding powder diffractogram.

The single crystals obtained from the second reaction route (A<sub>4</sub>Ge<sub>9</sub> + WO<sub>3</sub> + HgO) were mounted on an Oxford Xcalibur3 diffractometer with Mo-K $\alpha$  radiation, graphite monochromator and CCD detector. Full data collections at room temperature included four series of 138 frames with 30 sec exposure time and the

crystal-detector distance at 50 mm. The reflections were collected over the range  $2\theta_{max} = 55.5^\circ$  and corrected for absorption (numerical) using the program X-Shape (Stoe, Darmstadt). The data were processed using the SHELXTL package and solved by direct methods.

