Gas-Phase Bismuth Sulfide Clusters Produced by Gas-Aggregation Source

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Bismuth sulfide clusters Bi_xS_y were produced using a gas-aggregation source and investigated by time-of-flight mass spectrometry following ionization with a 266-nm YAG laser. Stable bismuth sulfide cluster ions $Bi_4S_{10}^+$ and $Bi_6S_{11}^+$, as well as $Bi_2S_2^+$, $Bi_3S_2^+$, $Bi_2S_6^+$, $Bi_3S_9^+$, $Bi_4S_7^+$, and $Bi_6S_4^+$, were observed, indicative of the production of stable neutral bismuth sulfide clusters in the gas phase. The cluster structure was predicted by density-functional calculations.

Bismuth sulfide Bi_2S_3 is important as a semiconductor material, having a bandgap E_g of 1.3 eV,[1] and the preparation of Bi_2S_3 particles[2] and films[3] has been studied extensively. Among the sulfide compounds of the group 15 elements, phosphorus sulfide and arsenic sulfide form molecular crystals, and some of the stable molecules occur in the gas phase.[4] Antimony and bismuth form complex sulfide structures,[5] and as yet, there have been no reports regarding the analysis of such cluster structures in the gas phase. Pure Bi clusters and pure S clusters in the gas phase have been studied in detail; the structures of Bi cluster ions have been shown to be consistent with polyhedral skeletal electronic pair theory (PSEPT),[6] whereas S cluster ions have ring structures.[7,8] Both Bi and S elements have a tendency to form catenated compounds, and mixed clusters of these two elements are expected to have unique structures. In this study, bismuth sulfide clusters in the gas phase are investigated, and the structures are predicted by density-functional calculations.

A gas-aggregation source was employed for cluster formation. A mixture of Bi and S powders was resistively heated in an alumina crucible and evaporated into a flow of He gas (0.5 – 1.5 standard L min^{-1}). The gas mixture was cooled down by a cold Cu block (77 K), resulting in the formation of neutral clusters by aggregation. The gas sample was introduced into an ionization area through two skimmers in combination with a mechanical booster pump and two diffusion pumps. Neutral clusters are then ionized with fourth-harmonic light from a Nd:YAG laser (Minilite-II, HOYA Contimum, 266 nm, 10 Hz). The cluster ions were accelerated in an electric field (1.6 kV), passed through a 45-cm time-of-flight tube, and detected by a micro-channel plate (MCP) in an area evacuated by a turbo molecular pump. The signals from the MCP were captured using a digital oscilloscope (LeCroy 9310A). At low crucible temperature, pure sulfur clusters S_x^+ (≈ 350 K) and pure bismuth clusters Bi_x^+ (≈ 500 K) appear as major products. After increasing the temperature of the crucible (> 600 K), bismuth sulfide clusters $Bi_xS_y^+$ appear in the mass spectrum. The typical time-of-flight mass spectrum for $Bi_xS_y^+$ clusters is shown in Figure 1.

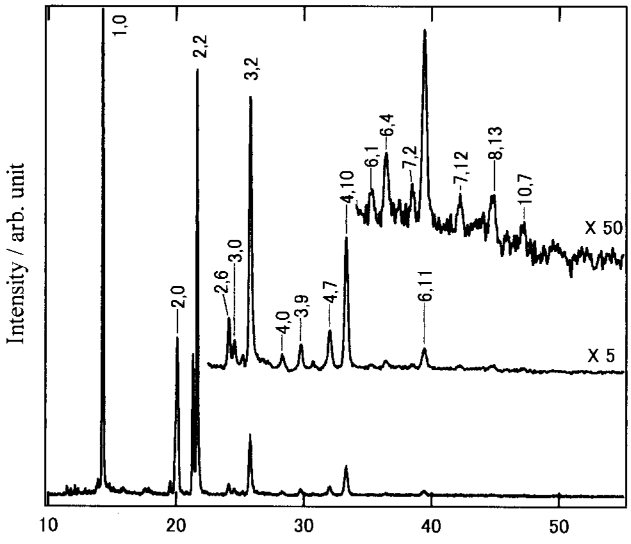

Figure 1. Time-of-flight mass spectrum of $Bi_xS_y^+$ clusters. Indicated numbers in the figure correspond to x,y in $Bi_xS_y^+$.

The bismuth sulfide cluster ions $Bi_xS_y^+$ observed in the spectrum did not exhibit a statistically distributed abundance, rather, unique clusters producing intense signals were apparent. Whereas $Bi_2S_2^+$ and $Bi_3S_2^+$ had very high intensities, other clusters, $Bi_xS_2^+$ (x>3) or $Bi_xS_1^+$, were not observed at all. $Bi_4S_{10}^+$ and $Bi_6S_{11}^+$ had very intense peaks, and are referred as magic number cluster ions. Other clusters, $Bi_2S_6^+$, $Bi_3S_9^+$, $Bi_4S_7^+$, $Bi_6S_4^+$, $Bi_7S_2^+$, $Bi_7S_{12}^+$, $Bi_8S_{13}^+$, and $Bi_{10}S_7^+$, were also observed as stable clusters. The relative intensities of the cluster ions varied depending on the formation conditions, such as bismuth and sulfur composition, He gas flow rate, crucible temperature, and laser intensity. However, cluster ions of particular compositions (magic number compositions) always produce intense signals and have the same distribution pattern in the mass spectra, regardless of ionization laser intensity and hence the extent of internal excitation and possible fragmentation. The strong intensity of the peaks of the species is attributed to the stability of the neutral molecules in the beam or the stability of the cluster ions produced by the ionization.

By analogy with phosphorus sulfide and arsenic sulfide molecules observed in gas phase or in molecular crystals, bismuth sulfide may form a stable structure in the gas phase as a neutral molecule. Density-functional calculations (ADF[9] using triple-zeta basis sets with frozen core) were applied in order to predict the geometry of the bismuth sulfide Bi_xS_y clusters. Each species was assumed to be in a low-spin state (S = 0 for Bi_2S_2, Bi_2S_6, Bi_4S_7, Bi_4S_{10}, Bi_6S_4, and Bi_6S_{11}; S = 0.5 for Bi_3S_2 and Bi_3S_9). The vertical ionization potentials and geometry of cluster ions $Bi_xS_y^+$ were also estimated. The optimized geometry for Bi_xS_y and $Bi_xS_y^+$ as well as the ionization potentials is shown in Figure 2. The calculation suggests that at least two photons are needed for the ionization of Bi_xS_y species, and that

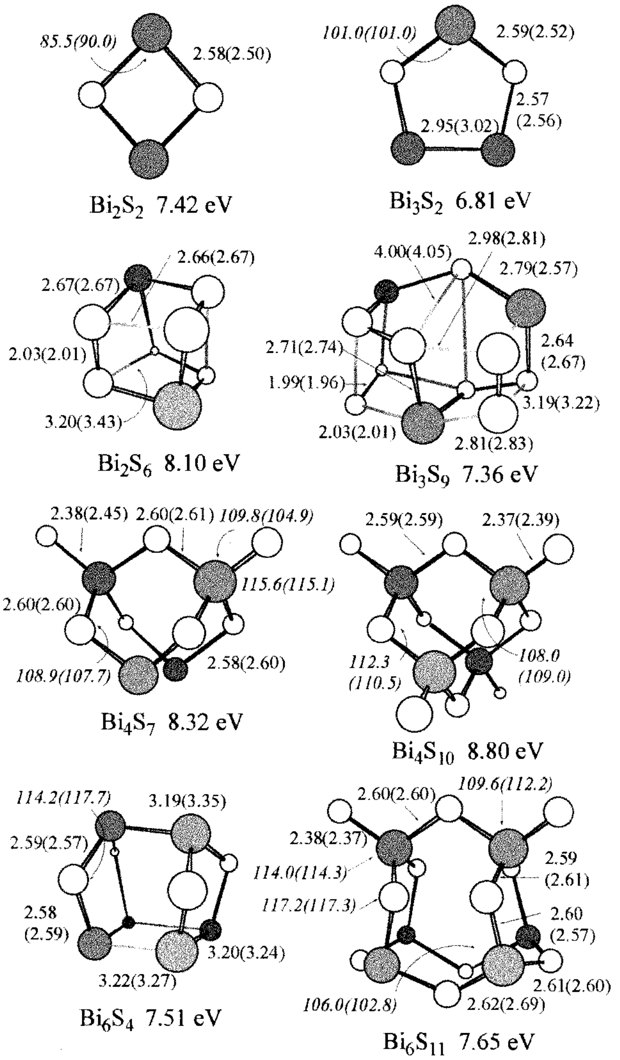

Figure 2. Optimized geometry for neutral Bi_xS_y and ionized $Bi_xS_y^+$ (in parentheses) using density-functional-calculation. Bond lengths are given in angstroms and angles in degrees.

the ionization makes little change in the geometry. Of the smaller clusters, Bi_2S_2 and Bi_3S_2 have a ring structure in which a S atom bridges two Bi atoms; a structure having a dimeric S_2 unit was also calculated and was found to be unstable. Bi_2S_6 has a cubic structure, in which three pairs of S_2 units connect two Bi atoms; a structure containing a ring Bi_2S_2 and two additional S atoms connected to each Bi atoms was also calculated and found to be unstable. Bi_3S_9 was calculated to have a structure consisting of two cubes (Bi_2S_6) with a common surface (BiS_3). A ring structure (six-membered ring, Bi_3S_3) with two S atoms connected to each Bi atom was also found to be unstable. If the cube structure were suitable for forming larger clusters, the series of $(BiS_3)_n$ should be observed. However, Bi_4S_{12} or larger clusters $(BiS_3)_n$ (n > 2) were not observed in the mass spectra. Bi_4S_7 and Bi_4S_{10} have structures similar to those of phosphorus sulfide P_4S_7[10] and P_4S_{10},[11] which were determined theoretically. The P_4S_{10} molecule was also successfully produced in the gas phase, and its infrared spectra in solid argon matrices have been reported.[12] Bi_4S_{10} has an adamantane-like structure consisting of three six-memberd rings, which is very stable, thus producing an intense signal in the mass spectrum. Larger clusters Bi_6S_4 and Bi_6S_{11} are unique, and similar sulfide compounds of group-15 elements have never been reported. Bi_6S_4 is considered to be the combination of two Bi_3S_2 rings, in which Bi atoms are connected to each other. Bi_6S_{11} is observed as a very intense signal, and is therefore considered stable in the gas phase. The structure is considered to be a combination of two six-membered rings and three eight-membered rings.

The stoichiometry of the observed Bi_xS_y clusters indicates that the structures do not reflect the bulk structure of the Bi_2S_3 solid. The clusters found in this study are therefore stable gas-phase cluster molecules, not fragments of solid Bi_2S_3. As a gas-aggregation source was employed for bismuth sulfide cluster formation, the neutral clusters in the gas phase were obtained efficiently. The strong intensity of the peaks of the species may be attributed to the stability of the neutral molecules. Some of these bismuth sulfide clusters have structures that are similar to other sulfides of group-15 elements in the gas phase or as molecular crystals. This is the first report of the observation of the unique structures Bi_6S_4 and Bi_6S_{11} in the gas phase.

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