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THIRD SEMIANNUAL TECHNICAL SUMMARY REPORT

FOR

NEW HIGH TEMPERATURE INFRARED TRANSMITTING GLASSES

Office of Naval Research Contract No. 3810(00)

in cooperation with
Advanced Research Projects Agency
Department of Defense

This Report Covers the Period
1 November 1963 through 30 April 1964

TEXAS INSTRUMENTS INCORPORATED
13500 NORTH CENTRAL EXPRESSWAY • DALLAS, TEXAS

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Prepared by

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A. Ray Hilton

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ABSTRACT

Glasses formed in the Ge-P-Te system have moderately high softening points (as high as 390°C) and are essentially transparent to the infrared out to 20 microns wavelength. Their refractive indexes are greater than 3, and their glass-forming composition region is the smallest of all the systems evaluated. We found no ternary glass system using the group IVA element Sn that should be evaluated. With the Si-As-Te and Ge-As-Te glass systems as bases, the effect on the optical properties, softening point, and hardness was determined when P, Sb, S, and Se were substituted into the glasses.

Efforts to definitely establish the origin of the undesirable absorptions in the most promising glasses will increase. Prisms made from these glasses will be cast and the refractive index accurately measured. Blending studies will continue.

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I. INTRODUCTION

For the past two years Texas Instruments has been evaluating three-component ternary glasses made with elements from groups IVA-VA-VIA for their potential application as infrared transmitting materials, particularly for the 8 to 14 micron region. This work has been carried out under contract Nonr 3810(00).

Ternary systems previously reported are Si-Sb-S, Si-Sb-Se, Si-P-Te, Ge-P-S, Ge-P-Se, and Ge-As-Te.[1-8] Results obtained in the evaluation of the Ge-P-Te system, in Sn-VA-VIA systems and in various blended glasses will be discussed in this report.

II. EXPERIMENTAL

A. Procedure for Evaluation

A detailed account of the glass preparation procedure has been given in previous reports[1-8] and will not be repeated here, since it has remained essentially unchanged throughout the investigation. High purity samples are prepared in evacuated quartz vials, reacted and mixed in a rocking furnace held at 1000°C, then quenched in air to room temperature.

The procedure employed in measuring the softening points of the glasses has been somewhat modified. This newer technique is more precise than the former method.[1] The apparatus is shown in Fig. 1 and consists of an Ames model 282M micrometer dial indicator to which a pointed quartz rod is attached. The movement of the glass specimen can be measured in increments of 0.01 mm, and the readings are quite reproducible. A load of approximately 100 grams is applied to the sample, and the glass is heated at a fixed rate until the dial indicator shows a slight movement, indicating a softening of the material. Although this is only a "relative" softening point, the results are most useful in comparing a family of glasses.

The method of calculating the optical constants has not changed, but the optical measurements are now made using a Perkin-Elmer model 337 infrared spectrometer. Transmission and reflectivity were measured on all samples from 2.5 to 25 microns.

Chemical stability and Knoop hardness were also studied under the current program.

B. Systems Selected for Evaluation

The ternary system Ge-As-Te produced good optical glasses[8] which had low softening points. Glasses containing P instead of As are found to have higher softening points. For this reason Ge-P-Te was selected for evaluation.

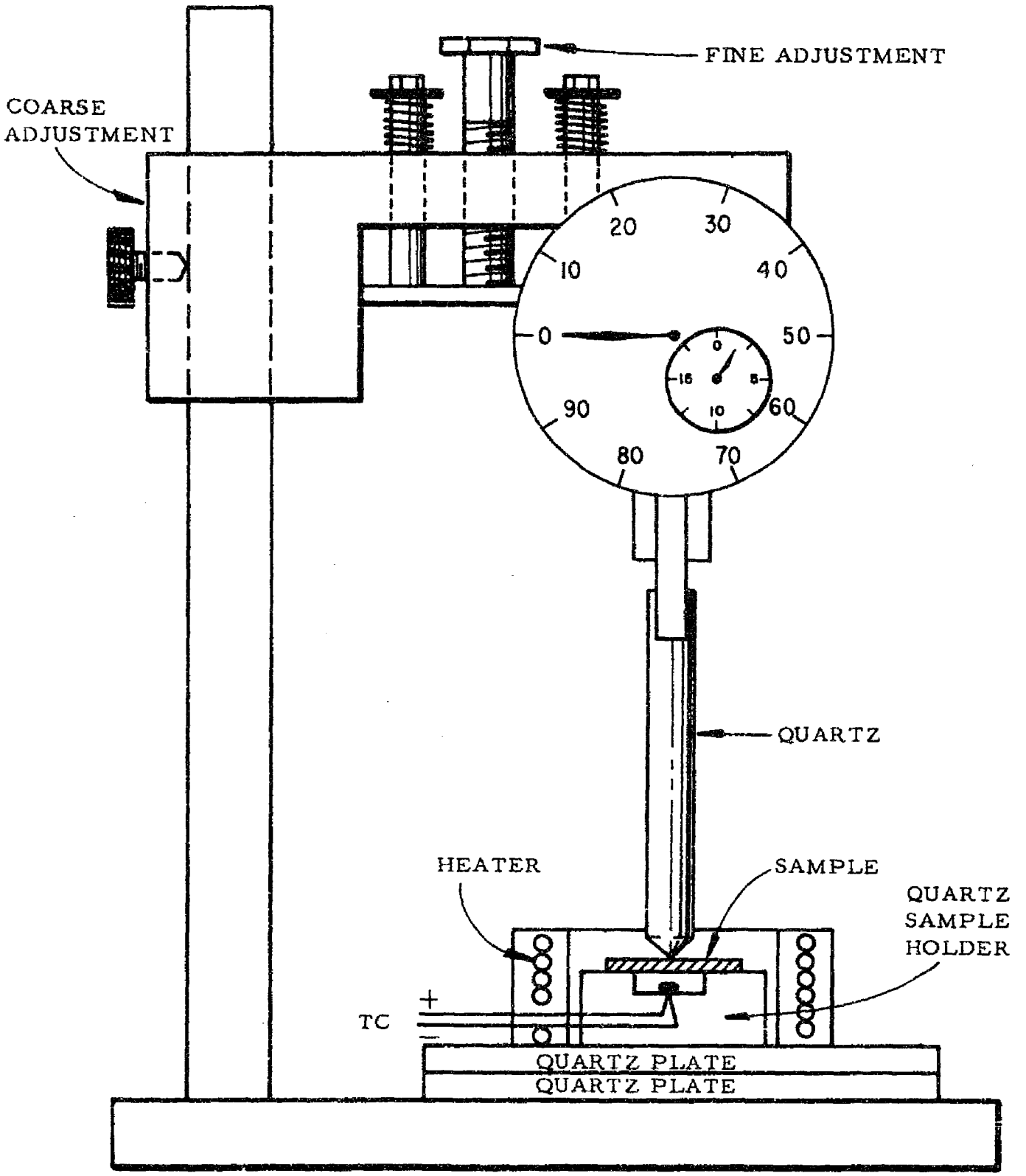

Fig. 1 "Soft-Point" Apparatus

Sn-VA-VIA systems were studied for glass-forming possibilities. From knowledge gained in studying previous IVA-VA-VIA glass composition diagrams, specific samples of Sn in combination with P, As, and Sb and S, Se, and Te were prepared in the usual manner to determine potential glass-forming compositions.

A few samples of glasses containing boron in place of the group IVA element were prepared. Since boron-silicate glasses have very good thermal and physical properties, a similar improvement in glasses based on S, Se, and Te could be expected.

C. Blending of Glasses

Glasses from a particular ternary system are characterized by specific physical and optical properties. These properties can be either enhanced or decreased by carefully blending a specific glass with a different glass system. A specific blend can be obtained by mixing the correct amounts of previously prepared glass or by weighing out the unreacted elements. The latter method has been used predominantly in our program.

Two base glass systems were chosen to study the effects of blending, as shown diagramatically in Fig. 2. The Si-As-Te system was chosen because it has been more fully characterized than the others, and the Ge-As-Te system because of its lack of absorption bands in the desired wavelength region. These two glasses were blended with each other, thus giving the effect of Ge in the Si-As-Te system, and vice versa. Si-As-Te was then blended with Si-P-Te, Si-Sb-Te, Si-As-Se, and Si-As-S, giving the effects of P, Sb, Se and S on the Si-As-Te system. The Ge-As-Te system was blended with Ge-P-Te, Ge-As-Se, Ge-As-S, and Ge-Sb-Te, giving the effects of P, Se, S and Sb on the Ge-As-Te system.

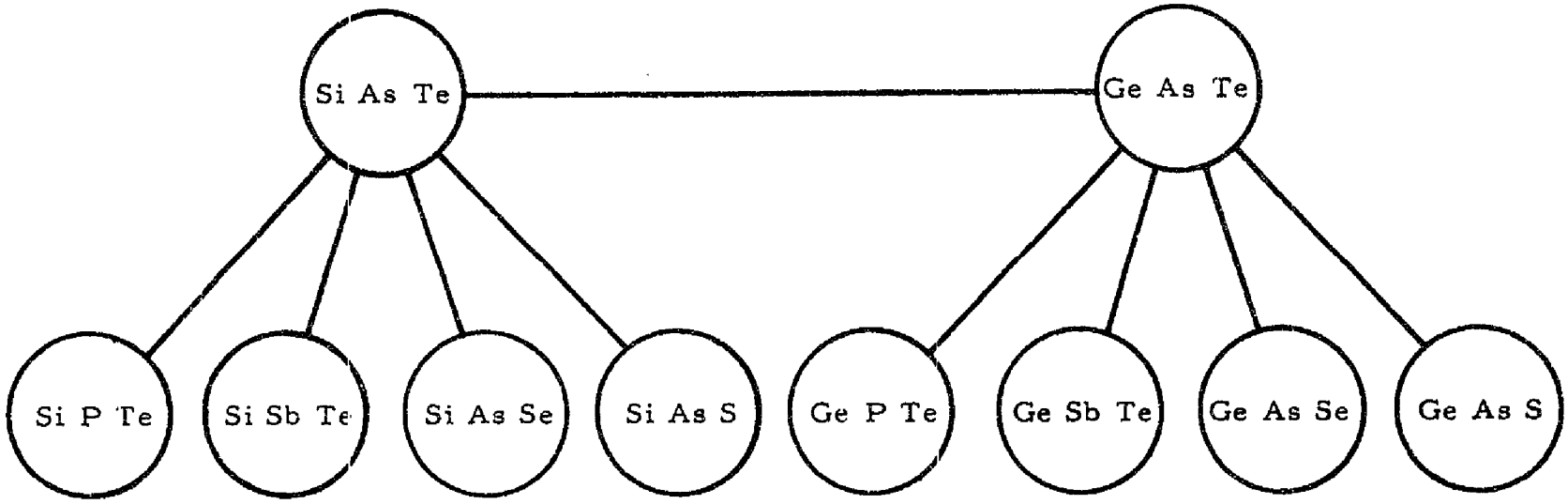

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Fig. 2 IVA-VA-VIA Glass Blends

III. RESULTS

A. The Ge-P-Te System

Results obtained from 27 samples of different compositions are shown in Table I. The measured softening points range from 130° to 390°C. The glass-forming region determined from these composition points is enclosed by the solid line shown in Fig. 3. This glass-forming region may extend further toward the phosphorus-rich region, but because of the high vapor pressures involved, no samples containing more than 30 atomic percent phosphorus were prepared. The chemical stability of some of these glasses was determined, and the results are shown in Table II, along with those for typical Ge-As-Te glasses. Although the Ge-P-Te glasses are somewhat less stable than Ge-As-Te glasses, the results indicate reasonable stability.

A plot of infrared transmission versus wavelength for the Ge-P-Te system is shown in Fig. 4. These glasses are essentially free of absorption bands out to 20 microns and show transmission over a greater wavelength range than any glass system previously reported. The refractive indexes, as in the case of the Ge-As-Te glasses, are greater than 3.

B. The Sn-VA-VIA Systems

Results obtained from 19 different compositions are shown in Table III. During the course of sample preparation, several violent explosions occurred at relatively low (< 600°C) temperatures, possibly because of pressure created by very exothermic reactions.

Only two compositions produced a glass, $SnAsSe_8$ and $SnAsSe_{18}$. The softening points of these glasses were 150° and 110°C, respectively. Because of the low softening points and the difficulty involved in preparing these compositions, we abandoned the work on the Sn-VA-VIA glasses in favor of blended glasses.

TABLE I

The Ge-P-Te System

Sample No.	Composition (Atom. %) Ge	P	Te	Softening Point °C
199	10	30	60	Exploded
200	15	15	70	145
201	30	10	60	Crystalline
202	25	25	50	Crystalline
203	35	15	50	Exploded
204	25	15	60	Crystalline
205	20	15	75	165
206	10	10	80	Crystalline
207	10	20	70	Crystalline
208	15	20	65	190
209	20	25	55	Crystalline
210	30	20	50	Crystalline
211	20	20	60	Crystalline
212	20	15	65	270
213	25	10	65	390
214	35	0	65	Crystalline
215	15	5	80	Crystalline
216	15	10	75	130
217	25	5	70	Crystalline
218	20	10	70	Crystalline
219	30	5	65	230
220	30	0	70	Crystalline
221	25	0	75	Crystalline
222	20	0	80	Crystalline
223	10	15	75	Crystalline
224	25	5	70	Crystalline
225	27	8	65	Crystalline

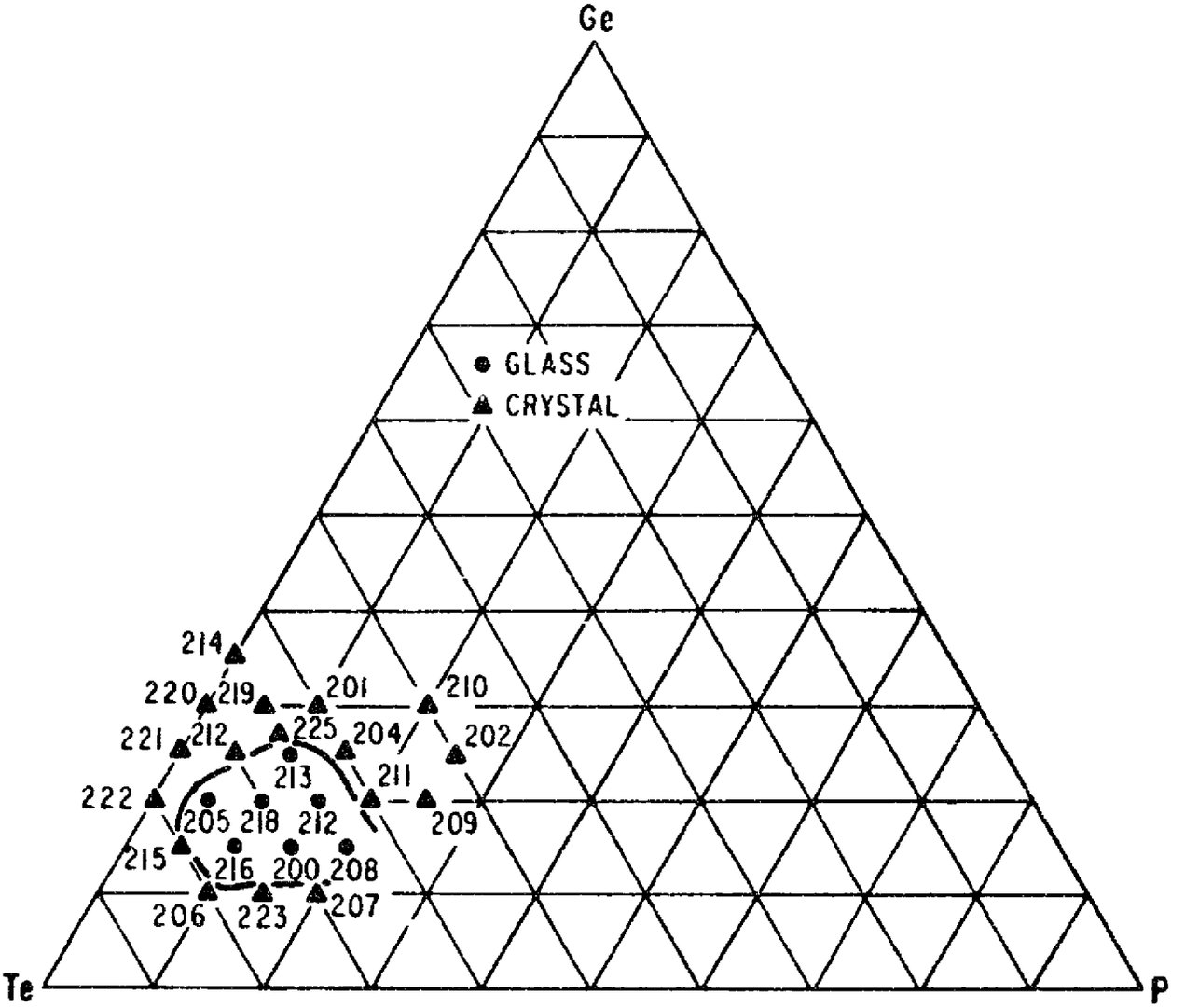

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Fig. 3 Composition Diagram for Ge-P-Te Glass System

TABLE II

Chemical Stability of Ge-P-Te Glass

(Weight Loss, Grams/Gram)

Composition	18 Hours in H_2O at 25°C	1.5 Hours in H_2O at 100°C	20 Hours in HCl - 5%	20 Hours in HNO_3 - 5%	20 Hours in NaOH - 5%
$Ge_3P_3Te_{14}$	0.0003	0.0002	0.0001	0.0083	0.0007
Ge_4PTe_{15}	0.0000	0.0016	0.0009	0.0000	0.0000
$Ge_3P_4Te_{13}$	0.0000	0.0048	0.0007	0.0012	0.0004
$Ge_4P_3Te_{13}$	0.0008	0.0005	0.0012	0.0018	0.0004
$Ge_3P_2Te_{15}$	0.0023	0.0000	0.0023	0.0034	0.0007
$GeAsTe_8$*	0.0001	0.0000	0.0006	0.0001	0.0004
$GeAs_6Te_{13}$*	0.0009	0.0000	0.0002	0.0003	0.0004

* Comparative Values

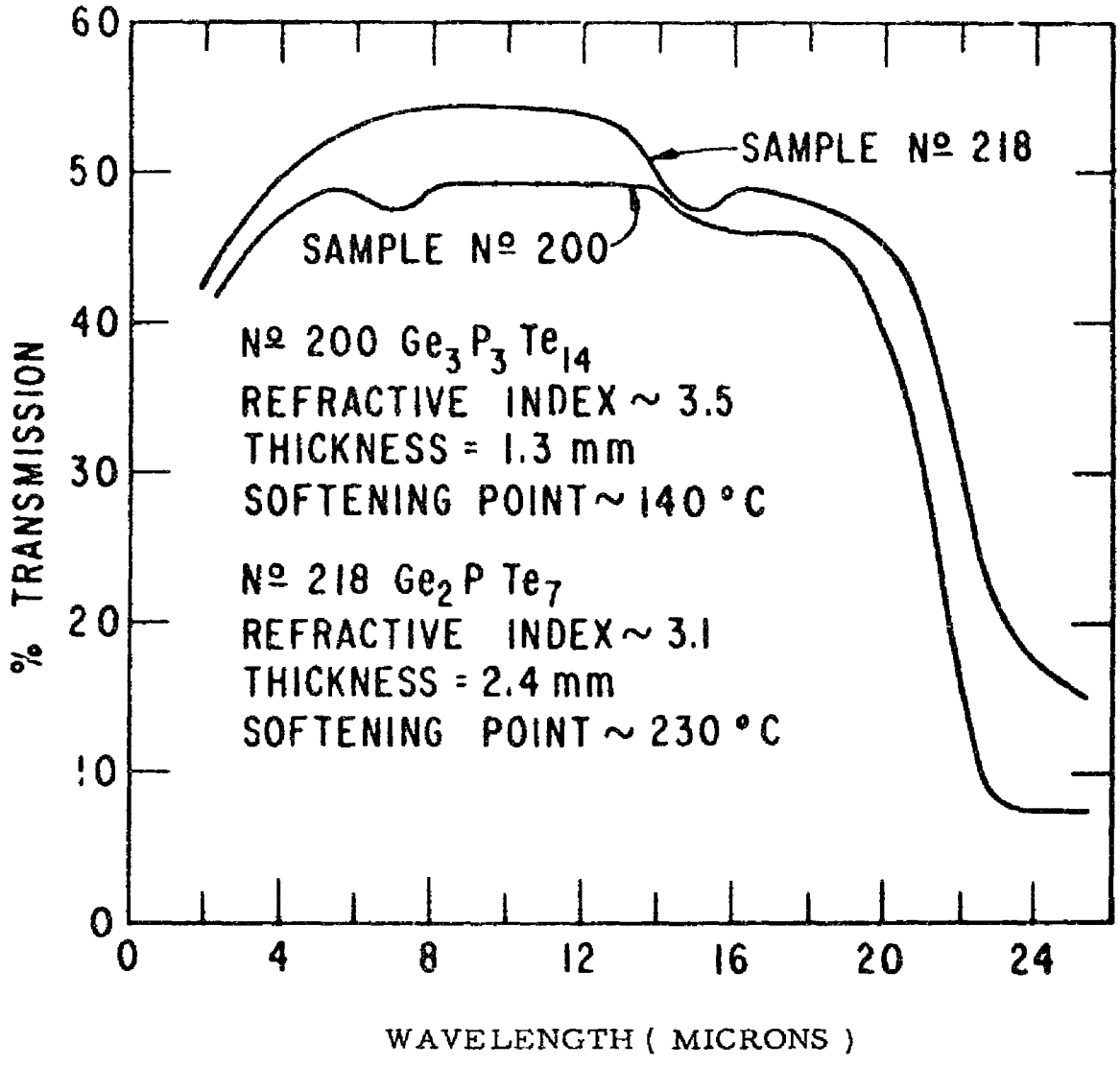

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Fig. 4 Infrared Transmission of Some Ge-P-Te Glasses

TABLE III

The Sn-VA-VIA System

Composition	Results
$SnPS_3$	Crystalline
$SnAsS_3$	Crystalline
$SnPSe_3$	Crystalline
$SnAsSe_3$	Crystalline
$SnPTe_3$	Exploded
$SnAsTe_3$	Crystalline
$Sn_3P_2S_{15}$	Crystalline
$Sn_3As_2S_{15}$	Crystalline
SnPS	Exploded
SnAsS	Exploded
$SnPS_{18}$	Exploded
$SnAsS_8$	Exploded
Sn_3AsS_{14}	Crystals in glassy matrix
$Sn_5As_4S_{11}$	Crystalline
$Sn_2As_5S_{13}$	Crystalline
$SnAsSe_8$	Glass - softening point ~ 150°C
$SnAsSe_{18}$	Glass - softening point ~ 110°C
$SnAsTe_8$	Crystalline
$SnAsTe_{18}$	Crystalline

C. B-As-VIA Glass

Three glass compositions--B_3AsS_6, B_3AsSe_6, and B_3AsTe_6-- were prepared as a preliminary study to determine the potential of boron as a glass-former in various chalcogenide systems. The composition containing tellurium did not form a glass; the other compositions were amorphous but were very reactive and decomposed when exposed to the atmosphere. Boron may be useful as a glass modifier, but it does not appear promising as a major glass constituent.

D. Blended Glass

1. Si-As-Te → Ge-As-Te

Table IV shows the effects on hardness and softening point when germanium was substituted for silicon in various Si-As-Te glasses. In all cases the glass was prepared from the elements in the usual manner. In general, adding germanium caused a slight decrease in the softening point of the glass. This effect is shown graphically in Fig. 5. As expected, the glasses with the largest amount of the group IVA element showed the greatest change in softening point. Glass rich in tellurium, especially a glass with a composition $Si_6As_8Te_{45}$, shows little change in softening point or hardness, indicating a structure somewhat different from that of a higher softening, lower tellurium-content glass such as $Si_7As_5Te_8$. This is probably a result of the type of bonding prevalent in the various glasses. Tellurium-rich glass undoubtedly contains Te-Te bonds and for this reason has a lower softening point. Addition or substitution of a relatively minor element should also have a lesser effect on the properties of the glass. The relationship between hardness measured on the Knoop scale and softening point is shown in Fig. 6. Since the low softening glasses are tellurium- or selenium-rich, it is expected that these glasses will be softer than those containing lesser amounts of the group VIA elements.

Another effect of germanium on the Si-As-Te system is to reduce the absorption coefficient, especially at 10 and 14 microns. This effect is shown in Fig. 7. At present the origin of these bands is unknown.

TABLE IV

Blended Glasses ($Si_{6-x}Ge_xAs_8Te_{26}$ → $Ge_{6-x}Si_xAs_8Te_{26}$)

Sample No.	Composition	Softening Point (°C)	Hardness (Knoop)
239	$Si_6As_8Te_{26}$	196	108.4
242	$Si_5GeAs_8Te_{26}$	190	126.5
245	$Si_4Ge_2As_8Te_{26}$	124	126.5
248	$Si_3Ge_3As_8Te_{26}$	200	136.8
251	$Si_2Ge_4As_8Te_{26}$	190	127.0
253	$SiGe_5As_8Te_{26}$	180	126.5
255	$Ge_6As_8Te_{26}$	Crystalline	-
258	$Si_6As_9Te_{45}$	160	108.4
260	$Si_5GeAs_9Te_{45}$	136	105.8
261	$Si_4Ge_2As_9Te_{45}$	148	110.9
262	$Si_3Ge_3As_9Te_{45}$	146	108.7
263	$Si_2Ge_4As_9Te_{45}$	148	109.0
264	$SiGe_5As_9Te_{45}$	150	113.4
265	$Ge_6As_9Te_{45}$	162	113.7
240	$Si_5As_5Te_{10}$	310	166.9
266	$Si_4GeAs_5Te_{10}$	290	156.5
267	$Si_3Ge_2As_5Te_{10}$	293	179.0
268	$Si_2Ge_3As_5Te_{10}$	256	151.2
269	$SiGe_4As_5Te_{10}$	Crystalline	-
241	$Si_7As_5Te_8$	434	207.8
244	$Si_6GeAs_5Te_8$	380	195.6
247	$Si_5Ge_2As_5Te_8$	394	198.6
250	$Si_4Ge_3As_5Te_8$	379	195.0
251	$Si_3Ge_4As_5Te_8$	Crystalline	-

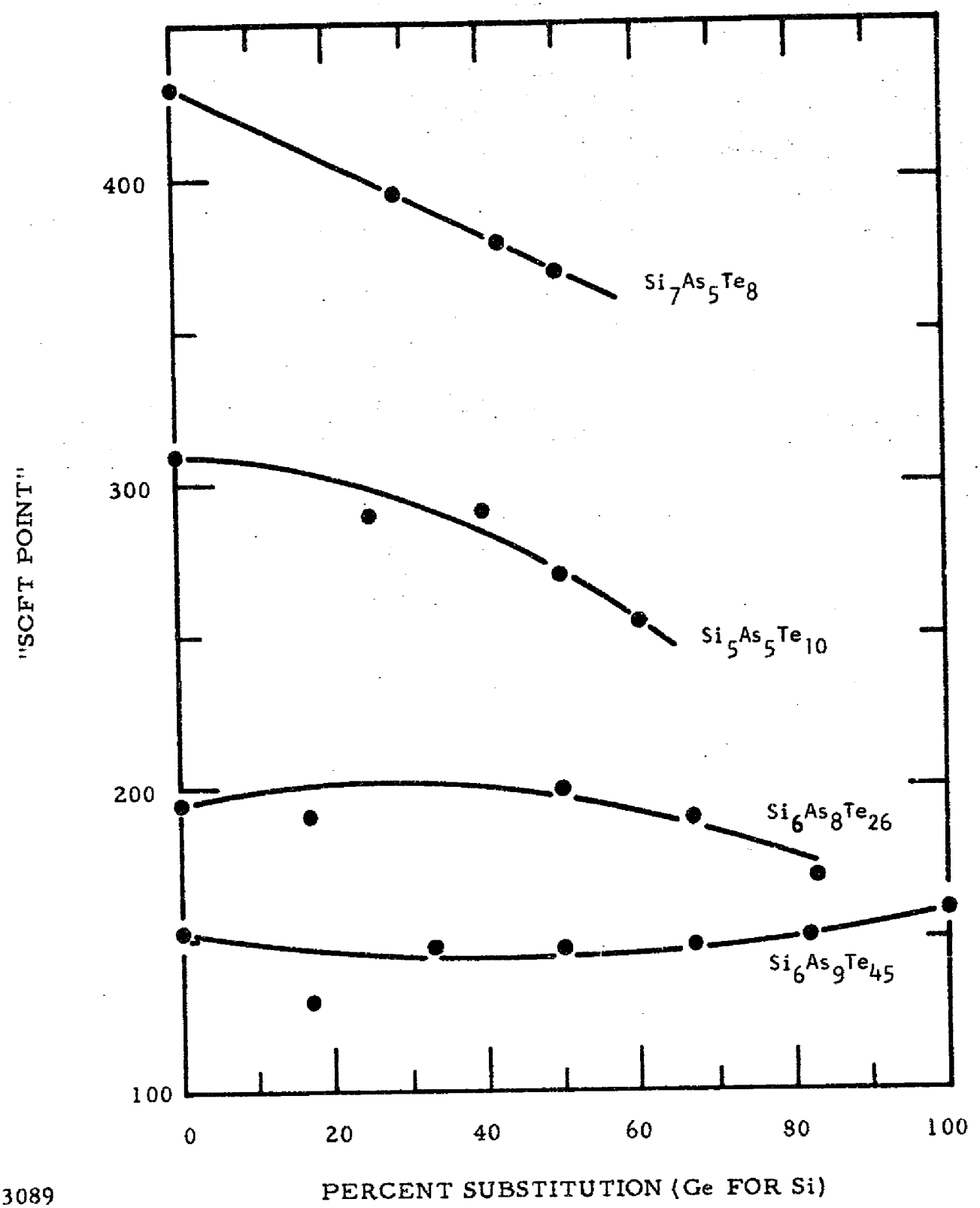

Fig. 5 Substitution of Ge for Si in Si-As-Te Glass: Effect on Softening Point

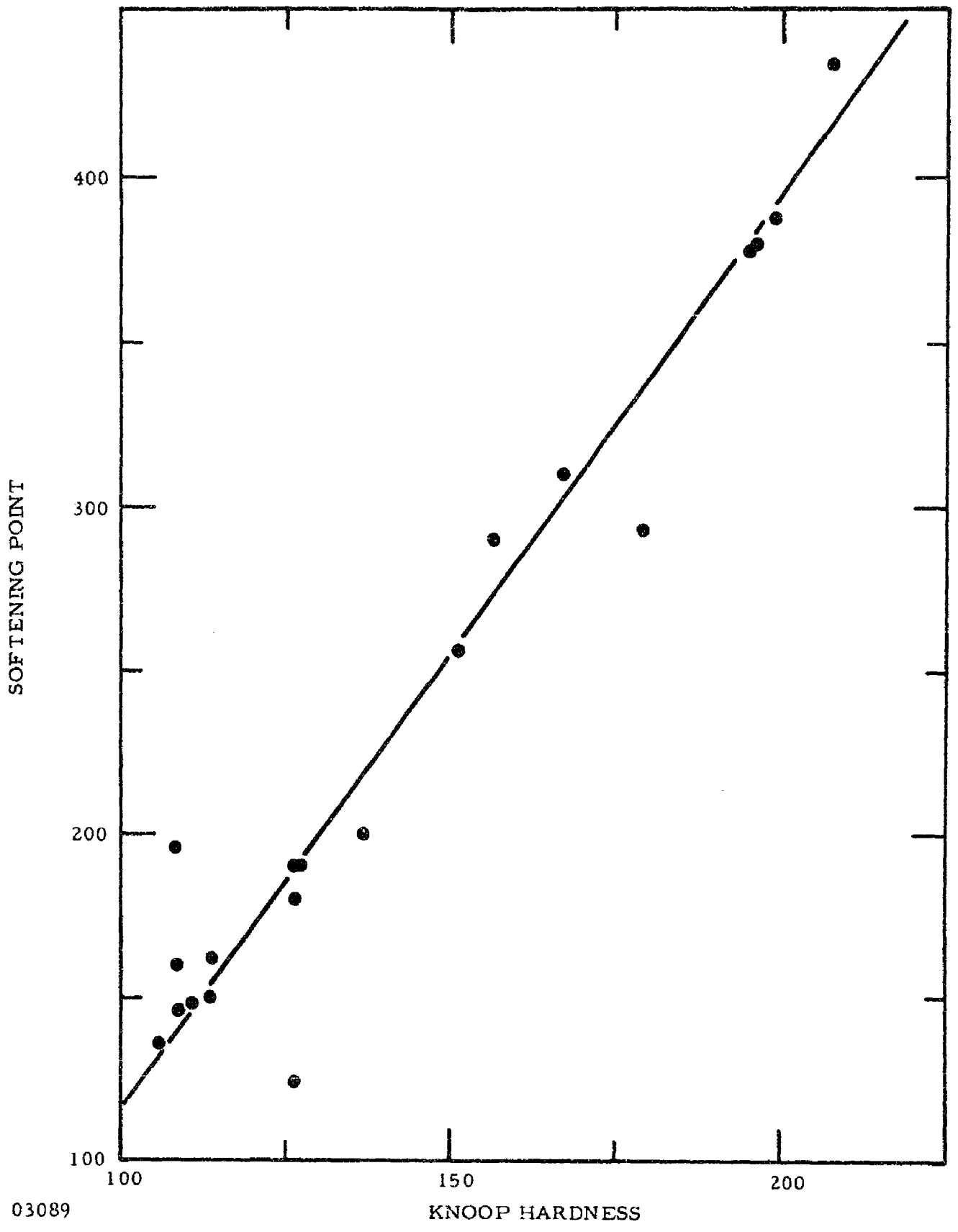

Fig. 6 Substitution of Ge for Si in Si-As-Te Glass:
Correlation between Knoop Hardness and "Soft-Point"

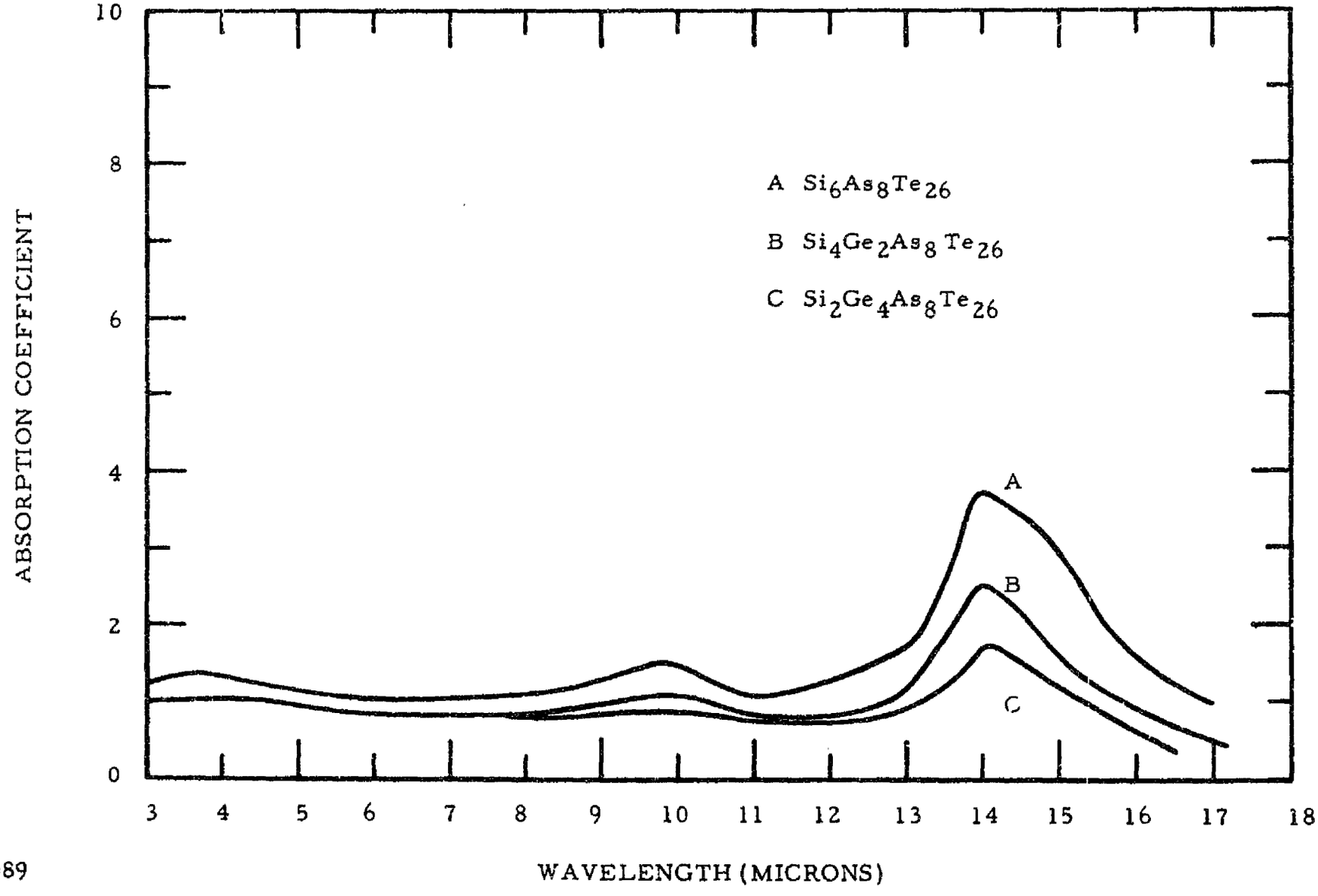

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Fig. 7 Absorption Coefficient of Si-As-Te → Ge-As-Te Glasses

Table V shows the effect on the softening point when Te is replaced with S in the Si-As-Te system. The softening point is not appreciably lowered until sulfur comprises about one-third of the group VIA elements. The refractive index is also lowered, as expected, by the addition of sulfur. The refractive index for $Si_{37}As_{30}Te_{33}$ is 3.12 at 8 μ, while the refractive index for $Si_{37}As_{30}Te_{18}S_{15}$ is 2.76 at the same wavelength. Sulfur also causes a loss in transmission, particularly at 10 microns. A typical plot of infrared transmission versus wavelength is shown in Fig. 8. Replacing only one-tenth of the tellurium with sulfur causes a factor of 4 decrease in transmission at 10 μ. Replacing one-fifth of the tellurium with sulfur causes a loss in transmission by almost a factor of 20.

3. Si-As-Te → Si-As-Se

Table VI shows the effect on the softening point when tellurium is replaced by selenium in the Si-As-Te system. In one family of glasses in which the ratio of tellurium and selenium to the IVA and VA elements was 1 to 1, the softening point increased slightly with an increase in selenium. In another family of glasses the ratio of tellurium and selenium to the IVA and VA elements was 2 to 1, and the softening points decreased slightly. Again, this is an indication of the presence of Te-Te or Te-Se bonds in the group VIA-rich glasses.

Infrared transmission was not adversely affected by addition of selenium. Bands are present at 10, 14 and 20 μ, as shown in Fig. 9.

4. Si-As-Te → Si-P-Te → Si-Sb-Te

Substituting phosphorus for arsenic caused the silicon to remain unreacted. The base glass, $Si_{15}As_{15}Te_{60}$, and the corresponding Si-P-Te glass were comparable and should have formed an amorphous material. This blend will be studied further to determine the reason for the unreacted silicon. Antimony substituted for arsenic in the Si-As-Te system produced little change in softening point and infrared transmission.

Results of these two systems are shown in Table VII.

TABLE V

The Si-As-Te → Si-As-S System

Sample No.	Composition	Softening Point (°C)
312	$Si_{37}As_{30}Te_{33}$	474
313	$Si_{37}As_{30}Te_{30}S_3$	478
314	$Si_{37}As_{30}Te_{27}S_6$	510
315	$Si_{37}As_{30}Te_{24}S_9$	480
316	$Si_{37}As_{30}Te_{21}S_{12}$	334
317	$Si_{37}As_{30}Te_{18}S_{15}$	294
318	$Si_{37}As_{30}Te_{15}S_{18}$	Reacts with the atmosphere
296	$Si_5As_5Te_{10}$	317
297	$Si_5As_5Te_9S$	300
298	$Si_5As_5Te_8S_2$	276
299	$Si_5As_5Te_7S_3$	Reactive
302	$Si_5As_5Te_6S_4$	170
303	$Si_5As_5Te_5S_5$	140
306	$Si_5As_5Te_4S_6$	198
307	$Si_5As_5Te_3S_7$	Reacts with the atmosphere

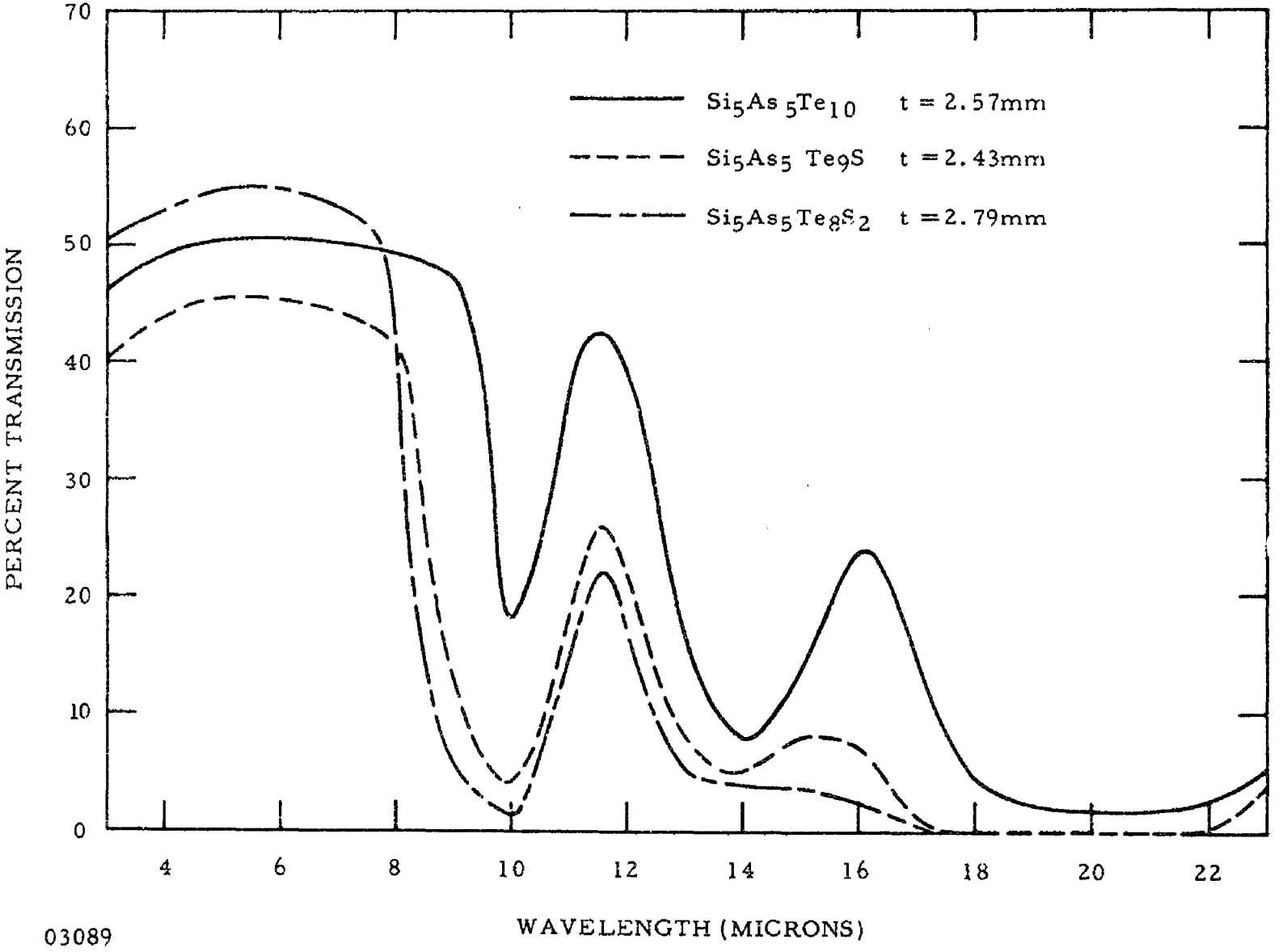

Fig. 8 Infrared Transmission of Si-As-Te – Si-As-S Glasses

TABLE VI

The Si-As-Te → Si-As-Se System

Sample No.	Composition	Softening Point (°C)
353	$Si_{25}As_{25}Te_{50}$	314
359	$Si_{25}As_{25}Te_{49.5}Se_{5}$	311
360	$Si_{25}As_{25}Te_{49}Se$	313
361	$Si_{25}As_{25}Te_{48}Se_{2}$	319
354	$Si_{25}As_{25}Te_{47}Se_{3}$	342
355	$Si_{25}As_{25}Te_{44}Se_{6}$	323
356	$Si_{25}As_{25}Te_{41}Se_{9}$	343
357	$Si_{25}As_{25}Te_{38}Se_{12}$	-
358	$Si_{25}As_{25}Te_{35}Se_{15}$	Too reactive, very brittle
362	$Si_{16.7}As_{16.7}Te_{66.6}$	200
363	$Si_{16.7}As_{16.7}Te_{64.6}Se_{2}$	-
364	$Si_{16.7}As_{16.7}Te_{62.6}Se_{4}$	218
365	$Si_{16.7}As_{16.7}Te_{60.6}Se_{6}$	205
366	$Si_{16.7}As_{16.7}Te_{58.6}Se_{8}$	227
367	$Si_{16.7}As_{16.7}Te_{56.6}Se_{10}$	187
368	$Si_{16.7}As_{16.7}Te_{54.6}Se_{12}$	176
369	$Si_{16.7}As_{16.7}Te_{52.6}Se_{14}$	165
370	$Si_{16.7}As_{16.7}Te_{50.6}Se_{16}$	Too reactive

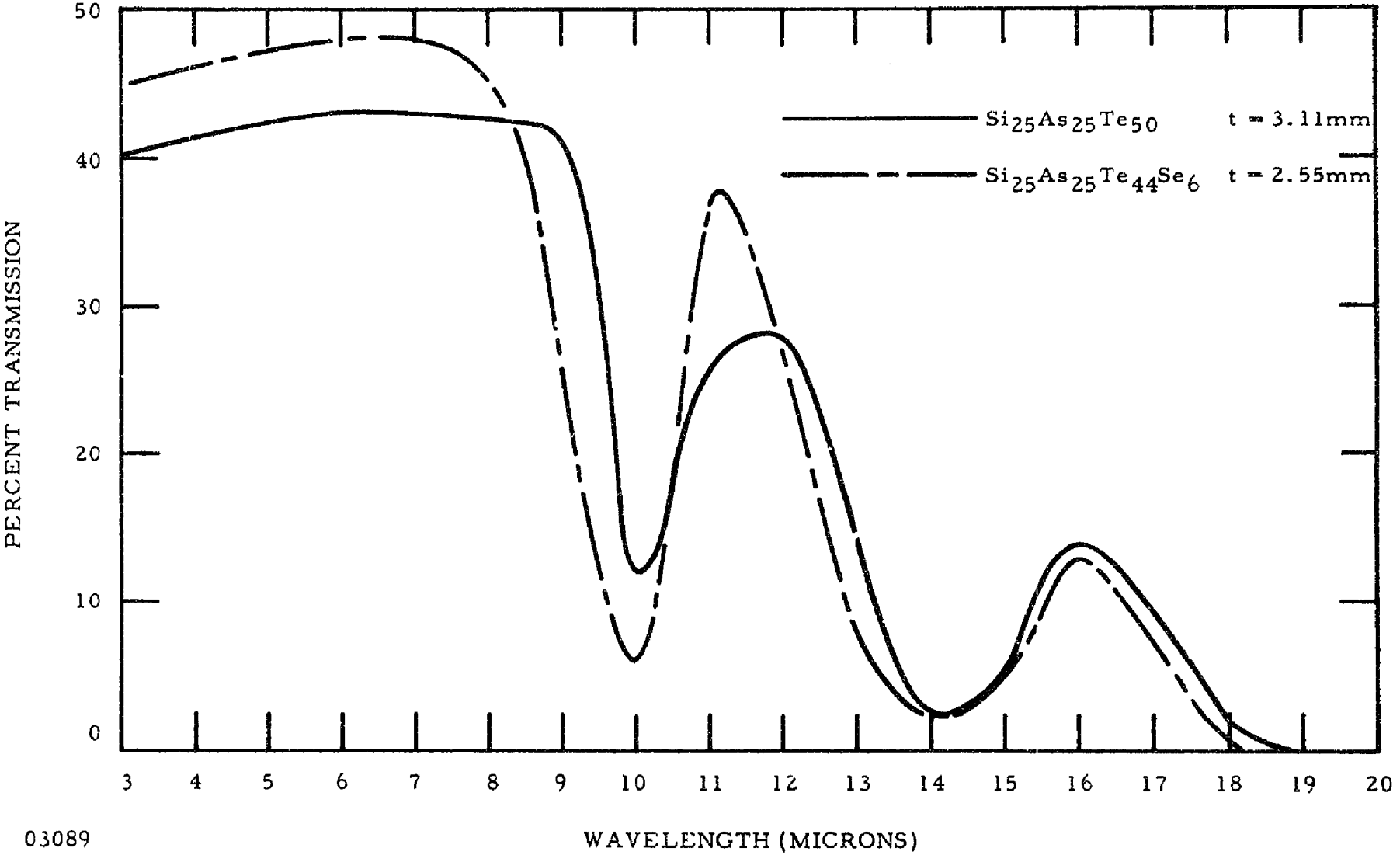

Fig. 9 Infrared Transmission of Si-As-Te and Si-As-Te-S Glass

TABLE VII

The Si-As-Te → Si-Sb-Te and Si-As-Te → Si-P-Te Systems

Sample No.	Composition	Softening Point (°C)
278	$Si_{14}As_{10}Te_{24}$	341
279	$Si_{14}As_{9}SbTe_{24}$	331
283	$Si_{14}As_{8}Sb_{2}Te_{24}$	334
284	$Si_{14}As_{9}Sb_{3}Te_{24}$	Crystalline
276	$Si_{10}As_{10}Te_{20}$	315
277	$Si_{10}As_{9}SbTe_{20}$	315
280	$Si_{10}As_{8}Sb_{2}Te_{20}$	301
281	$Si_{10}As_{7}Sb_{3}Te_{20}$	300
282	$Si_{10}As_{6}Sb_{4}Te_{20}$	Crystalline
347	$Si_{15}As_{25}Te_{60}$	203
348	$Si_{15}As_{23}P_{2}Te_{60}$	Silicon did not react
349	$Si_{15}As_{21}P_{4}Te_{60}$	Silicon did not react
350	$Si_{15}As_{19}P_{6}Te_{60}$	Silicon did not react
351	$Si_{15}As_{17}P_{8}Te_{60}$	Silicon did not react

5. Ge-As-Te → Ge-As-S

When tellurium is replaced by sulfur in the Ge-As-Te system, the softening point increases with an increase in sulfur content, as shown in Table VIII. This effect is large, since the ratio of VIA elements to IVA and VA elements is only 0.67, indicating the absence of Te-Te or Te-S bonds. Absorption at 13 microns is increased by addition of sulfur, and the refractive index is lowered. $Ge_4As_{20}Te_{16}$ has a refractive index of 3.57 at 8 μ, and $Ge_4As_{20}Te_{10}S_6$ has 3.12 at the same wavelength. A typical plot of infrared transmission versus wavelength for these two glasses is shown in Fig. 10.

6. Ge-As-Te → Ge-As-Se

Table IX shows the effect on the softening point of substituting selenium for tellurium in the Ge-As-Te system. In one family of glass, $Ge_{15}As_{15}Te_{70}$, where the group VIA element comprises 70% (atomic) of the composition, the softening point is not significantly affected by this substitution. However, when the group VIA element comprises only 40% (atomic), as in $Ge_{15}As_{45}Te_{40}$, the softening point is substantially increased.

Figure 11 shows change in refractive index as a function of composition for a $Ge_{15}As_{15}Te_{70-x}Se_x$ glass. The refractive index is found to change linearly from ~ 3.5 at 8 μ for $Ge_{15}As_{15}Te_{70}$ to 2.9 at 8 μ for $Ge_{15}As_{15}Te_{20}Se_{50}$. A typical plot of infrared transmission as a function of wavelength is shown in Fig. 12. The band at 13 μ is reportedly caused by an impurity.[9]

TABLE VIII

The Ge-As-Te → Ge-As-S System

Sample No.	Composition	Softening Point (°C)
308	$Ge_4As_{20}Te_{16}$	215
309	$Ge_4As_{20}Te_{14}S_2$	223
310	$Ge_4As_{20}Te_{12}S_4$	236
311	$Ge_4As_{20}Te_{10}S_6$	251
318	$Ge_4As_{20}Te_8S_8$	229
319	$Ge_4As_{20}Te_6S_{10}$	280
340	$Ge_4As_{20}Te_4S_{12}$	285
341	$Ge_4As_{20}Te_2S_{14}$	278
342	$Ge_4As_{20}S_{16}$	260

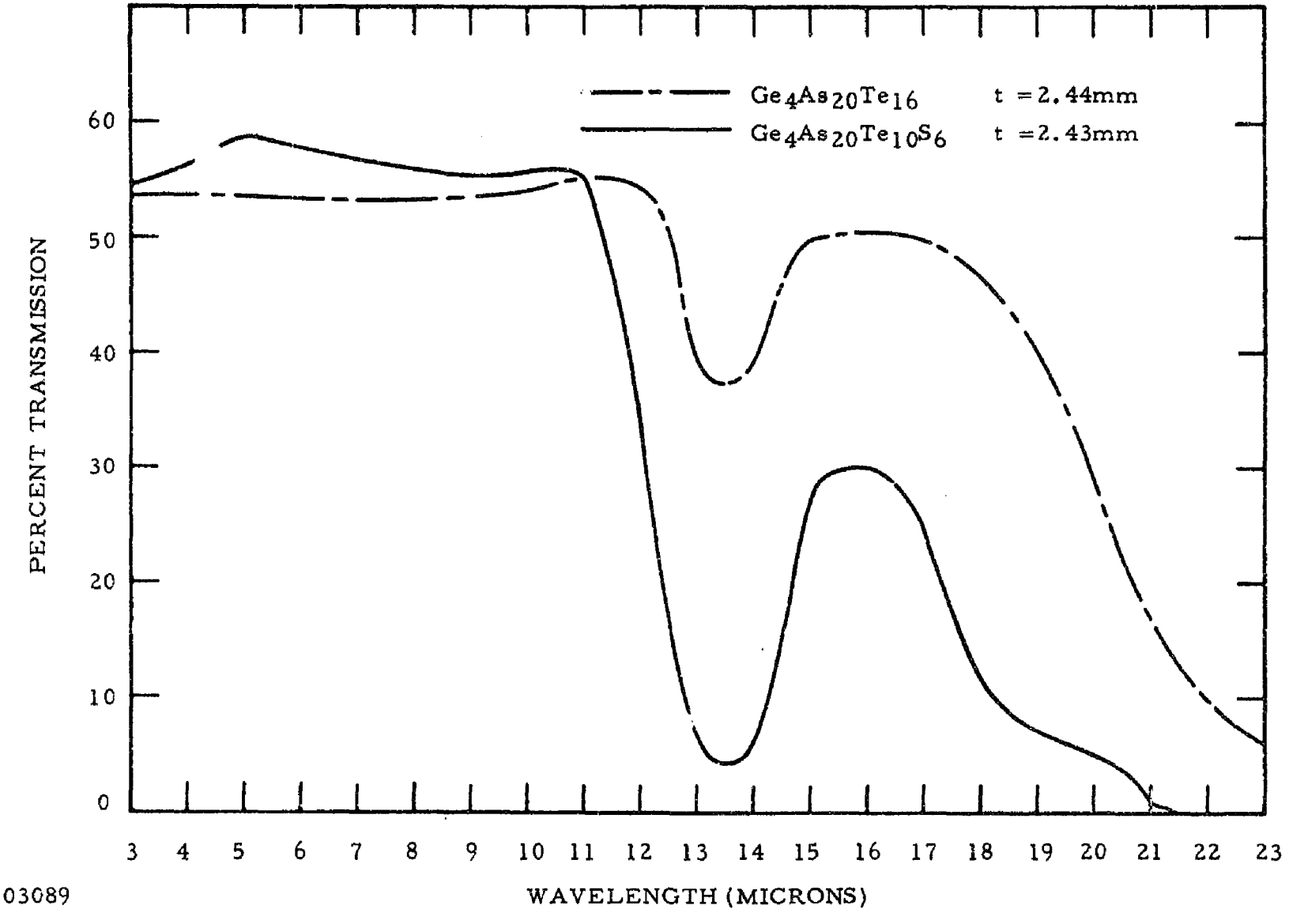

Fig. 10 Infrared Transmission of Ge-As-Te and Ge-As-Te-S Glass

TABLE IX

The Ge-As-Te → Ge-As-Se System

Sample No.	Composition	Softening Point (°C)
320	$Ge_{15}As_{15}Te_{70}$	160
321	$Ge_{15}As_{15}Te_{65}Se_{5}$	194
322	$Ge_{15}As_{15}Te_{60}Se_{10}$	192
323	$Ge_{15}As_{15}Te_{55}Se_{15}$	174
328	$Ge_{15}As_{15}Te_{50}Se_{20}$	192
329	$Ge_{15}As_{15}Te_{45}Se_{25}$	184
330	$Ge_{15}As_{15}Te_{40}Se_{30}$	182
331	$Ge_{15}As_{15}Te_{35}Se_{35}$	210
336	$Ge_{15}As_{15}Te_{30}Se_{40}$	202
337	$Ge_{15}As_{15}Te_{25}Se_{45}$	210
338	$Ge_{15}As_{15}Te_{20}Se_{50}$	206
339	$Ge_{15}As_{15}Te_{15}Se_{55}$	222
344	$Ge_{15}As_{15}Te_{10}Se_{60}$	240
324	$Ge_{15}As_{45}Te_{40}$	247
325	$Ge_{15}As_{45}Te_{35}Se_{5}$	259
326	$Ge_{15}As_{45}Te_{30}Se_{10}$	266
327	$Ge_{15}As_{45}Te_{25}Se_{15}$	283
332	$Ge_{15}As_{45}Te_{20}Se_{20}$	308
333	$Ge_{15}As_{45}Te_{15}Se_{25}$	317
334	$Ge_{15}As_{45}Te_{10}Se_{30}$	322
335	$Ge_{15}As_{45}Te_{5}Se_{35}$	315
343	$Ge_{15}As_{45}TeSe_{40}$	355

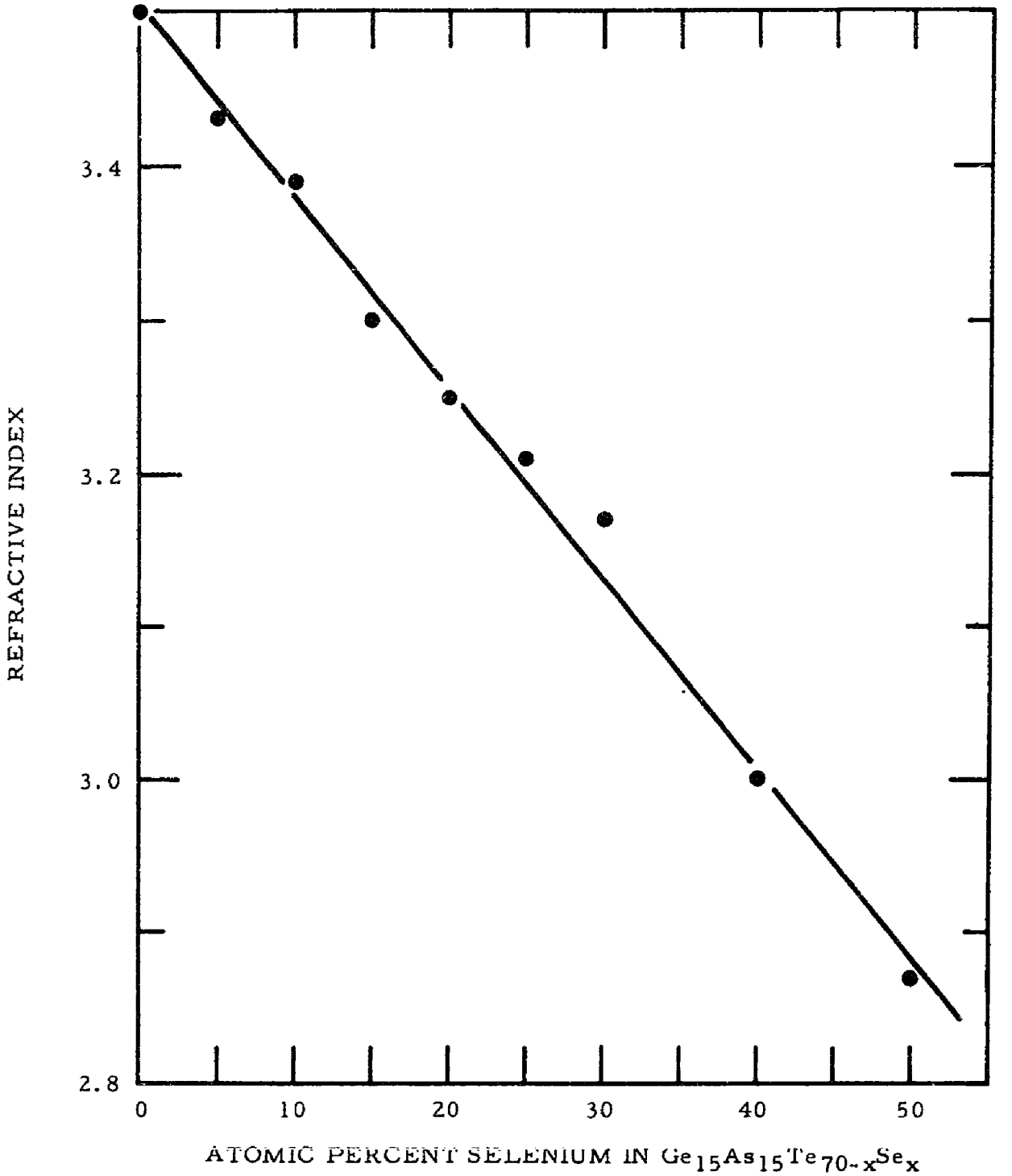

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Fig. 11 Refractive Index for the $Ge_{15}As_{15}Te_{70} \rightarrow Ge_{15}As_{15}Te_{20}Se_{50}$ System

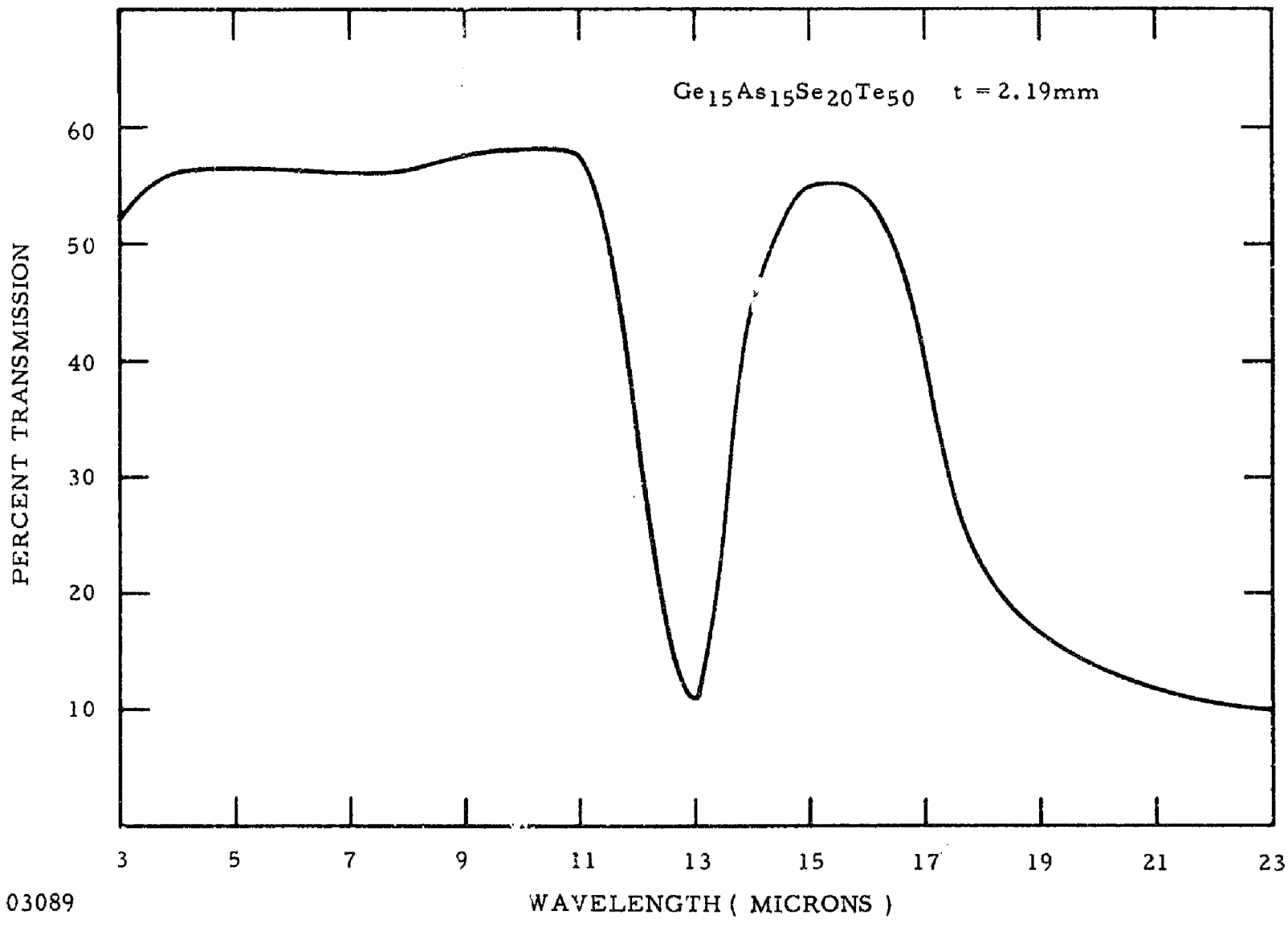

Fig. 12 Infrared Transmission of $Ge_{15}As_{15}Se_{20}Te_{50}$

IV. CONCLUSIONS

1. The Ge-P-Te system produces a glass with good optical properties. Good infrared transmission is obtained out to 20 microns. However, the glass-forming region is the smallest of all the systems studied, and the glasses have moderately low softening points. This glass would be excellent for low temperature applications.

2. The Sn-VA-VIA system does not have good glass-forming characteristics, and the two glasses obtained were essentially tin-modified selenium glasses.

3. The optical properties of Si-As-Te glasses are enhanced by replacing some of the silicon with germanium. Softening point and hardness are not drastically changed.

4. Sulfur does not appear to be a desirable constituent in either the Si-As-Te or Ge-As-Te based glasses because of an increase in the absorption coefficient at 10 and 14 microns.

5. Optical and physical properties of a glass composed of essentially a chalcogenide are not greatly affected by substituting one group IVA or VA element for another. However, if the chalcogenide is not present as the dominant element, the effects can be great.

V. FUTURE WORK

1. The Si-As-Te, Ge-As-Te, Ge-P-Te, and Ge-S glasses are the most promising optical materials. Slight absorption bands are found in the Ge-S and Si-As-Te glasses. Work carried out in this laboratory pouring molten glasses from open containers and results obtained by Jerger[9] indicate that some of these absorptions result from volatile impurities. Several samples will be placed in a Knudsen cell, heated to a molten state, and the volatile components identified using a Bendix time-of-flight mass spectrometer.

Another approach to resolving the identity of the absorption bands will be an ultra-purification of the starting materials. Both emission and mass spectrographic techniques will be used to identify impurities in the starting material.

2. Several compositions from the most promising systems will be selected and attempts made to cast prisms of the material. If these attempts are successful, accurate refractive index measurements will be carried out to permit precise calculation of the absorption coefficient. Other pertinent physical properties will be carefully measured.

3. Studies will be made to determine the cause for the unreacted silicon in the Si-As-Te → Si-P-Te system.

4. We will study the effect on the softening point and refractive index when sulfur is substituted for tellurium in a system comprising a high ratio of chalcogenide to Ge and As in the Ge-As-Te → Ge-As-S system.

REFERENCES

1. "First Annual Technical Summary Report for New High Temperature Infrared Transmitting Glasses," Contract Nonr 3810(00), Texas Instruments Incorporated, Report No. 08-63-50, May 1963.

2. "First Quarterly Technical Report for New High Temperature Infrared Transmitting Glasses," Contract Nonr 3810(00), Texas Instruments Incorporated, August, 1962.

3. "Second Quarterly Technical Report for New High Temperature Infrared Transmitting Glasses," Contract Nonr 3810(00), Texas Instruments Incorporated, October 1962.

4. "First Semiannual Technical Summary Report for New High Temperature Infrared Transmitting Glasses," Contract Nonr 3810(00), Texas Instruments Incorporated, November 1962.

5. "Third Quarterly Technical Report for New High Temperature Infrared Transmitting Glasses," Contract Nonr 3810(00), Texas Instruments Incorporated, January 1963.

6. "Fourth Quarterly Technical Report for New High Temperature Infrared Transmitting Glasses," Contract Nonr 3810(00). Texas Instruments Incorporated, Report No. 08-63-38, April 1963.

7. "Fifth Quarterly Technical Report for New High Temperature Infrared Transmitting Glasses," Contract Nonr 3810(00), Texas Instruments Incorporated, Report No. 08-63-97, August 1963.

8. "Second Semiannual Technical Summary Report for New High Temperature Infrared Transmitting Glasses," Contract Nonr 3810(00), Texas Instruments Incorporated, Report No. 08-63-167, November 1963.

9. "Semiannual Technical Summary Report, Investigate the Properties of Glasses Transmitting in the 3 to 5 and 8 to 14 Micron Windows," Contract Nonr-4212(00), J. Jerger, Servo Corporation, 31 December 1963.