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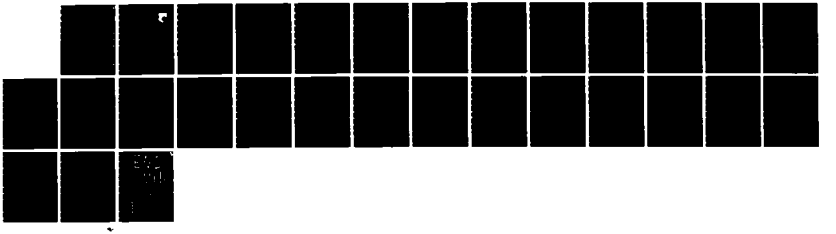

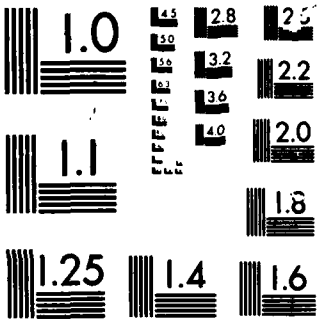


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AFWAL-TR-85-4092

# CHALCOGENIDE GLASSES (PART II)

## OPTICAL THICKNESS - TEMPERATURE RELATION IN CHALCOGENIDE GLASS FILMS



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February 1986

Final Report for Period 1 October 1983 - 30 September 1984

Approved for public release; distribution unlimited



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SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

| | |
|---|---|
| 1a REPORT SECURITY CLASSIFICATION: Unclassified | 1b RESTRICTIVE MARKINGS |
| 2a SECURITY CLASSIFICATION AUTHORITY | 3 DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release, distribution unlimited |
| 2b DECLASSIFICATION/DOWNGRADING SCHEDULE | |
| 4 PERFORMING ORGANIZATION REPORT NUMBER(S): AFWAL-TR-85- 4092 | 5. MONITORING ORGANIZATION REPORT NUMBER(S) |
| 6a NAME OF PERFORMING ORGANIZATION: Air Force Wright Aeronautical Laboratories, Material's Lab. / 6b OFFICE SYMBOL (If applicable): AFWAL/MLPJ | 7a NAME OF MONITORING ORGANIZATION |
| 6c ADDRESS (City, State and ZIP Code): Wright-Patterson Air Force Base, Ohio, 45433 | 7b. ADDRESS (City, State and ZIP Code) |
| 8a NAME OF FUNDING/SPONSORING ORGANIZATION / 8b OFFICE SYMBOL (If applicable) | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER |
| 8c ADDRESS (City, State and ZIP Code) | 10 SOURCE OF FUNDING NOS |

| PROGRAM ELEMENT NO. | PROJECT NO | TASK NO | WORK UNIT NO |
|---|---|---|---|
| 62102F | 2422 | 242204 | 24220401 |

11 TITLE (Include Security Classification): Chalcogenide Glasses (Part II) Optical Thickness-Temperature Relation in Chalcogenide Glass Films

12 PERSONAL AUTHOR(S): White, Koto, Phillippi, Conrad, M. and Rea, Laura, S.

| 13a TYPE OF REPORT | 13b TIME COVERED | 14 DATE OF REPORT (Yr., Mo., Day) | 15 PAGE COUNT |
|---|---|---|---|
| Final | FROM 10-1-83 TO 9-30-84 | 1986 February | 28 |

16 SUPPLEMENTARY NOTATION

| 17 COSATI CODES | | |
|---|---|---|
| FIELD | GROUP | SUB GR |
| 20 | 06 | — |
| | | |

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number): chalcogenide glass films, optical thickness, refractive index film thickness, thermal expansion, spectrophotometry, Tg

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The optical thickness, which is a multiplication of the refractive index and the physical thickness of a film, is the most important parameter in designing a spectral interference filter. This quantity should be stable against all environmental effects, particularly the heating effect. The changes in optical thickness due to heating may be devided into two categories; a reversible change and irreversible change. This report describes the reversible portion of changes in refractive index, film thickness and optical thickness with temperature, caused by temperature coefficient of refractive index and thermal expansion coefficient of chalcogenide glass films. Film compositions studied were; $As_2S_3$, $As_3S_7$, $AsS_4$, $Ge_3S_7$, and $Ge_5As_{38}S_{57}$. This report also describes the spectrophotometric technique utilized to determine the optical parameters.

| 20 DISTRIBUTION/AVAILABILITY OF ABSTRACT | 21 ABSTRACT SECURITY CLASSIFICATION | |
|---|---|---|
| UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS ☐ | Unclassified | |
| 22a NAME OF RESPONSIBLE INDIVIDUAL: White, Koto | 22b TELEPHONE NUMBER (Include Area Code): (513)255-3228 | 22c OFFICE SYMBOL: AFWAL/MLPJ |

DD FORM 1473, 83 APR — EDITION OF 1 JAN 73 IS OBSOLETE

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## FOREWORD

This report describes in-house research performed at the Laser hardened materials branch of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, from October 1, 1983 to September 30, 1984 under work unit number 24220401. This is the part II of a four part study on chalcogenide glasses.

The authors would like to achnowledge Dr. Binod Kumar of UDRI for useful discussions, Mr. George Orbit of SAIC, Dayton for technical assistance in spectrophotometric instrumentation, Mr.T.Kerschner for chemical analysis and Mr. J.D.Wolf of UDRI for conducting SEM and EDAX analyses.

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# I. INTRODUCTION

Chalcogenide glasses are glasses based on sulfur, selenium and tellurium. They have been utilized in far infrared optical applications because of their good spectral transparency in far infrared wavelength region. The sulfide glasses transmit from 0.6μm to 11.5μm, selenide glasses from 1.0μm to 15.0μm and telluride glasses from 2.0μm to 20.0μm, while oxide and fluoride glasses become opaque around 6μm and 9μm respectively. The chalcogenide glasses are more resistant to moisture as compared to other far infrared materials such as alkali halides. In addition, they are good glass formers and large glass-forming regions are found among many chalcogenide compositions. A majority of the literature on chalcogenide glasses is concerned with bulk properties, and data on chalcogenide films are scarce.

The optical thickness, which is a multiplication of the refractive index and the film thickness, is the most important parameter in designing a spectral interference filter. This quantity should be stable against all environmental effects. Changes in optical thickness may be divided into two categories; a reversible change and an irreversible change. The reversible change is due to temperature coefficient of refractive index and thermal expansion of the film. The irreversible change is due to stabilization effects such as chemical bonding change, densification and stress annealing effects. The irreversible change in films has been discussed elsewhere [Ref.1]. In this report, we will discuss the reversible change in optical

thickness.

## II. EXPERIMENTAL PROCEDURE

### 1. Film Synthesis

The glass films were synthesized from bulk compositions by a vapor deposition process. Chalcogenide compositions were chosen from the glass-forming region of As-Ge-S ternary system as shown in Figure 1 * [Ref.2]. Five compositions reported in this study are indicated as (●). The starting materials were arsenic trisulfide (Servofrax® glass), germanium (lump, 99.99 % pure) and sulfur (lump, 99.95 % pure). 30-gram batches of the starting mixtures were placed in fused silica ampoules and sealed under vacuum of around $10^{-6}$ torr. The mixtures were heated at 300°C to 450°C for 24 to 200 hours until all free sulfur was reacted. The complete reaction and homogenization were then performed in a rocking furnace at 450°C to 850°C, which are above the liquidus temperature of the corresponding crystalline compositions. The melts at these temperatures were very fluid. The homogenized melts were subsequently quenched in water to form the bulk glasses.

The bulk glasses were crushed and evaporated from a resistance heated tungsten boat onto two types of substrate held near room temperature, in a vacuum of $10^{-6}$ torr. The films for spectrophotometric measurements were deposited on cleaned Servofrax® glass substrates placed 30 cm above the boat. The

* Figures and Tables are located at the end of report.

free standing films for other characterizations were prepared simultaneously by depositing films on microscope slides which were pre-coated with sodium chloride films. The films were removed by dissolving the salt in water and then drying in a vacuum chamber for several days. The film thicknesses and deposition rates were measured with a quartz crystal monitor (Veeco Instruments Model QM-300/RI-100), during depositions. All films were deposited at rates between 30 and 50 $\mathring{A}$/sec. The boat temperature was measured by a Pt/Pt-10%Rh thermocouple spot welded to the boat, and was constant to within $10^{\circ}C$ throughout a deposition.

2. Film Characterization

The chemical compositions of deposited films were analyzed by the Schoninger sulfur combustion method and by atomic absorption spectroscopy. The experimental accuracy was 0.3 percent and 5 percent in the Schoninger method and in atomic absorption, respectively. Although these techniques worked well with the binary compositions, they left uncertainty in the arsenic to germanium ratio of the ternary compositions. Several films were cross sectioned and examined with a scanning electron microscope and an electron microprobe to detect any compositional variation or inhomogeneity that might exist through the thickness of the film. X-ray or electron diffraction and transmission electron microscope were used to determine the morphology of the films. Thicknesses of the films were measured on a mechanical stylus instrument (Sloan Technology Corp. Dektak IIA) for comparison

with thicknesses calculated from the optical interference fringe patterns measured by the spectrophotometer. The stylus weight was set at the lowest possible value ($\sim$ 10 mg) which did not cause noise in the data, so that the sharp point would not score the soft film surfaces. Reproducibility of measurements was within 0.2 percent on successive measurements at the same location when the step height was about 10 $\mu$m. However, various factors degraded the accuracy of reported thickness to an estimated $\sim$5 percent.

The glass transition onset temperatures Tg of the films were determined by differential scanning calorimeter (Perkin-Elmer Model DSC II) in a flowing nitrogen atmosphere at a heating rate of 10$^{\circ}$K/minute. The DSC samples were pieces of free standing films weighing about 10 mg. The glass transition temperature may be regarded as the upper temperature limit of a particular composition's useful working range, since glassy materials soften above this temperature.

3. Spectrophotometer

The optical thickness and the refractive index of a transparent film can be determined from its optical interference fringe pattern either in transmission mode or in reflection mode [Ref.3]. In this study, the optical transmission of films and their substrates was measured as a function of the wavelength at a fixed angle of incidence, using an infrared spectrophotometer (Perkin-Elmer model 983) with a in-situ heating sample chamber [Ref.4]. Servofrax® glass plates were used as substrates because

of (1) good film adhesion, (2) its excellent transparency in the wavelength range of our interest, (3) negligible dispersion and negligible change in optical absorption with temperature to simplify the calculations as much as possible. A Servofrax® glass with no film coating was placed in the reference beam to compensate for the absorption due to water in the substrate material, so that the fringe patterns do not have to be corrected for this absorption effect. All film specimens , which had been annealed and stabilized prior to this study [Ref.1], were heated to 50°C, 75°C, 100°C, 125°C, 150°C (and 175°C in one case) in nitrogen atmosphere and their optical interference fringes were recorded at each temperature.

Figure 2 shows the cross section of a film specimen. $n_f$, $n_s$ and $n_o$ represent refractive indices of the film, substrate, and nitrogen atmosphere, respectively. The physical thickness of a film $t_f$ is smaller than the coherence length of the spectrophotometer's probing radiation, while the thickness of a substrate $t_s$ is sufficiently large so that the light transversing it loses phase coherence and may be treated in the limit of geometrical optics. Transmittance (transmitted energy) $T_1$ at the front side of the specimen, taking the multiple reflection within the film into account, can be expressed as;

$$T_1 = \frac{8n_o n_f^2 n_s}{(n_o^2 + n_f^2)(n_f^2 + n_s^2) + 4n_o n_f^2 n_s + (n_o^2 - n_f^2)(n_f^2 - n_s^2)\cos\frac{2\pi n_f t_f}{\lambda}}$$

Transmittance $T_2$ at the exit side of the specimen can be expressed as;

$$T_2 = \frac{4n_o n_s}{(n_o + n_s)^2}$$

The resultant transmittance through the specimen, considering the multiple reflection inside the substrate [Ref. 5], can be written as;

$$T_s = \frac{T_1 T_2}{T_1 + T_2 - T_1 T_2}$$

$$\frac{8 n_o n_f^2 n_s}{n_f^4 + 3 n_f^2 n_o^2 + 3 n_f^2 n_s^2 + n_o^2 n_s^2 + (n_o^2 - n_f^2)(n_f^2 - n_s^2)\cos\frac{2\pi n_f t_f}{\lambda}} \qquad (1)$$

The resultant transmittance in the reference side is;

$$T_r = \frac{2 n_o n_s}{n_o^2 + n_s^2} \qquad (2)$$

As we can see from the equation (1), Ts is a periodic function of wave number $1/\lambda$ , where $\lambda$ is a wavelength, with a period = $1/n_f t_f$. A fringe pattern, or a plot of m versus $1/\lambda$ as shown in Figure 3, is obtained as an output of the spectrophotometer. The measured transmission values (T) appear as T = (Ts/Tr)•F. Maxima and minima in transmission occur as;

$$T = \frac{2 n_o n_s}{n_o^2 + n_s^2} \cdot F' \qquad (3) \quad \text{when} \quad n_f t_f = m \bullet \lambda_m \qquad (4)$$

$$T = \frac{4 n_o n_f^2 n_s}{(n_o^2 + n_f^2)(n_f^2 + n_s^2)} F' \qquad (5) \quad \text{when} \quad n_f t_f = (m+1/2) \bullet \lambda_{m+1/2} \qquad (6)$$

where F and F' are instrumental correction factors.

Using equations 3 through 6, two informations can be extracted from one interference fringe pattern; the optical

thickness of the film ($n_f t_f$) from equations 4 and 6, and the refractive index of the film ($n_f$) from equations 3 and 5. The optical thickness can be determined from the slope of m versus $1/\lambda$ plot, using the linear regression analysis. A typical correlation factor for the straight line was around 99.998, indicating an excellent fit between theory and the experimental data. The value of m when $1/\lambda = 0$ (X-axis intercept) reveals the relative magnitude of indices, $n_f < n_s$ or $n_f > n_s$.

Determination of $n_f$ from equations 3 and 5 is less straight forward and more subjective to instrumental errors. This problem was solved by an innovative use of a correction factor F', taken as a ratio of measured transmission and expected transmission. The expected transmission was calculated from equation 3 with an assumption that the refractive index of Servofrax substrate was that as reported by Malitson, et al [Ref.6], in the form of a set of coefficients for Sellmeier's dispersion equation. The correction factors were calculated at m and m+1 , and their average value was applied at m+1/2 to equation 5. $n_f$ was calculated from equation 5 based on this corrected T value and known $n_s$. This process was repeated for all m's through the entire spectrum, and the average of all $n_f$'s was taken as the film refractive index. The physical thickness of the film was calculated from;

$$t_f = \frac{n_f t_f \text{ (from fringe period)}}{n_f \text{ (from } T_{max} \text{ and } T_{min} \text{)}}$$

## III. RESULT AND DISCUSSION

All as-deposited films were found to be amorphous and featureless in electron microscope, x-ray and electron diffraction. Electron microprobe and electron microscope revealed that films used in this experiment were free from inhomogeneity and compositional variation across the thickness of the film. Results of chemical compositional analysis, glass transition temperatures (Tg), refractive indices, film thicknesses determined from optical fringes, and film thicknesses measured by the mechanical stylus are listed on Table 1. The vapor deposited films were found to be sulfur deficient by a few percent as compared to their corresponding bulk compositions. This sulfur deficiency was more severe in the compositions higher in sulfur. A separate study [Ref.7] revealed, for $As_2S_3$ films, that the sulfur deficiency increases with increasing deposition rate. This may be caused from the free sulfur dissociation during deposition process [Ref.8,9, and 10]. The physical thicknesses calculated from the optical interference fringes agreed within 5 percent with the stylus thickness measurements performed at room temperature.

Figure 4 through figure 8 show the normalized optical thicknesses, refractive indices, and normalized physical thicknesses as a function of temperature. All normalizations were executed with respect to the corresponding room temperature values. The calculated slope are also shown on these figures. The normalized physical thickness is the thermal expansion

coefficient ($\alpha$).

The behavior of the optical constants above Tg can be seen clearly in Figures 5 and 6. The significant change in these properties at their corresponding Tg may be explained by considering the specific volume as a function of temperature for glassy materials as shown in Figure 9 [Ref.11]. As a glassy material is heated beyond its Tg, the specific volume increases more rapidly with temperature. Therefore, thermal expansion coefficient increases above Tg. This, in turn, affects dn/dT in the opposite direction according to the Lorentz-Lorenz equation [Ref.12]. The combined effects in this case gives rise to a sharp increase in optical thickness, because the increase in thermal expansion was more rapid as compared to the decrease in dn/dT. Data points above Tg are indicated by open squares (□), and they were excluded from the calculations for the slopes, because these data points do not represent the reversible effect.

Improbably large dn/dT and $\alpha$ values obtained for the $Ge_5As_{38}S_{57}$ composition are most likely caused by a temperature dependent optical absorption effect which was not incorporated in the equations 4 and 6 used in this study. Including the optical absorption term in equations 4 and 6 will be achieved in future. The slope of the normalized optical thickness is $^{1}/_{nt} \cdot {}^{d(nt)}/_{dT}$, and the results from this experiment are shown in Figure 10, as (■), along with the literature values for other optical materials [Ref.12 and 13]. Our experimental values for the $As_2S_3$ film fit in the same range as the bulk data reported in Ref.13 ($\alpha = 25 \times 10^{-6}$ /°C and dn/dT = $-8.6 \times 10^{-6}$/°C). Literature values for other

compositions in our study, either for bulk or for film, have not been found. Of the compositions studied, $As_2S_3$ had the greatest thermal stability in optical properties up to 150°C. The addition of sulfur or germanium to $As_2S_3$ decreased the thermal stability.

## IV. SUMMARY

(1) We have developed the methodology to evaluate the thermal stability of vapor deposited glassy chalcogenide films for spectral interference filter applications.

(2) Of the compositions studied, $As_2S_3$ had the greatest thermal stability up to 150°C. The addition of sulfur or germinium to $As_2S_3$ decreased the thermal stability.

(3) A formal transmittance equation which incorporates the optical absorption effect should be developed and used in future to obtain more accurate values of dn/dT and $\alpha$ for absorbing films.

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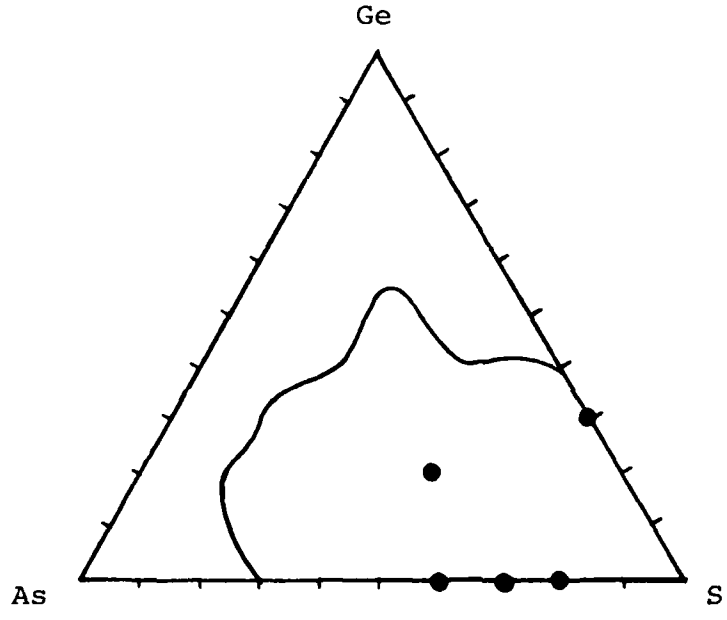


FIGURE 1. Glass Forming Region in As-Ge-S Ternary System

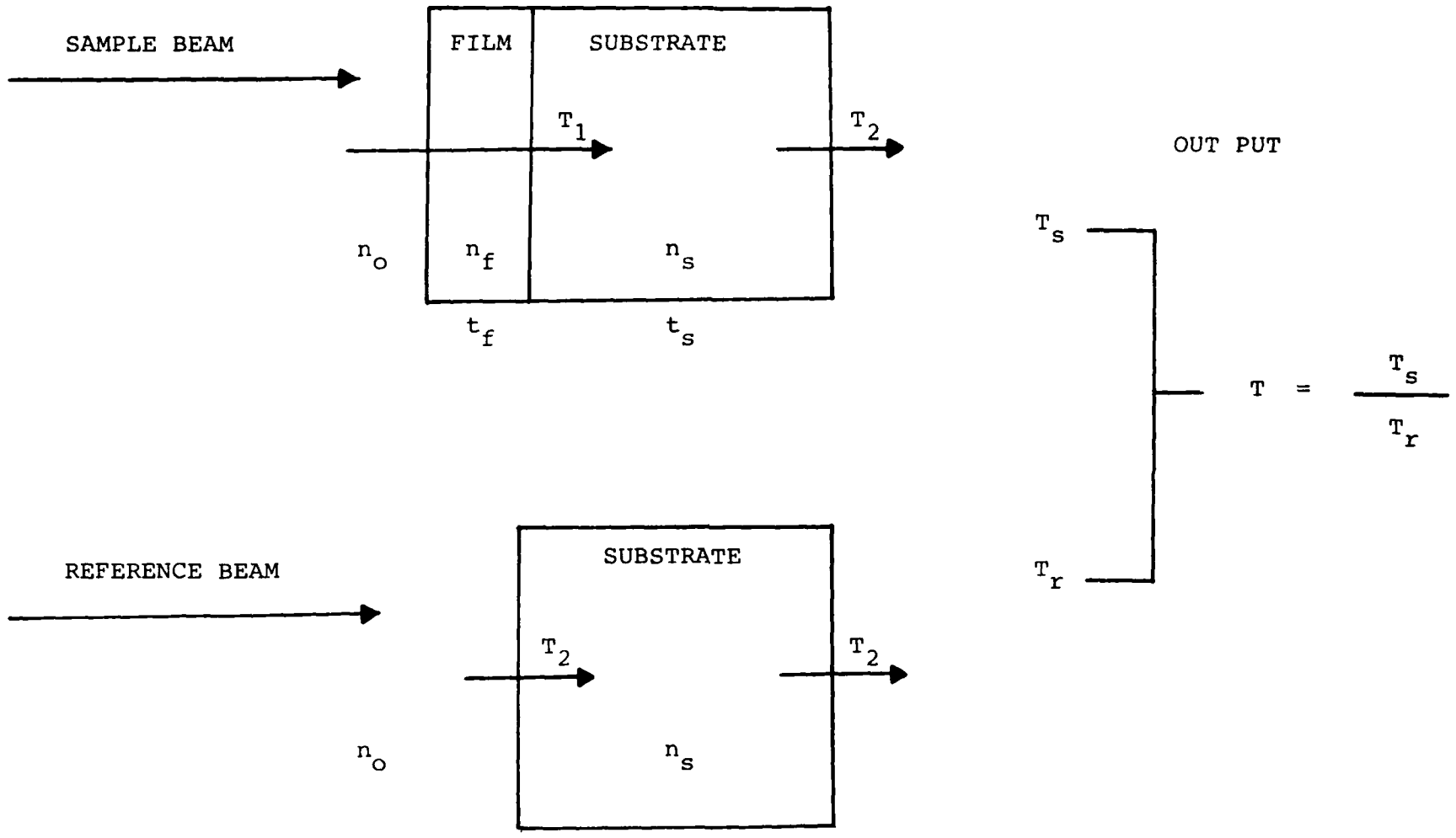


FIGURE 2. Spectrophotometry

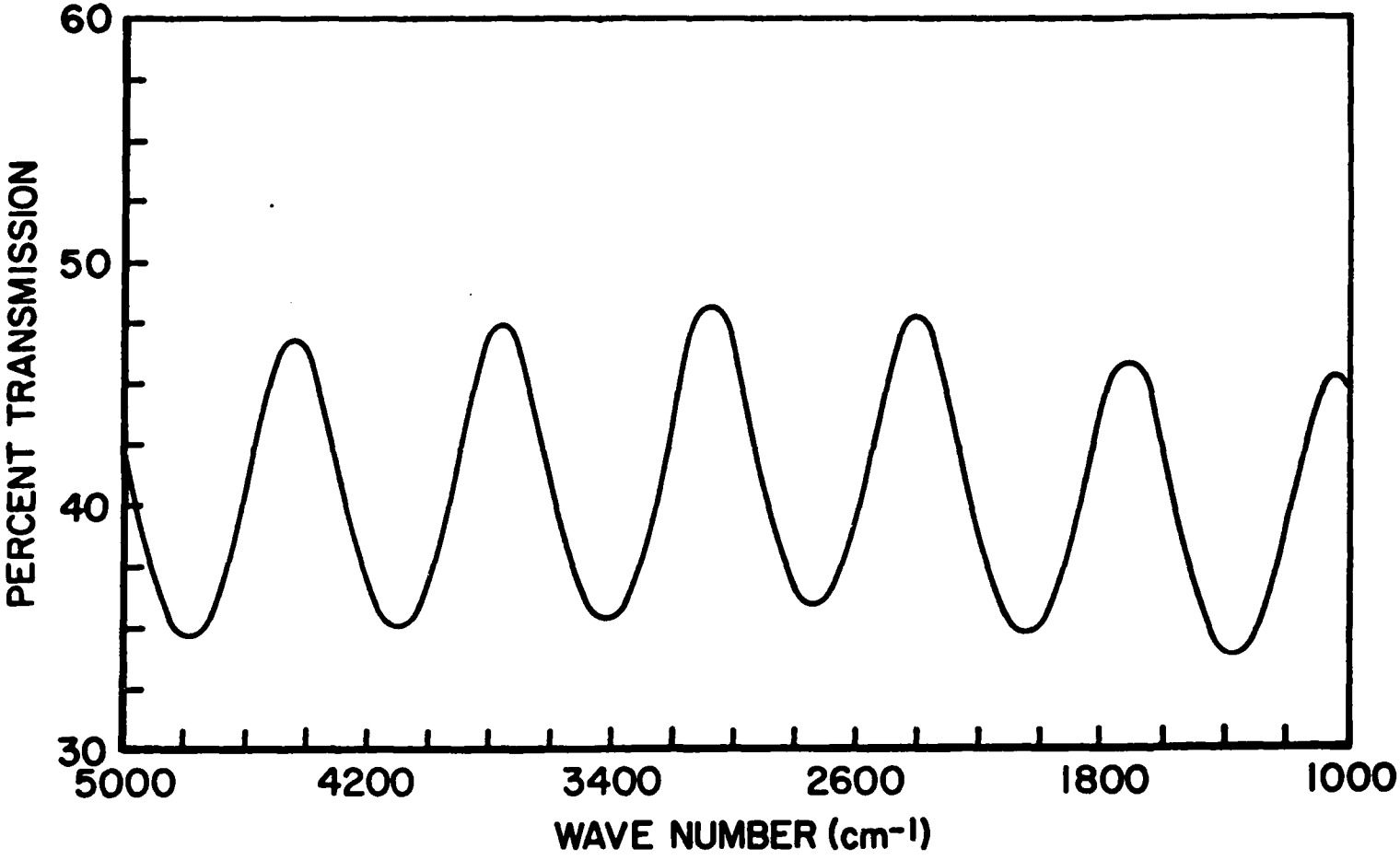


FIGURE 3. Optical Transmission Interference Fringe Pattern

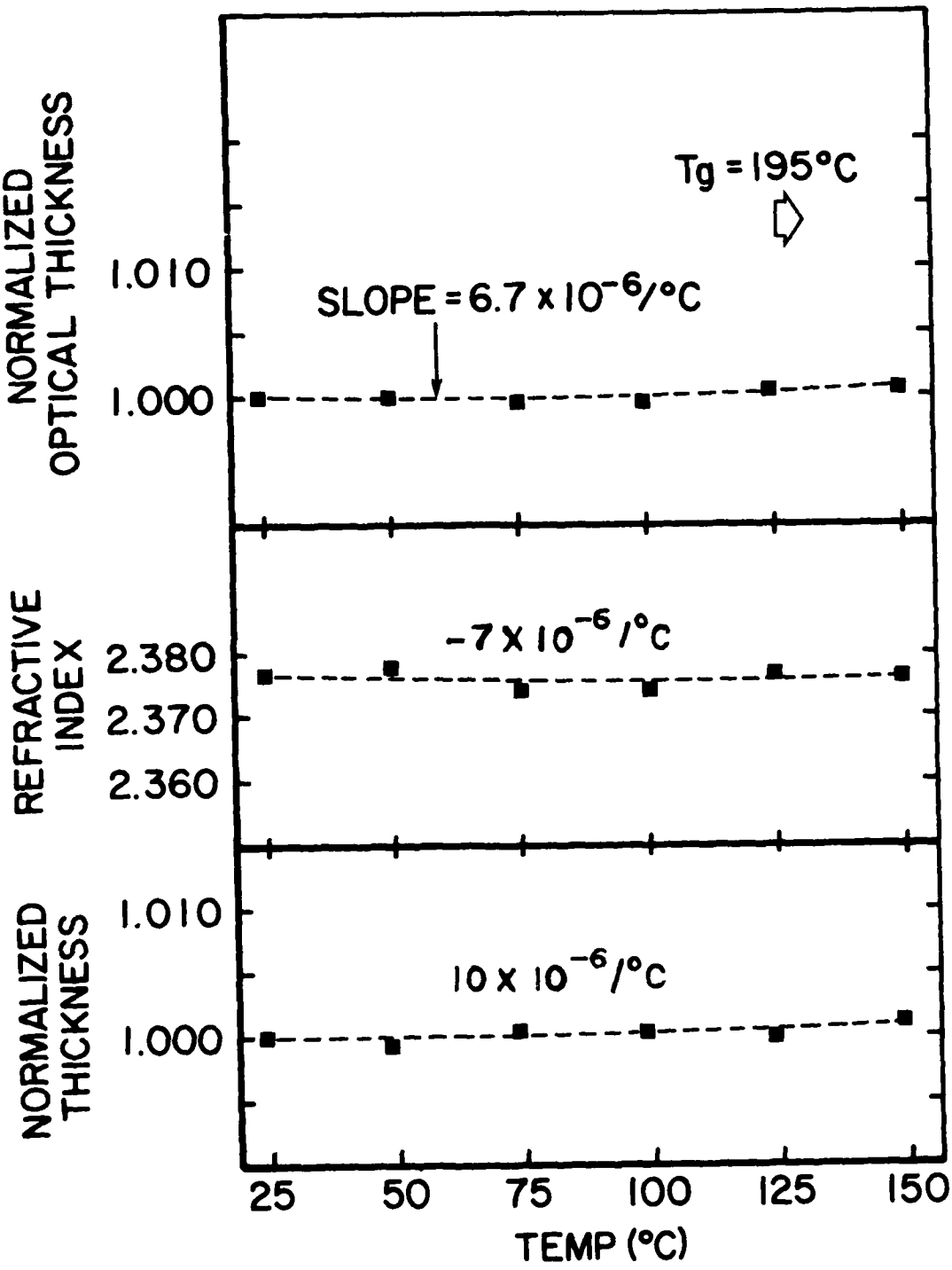


FIGURE 4. Calculated Properties of $As_2S_3$ Film as a Function of Temperature

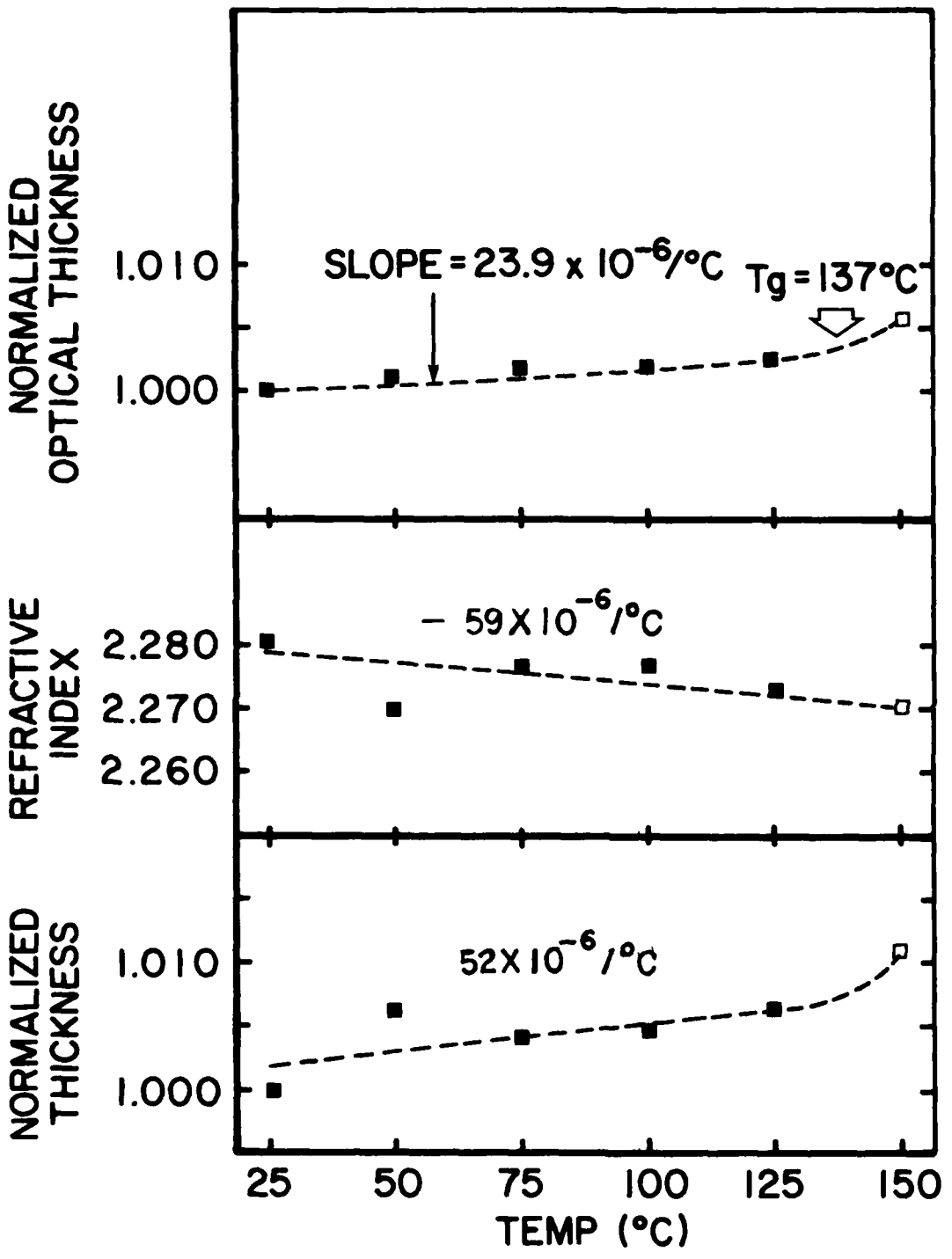


FIGURE 5. Calculated Properties of $As_3S_7$ Film as a Function of Temperature

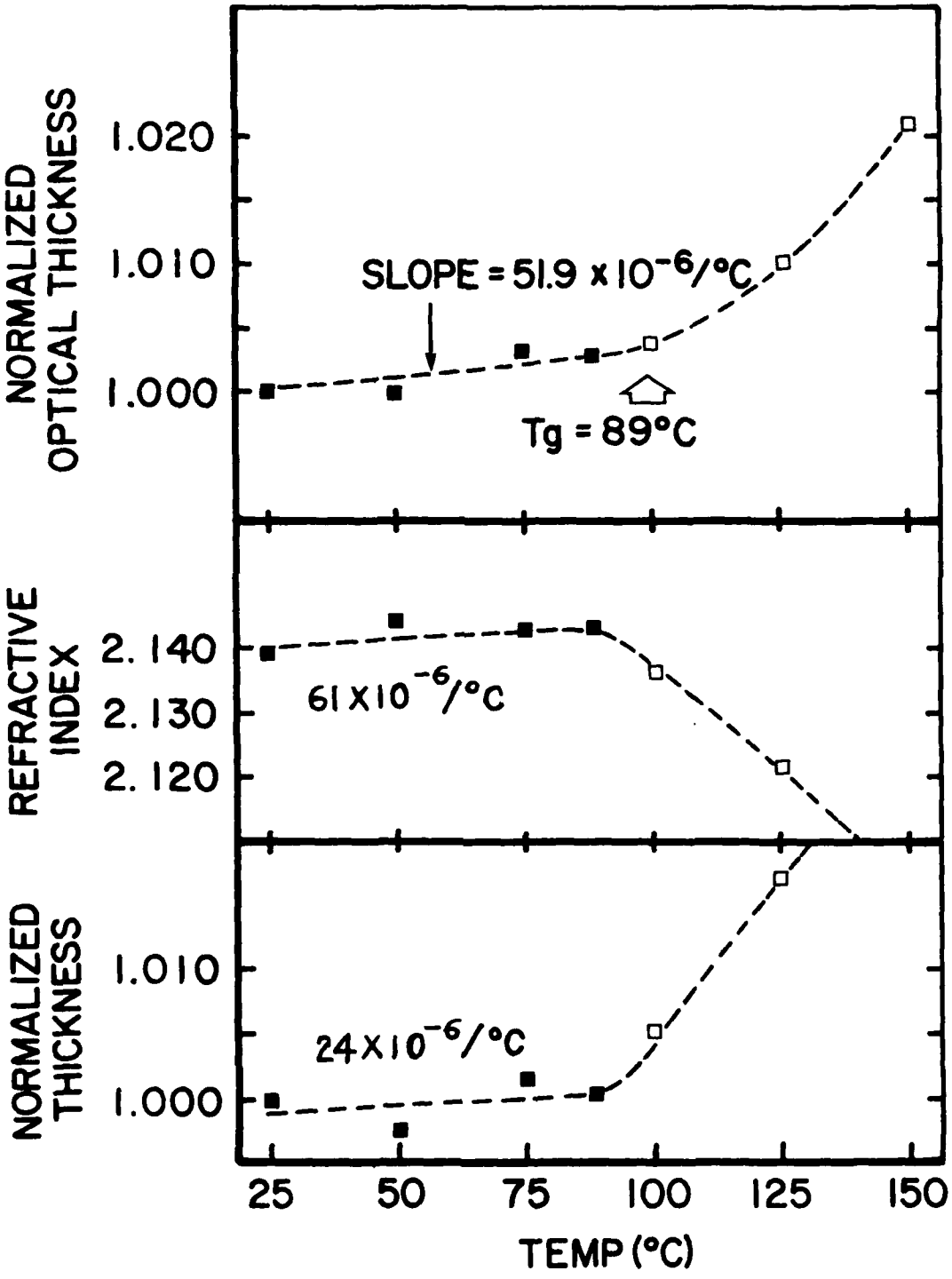


FIGURE 6. Calculated Properties of As $S_4$ Film as a Function of Temperature

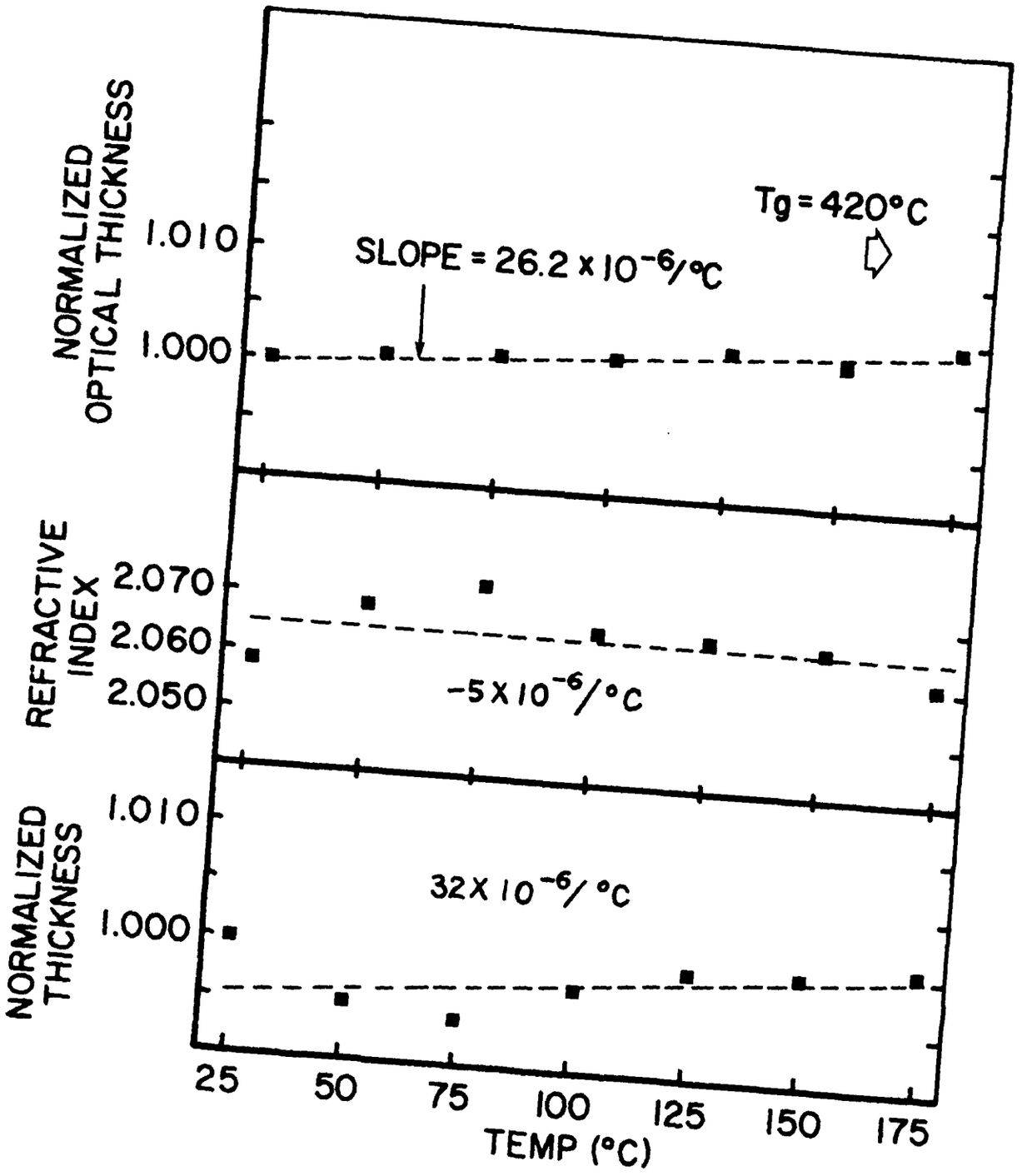


FIGURE 7. Calculated Properties of $Ge_3S_7$ Film as a Function of Temperature

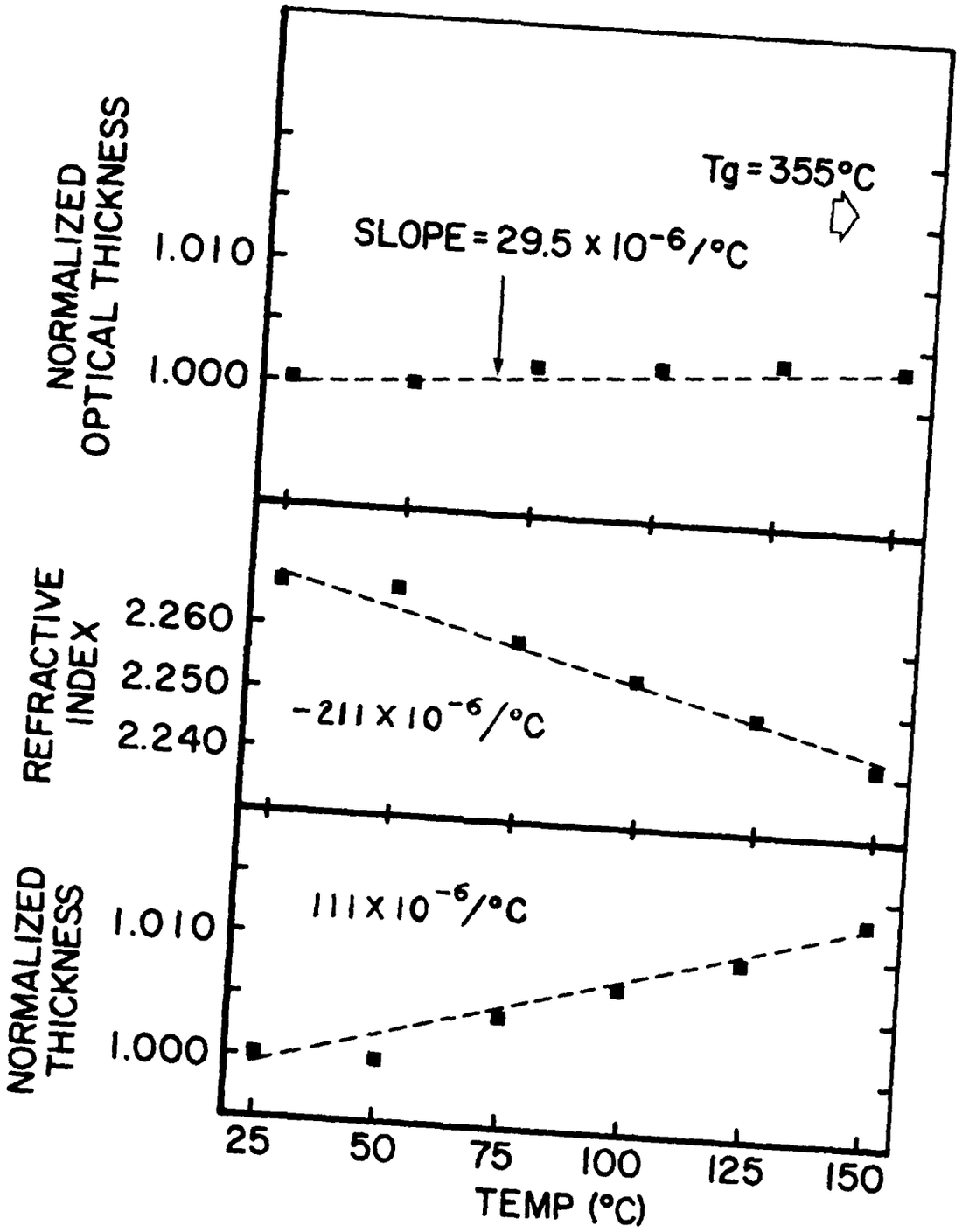


FIGURE 8. Calculated Properties of $Ge_5As_{38}S_{57}$ Film as a Function of Temperature

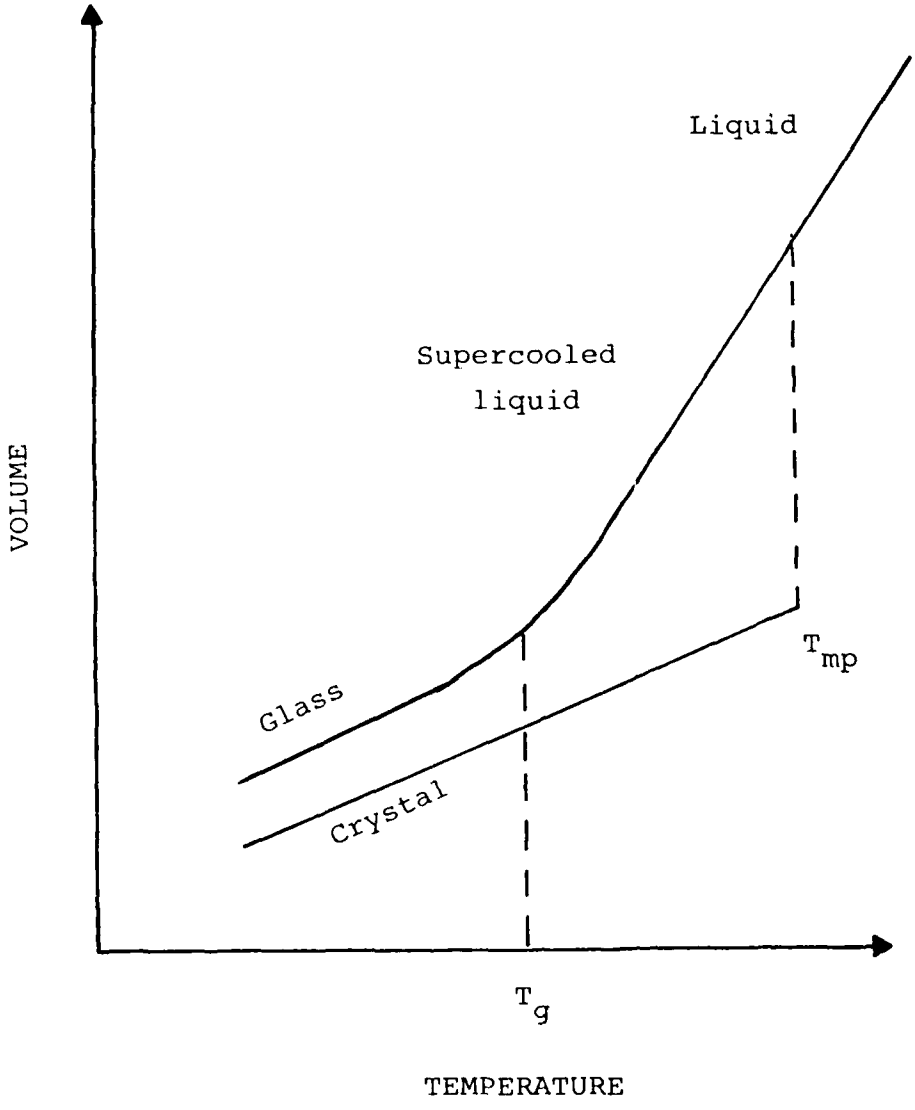


FIGURE 9. Specific Volume as a Function of Temperature for Glassy Materials

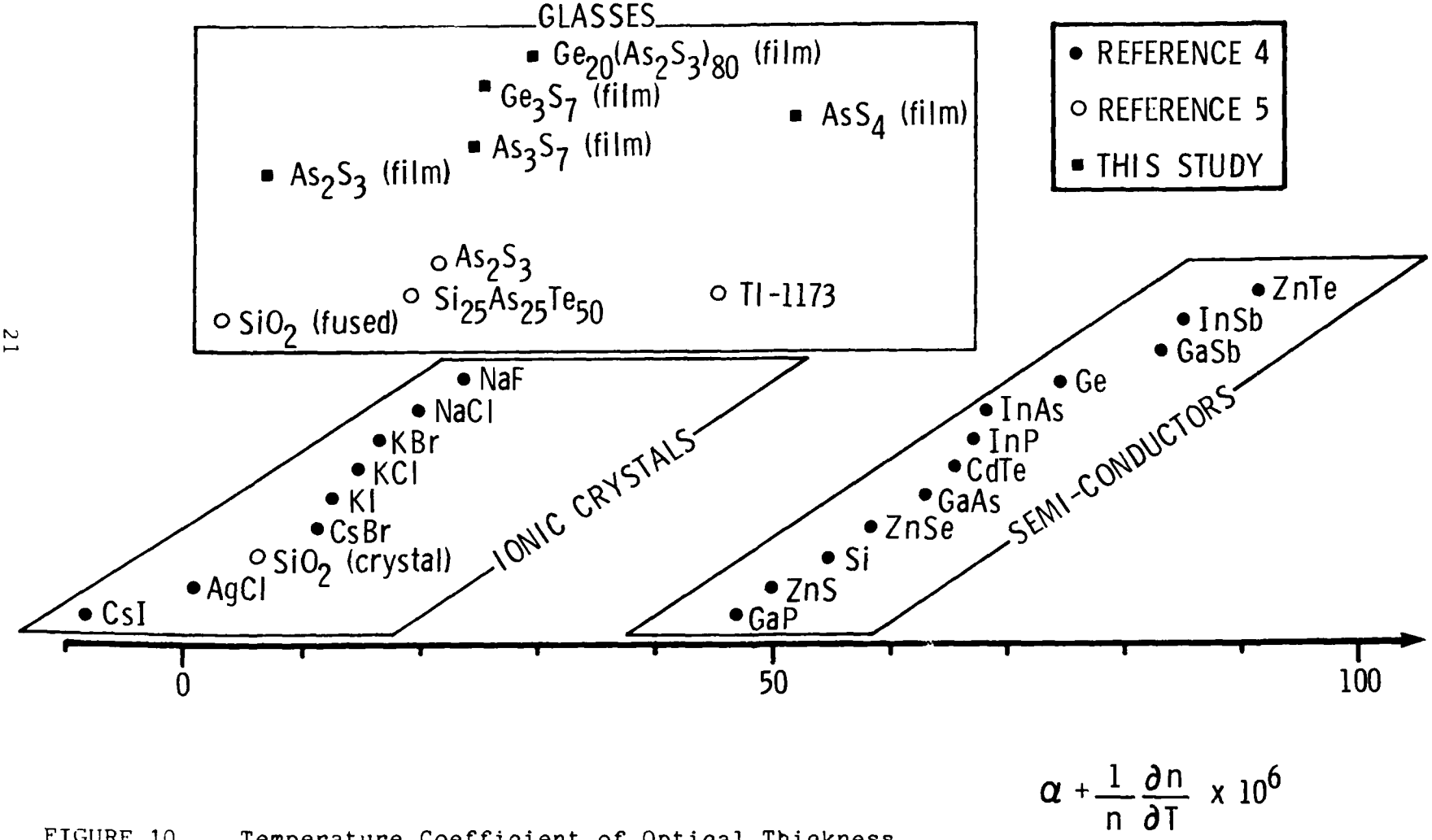


FIGURE 10. Temperature Coefficient of Optical Thickness for Infrared Transmitting Materials

| STARTING COMPOSITION | ANALIZED COMPOSITION | $T_g$ | n | PHYSICAL THICKNESS | |
|---|---|---|---|---|---|
| | | | | FRINGE μM | STYLUS μM |
| $AsS_4$ | $As_{25.0}S_{75.0}$ | 89 °C | 2.137 | 5.407 | 5.6 |
| $As_3S_7$ | $As_{31.9}S_{68.1}$ | 137 °C | 2.284 | 7.745 | 7.7 |
| $As_2S_3$ | $As_{40.8}S_{59.2}$ | 195 °C | 2.337 | 10.196 | 10.0 |
| $Ge_3S_7$ | $Ge_{31.5}S_{68.5}$ | 420 °C | 2.056 | 4.302 | 4.4 |
| $Ge_5As_{38}S_{57}$ | 52.5 % S | 355 °C | 2.267 | 6.203 | 6.2 |

TABLE 1. List of Measured Values

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