Generation of Gas-Phase Ge, Sn, and Pb Cluster Anions from Various Sources and Comparison to Solid-State Analogues

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Time-of-flight mass-spectrometric investigations show that laser desorption leads to anionic, large clusters of the elements (E) Ge, Sn, and Pb without special gas-phase clustering conditions and additional ionization processes. Ion formation strongly depends on the nature of the starting materials used during desorption experiments. Cluster anions from pure elements E were observed with a maximum of 6 atoms and their relative intensities decreased exponentially with increasing cluster size. Larger clusters are observed if alkali metals (K, Rb, and Cs) are present. Binary phases of nominal composition K_4E_9, ethylenediamine solutions of these phases, and crystalline compounds containing well-defined cluster anions as in $[K([2.2.2]\text{-crypt})]_3E_9$ are used as sources for desorption experiments. The latter results in the formation of clusters of 11 (Ge), 15 (Sn), and 13 (Pb) E atoms. Under similar conditions cations are observed at much lower intensities and the maximum cluster size is 6. For E = Ge anions containing two different kinds of atoms KGe_n^- are observed with relatively high abundance for n = 5, 9, and 10; KGe_{11}^- and KGe_{13}^- are also detected. The results are compared to the formation of clusters in binary alloys. Analogies to structurally characterized Zintl ions E_n^{x-} (x = 2, 3, 4) are given. The enhanced formation of cluster anions during the laser desorption process in the presence of electropositive metals indicates a more general application for anion formation in the gas phase.

Introduction

The relationship between the stability of gas-phase clusters and Zintl ions is of considerable interest[1][2]. The remarkable feature of anions of group-14 elements E (E = Ge, Sn, Pb) is their distinct tendency towards *cluster* formation in the solid state, in solution, and in the gas phase. The earliest studies on soluble E_n clusters were reported more than 100 years ago[3]. The systematic work of Kraus, Smyth, and Zintl[4][5] proved the existence of polyanions, such as Pb_9^{4-} and Pb_7^{4-}. Since then, several homoatomic cluster anions − so-called *Zintl ions* − have been structurally characterized, most of them as their $[K([2.2.2]crypt)]^+$ and $[Na([2.2.2]crypt)]^+$ salts[6]: E_5^{2-}, E_9^{x-} (x = 3, 4), and Ge_{10}^{2-}. Sn_9^{4-} and Pb_9^{4-} clusters stabilized by $Cr(CO)_3$ have also been isolated (Figure 1)[7]. Interestingly, there is only one structural report of an octahedral group-14 species $[SnCr(CO)_5]_6^{2-}$ characterized as $[K([2.2.2]crypt)]^+$ salt[8].

The enhanced stability of these anions can be understood using Wade's electron counting rules for clusters[9]. Deltahedral n-vertex clusters are stable with $2n + 2$, $2n + 4$ and $2n + 6$ skeletal electrons and form *closo*-, *nido*-, and *arachno*-type clusters, respectively. As a result, E_n^{x-} clusters which are build up from group-14 elements should be especially favored independent of cluster size with the same relatively low charges of −2, −4, and −6. Deltahedral *closo* structures were predicted for $n \leq 24$[10] and are known for boranes and caboranes for $4 \leq n \leq 12$.

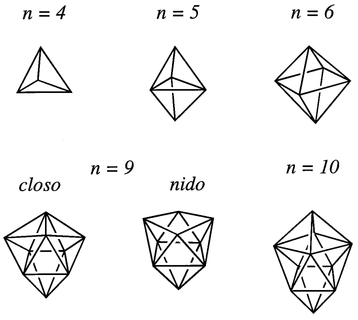


Figure 1. Structurally characterized homoatomic deltahedra E_n with n = 4, 5, 6, 9, 10 vertices; nine-atom clusters occur with different electron counts and structures between the *closo* and *nido* type; octahedral clusters are only known with stabilizing organometallic ligands (for further details see text)

Several homoatomic clusters of the heavier group-14 elements were characterized by mass spectrometry. Under equilibrium conditions in Knudsen cell effusion, the abundance of tetrameric molecules is independent of the composition of the condensed starting material. Such precursors include binary to quaternary systems of group-14 to -16 elements, some of which also contain alkali metals[11]. The stability of these molecules correlates with their electron numbers (20 and 22 electrons) and hence with their possible structures (planar and tetrahedral)[12]. Cooling hot metal vapors using different techniques enables the production of larger cluster species and ultrasmall particles[1][13][14][15]. In many cases electron bombardment or laser ionization generates positive cluster ions from neutral cluster beams. Positively and negatively charged cluster ions can be obtained by laser desorption[13] or injecting electrons from a biased filament[16]. Several mass-spectrometric investigations of larger group-13 to -16 clusters use the corresponding elements as ion sources. Gas-phase reaction and gas-aggregation techniques used for the binary systems Cs/Sn and Cs/Pb show intensity maxima for the molecules $Cs_3Sn_5^+$, $Cs_3Sn_9^+$, $Cs_5Sn_9^+$, and $Cs_3Pb_5^+$. Sn_{10}^+ is observed at low intensity. Larger clusters were not observed due to the limitation of the mass spectrometer[1].

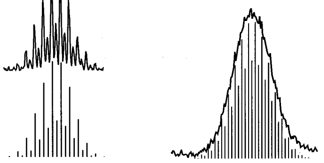
The facile synthesis and isolation of molecular paramagnetic clusters E_9^{3-} in good yields[17] prompted us to investigate the gas-phase ion formation from samples that contain discrete cluster units. Here we report our time-of-flight (TOF) mass-spectrometric studies of $E_n^{+/-}$ ions (E = Ge, Sn, and Pb) generated by laser desorption in a commercially available TOF mass spectrometer. The generation of large, anionic clusters is achieved by laser desorption without gas-phase aggregation techniques.

In order to evaluate the dependency of the gas-phase cluster-ion formation on the ability of electron transfer and thus ion formation in the precursors, we investigated the following series of samples: pure elements (Ge, Pb); mixtures of the elements K and E = Ge, Pb; binary phases K_4E_9 (E = Ge, Sn, and Pb); ethylenediamine solutions of A_4E_9 (A = alkali metal, E = Ge, Sn, and Pb); $[K([2.2.2]crypt)]_3E_9$ salts containing isolated Zintl ions E_9^{3-} (E = Ge, Sn, and Pb).

Results

The resolution of the TOF spectrometer allows the identification of the isotopic distribution in the clusters up to a maximum cluster size of six atoms. As an example, the observed and simulated spectrum of Ge_4 is shown in Figure 2a, left where the five most abundant isotopes are used for the calculation (isotope mass, relative abundance: 69.9, 0.56; 71.9, 0.75; 72.9 ,0.21; 73.9, 1.00; 75.9, 0.21). Larger clusters appear as broader signals (Figure 2b, right). Typical mass spectra of the investigations are shown in Figures 3−5. The inserts show the mass spectra of delayed extraction. In Figures 3c and 4a higher mass regions are shown on enlarged intensity scales.

Figure 2. Comparison of the measured and simulated (lines) mass spectra of Ge_4 and Ge_{10}



Pure Elements E = Ge, Pb

A typical spectrum of negatively charged Ge clusters generated by laser desorption from elemental germanium is shown in Figure 3a. All ion signals have the expected mass distribution due to the abundance of the different isotopes of Ge. The largest detected ion is a six-atom cluster. The relative intensities of the ion signals decrease exponentially with increasing cluster size. The relative intensities differ clearly from those recorded using vapor-phase condensation techniques. In these experiments cluster-size "magic numbers"[15][16][18] appear and a dependency of the cluster size distribution on the gas-aggregation technique is observed[14][19]. The size distribution for Ge and Pb cations are very similar, however, in the case of Pb also oxide formation Pb_3O_y with $y = 1-4$ is found.

Mixtures of K and E = Ge, Pb

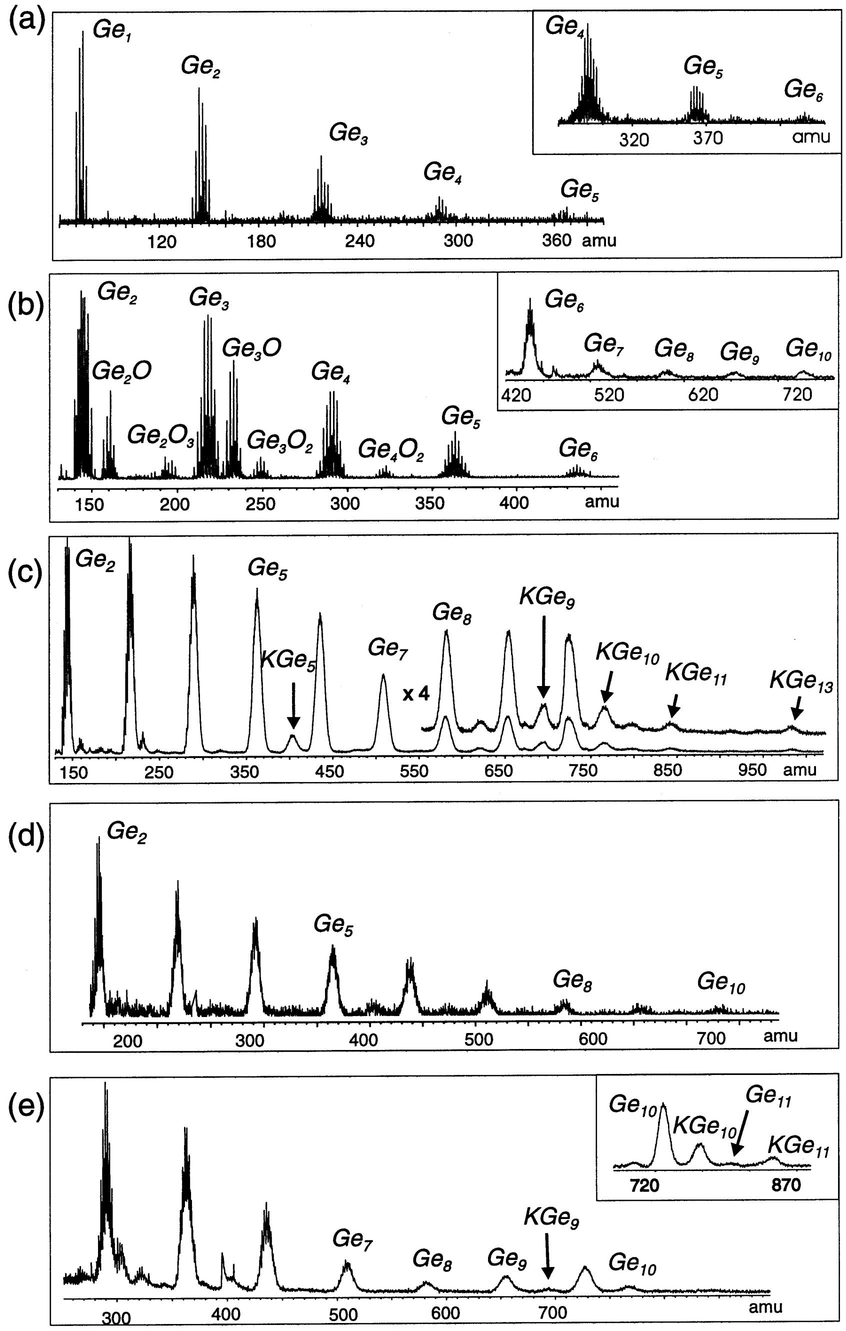
If potassium is present during the laser evaporation process, the formation of larger anionic clusters occurs. The mass spectrum in Figure 3b reveals an exponential decay of the anion intensities from $n = 1$ to 6 for Ge. After a drop of relative intensity, larger clusters ($n = 7-10$) appear with similar intensities. An analogous spectrum is obtained with E = Pb (not shown). No mixed atom clusters KE_n^- are present. For E = Ge and Pb several oxide-containing anions are observed: Ge_2O^-, $Ge_2O_2^-$, $Ge_2O_3^-$, Ge_3O^-, $Ge_3O_2^-$, $Ge_3O_3^-$, $Ge_4O_2^-$ and the series $Pb_nO_{n+1}^-$ as well as $KPb_nO_{n+1}^-$ ($n = 2-6$) are predominant. The enhanced formation of oxides is probably caused by oxygen impurities in elemental potassium or partial oxidation of the surface of the samples during sample transfer to the mass spectrometer. Certainly, the alkali metal acts as an electron donor, and thus promotes the anion cluster formation in the plasma. Lead cation abundance using the mixture as source is similar to the mass distributions from pure metal sources.

Binary Phases of Nominal Composition "K_4E_9" (E = Ge, Sn, and Pb)

Recently, binary A/E = 4:9 phases have been structurally characterized for E = Ge and Sn and A = K, Rb, Cs[20]. They contain discrete E_9^{4-} cluster ions. In the case of E = Pb the existence of a 4:9 phase was discussed earlier[5]. The results of the desorption experiments are shown in Figure 3c for E = Ge. Clusters with maximum size $n = 13$ are observed. The ion signals of the homoatomic clusters Ge_n^- show a decay in intensity up to cluster size $n = 8$. The nine- and ten-atom clusters occur with similar intensities as the eight-atom cluster. Species containing 11 to 13 atoms are detected at lower relative intensities. The formation of mixed metal clusters KGe_n^- for $n = 5$, 9, and 10 is favored, accompained by ions with $n = 8$, 11, and 13 at lower intensities.

In the case of E = Sn and Pb, the anionic clusters occur with a stronger decay in relative intensity in the higher mass

Figure 3. Mass spectra of Ge_n^- clusters obtained from a) elemental Ge, b) mixture of K and Ge, c) K_4Ge_9, d) ethylenediamine extract of K_4Ge_9, and e) $[K([2.2.2]crypt)]_3Ge_9$, containing discrete Ge_9^{3-} clusters; inserts show spectra optimized for the higher mass regions (delayed extractions)



region and reach a maximum cluster size of 10 atoms. Mixed metal clusters KSn_n^- or KPb_n^- are absent but the anions $KSn_2O_3^-$, $KSn_3O_4^-$, KPb_9O^-, and $KPb_{10}O^-$ are present.

Ethylenediamine (en) Solutions of Phases of Nominal Composition "A_4E_9" (E = Ge, A = Na, K, Rb; E = Sn, Pb, A = K)

If phases of nominal composition Na_4E_9 (E = Ge, Sn) are dissolved in en, the crystalline product $[Na_4 \cdot x\ en]\ E_9$ ($x = 0-7$) can be isolated after slow evaporation of the solvent[21]. Using K instead of Na leads to products with similar compositions. The mass spectra of residues of en solutions of K_4Ge_9, K_4Sn_9, and K_4Pb_9 are shown in Figures 3d, 4a, and 5a, respectively. The spectra of the en solutions of Na_4Ge_9 (not shown), K_4Ge_9, Rb_4Ge_9 (not shown), and K_4Pb_9 reveal very similar mass distributions and relative intensities. E_n^- clusters are observed with an exponential decay of their intensities with increasing mass for $n \leq 10$. $NaGe_5^-$, KGe_5^-, KGe_6^-, $RbGe_5^-$, and $RbGe_{10}^-$ are also observed. In the lead system several oxides as discussed earlier are present. In K_4Sn_9 the occurrence of ion pairs Sn_n^- and $Sn_n^- + 56$ (±1) amu, corresponding to the mass of Sn_n and KSn_nO, respectively, is prominent. These peaks are present for $7 \leq n \leq 12$ (Figure 4a). Notice the high abundance of the $KSn_{11}O^-$ anion. For larger n the ternary ions show higher abundance than Sn_n^- anions.

Figure 4. Mass spectra of Sn_n^- clusters obtained from a) ethylenediamine extract of a solidified melt of nominal composition K_4Sn_9, and b) $[K([2.2.2]crypt)]_3Sn_9$, containing discrete Sn_9^{3-} clusters; for insert cf. caption of Figure 3

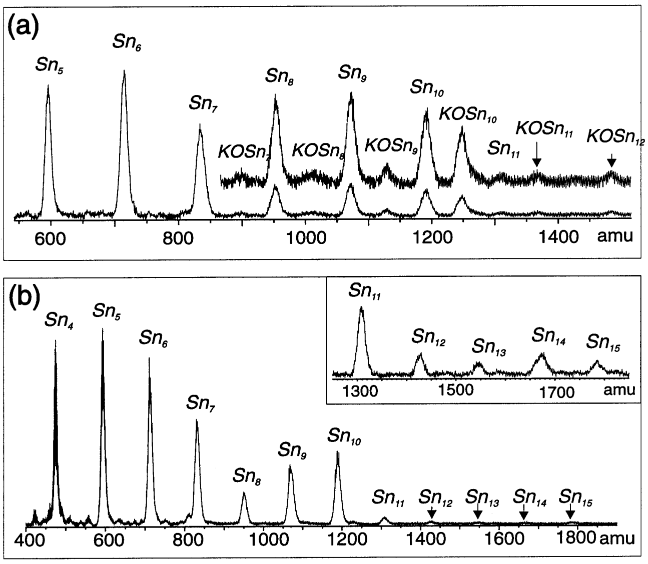
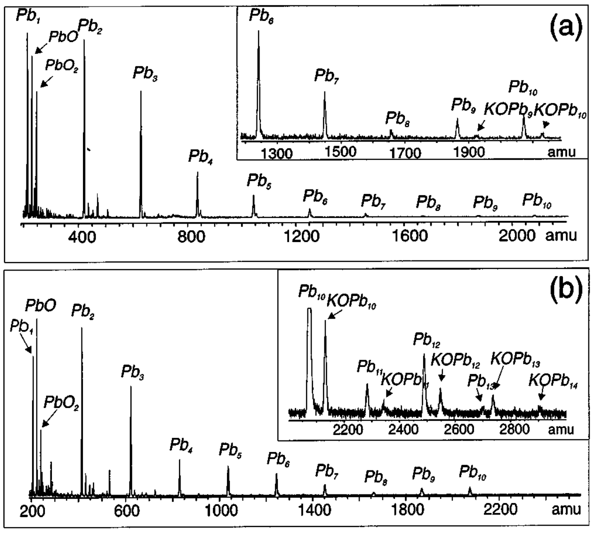


Figure 5. Mass spectra of Pb_n^- clusters obtained from a) ethylenediamine extract of a solidified melt of nominal composition K_4Pb_9, and b) $[K([2.2.2]crypt)]_3Pb_9$, containing discrete Pb_9^{3-} clusters; for inserts cf. caption of Figure 3



Compounds Containing E_9^{3-} Zintl Ions Separated by K-[2.2.2]crypt Units (E = Ge, Sn, Pb)

On use of the alkali-metal-sequestering reagent [2.2.2]crypt[6] crystalline compounds $[K\text{-}[2.2.2]crypt)]_3E_9$ containing discrete polyanions can be isolated from the en solutions of the A_4E_9 alloys[7][17]. Photodesorption and photoionization of these Ge, Sn, and Pb compounds leads to the formation of ions of size $1 \leq n \leq 11$ (Figure 3e), $1 \leq n \leq 15$ (Figure 4b), and $1 \leq n \leq 13$ (Figure 5b), respectively. An exceptional increase of abundance with respect to smaller clusters of cluster size $8 \leq n \leq 10$ is observed. The intriguing difference to the other experiments is the occurrence of larger clusters. For E = Ge the spectrum is very similar to that of "K_4Ge_9" (Figure 3c); however, mixed metal anions are less frequent. The same holds for E = Sn, where a very high abundance of E_{10} and the occurrence of a cluster series with $11 \leq n \leq 15$ at lower intensities is visible (Figure 4b). Desorption of the lead compound leads to a series of clusters $1 \leq n \leq 10$ with exponential decay of intensity (Figure 5b). The maximum size of Pb_n clusters is limited to $n = 13$. The higher mass region shows predominant peaks of ion pairs [$Pb_n + 56$ (±1) amu] as found in the case of Sn (Figure 4a), corresponding to the series KPb_nO^- with $n = 10-14$.

Discussion

We found that the relative abundance of ions depends strongly on the nature of the starting material used for the desorption process. The desorption conditions used in this investigation generate *cluster anions* from pure elements E with a maximum size of 6 atoms and display an exponential and monotone decrease of their relative intensities with increasing cluster size. In the case of E = Sn the results are consistent with a recent investigation using direct laser ablation of tin metal in an ICR cell[22]. We observe larger anionic clusters in the presence of alkali metals, e.g. from mixtures of the elements K/E, from phases of nominal composition K_4E_9, and from residues of ethylenediamine solutions of these phases. Clusters E_n with maximum size of 13, 12, and 10 atoms are found for E = Ge, Sn, and Pb, respectively. On use of compounds containing preformed E_9^{3-} clusters separated by large counterions $(K\text{-}[2.2.2]crypt)^+$, gas phase species with maximum sizes up to 15 E atoms are found (KGe_{11}^-, Sn_{15}^-, and KPb_{14}^-). The general feature of the spectra is a decay of intensity as the number of constituent cluster atoms increases from one to seven and a minimum in intensity for clusters of eight atoms. Nine- and ten-atom clusters are found with similar or increased intensity relative to the abundance of eight-atom clusters. The increase of intensity of clusters with $n = 9$ and 10 are most pronounced in $[K\text{-}([2.2.2]crypt)]_3E_9$ as source. The maximum cluster size for *cations* is 6 atoms, however, much smaller intensities are measured.

The ion distributions do not correlate to photoelectron threshold energies and thus electron affinities of the E_n clusters, generated by other techniques. Higher values are observed for $n = 5$ and 9 for Ge[23], 5 and 8 for Sn, and 5, 10, and 11 for Pb[18]. This is in contrast to the relative intensities observed in our experiments, where exponential decays with increasing size or intensity minima for $n = 8$ are found. Also, if electron affinity would dominate the occurrence of specific mass peaks in the spectra, a similar abundance of clusters should be found, independent of the sample used as starting material.

Conclusions and Comparison to Solid-State Analogues

Naked polyatomic ions of the type E_n^{x-} belong to the class of Zintl ions. Many of these ions cannot be described using classical electron counting rules such as the octet rule; thus, bonding models with electron delocalization (e.g. molecular orbital theory and related electron counting rules for clusters) are used for their electronic description. According to electron-counting rules for deltahedral clusters an n-vertex *closo*-deltahedron is stable if $n + 1$ skeletal orbitals are filled. As cluster size increases, a deviation from the expected number of electrons (or structures) is possible. Variable electron counts are especially observed for clusters of the heavier elements E, which have smaller HOMO-LUMO gaps[24]. Interestingly, ligand-free polyhedral clusters E_9 occur more frequently with additional electrons. E_9^{3-} and E_9^{4-} clusters with 21 and 22 skeletal electrons, respectively, possess deltahedral structures, albeit distorted and a compromise between tricapped trigonal prismatic (*closo*) and monocapped quadratic antiprismatic (*nido*)[7]. The E_n^- anions investigated here in the gas phase might correspond to $2n + 1$ skeletal electron clusters and might therefore also adopt to deltahedral structures. In other words the single-charged gas-phase anions might be regarded as *closo*-type clusters with a deficiency of one electron. Indeed, density functional studies on anionic Sn_n^- clusters confirm that the species adopt *closo* structures at the optimized minimum energies for $n = 5$, 6, and 7[22].

It has been pointed out earlier that clusters with one negative charge (e.g. E_n^-) are probably not stable in the solid state due to an inherent insufficient cation presence for anion separation[25]. Although no E_9^- species has been hitherto isolated from solution, the variability of electron numbers for these clusters makes the existence of singly charged ions with deltahedral structures more likely. Recent electrochemical investigations show that Ge_9^{3-} undergoes two pseudo reversible oxidative electron processes and therefore Ge_9^- might be a stable cluster. Oxidation of Sn $_9^{3-}$ and Pb_9^{3-} in solution is possible, but is accompanied by an adsorption process making the interpretation more difficult[26]. Even more intriguing is the high abundance of KE_n^- ions. The formation of the mixed element clusters KGe_n^- for $n = 5$, 9, and 10 is predominant beside $n = 8$, 11, and 13 at lower intensities. Applying the *Zintl-Klemm-Busmann*[27] concept applicable to binary phases also to the KGe_n^- ions[1] – in other words transferring the valence electron from the more electropositive K atom to the element cluster – the doubly charged and according to Wades rules electron-precise Ge_n^{2-} Zintl ions result.

The exceptional occurrence of KGe_{13}^- and Sn_{15}^- anions attests to the possible existence of large Zintl ions. Remarkable is the fact that the counterion [K-[2.2.2]crypt]$^+$ is capable of good crystal packing also with very large anions such as C_{60}^{2-}[28]. However, large n-vertex polyhedra with $n > 10$ of the elements Ge and Sn are known only as structural units in three-dimensional anionic networks of Zintl phases. Pentagonal dodecahedra E_{20} which are centered by A atoms are found as linked building blocks in the Zintl phases A_4E_{22}[29] and $A_{6+x}E_{25}$[30].

In summary, we see a tendency for the formation of larger clusters, especially if preformed cluster units or electropositive elements are already present in the precursor. The latter point indicates a more general application for anion formation in plasmas. Owing to the possible variable electron counts of polyhedral clusters, the gas-phase monoanionic Zintl ions are in close relation to polyanions found in solution and in the solid state. Therefore these results suggest the possibility that large, discrete main-group clusters of Ge, Sn, and Pb may also exist in solution or in the solid state.

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Experimental Section

The elements Ge, Sn, Pb, and K, Na, Rb were purchased from Fluka and Aldrich and used without further purification. The syntheses of the binary phases, the ethylenediamine solutions of the latter, and the compounds [K-[2.2.2]crypt]$_3E_9$ are described elsewhere[17]. The mixtures of the elements K/E were prepared in an argon-filled dry-box by stirring the corresponding group-14 element with a slight excess (by weight) of molten alkali metal at 200°C. The solid samples were pressed in a recess of a stainless steel target of 3 mm in diameter. The ethylenediamine solutions of the binary A_4E_9 phases, as well as the acetonitrile solutions of [K-[2.2.2]crypt]E_9 salts were transferred to the target in an argon-filled dry-box and the solvent was subsequently removed under vacuum. During the transfer of the targets into the mass spectrometer, the samples were briefly exposed to air (approx. 5–10 s).

The mass analysis was carried out with a reflector time-of-flight (RETOF) mass spectrometer (Bruker Reflex™). Desorption and ionization of the clusters were achieved in a single step with a pulsed N_2 laser (337 nm, 3.7 eV, pulse duration: 3 ns; pulse frequency: 3–5 Hz) operating at a maximum pulse energy of 0.1 mJ. The spectra shown here are accumulations of 20–50 laser shots at acceleration voltages ranging from 7–15 kV in the negative ion mode. For each accumulation the laser power is adjusted slightly above the threshold level for detection of ion signals by the use of a variable attenuator. In order to enhance the intensity and resolution of ions with masses greater than 600 amu, ions of lower masses, i.e. shorter flight times, are ejected by applying an electric field between the two deflection plates by a rectangular signal triggered by the pulsed laser (delayed extraction). We like to emphasize that no special clustering conditions (e.g. gas expansion) are used for the generation of the clusters.

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