Theses of the Ph. D dissertation

Modeling of the structure of arsenic and germanium chalcogenid glasses and investigation of their applicability in fiber optics

Fejes István

Supervisor

Dr. Billes Ferenc

Budapest University of Technology and Economics, Physical Chemistry Department of Faculty of Chemical Engineering

2002

1. The aim of the work and previous results

Optoelectronics and fiber optics belong to the most dynamically developing industries of our days. The optical fibers made of high purity glasses slowly penetrate in our all-days life. The optical information transfer got the alternative of the electronic one when the attenuation of the quartz fibers were decreased to some decibel/kilometer. Therefore the bulk of the glass fibers is made of quartz. However, the researchers look for new materials in which the amplification of the signals is not necessary. At first the different fluorides were investigated. Their advantage is their Rayleigh scattering that is hundred times lower then that of quartz based glasses. The stability of these substances, however, could not fulfill the expectations, since their lifetime is shortened by the contacting moisture and the crystallization during the fiber dragging.

Elaborating fibers of small energy loss, the central problem of the researchers became the application of optical fibers to the transfer of giant gas laser pulses. Above all the possibility of the transfer of high power infrared (IR) radiation was the subject of the investigations. The first fibers for IR radiation transfer were produced form chalcogenides, i.e. from sulfide, selenide and telluride based glasses. In contrary to quartz that absorbs the IR light above 2-3 μm, the chalcogenides are applicable in a wide range of the infrared region. The arsenic and germanium sulfides are transparent approximately till 6 μm, the selenide and telluride variants over 10 μm, i.e. also in the usual region of the CO_2 lasers.

It is awaited that the IR transfer fibers can be applied in the surgery as flexible, elastic and antiseptic lancets. The high power lasers can generate already energy pulses at 2.94 μ wave length - the water has the highest absorption at the neighborhood of this wavelength in the infrared spectral region. The biological tissues absorb to an important extent this type of laser radiation, therefore the surgeons can treat the internal tissues though very small cuts or though the natural openings of the body.

The subjects of my research work are substances belonging to one of the most important groups of the chalcogenide glasses. Starting up with my work I based on the results obtained during the investigation of similar glasses. According to these results there exists beside the short range ordering also a middle range one in the chalcogenide glasses, i.e. a correlation between the atoms of a distance of about 15-20 Å (that means the atoms within this distance do not show a completely random distribution). The "cluster model" was elaborated for the explanation of this phenomenon. The essence of this model is that the geometric units insuring the short range ordering (those are in the case of arsenic chalcogenides the AsX_3 pyramids, for the germanium ones the GeX_4 pyramids) are joined one another in a well-defined manner resulting clusters of different sizes.

The aims of my work were the quantum chemical modeling of different possible structural elements in these glasses, the theoretical prediction of their vibrational spectra, then comparing these results with the experimental ones, choosing those structural units that can be the really components of the glass in question.

2. Applied methods of investigations

For the quantum chemical calculations the Gaussian 98 program package was used with the Hartree-Fock method and the LANL2DZ basis set.

The results of these calculations were elaborated by normal coordinate analysis and spectrum simulation. In this way it succeeded to identify the frequencies of the normal modes and to determine their characters (i.e. the weight of the individual coordinate types in the given normal mode) and the strong absorption bands of the glasses. These can give important information for the applications.

3. New scientific results

1. Our investigations were above all of theoretical character. Since according to our best knowledge methods of ab initio level were not applied for the calculation of chalcogenide clusters till now, the first task was to find a suitable method for high quality the calculations of the structures and the spectra of the clusters considering their heavy atoms. This request can be realized by the good approach of the calculated frequencies to the experimental ones. After several trials this request was fulfilled at a high level by the LANL2DZ basis set in the frame of the Hartree-Fock method. The level of the approximation is well characterized by the fact that during the elaboration of the calculated entries with normal coordinate analysis scaling was not necessary, i.e. the agreement between the calculated and experimental data was very good.

2. Modeling with quantum chemical methods the structures of various possible arsenic and germanium clusters, calculated their vibrational spectra and comparing the calculated and experimental data, there were found the really possible components of the structure of the glass in question. The possible cluster types yielded in this way are for the arsenic chalcogenides as follows: As_2X_5, As_4X_6, As_6X_9 [X=S, Se, Te] and for germanium chalcogenides the clusters Ge_3X_6, Ge_4X_8, Ge_5X_{10}, and Ge_6X_{12}.

3. A method was elaborated for the simulation of the spectra with the request to present the spectra prepared form the quantum chemical data in a form comparable with that of the experimental ones. In the course of simulation the calculated intensity was regarded as the integrated intensity of the band, Lorentz type bands were assumed and the applied fwhh was 15 cm^{-1} in all cases. This method was used also for the comparison of the spectra of the various clusters, i.e. for the study of the several effects on the spectra, that of the chain length, the change in the atomic quality and the isomerism.

4. The chain structure is characteristic of the chalcogenide glasses. If one wish to build up their structure the problem of the cut-off of the chain arises. Analyzing the optimized geometric parameters we could establish that double bounds exist on the chain ends in the case of germanium chalcogenides, however, in the case of the arsenic chalcogenides - curiously - even AS-S-S three-member rigs can play role. The characteristic frequencies calculated for this group were observed in the experimental Raman spectrum of arsenic sulfide.

5. With increasing chain length the fundamental frequencies build groups and band structure form. These is above all characteristic of the arsenic chalcogenides. Similarly, with increasing chain length the bands in the simulated spectra shift generally to the lower frequencies.

6. It is demonstrated for the various chalcogenid glasses, which infrared regions are suitable for fiber optical and optoelectronical applications. For similar purposes the glasses containing more than one chalcogenides complete well the series of those with only one chalcogenide. Using also glasses of multichalcogenide types the range of the infrared spectral region suitable for information transfer extends further.

Scientific articles:

1. Billes, F., Mitsa, V., Fejes, I., Mateleshko, N. Fejsa, I.: IR spectra calculations of arsenic sulfide clusters
   J. Mol. Structure, **513**, 109-115 (1999).

2. Billes, F., Mitsa, V., N. Mateleshko, I. Fejsa, I. Fejes: Calculations of vibrational spectra of chalcogenide glasses by ”ab initio” method
   Functional Materials, **6**, 585-588 (1999).

3. Fejes, I., Billes, F., Mitsa, V.: A theoretical study of the effect on the vibrational spectrum of the stepwise sulfur by selenium substitution in arsenic pentasulfide
   J. Mol. Structure (THEOCHEM) **531,** 407-414 (2000)

4. Fejes I. Billes F. :Investigation of the structural units of germanium sulfide and selenide by quantum chemical methods Int. J. Quantum Chemistry **85**, 85-91 (2001).

5. Fejes I., Billes F.: Kalkogenid üvegek szerkezetvizsgálata (Structural investigation of chalcogenide glasses)
   Magy. Kém. Foly. (in hugarian) **107/9**, 375-384 (2001).