

Mass spectrometry of chalcogenide glasses

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Chalcogenide glasses are based mostly on sulfur, selenium, tellurium, etc., and elements from the 14-15th group of the periodic system (germanium, arsenic, antimony, etc.). They are high-tech materials with strategic importance for manufacturing phase change memory, optical fibers, etc. However, the analysis of these glasses by mass spectrometry is not easy. We cannot use MALDI for the ionization here, we have to apply laser desorption ionization or laser ablation of the materials with Time Of Flight (TOF) MS. The possibilities of TOF MS for the characterization of chalcogenide glasses and/or their structure elucidation are studied and evaluated here for four selected cases.

- (i) The formation of binary antimony selenides was studied via laser ablation synthesis (LAS) from various mixtures of antimony and selenium was followed and 24 new Sb_mSe_n clusters were identified [1].
- (ii) When Sb_2Se_3 polycrystalline materials were analyzed, six high mass clusters were detected for the first time ($Sb_4Se_4^+$, $Sb_5Se_3^+$, $Sb_5Se_4^+$, $Sb_5Se_5^+$, $Sb_5Se_6^+$, and $Sb_7Se_4^+$) [2].
- (iii) Chalcogenide's properties can be changed via doping with the other elements. Silver doping of the ternary Ge-Sb-S glasses was studied and the results of MS were compared with Raman spectroscopy. It was found that while Raman spectroscopy detects the basic structural units, MS shows mostly just their fragments [3].
- (iv) Similarly, doping of ternary Ge-Sb-Se system with Te, while Se was partially replaced by Te, was studied. A higher number of clusters is produced after the addition of Te to the Ge-Sb-Se mixtures of elements [4] while many are quaternary.

In contrast to Raman spectroscopy, which is not fragmenting the structures, LDI or LA techniques with TOF MS can be used anyway to examine the formation of structural entities (clusters). MS instrument can be considered as a kind of synthesizer. Often, new clusters are synthesized in comparison to those formed via laser fragmentation of known structures.

Concluding, LDI TOF MS is a powerful and useful tool to elucidate the composition of clusters formed from chalcogenide glasses (determining their stoichiometry). Even if LDI TOF MS causes chalcogenides structure to smaller clusters, this information is important. The fragmentation of chalcogenides can be suppressed by mixing the samples with paraffin.

References:

- [1] F. Huang et al., Laser Ablation Generation of Antimony Selenide Clusters: Laser Desorption Ionization (LDI) Quadrupole Ion Trap Time of Flight Mass Spectrometry. *J. Am. Soc. Mass Spectrom.* 30, 634-638 (2019).
- [2] F. Huang et al., Comparison of clusters produced from Sb_2Se_3 homemade polycrystalline material, thin films and commercial polycrystalline bulk using laser desorption ionization with time of flight quadrupole ion trap mass spectrometry. *J. Am. Soc. Mass Spectrom.* 30, 2756-2761 (2019).
- [3] F. Huang, et al., Laser Desorption Ionization Time-of-Flight Mass Spectrometry of Silver-Doped $(GeS_2)_{50}(Sb_2S_3)_{50}$ Chalcogenide Glasses. *ACS Omega* 5, 28965–28971 (2020).
- [4] F. Huang, et al., Doping of Ge-Sb-Se thin films with tellurium: clusters formation by Laser Ablation of thin films and comparison with clusters formed from the mixtures of elements. Quadrupole ion trap time of flight mass spectrometry study, to be published.