# XAs₂S₃-(1-X)GeS₂ 유리의 Multiphonon 영역에서의 적외선 흡수

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# Infrared Absorption in XAs₂S₃-(1-X)GeS₂ Glasses in Multiphonon Region

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초 록

2.5~40μm 영역에서 XAs₂S₃-(1-X)GeS₂ 유리의 적외선 흡수에 관하여 연구했다. Lucovsky와 그의 연구팀이 제창한 "분자모델"에 의하면 8~20μm 영역에서 위의 유리물질의 multiphonon 흡수대는 고립된 각 분자의 기본진동대의 overtone 및 combination 과 같다. 그러므로 multiphonon 흡수영역에서 AsY₃와 GeY₄의 기본진동수를 모두 가지고 있는 combination 대는 관찰되지 않고 또한 혼합된 As₂Y₃-GeY₂ 유리의 흡수계수는 순수한 As₂Y₃ 및 GeY₂ 유리의 흡수계수를 더한것으로 표현된다. 실험에서 얻은 흡수계수는 이 분자모델로 부터 예상되는 값과 잘 일치한다.

## I. INTRODUCTION

Lucovsky and co-workers[1,2,3,4] have proposed a "Molecular Model" for vibrational properties of chalcogenide glasses such as such as As₂Y₃ and GeY₂, where Y is S or Se. This model suggests that multiphonon absorption bands in these network glasses should be analogous to overtone combination vibrational bands in isolated molecules. As₂S₃ glass has a two-dimensional layer structure which consists of pyramidal AsS groups bridps bridged by bent As-S-As groups[5]. GeS₂ glass possesses a three-dimensional network structure which consists of tetrahedral GeS₄ groups bridged by bent Ge-S-Ge group[6,7,8]. The structure of the mixed As₂S₃-GeS₂ presumably consists of AsS₃ pyramids and GeS₄ tetrahedra linked by S atom bridges. The structures of these chalcogenide glasses (As₂Y₃ and GeY₂) are shown in Fig. 1.

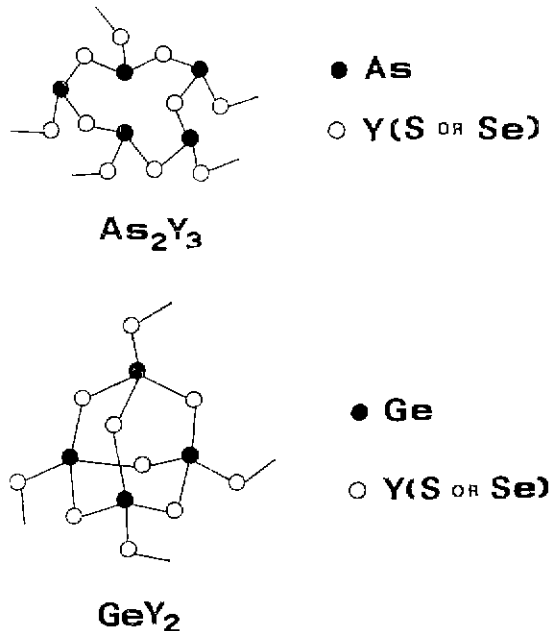The "Molecular Model" predicts that the vibrations of neighboeing AsS₃ and GeS₄ groups in As₂S₃-GeS₂



Fig. 1. Local structure in chalcogenide glasses, As₂Y₃ and GeY₂ (Y=S or Se).

glasses should be only very loosely coupled. Therefore, in a multiphonon absorption region one expects that no combination bands containing both AsS$_3$ and GeS$_4$ fundamental frequencies will be observed. Further, one expects that the intensities of the multiphonon bands due only to AsS$_3$ overtones and combinations should be proportional to the AsS$_3$ volume fraction in the glass, and similarly for the GeS$_4$ overtones and combinations. This in turn means that at each wavelength the absorption coefficients of XAs$_2$S$_3$-(1-X)GeS$_2$ glass should be calculable on the assumption of additivity of absorption coefficients of the pure As$_2$S$_3$ and GiS$_2$ and GeS$_2$ glasses.

Moynihan and his coworkers[9),10)] tested the "Molecular Model" for two mixed chalcogenide glass systems: As$_2$S$_3$-As$_2$Se$_3$ and As$_2$Se$_3$-GeSe$_2$. They found that the "Molecular Model" correctly predicted additivity of absorption coefficients in the 2-phonon region when the high coordination center atoms are mixed, as in As$_2$Se$_3$-GeSe$_2$ glasses. However, with mixed As$_2$S-As$_2$Se$_3$ glasses deviations from additivity were observed when the bridging chalcogen atoms were mixed, leading to the formation of mixed AsSSe$_2$ and AsS$_2$Se high coordination groups. With the As$_2$Se$_3$-GeSe$_2$ glasses intrinic absorption in the 3-phonon region was partly masked by oxide impurity absorption band[10)], precluding a test of the "Molecular Model" in this region. This test is possible with the sulfide glasses of the present study, for which the intensity of oxide impurity absorpiton bands in the 2-and 3-phonon regions is negligible compared to the intrinsic absorption bands. In this paper infrared absorption due to the intrinsic multiphonon process has been investigated in mixed As$_2$S$_3$-GeS$_2$ glasses.

## II. EXPERIMENTAL SECTION

XAs$_2$S$_3$-(1-X)GeS$_2$ glasses (X=0.1 to 1.0 in steps of 0.1), where X is the mole fraction of As$_2$S$_3$, were compounded in 15 g batches by using the general procedure[11),12)] from commercially available high purity elements: As (Cominco American, purity 99.999 9%), Ge (Atomergic Chemicals, semiconductor grade), and S (Atomergic Chemicals, purity 99.9999%). These were stored, weighed, and handled in a Vac-

uum Atmospheres N$_2$-filled inert atmosphere box to avoid any contamination from atmospheric oxygen and moisture. The glasses were prepared by melting the batches sealed under vacuum in Vycor and fused quartz tubes for 24-72 hours at 850~950°C in a rocking furnace. Prior to filling, the reaction tubes were baked out overnight at 850~900°C under vacuum. After melting the glass samples were cooled to room temperature, removed from the reaction tubes, and sealed under vacuum into Pyrex tubes. The samples were then annealed at 190 to 330°C for 2 hours, cooled slowly to room temperature, and removed from the Pyrex tubes. The detailed sample preparation procedures are given in Table I. IR spectra of the glasses in the frequency range 250~4000cm$^{-1}$ were measured by using Perkin-Elmer Model 467 double beam spectrometer[11),12)]. Absorption coefficients $\alpha$ were calculated from the IR spectra using the expression

$$T=(1-R)^2\exp(-\alpha x)/[1-R^2\exp(-2\alpha x)], \qquad (1)$$

where $T$ is transmission, $R$ the reflectivity, and $x$ the sample thickness. For each spectrum the reflectivity used in eq. (1) was determined from the apparent transmission $T_o$ in regions of negligible bulk absorption via the equation:

$$R=(1-T_o)/(1+T_o) \qquad (2)$$

**Table I.** Detailed Sample Preparation Procedures.

| Sample Composition | Preparation Procedure |
|---|---|
| As$_2$S$_3$ | melted for 20 h at 850°C annealed for 2 h at 190°C |
| 0.9As$_2$S$_3$-0.1GeS$_2$ | melted for 20 h at 900°C annealed for 2 h at 190°C |
| 0.8As$_2$S$_3$-0.2GeS$_2$ | melted for 20 h at 900°C annealed for 2 h at 215°C |
| 0.7As$_2$S$_3$-0.3GeS$_2$ | melted for 20 h at 900°C annealed for 2 h at 215°C |
| 0.6As$_2$S$_3$-0.4GeS$_2$ | melted for 40 h at 900°C annealed for 2 h at 215°C |
| 0.5As$_2$S$_3$-0.5GeS$_2$ | melted for 40 h at 900°C annealed for 2 h at 280°C |
| 0.4As$_2$S$_3$-0.6GeS$_2$ | melted for 40 h at 900°C annealed for 2 h at 300°C |
| 0.3As$_2$S$_3$-0.7GeS$_2$ | melted for 65 h at 900°C annealed for 2 h at 300°C |
| 0.2As$_2$S$_3$-0.8GeS$_2$ | melted for 65 h at 935°C annealed for 2 h at 310°C |
| 0.1As$_2$S$_3$-0.9GeS$_2$ | melted for 65 h at 935°C annealed for 2 h at 330°C |

Densities ($\rho$) of XAs$_2$S$_3$-(1-X)GeS$_2$ glasses were determined by the Archimedes principle using a specific gravity bottle. The bottle was filled with distilled water and its mass (m$_1$) determined to 0.0001g by weighing. The glass sample mass (m$_2$) was determined. After this, the sample was placed in the specific gravity bottle, the remaining volume in the bottle filled with distilled water, and the mass (m$_3$) of the bottle+water+sample determined. The density ($\rho$) of the glass sample is then given by

$$\rho = m_2 \rho H_2O / (m_1 + m_2 - m_3)$$

where $\rho H_2O$ is the density of water at ambient temperature.

## III. RESULTS AND DISCUSSION

In Figs. 2 to 5 are shown semilogarithmic plots $\alpha$ vs. $\bar{\nu}$ in the multiphonon region for mixed XAs$_2$S$_3$-(1-X)GeS$_2$ glasses. The solid curves are the absorption coefficients predicted on the basis of additivity of the $\alpha$ values of the end number compositions As$_2$S$_3$ and GeS$_2$:

$$\alpha = f\alpha_1 + (1-f)\alpha_2 \qquad (3)$$

$$f = (XM_1/\rho_1) / \{(XM_1/\rho_1) + ((1-X)M_2/\rho_2)\} \qquad (4)$$

where $f$ is the volume fraction of As$_2$S$_3$ glass, $\alpha_1$, $\rho_1$, and $M_1$ respectively the absorption coefficient, density and formula weight of As$_2$S$_3$ glass, and $\alpha_2$, $\rho_2$, and $M_2$ respectively the absorption coefficient, density and formula weight of GeS$_2$ glass. The ambient temperature densities of XAs$_2$S$_3$-(1-X)GeS$_2$ glasses are given in Table II. Within experimental error the molar voumes are additive, as shown in Fig. 6, justifying the use of Eq. (4) in calculating the volume fractions. This study of the stoichiometric glasses covers the composition range X=0.1 to X=1.0 in steps of 0.1. Since the pure GeS$_2$ glass could not be prepared by rapid quenching[12),13),14)] the $\alpha_2$ values were calculated from Eq. (3) using the experimental $\alpha$ values for the 0.1 As$_2$S$_3$-0.9 GeS$_2$ glass. The calculated $\alpha_2$ values were then used to calculate the solid curves (Figs. 2 to 5) for the other mixed compositions X=0.2 to 0.9. The agreement between the experimental and calculated additive $\alpha$ vs. $\bar{\nu}$ curves in the region below 1200 cm$^{-1}$ is within experimental error (within about 20 percent).
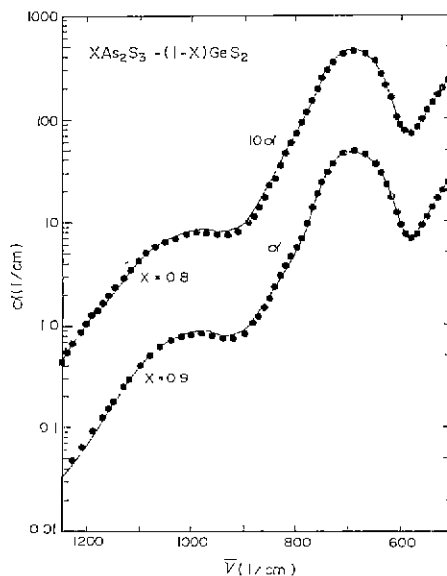


Fig. 2. Absorption coefficient versus frequency for 0.8 As$_2$S$_3$-0.2 GeS$_2$ and 0.9 As$_2$S$_3$-0.1 GeS$_2$ glasses in the multiphonon region.
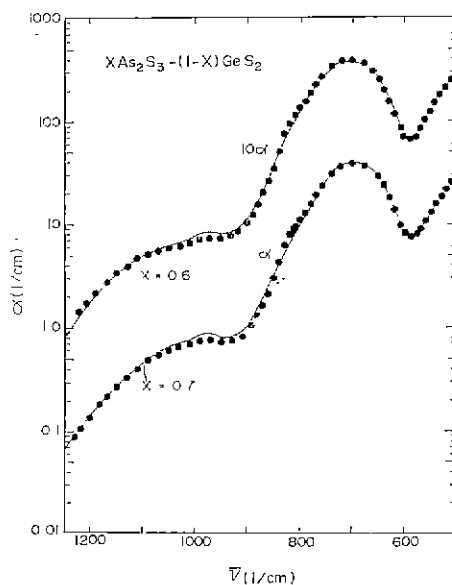


Fig. 3. Absorption coefficient versus frequency for 0.6 As$_2$S$_3$-0.4 GeS$_2$ and 0.7 As$_2$S$_3$-0.3 GeS$_2$ glasses in the multiphonon region.
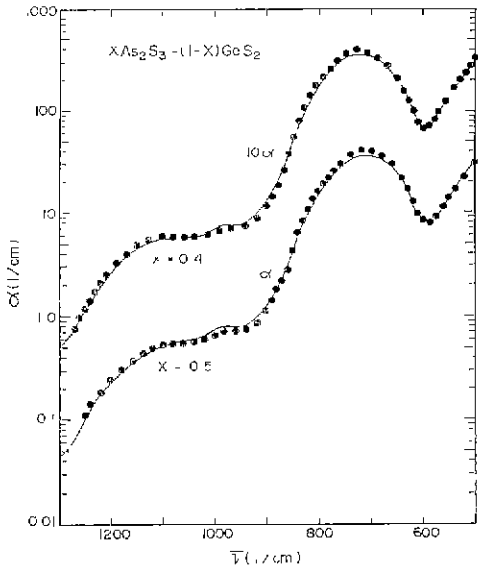
**Fig. 4.** Absorption coefficient versus frequency for 0.4 As$_2$S$_3$-0.6 GeS$_2$ and 0.5 As$_2$S$_3$-0.5 GeS$_2$ glasses in the multiphonon region.
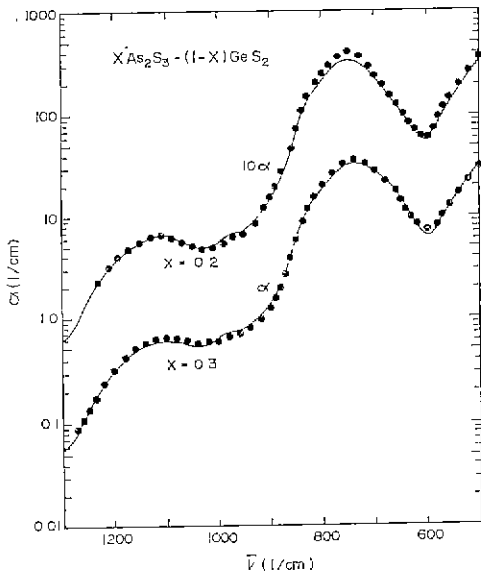


**Fig. 5.** Absorption coefficient versus frequency for 0.2 As$_2$S$_3$-0.8 GeS$_2$ and 0.3 As$_2$S$_3$-0.7 GeS$_2$ glasses in the multiphonon region.

**Table** II. Densities and Molar Volumes of XAs$_2$S$_3$-(1-X)GeS$_2$ Glasses at Ambient Temperature

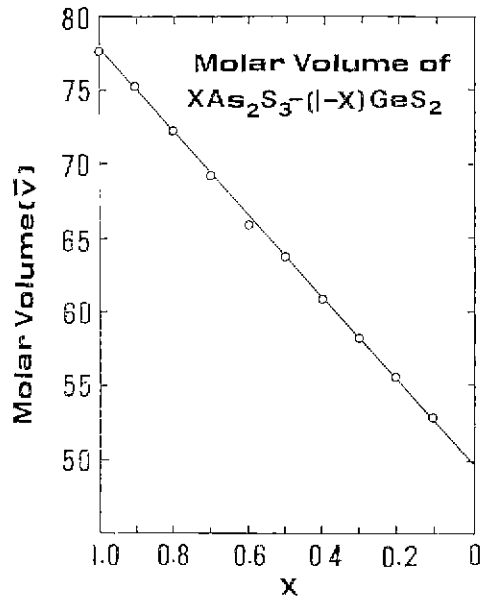| X | $\rho$(g/cm$^3$) | $\bar{V}$ (cm$^3$/mol) |
|---|---|---|
| 1.0 | 3.18 | 77.4 |
| 0.9 | 3.12 | 75.3 |
| 0.8 | 3.10 | 72.3 |
| 0.7 | 3.09 | 69.1 |
| 0.6 | 3.08 | 65.7 |
| 0.5 | 3.01 | 63.7 |
| 0.4 | 2.97 | 60.8 |
| 0.3 | 2.91 | 58.2 |
| 0.2 | 2.87 | 55.4 |
| 0.1 | 2.80 | 52.7 |



**Fig. 6.** Molar volumes of XAs$_2$S$_3$-(1-X)GeS$_2$ glasses versus composition.

boring AsS$_3$ and GeS$_4$ groups should be only very loosely coupled, in agreement with the "two-mode" vibrational behavior observed for mixed As$_2$S$_3$-GeS$_2$ glasses in the fundamental region[15],[16]. Hence in the multiphonon absorption region of the mixed glasses one expects (a) to see no combination bands of AsS$_3$ and GeS$_4$ fundamental frequecies and (b) that the AsS$_3$ groups and GeS$_4$ groups should contribute independently and hence additively to the total absorption coefficient. The frequency range of Figs. 2 to 5 is that in which 2- and 3-phonon processes involving

From Fig. 1 the structure of the mixed As$_2$S$_3$-GeS$_2$ glasses is expected to consist of AsS$_3$ pyramids and GeS$_4$ tetrahedra linked by S atom bridges. The "Molecular Model" predicts that the vibrations of neigh-

the $AsS_3$ and $GeS_4$ stretching modes are predicted to occur. Hence the agreement of the spectra of the mixed $As_2S_3$-$GeS_2$ glasses in this region with those predicted from Eq. (3) is in complete agreement with the above hypotheses.

# Ⅳ. CONCLUSION

IR spectra have been measured for the $XAs_2S_3$-$(1-X)GeS_2$ glasses (X=mole fraction of $As_2S_3$) in the 8 $\sim$20 $\mu$m(1250-500 cm$^{-1}$) region where two and three multiphonon processes predominate The measured absorption coefficients are in good agreement with the prediction of "Molecular Model" on the basis of additivity.

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