

MULTIPHONON ABSORPTION IN As₂S₃ AND GeS_{2.1} GLASSES

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As₂S₃ 유리와 GeS_{2.1} 유리의 Multiphonon 영역에서의 흡수

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초 록

2.5~40 μm 영역에서 As₂S₃ 및 GeS_{2.1} 유리의 적외선 흡수에 관하여 연구했다. Lucovsky 와 그의 연구팀이 제창한 분자 모델에 의하면 8~20 μm 영역에서 위의 유리물질의 multiphonon 흡수대는 고립된 각 분자의 기본진동대의 overtone 및 combination 과 같다. Lucovsky 와 Galeener 는 이 이론에 입각하여, network 구조를 갖는 유리가 적외선 및 라만 스펙트럼에서 나타나는 multiphonon combination 과 overtone 진동수를 예언하는 실현적 선택률을 제안했다. 우리가 얻은 As₂S₃ 및 GeS_{2.1} 유리의 적외선 스펙트럼은 이 유리에 대해 적용한 위의 실험법칙과 잘 일치한다.

I. INTRODUCTION

Chalcogenide glasses, which have network structures based on sulfur or selenium rather than on oxygen, are an important class of infrared transmitting materials in the wavelength region 5 to 15 microns (2000 to 667cm⁻¹)—a region in which oxide glasses are opaque. They owe their transparency in this region to the fact that the heavier S and Se atoms give rise to lower vibrational frequencies in comparison to oxide glasses, shifting the region of intense infrared absorption to correspondingly longer wavelengths. Near this long wavelength limit to transparency there are two sources of infrared absorption in these materials: intrinsic multiphonon bands and light atom impurity absorption bands, the latter due to the presence of oxygen. In this paper infrared absorption due to the

intrinsic multiphonon process has been investigated in As₂S₃ and GeS_{2.1} glasses.

Lucovsky and co-workers^{1),2),3),4)} have proposed a "Molecular Model" for vibrational properties of chalcogenide glasses 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 and combination vibrational bands in isolated molecules. As₂S₃ glass has a two-dimensional layer structure which consists of pyramidal AsS₃ groups bridged by bent As-S-As groups⁵⁾. GeS₂ glass possesses a three-dimensional network structure which consists of tetrahedral GeS₄ groups bridged by bent Ge-S-Ge Groups^{6),7),8)}. The structures of these chalcogenide glasses (As₂Y₃ and GeY₂) are shown in Fig. 1.

The "Molecular Model" predicts that the vibrations

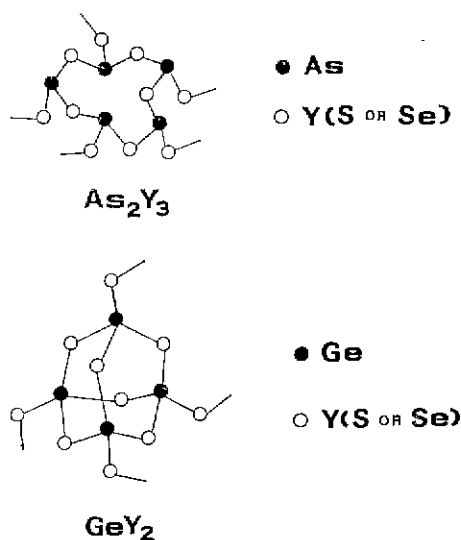


Fig. 1. Local structure in chalcogenide glasses, As₂Y₃ and GeY₂ (Y=S or Se).

of neighboring AsS₃ and GeS₄ groups in As₂S₃ and GeS₂ glasses should be only very loosely coupled. Therefore, in a multiphonon absorption region one expects that only combination bands containing AsS₃ or GeS₄ fundamental frequencies will be observed. On this basis, Lucovsky and Galeener^{6) 7)} have proposed an empirical selection rule scheme for predicting the multiphonon combination and overtone frequencies which appear in the IR and Raman spectra of chalcogenide glasses. This scheme was tested for a 0.5As₂S₃-0.5 GeS₂ glass in an earlier study⁹⁾ and is tested here for As₂S₃ and GeS_{2.1} glasses.

II. EXPERIMENTAL SECTION

1. Sample preparation

As₂S₃ and GeS_{2.1} glasses were compounded in 15 g batches from commercially available high purity elements: As(Cominco American, purity 99.9999%), Ge(Atomergic Chemicals, semiconductor grade), and S(Atomergic Chemicals, purity 99.9999%). As a further starting material purification step, sulfur was distilled under vacuum through a fritted disc to remove particulate matter and any adsorbed oxides. To avoid any contamination from atmospheric oxygen and moisture, storage, weighing and handling of the elements

were carried out in a Vacuum Atmospheres N₂-filled inert atmosphere box^{10), 11)} containing no more than 1 ppm O₂ and 1 ppm H₂O.

As₂S₃ glass was melted in 1.3 cm o. d. 1.0 cm i. d. Vycor reaction tube of about 18 cm length, and GeS_{2.1} glass melted in fused quartz tube^{12), 13)}. The reaction tubes were sealed at one end, washed, baked overnight under vacuum ($p \leq 1 \mu\text{m}$) at 850~900°C to remove absorbed water, and transferred to the inert atmosphere box. The glass components were weighed and loaded into the tubes, which were then capped, removed from the box and sealed off under vacuum at room temperature. The glasses were melted by heating the sealed, evacuated tubes in a rocking furnace at 700~950°C for 20~70 hours. The melts were removed from the furnace and allowed to cool slowly to room temperature. After cooling, the sample tubes were broken open and the glasses transferred to Pyrex tubes, which were sealed under vacuum. The samples were then annealed at 190°C(As₂S₃) and 330°C(GeS_{2.1}) for two hours, cooled slowly to room temperature, and removed from the Pyrex tubes.

We attempted to make bulk GeS₂ glass, but unfortunately were unable to obtain large GeS₂ samples in the glassy state, even by rapid quenching contrary to the reports of other investigators^{14), 15), 16)}. These investigators, however, prepared only relatively thin GeS₂ specimens, which could be quenched very rapidly in air, water or a NaOH-H₂O solution. An earlier report, however, of the glass-forming regions in Ge-As-S system¹⁷⁾ indicated that GeS₂ is not glass-forming, but that glasses can be obtained by rapid quenching if one goes slightly off stoichiometry, e. g., to GeS_{2.03}^{18), 19)}. Hence, we were able to obtain bulk GeS_{2.1} glass (instead of GeS₂ glass) by rapid quenching.

2. Infrared Absorption Measurements

Cylindrical specimens for IR absorption measurements were prepared by cutting slices from the 1.0 cm o. d. glass boules and polishing the opposite faces plane parallel. The thickness of the glass samples ranged from about 0.04 to 2.0 cm. In color the samples were deep orange-red(As₂S₃) and yellow(GeS_{2.1}). The polished specimens were examined under a metallographic microscope (FJW Industries) equipped with

an IR-to-visible image converter Those found to contain bubbles or gross amounts of particulate matter were not used for IR transmission measurements.

A Perkin-Elmer Model 467 double beam spectrometer was used to measure IR transmission of polished glass samples over the range 2.5~40 μ m (4000-250 cm^{-1}) at ambient temperature. Prior to recording the spectrum, the instrument was adjusted using the instrument controls and a comb attenuator in the reference beam to give a reading of 100% transmission with no sample in the sample beam and 0% transmission with the sample beam blocked.

The absorption coefficients of the chalcogenide glasses were determined at various wavelengths from the IR spectra via the equation¹³⁾

$$T \equiv I/I_0 = (1-R)^2 \exp(-\alpha X) / (1-R^2 \exp(-2\alpha X)) \quad (1)$$

where

- I_0 =incident intensity of the light
- I =transmitted intensity
- T =transmission
- X =sample thickness
- R =reflectivity
- α =absorption coefficient.

This equation is valid for normal incidence of the light beam on the sample surface in the region in which $\alpha\lambda \ll 1$. The reflectivity R used in Eq. (1) was calculated from

$$R = (1 - T_0) / (1 + T_0) \quad (2)$$

where T_0 is the transmission measured in a wavelength region (e.g., the flat region of the spectrum between 5 and 6 μ m in Fig. 2) where the attenuation of

light due to absorption is negligible ($\alpha X \approx 0$) and apparent losses are due entirely to reflection.

III. RESULTS AND DISCUSSION

In Figs. 2 and 3 are shown respectively the IR transmission spectra of As_2S_3 and $\text{GeS}_{2.1}$ glasses of different thicknesses. At short wavelengths ($< 7\mu\text{m}$) for As_2S_3 glass three absorption bands due to impurities are visible. The band at 3455 cm^{-1} is caused by the O-H stretching vibration, the band at 2495 cm^{-1} by the S-H stretching, and that at 1585 cm^{-1} by H_2O bending vibrations¹⁴⁾. The $\text{GeS}_{2.1}$ glass spectrum contains three previously observed¹⁵⁾ impurity bands: the S-H stretching band at 2520 cm^{-1} and vibration bands of the linear COS and CS_2 molecules at 2030 and 1510 cm^{-1} respectively. In Tables I and II both bulk and impurity IR absorption maxima in As_2S_3 and $\text{GeS}_{2.1}$ glasses are categorized.

In Fig. 4 are shown semilogarithmic plots of α vs. wavenumber $\bar{\nu}$ in the 2- and 3-phonon multiphonon absorption region for As_2S_3 and $\text{GeS}_{2.1}$ glasses. Lucovsky and Galeener's scheme^{6),7)} for predicting the multiphonon bands of network glasses assigns an "activity factor" (+ or -) to each of the high frequency first order vibrational bands: "+" if the band is strong in the Raman spectrum, and "-" if the band is strong in the IR spectrum. Combinations of these first order frequencies are strong in the multiphonon Raman spectrum if the "product" of their activity factors is "+" and strong in the multiphonon IR spectrum if the "product" is "-". We applied this scheme successfully to prediction of IR-active multiphonon bands in 0.5

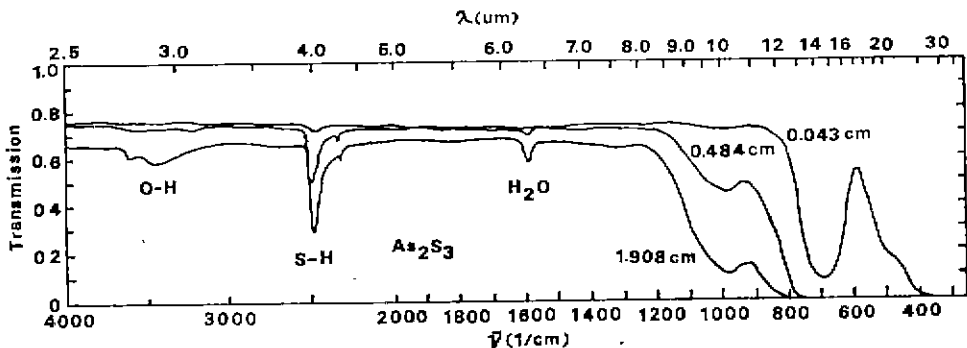


Fig. 2. IR spectra for As_2S_3 glass specimens of different thicknesses.

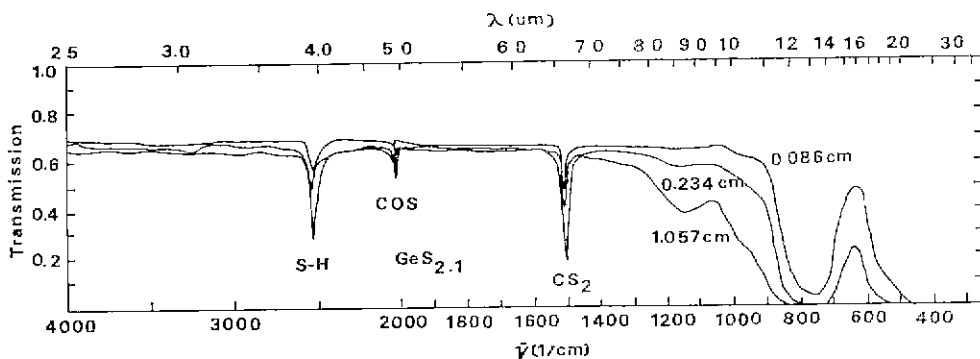


Fig. 3. IR spectra for GeS_{2.1} glass specimens of different thicknesses.

Table I. Bulk and impurity IR absorption maxima in As₂S₃ glass in the 250~4000 cm⁻¹ region.

ν (cm ⁻¹)	λ (μ m)	Relative Intensity(a)	Assignment
685	14.6	s	Intrinsic 2-phonon process
980	10.2	m	Intrinsic 3-phonon process
1585	6.31	w	H ₂ O bending
2495	4.01	w	S-H stretching
3455	2.89	w	O-H stretching

(a) s=strong, m=medium, w=weak

Table II. Bulk and impurity IR absorption maxima in GeS_{2.1} glass in 250~4000 cm⁻¹ region.

ν (cm ⁻¹)	λ (μ m)	Relative Intensity(a)	Assignment
760	13.2	s	Intrinsic 2-phonon process
1140	8.77	m	Intrinsic 3-phonon process
1510	6.62	w	Molecular CS ₂
2030	4.93	w	Molecular COS
2520	3.97	w	S-H stretching

(a) s=strong, m=medium, w=weak

As₂Se₃-0.5 GeSe₂ glasses in an earlier paper⁹⁾. In what follows we apply it to the data of Fig. 4.

From the data of Lucovsky et al.¹⁶⁾ the frequencies and activity factors of the high frequency first order bands in As₂S₃ glass are 310(-), 340(+) and 375 (-) cm⁻¹. Frequencies of IR active multiphonon bands in As₂S₃ glass predicted by the above selection rule are shown by arrows(↓) in Fig. 4 (e.g., the lowest frequency predicted band at 650 cm⁻¹ is a combination of the 310(-) and 340(+) cm⁻¹ As₂S₃ first order fre-

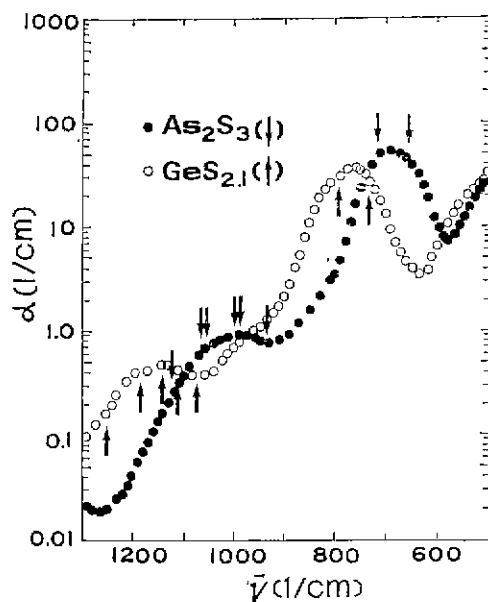


Fig. 4. Absorption coefficient versus frequency for As₂S₃ and GeS_{2.1} glasses in the multiphonon region.

quencies). The predicted 2-phonon frequencies correspond well to the peak at 685 cm⁻¹ and the predicted 3-phonon frequencies to the peak at 980 cm⁻¹ in Fig. 4.

The same scheme has been applied to the GeS_{2.1} glass using first order band frequencies of 348(+), 370(-) and 440(-) cm⁻¹ observed for GeS₂ glass¹⁶⁾ and the results are also shown by arrows (↑) in Fig. 4. The predicted 2-phonon frequencies correspond well to the 760 cm⁻¹ peak and the predicted 3-phonon frequencies to the peak at 1140 cm⁻¹ in Fig. 4. There

is a shoulder in the $\text{GeS}_{2.1}$ glass α vs. $\bar{\nu}$ plot at about 980cm^{-1} which is not predicted using GeS_2 glass data. However, the non-stoichiometric $\text{GeS}_{2.1}$ glass should contain some S-S bonds in addition to G-S bonds¹⁰. The S-S vibration has a fundamental mode at 490cm^{-1} ⁶. Hence the shoulder at 980cm^{-1} is probably a 2-phonon combination of this S-S combination band.

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