Solid-Sate Chemistry

DOI: 10.1002/anie.201105033

At the Border of Intermetallic Compounds and Transition-Metal Oxides: Crystal Intergrowth of the Zintl Phase Cs_4Ge_9 and Cs_2WO_4 or Cs_3VO_4 as well as Nine-Atom Cluster Relocation in the Solid State**

*Viktor Hlukhyy and Thomas F. Fässler**

In recent years significant progress in the research on nine-atom clusters of germanium has been made. Nine-atom clusters E_9 of group 14 elements are species of captivating beauty and simplicity, which can be regarded as small charged element units that open new possibilities for chemical reactions and the development of nanoscaled materials.[1,2] The isolated clusters Ge_9 are well-known in solution and have been stabilized with a variety of counter ions and as solvates,[1] however, in neat solids they are characterized only in a few binary intermetallic phases such as A_4Ge_9[3] and $A_{12}Ge_{17}$[4] (A = Na, K, Rb, and Cs), in which they mostly show a strong structural disorder. These compounds represent typical salt-like intermetallic compounds, and their solubility in polar solvents makes them valuable precursors for subsequent chemical reactions. Most interesting to materials chemists is the oxidation reaction of $[Ge_9]^{4-}$ clusters which leads to the formation of $([Ge_9]^{2-})_n$ oligomers and polymers ($n = 2$, 3, 4, and ∞, respectively).[5] A $[Ge_{45}]^{12-}$ anion has been found to complex Au atoms,[6] and full oxidation leads to the crystalline modification of clathrate-II-type germanium.[2,7] Further stable Ge modifications based on Ge_9 clusters as building blocks are predicted from theoretical calculations.[8] Although deltahedral germanium Zintl anions have been known for a long time and have intensively been studied in solution,[9] their chemistry in the solid state is almost unexplored. The formation of the few reported double salts containing deltahedral Zintl clusters shows, however, Zintl anions to form rather unusual compounds. In the tetrelide–tetrelate compounds $Cs_{10}[Si_4][Si_3O_9]$ and $Rb_{14}[E_4][Si_6O_{17}]$ (E = Si, Ge) negative and five-fold positive oxidation states of the tetrel elements simultaneously appear.[10] Unfortunately, it was not possible to expand this compound family in which bare element cluster anions are stable in the presence of the respective oxide.

Therefore, we investigated the chemical behavior of germanium Zintl clusters in the presence of transition-metal oxides. An energetically high-lying HOMO of the Zintl clusters might be combined with a low-lying conduction band of the transition-metal oxide such as it appears, for example, in tungsten bronzes.[11]

In the course of our exploration of the reactions of deltahedral germanium Zintl anions with oxometallates in solid-state reactions, we found synthetic access to a series of novel intergrowth structures containing the reduced *nido* cluster $[Ge_9]^{4-}$ and oxidized transition metals, which are generally reduced more easily than silicates.[12] We describe here the synthesis, crystal structure, and spectroscopic properties of the compounds $Cs_{10}[Ge_9]_2[WO_4]$ and $Cs_{11}[Ge_9]_2[VO_4]$ containing $[Ge_9]^{4-}$ clusters and oxometallate anions $[MO_4]^{x-}$. The extremely air- and moisture-sensitive ruby-red single crystals of the title compounds have been obtained by reaction of mixtures of Cs_4Ge_9 and Cs_2WO_4 (Cs_3VO_4), or by the reaction of mixtures of Cs_4Ge_9, WO_3 (V_2O_5) and HgO (as a mere oxygen provider) with elemental Cs in sealed niobium containers. We show here, that ion packing in the new structures allows to adapt the alkali metal content to the charge of the anions WO_4^{2-} or VO_3^{3-} and probably other anions.

$Cs_{10}[Ge_9]_2[WO_4]$ and $Cs_{11}[Ge_9]_2[VO_4]$ crystallize in the space group $P2_1/c$.[13] From a crystallographic point of view the former crystallizes in a new structure type, whereas the latter can be considered as the filled structure variant of the former with one additional Cs atom and neglecting the different cluster orientations (Figure 1 a,b). $Cs_{10}[Ge_9]_2[WO_4]$ and $Cs_{11}[Ge_9]_2[VO_4]$ both contain two crystallographically independent Ge_9 clusters (**A** and **B**) and oxo-bonded WO_4^{2-} and VO_4^{3-} anions (**C**), respectively, in the stacking sequence **ACBCA**.

The Raman spectrum of $Cs_{10}[Ge_9]_2[WO_4]$ (Figure 2) shows the typical signals for nine-atom Ge clusters and tetrahedral WO_4 including the very strong breathing mode around 221 cm^{-1}, and further bands at around 163 and 154 cm^{-1} for the Ge_9 unit.[4a,14] However, an intense low-range peak at 54 cm^{-1} has been observed for the first time for the Ge_9 cluster in this study which is attributed to a librational mode of the cluster. The peaks assigned to the WO_4^{2-} anion around 320 and 916 cm^{-1} are in good agreement with those reported in the literature.[15]

The substitution of WO_4^{2-} in $Cs_{10}[Ge_9]_2[WO_4]$ for VO_4^{3-} to give $Cs_{11}[Ge_9]_2[VO_4]$ is counterbalanced by one additional Cs position in the structure. Therefore, according to the ratio of Cs^+ cations to germanide cluster and oxometallate anions, the clusters in both structures are clearly four-fold negatively charged. The expected diamagnetism for the species $[Ge_9]^{4-}$, WO_4^{2-}, and VO_4^{3-} is confirmed by the negative values of the

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[*] Dr. V. Hlukhyy, Prof. Dr. T. F. Fässler
Departement Chemie, Technische Universität München
Lichtenbergstr. 4, 85747 Garching (Germany)
E-mail: thomas.faessler@lrz.tum.de

[**] The authors thank Prof. R. Niessner and Dr. N. P. Ivleva, Institute of Hydrochemistry, Technische Universität München for the Raman spectroscopy measurements and Dr. A. Schier for the revision of the manuscript.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105033.

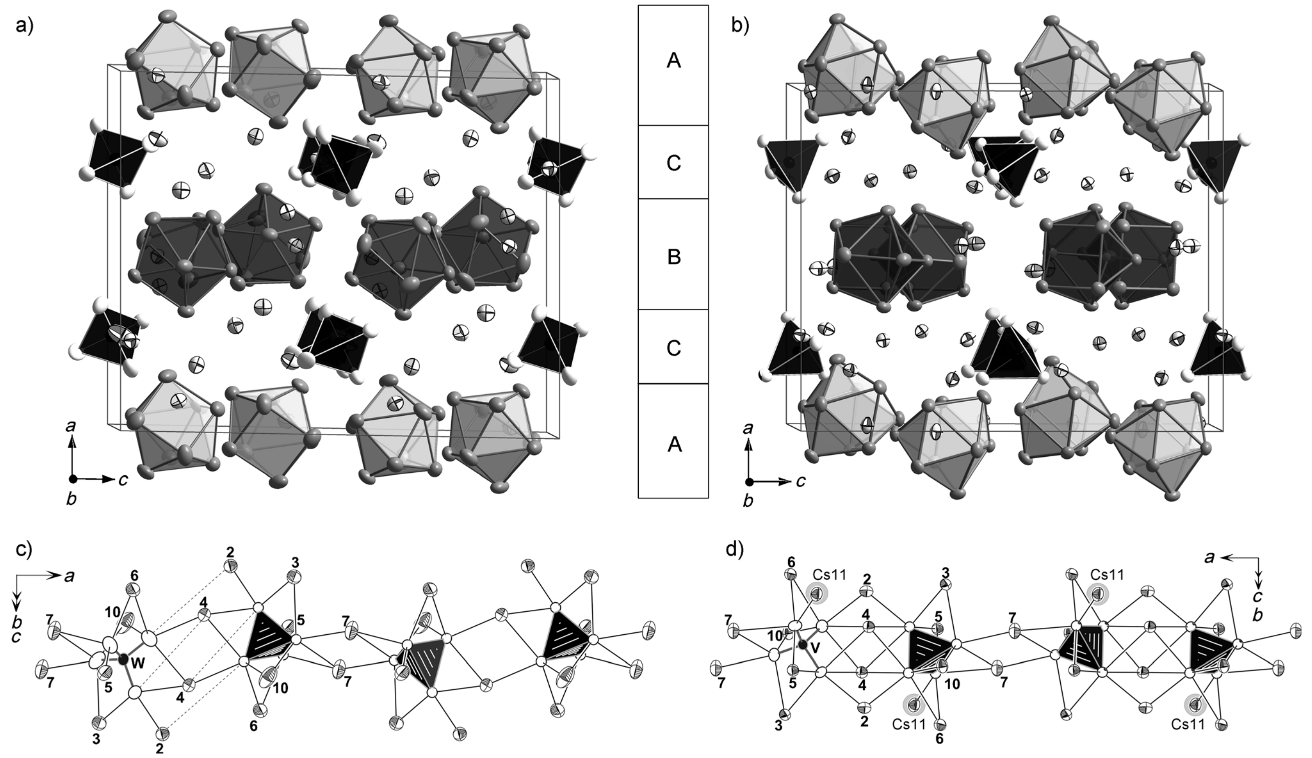

Figure 1. View of a) the $Cs_{10}[Ge_9]_2[WO_4]$ and b) the $Cs_{11}[Ge_9]_2[VO_4]$ structures (at 150 K) along the *b* axis showing alternating layers of germanides (**A** and **B**) and oxometallates (**C**) with the sequence **ACBCA**. The anions WO_4^{2-} and VO_4^{3-} and the Ge_9 clusters **A** and **B** are shown as black, white and grey polyhedra, respectively. View of the coordination of the MO_4 anions by the closest Cs^+ cations in c) $Cs_{10}[Ge_9]_2[WO_4]$ and d) $Cs_{11}[Ge_9]_2[VO_4]$. The additional Cs position (Cs11) in $Cs_{11}[Ge_9]_2[VO_4]$ (d) is emphasized. Isolated crossed ellipsoids are Cs^+ cations. Ge, W (V), O atoms are drawn in grey, black, and white, respectively. The displacement ellipsoids are drawn at the 70% probability level. The numbering scheme is shown for Cs atoms only (c, d).

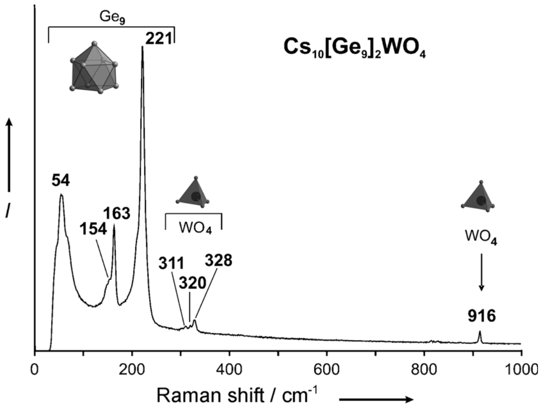

Figure 2. Raman spectrum obtained from single crystals of the double salt $Cs_{10}[Ge_9]_2[WO_4]$.

magnetic susceptibility measured at various fields for $Cs_{10}[Ge_9]_2[WO_4]$ and $Cs_{11}[Ge_9]_2[VO_4]$.[16]

In $Cs_{10}[Ge_9]_2[WO_4]$ and $Cs_{11}[Ge_9]_2[VO_4]$ each of the two symmetry-independent $[Ge_9]^{4-}$ cluster anions **A** and **B** are ordered in contrast to the situation in double salts with smaller cations A^+ in $A_{10}[Ge_9]_2[WO_4]$ ($A = K$, Rb), where the type **B** cluster is strongly disordered.[17] Since the same behavior is observed for the binary phases Cs_4Ge_9 (ordered) and K_4Ge_9 (disordered) the size of the surrounding cations seems to play a crucial role for cluster ordering. Whereas in the structures of $A_{10}[Ge_9]_2[WO_4]$ ($A = K$, Rb) the orientational disorder of the Ge_9 cluster can be considered as a superposition of two or more conformations, in $Cs_{11}[Ge_9]_2[VO_4]$ different cluster rearrangements in the solid state are observed, associated with a phase transition. Upon heating a single crystal of $Cs_{11}[Ge_9]_2[VO_4]$ on the diffractometer, the lattice parameters discontinuously increase between 167 K and 175 K (see Figure S1 and Table S1 in the Supporting Information). This abrupt change of the lattice parameters (i.e. “jump over tetragonality”) is caused by a conformational transition of the Ge_9 clusters **A** as proven by a structure refinement of the high-temperature data (HT $Cs_{11}[Ge_9]_2[VO_4]$).[13] The monocapped square antiprismatic configuration of the *nido* clusters $[Ge_9]^{4-}$ (**A**) appears in a different orientation. A least-motion pathway in analogy to the known diamond-square-diamond process established for borane and carbaborane polyhedra[1c] can be established also here by shifting six atoms of the cluster **A** followed by a rather small rotation as shown in Figure 3. Atom rearrangements of nine atom clusters has been found in solution long time ago by NMR methods for $[Sn_9]^{4-}$ and $[Pb_9]^{4-}$ clusters[18a,b] and is here established for the first time also for $[Ge_9]^{4-}$ clusters in the solid state.[18c] Driving force of the rearrangement might be traced back to the rather short Ge–Ge intercluster distance Ge2A–Ge2A of 3.205(2) Å in the low-temperature (LT) $Cs_{11}[Ge_9]_2[VO_4]$ cluster relative to the distance of 3.693(5) Å

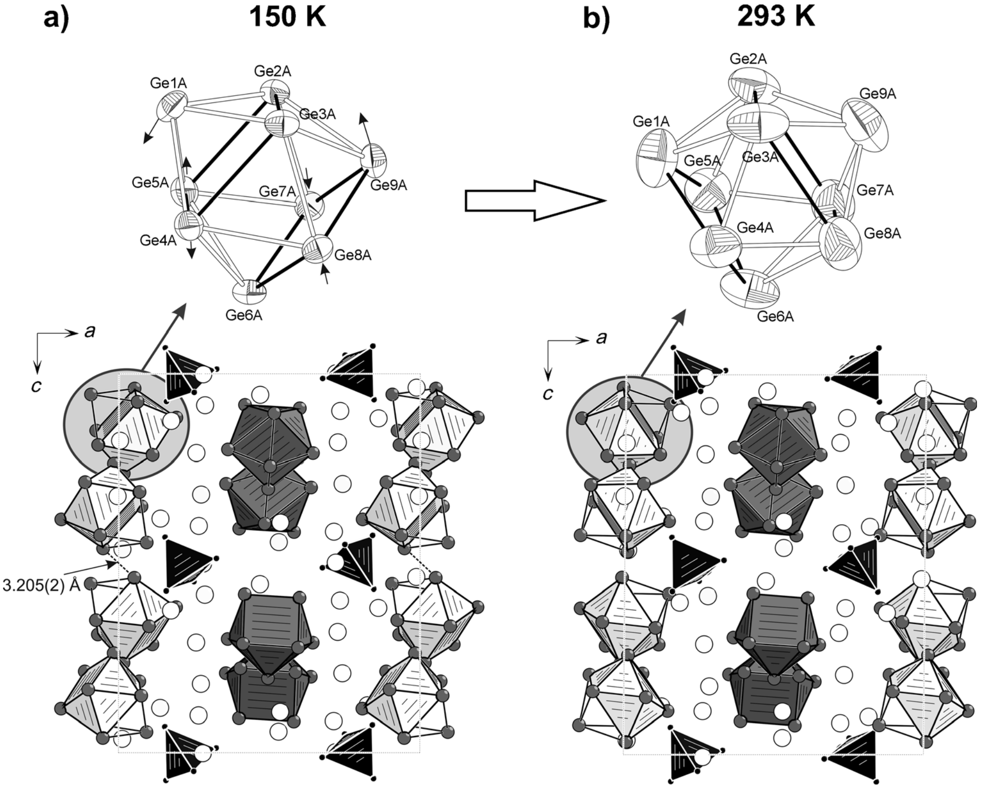

Figure 3. Rearrangement of the nine-atom clusters in the solid state of $Cs_{11}[Ge_9]_2[VO_4]$. a) Low-temperature (150 K) structure with short intercluster Ge_9–Ge_9 distances. b) High-temperature structure at 293 K. The conformation of the Ge_9 clusters **A** is shown in detail: the square anti-prisms are emphasized, and the shift directions of the atoms Ge1 A and Ge9 A are shown. The displacement ellipsoids of the Ge atoms in the Ge_9 clusters (top) are shown at the 70 % probability level.

in the HT form (at 293 K). In $Cs_{10}[Ge_9]_2[WO_4]$ and the parent Cs_4Ge_9 the minimum intercluster distances are larger (3.628(5) and 3.96 Å, respectively), and this transition has by now been observed only for LT-$Cs_{11}[Ge_9]_2[VO_4]$. Differential scanning calorimetry (DSC) measurements show a weak reversible effect around 175 K (see Figure S2 in the Supporting Information).[19]

The ordered Ge_9 clusters (**B** in $Cs_{10}[Ge_9]_2[WO_4]$, LT-, and HT-$Cs_{11}[Ge_9]_2[VO_4]$; as well as **A** in LT-$Cs_{11}[Ge_9]_2[VO_4]$) have similar shapes with an almost ideal C_{4v} symmetry as visible from the ratio of diagonal lengths of the open basal square $d_1/d_2 > 1.06$ and dihedral angles $\alpha > 3.5°$. Clusters **A** in $Cs_{10}[Ge_9]_2[WO_4]$ and HT-$Cs_{11}[Ge_9]_2[VO_4]$ suffer from a small C_{2v}-symmetric distortion with $d_1/d_2 = 1.18$ and larger dihedral angles α of approximately 12.0° (see Figure S3 and Table S2 in the Supporting Information:). The Ge–Ge distances within the Ge_9 clusters correspond to the pattern found for all fully isolated E_9 *nido* clusters. The distances between five-coordinated Ge atoms within the capped square are slightly longer (2.67(1) Å–3.09(1) Å) than the other distances which are observed in the range from 2.49(1) to 2.65(1) Å. Similar bond lengths are found in other ordered $[Ge_9]^{4-}$ clusters of the binary system Cs_4Ge_9 (2.52 to 3.01 Å).[3a] Further, the Ge_9 clusters **A** in $Cs_{11}[Ge_9]_2[VO_4]$ (LT and HT) are surrounded by 16 closest Cs^+ cations, whereas clusters **A** of $Cs_{10}[Ge_9]_2[WO_4]$ and clusters **B** in all structures have 17 closest Cs^+ neighbors each with several cations capping the polyhedral faces (see Figure S4 in the Supporting Information) in a rather similar way as observed in the binary phase Cs_4Ge_9 with 16 closest Cs^+ cations.[3a] The shortest Cs–Ge distances are 3.51(2), 3.50(1), and 3.56(1) Å for $Cs_{10}[Ge_9]_2[WO_4]$, LT-$Cs_{11}[Ge_9]_2[VO_4]$, and HT-$Cs_{11}[Ge_9]_2[VO_4]$, respectively, whereas for the parent Cs_4Ge_9 it is 3.49 Å.

The W–O distances in $Cs_{10}[Ge_9]_2[WO_4]$ range from 1.77(2) to 1.82(2) Å as observed in K_2WO_4 (1.76 to 1.81 Å).[20] The anionic WO_4^{2-} unit in the Cs double salt is surrounded by 9 Cs^+ cations which is less than the 11 Cs^+ neighbors found in Cs_2WO_4 (Figure 1 c). The distances between Cs and O atoms vary from 2.82(2) to 3.44(2) Å. In the double salt $Cs_{11}[Ge_9]_2[VO_4]$ the V–O distances range from 1.71(1) to 1.73(1) Å and are close to those in γ-K_3VO_4 (1.73 Å), but longer than the ones in β-K_3VO_4 (1.62 Å).[21] The anionic VO_4^{3-} unit shows contacts to 11 Cs^+ cations, whereas it has 10 contacts to K^+ in γ-K_3VO_4 and 12 in β-K_3VO_4 (Figure 1 d).[21] The additional Cs11 position in $Cs_{11}[Ge_9]_2[VO_4]$ causes a change in the relative orientation of the VO_4 tetrahedra if compared to $Cs_{10}[Ge_9]_2[WO_4]$. As a consequence of an additional Cs11–O contact the dashed lines shown in Figure 1 c become shorter in $Cs_{11}[Ge_9]_2[VO_4]$, and thus four instead of two bridging alkali metal atoms occur (Figure 1 c,d).

The packing of the cluster units into more complex structures can be traced back to the atom packing in more simple structure types.[22] The topological analysis of the structures of the title compounds shows that they are hierarchical derivatives of the initiator Al_2Cu ($I4/mcm$)[23] with the Ge_9 clusters at the Al and the MO_4 anions at the Cu positions, whereas the Cs^+ cations are located in the resulting tetrahedral voids of the structure (see Figure S5 in the Supporting Information).[24] The relationship between the basic structure Al_2Cu and the hierarchical derivative structure by atom-by-cluster replacement plus filling of tetrahedral voids can be written: $\square_{17}Al_2Cu \cong \square_7Cs_{10}[Ge_9]_2[WO_4]$ or $\square_{17}Al_2Cu \cong \square_6Cs_{11}[Ge_9]_2[VO_4]$ (□ denoted tetrahedral voids). Based on this consideration of hierarchical variants it becomes clear that further double salts might form stable packings: the structure can accommodate more extra cations by filling the second tetrahedral void which could counterbalance an MO_4^{4-} oxometallate anion such as TiO_4^{4-}. Attempts to synthesize $Cs_{12}[Ge_9]_2[TiO_4]$ are in progress.

Both the stoichiometry and the coordination of the anions by Cs cations indicate a "merging" of the structures of the Zintl phase Cs_4Ge_9 and the parent oxides Cs_2WO_4 and Cs_3VO_4 in $Cs_{10}[Ge_9]_2[WO_4]$ and $Cs_{11}[Ge_9]_2[VO_4]$ according to $Cs_{10}[Ge_9]_2[WO_4] = [Cs_4Ge_9]_2{\cdot}[Cs_2WO_4]$ and $Cs_{11}[Ge_9]_2[VO_4] = [Cs_4Ge_9]_2{\cdot}[Cs_3VO_4]$, respectively. The existence of such an intergrowth of a Zintl phase and a classical salt puts further strength on the term "saltlike" compound.

The title compounds are nice examples for crystal-engineered all-inorganic composite materials,[25,26] but the formation of such composite materials from two simple parent compounds is unpredictable. At first glance it emphasizes the good topological compatibility of the two anions and their first coordination sphere of cations. Hence, it is likely that the main factor behind the existence of these hybrid compounds is the slightly higher Madelung energy of the crystal intergrowth compound relative to the one of the parent compounds. The volume per formula unit of the composite materials at room temperature is virtually the same as the sum of the volumes of the two parent compounds, whereas a small volume increase of about 3.5 % is observed for the tetrelide–tetralate compounds.[10,27]

Homoatomic Zintl cluster ions of the main group elements can be regarded as small charged element particles that open new possibilities for chemical reactions, and they are versatile building blocks for novel nanoscaled materials. Materials belonging to the tungstate and vanadate families have a long history of practical applications and have been the object of extensive research over the last decades because of their excellent optical properties.[28] A "fusion" of these systems may give rise to materials in which a variety of properties coexist, or to materials with completely new properties because of the mutual interaction between the two individual networks.

Experimental Section

Synthesis: All manipulations were carried out under a purified argon atmosphere using standard glove box techniques. The reactants were elemental Cs (Riedel-de-Haën, 99.9 %) and Ge (Chempur, 99.9999+%), the oxides WO_3 (Aldrich, 99+%), V_2O_5 (Aldrich, 99+%), and HgO (99.0 %, Alfa Aesar), and the oxometallates Cs_2WO_4 (99.9 %, Alfa Aesar) and Cs_3VO_4 (99.9 %, Alfa Aesar). The solids were weighed and loaded in Nb crucibles (99.9 %, Osnabruegge; or Nb ampoules with an inner corundum crucible) which were in turn sealed by welding on both sides and jacketed in a fused silica Schlenk tube under argon and evacuated to prevent oxidation of the crucibles at high temperatures. The precursor Cs_4Ge_9 was prepared from stoichiometric amounts of the elements in sealed niobium containers. These containers were encapsulated in evacuated fused silica tubes, heated to 1173 K for 4 h, and slowly cooled to room temperature at a rate of $0.2\,K\,min^{-1}$.

The double salt $Cs_{10}[Ge_9]_2WO_4$ was obtained directly from the parent compounds Cs_4Ge_9 and Cs_2WO_4 in a sealed niobium ampoule with an inner corundum crucible using the following thermal treatment: the sample was first heated in a muffle furnace to 1223 K and held at that temperature for 12 h. Next, the temperature was lowered at a rate of $-6\,K\,h^{-1}$ to 923 K, held at that temperature for 120 h, and finally quenched on air. This procedure yielded high-quality single crystals of $Cs_{10}[Ge_9]_2WO_4$ in the form of ruby-red transparent plates and single-phase microcrystalline powders (see Figure S6 in the Supporting Information).

$Cs_{11}[Ge_9]_2VO_4$ was obtained by heating a mixture of Cs/Cs_4Ge_9/V_2O_5/HgO at a ratio of 6:4:1:3 in a sealed niobium ampoule with an inner corundum crucible using a thermal treatment similar to that described above for $Cs_{10}[Ge_9]_2WO_4$. The $Cs_{11}[Ge_9]_2VO_4$ double salt can also be obtained directly from the parent compounds Cs_4Ge_9 and Cs_3VO_4 as described above for $Cs_{10}[Ge_9]_2WO_4$.

The chemical composition of the single crystals extracted from the reaction products were investigated with a scanning electron microscope JEOL-SEM 5900LV equipped with an integrated energy dispersive X-ray system and a LINK AN 10000 detector system for EDX analysis. A quantitative estimation of the atomic ratio was difficult to perform because of the extreme air and moisture sensitivity of the compounds. However, an atomic ratio of Cs/Ge close to 1:2 was observed for most of the analyzed crystals, as well as a Ge/W(V) atomic ratio close to or larger than 10:1.

Crystal structure determination: Transparent ruby-red irregular crystals of $Cs_{10}[Ge_9]_2WO_4$ and $Cs_{11}[Ge_9]_2VO_4$ were selected under perfluoropolyalkyl ether and mounted on top of a glass fiber. Single-crystal intensity data were collected on an Oxford XCalibur3 diffractometer at 150 K for $Cs_{10}[Ge_9]_2WO_4$ and at 150, 167, 175, 225, and 293 K for $Cs_{11}[Ge_9]_2VO_4$. The crystals were systematically twinned with varying twin fractions; the corresponding twin law was considered in the structure refinement. The unit cell angles are all close to 90°, but on the basis of systematic extinction, the structure was solved in the space group $P2_1/c$. The structures were solved by direct methods, using SHELXS-97 and refined by employing the full-matrix least-squares procedure SHELXL-97.[13] The O positions were localized on the residual electron density map around the W(V) position. All atoms were refined using anisotropic displacement parameters. Atomic coordinates, displacement parameters, and selected bond lengths are given in Tables S3–S8 in the Supporting Information.

Raman spectra: A LabRAM HR Raman microscope system with 785 nm excitation wavelength of the laser diode, Raman edge filter ($<50\,cm^{-1}$), and 10× objectives (NA 0.25) was used for the measurement of single crystals of $Cs_{10}[Ge_9]_2WO_4$ (sealed in a capillary of 0.3 mm in diameter, 0.01 mm wall thickness). At least three measurements were made on different crystals in each case to assure reproducibity.

Wavenumbers: $\tilde{\nu} = 54$ (Ge_9), 154 (Ge_9), 163 (Ge_9), 221 (Ge_9), 311 (WO_4), 320 (WO_4), 328 (WO_4), 916 cm^{-1} (WO_4). The Raman spectra fit well into the series of the already known Ge_9-containing compounds, showing the very strong breathing mode at around 221 cm^{-1} (n_2, A_1) as well as further bands at around 163 and 154 cm^{-1}, which are not single fundamentals but result from a superposition of separated groups of modes, that is, (A_1+B_1+E) and ($2B_2+E$), respectively. As shown by other investigations the modes of the WO_4^{2-} anion are sensitive to the environment[15] in contrast to the frequencies of the Ge_9 cluster, the positions of which are practically constant, that is, independent of the counter ions and coordination polyhedron.

Received: July 18, 2011

Keywords: cluster compounds · germanium · oxometallates · tungsten brass · Zintl phases

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[13] a) Details of the crystal structure determination of Cs$_{10}$Ge$_{18}$WO$_4$ (at 150 K): crystal size $0.20\times0.20\times0.20$ mm^3; cell parameters at 150 K: $a=14.9565(7)$, $b=15.7672(9)$, $c=18.5289(8)$ Å, $\beta=91.079(4)°$, $V=4368.7(4)$ Å^3; monoclinic, space group $P2_1/c$ (no. 14), $Z=4$, $\rho_{\text{calc}}=4.38$ g cm^{-3}, $\mu=23.0$ mm^{-1}; $\Theta_{\max}=27.50°$, 29037 measured reflections, 10035 independent reflections, $R_{\text{int}}=0.161$; $R_1=0.091$ and $wR_2=0.223$ for $I\geq2\sigma(I)$. Details of the crystal structure determination LT-Cs$_{11}$Ge$_{18}$VO$_4$ (at 150 K): crystal size $0.10\times0.10\times0.12$ mm^3; cell parameters: $a=14.1536(3)$, $b=17.7120(4)$, $c=17.8233(3)$ Å, $\beta=90.081(2)°$, $V=4468.1(1)$ Å^3; monoclinic, space group $P2_1/c$ (no. 14), $Z=4$, $\rho_{\text{calc}}=4.29$ g cm^{-3}, $\mu=20.9$ mm^{-1}; $\Theta_{\max}=30.00°$, 87230 measured reflections, 13378 independent reflections, $R_{\text{int}}=0.077$; $R_1=0.035$ and $wR_2=0.074$ for $I\geq2\sigma(I)$. Details of the crystal structure determination HT-Cs$_{11}$Ge$_{18}$VO$_4$ (at 293 K): Crystal size $0.10\times0.10\times0.12$ mm^3; cell parameters: $a=14.0321(9)$, $b=18.269(1)$, $c=17.795(1)$ Å, $\beta=90.468(6)°$, $V=4561.6(5)$ Å^3; monoclinic, space group $P2_1/c$ (no. 14), $Z=4$, $\rho_{\text{calc}}=4.20$ g cm^{-3}, $\mu=20.5$ mm^{-1}; $\Theta_{\max}=27.50°$, 71396 measured reflections, 10455 independent reflections, $R_{\text{int}}=0.115$; $R_1=0.078$ and $wR_2=0.218$ for $I\geq2\sigma(I)$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-423295 (Cs$_{10}$Ge$_{18}$WO$_4$), -423296 (LT-Cs$_{11}$Ge$_{18}$VO$_4$), and -423297 (HT-Cs$_{11}$Ge$_{18}$VO$_4$); b) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Universität Göttingen, **1997**; c) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Universität Göttingen, **1997**.

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