School of Engineering

VANDERBILT UNIVERSITY

Nashville, Tennessee 37203

THIRD SEMIANNUAL TECHNICAL REPORT

7/1/71 - 12/31/71

Structural Effects on Electrical Properties in Amorphous Semiconductors

School of Engineering
Vanderbilt University
Nashville, Tennessee 37235

D. L. Kinser, Co-Principal Investigator 615-322-2413

L. K. Wilson, Co-Principal Investigator 615-322-2771

Sponsored by

ADVANCED RESEARCH PROJECTS AGENCY

ARPA ORDER: 1562

PROGRAM CODE: 61101D

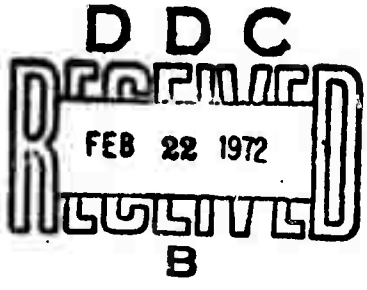
CONTRACT NUMBER: DAHC04-70-C-0046

AMOUNT OF CONTRACT: $88,136.00

EFFECTIVE DATE OF CONTRACT: June 1, 1970

CONTRACT EXPIRES: May 31, 1972

Date Submitted: January 31, 1972



ABSTRACT

During this report period, work has been concentrated on a survey of the structure, electrical and magnetic properties of transition metal oxide-phosphate glasses and glasses in the As_2Te_3-As_2Se_3 system which possess electrical or magnetic device potential. Results of magnetic and electrical observations in several transition metal-phosphate glasses have revealed a high degree of magnetic and structural order. The pronounced influence of glass-glass phase separation and compositional segregation has also been noted.

Examination of a series of FeO-P_2O_5 glasses has revealed a glass forming range which extends to 80 mole % FeO. Susceptibility and Mössbauer spectroscopy results on these glasses are reported herein. Results on a CuO-P_2O_5 glass indicate that the conduction mechanism in this system is partially ionic and thermal treatments can change the ionic mechanism to electronic. These glasses exhibit microstructural features resembling crystals but no crystals have been detected using x-ray techniques.

Detailed studies of the As_2Te_3-As_2Se_3 system has shown switching behavior which can be controlled with compositional variation. The compositional variation of the microstructure is noted in micrographs included in this report.

Statement of Problem

The device potential in amorphous semiconducting materials is a largely unexploited area, despite extensive research in this area. This is the result of a lack of systematic structure-property oriented research in these materials. A fundamental understanding of the structural features of this class of materials will allow rational interpretation and control of relationships between glass preparation variables and important electrical and magnetic properties.

Electronic conduction in amorphous solids has become the subject of interest to a number of theoreticians and has been reviewed by Mott[1,2] Gubanov[3] and numerous others. Virtually all of these works have begun with an assumption that amorphous solids are uniformly random, even though they recognize glasses are generally heterogenous. These theoreticians have developed analytical descriptions of several systems which have been experimentally verified in some cases. Attempts to extend this approach to microscopically heterogenous systems have had notably little success. There remains a considerable body of experimental results, including Hall and Seebeck coefficients, which are not rationalized by present theory.

Pearson[4] has suggested that heterogenous structure in these materials may explain these anomalies if the separated phase is crystalline. It appears that heterogenous transport analysis similar to that of Volger[5] or Bube[6] is required to ascertain the transport behavior in each phase.

Another important anomaly between theory and observation concerns the theoretically predicted insensitivity of amorphous semiconductors to doping. Early experimental observations by Kolimets, et. al.,[7] conformed to the theoretical predictions, but recent work by Mackenzie[8] clearly conflicts with the theory and the early work. It appears that the above anomalies are the result

of inadequate structural characterization, rather than fundamental theoretical problems.

Further evidence that structrual heterogenities lie at the root of these anomalies can be inferred from work by Kinser, et al.,[9] in K_2O-P_2O_5-V_2O_5 glasses. This work has shown that marked changes in dielectric behavior occur during thermal treatments customarily used to stress relieve glasses. These changes have been shown to be the result of structural changes involving precipitation of small amounts of crystals.

Wilson and Kinser[10] have observed similar, but somewhat more complex, behavior in FeO-P_2O_5 glasses after thermal treatments corresponding to annealing. Electron spin resonance (ESR) results have shown the onset of structural changes during thermal treatment prior to their observation by other commonly employed techniques.[11]

It is thus apparent that homogenous glasses, semiconducting or otherwise, are the exception rather than the rule.

General Methodology

The electrical and magnetic property changes accompanying structural modifications during glass processing are of prime interest in the present work. The above questions can only be answered with detailed structural characterization of representative glasses from the oxide and chalcogenide groups. The initial oxide glass examined was the 55FeO-45P_2O_5 glass along with glasses from the V_2O_5-P_2O_5, CuO-P_2O_5, TiO_2-P_2O_5 and MnO-P_2O_5 systems. The initial chalcogenide glasses are from the As_2Te_3-As_2Se_3 system with Ag-As-s glasses in preliminary stages of study.

Structural characterization of these systems is being accomplished using electron microscopy, Guinier-DeWolff x-ray, electron spin resonance spectroscopy, magnetic susceptibility, electron microprobe, dielectric

relaxation, Mössbauer spectroscopy and differential thermal analysis techniques.

In conjunction with the structural tools, it is necessary that the conductivity, switching behavior and Seebeck coefficient be monitored to allow direct structure-property correlations.

Transition-Metal Phosphate Glasses

Experimental results during this report period have justified our previous assumption[12] that the interactions between ions in the amorphous metals oxide-phosphates are similar to those in crystalline oxide containing the same ions. Such interactions are principally negative superexchanges. Interesting magnetic observations have led to the conclusion that the magnetic susceptibility is a result of both interacting and non-interacting (partially isolated) ions. Such an assumption can be used to explain the unique downward curvatures of the reciprocal magnetic susceptibility versus temperature curves at low temperatures.

Iron-oxide-phosphate

Previously published data on the iron-oxide phosphate glass system has been restricted to 55 mole% FeO-45 mole% P_2O_5. Recently a glass forming study of the FeO-P_2O_5 system has shown that the glass forming range extends to 80 mole% FeO when the glasses are melted in an oxidizing atmosphere. Glasses above 80 mole% FeO spontaneously crystallized to α-Fe_2O_3 while intentionally devitrified glasses of compositions below 80% crystallized to $FePO_4$.

The reciprocal magnetic susceptibility versus temperature curves for four representative glasses are shown in Figure 1. These data indicate that all the glasses antiferromagnetically coupled and the magnetic interactions are attributable to negative superexchange. The downward curvature of the

curves are a direct consequence of the amorphous nature of the glasses.[13] The matrix of interacting ions is responsible for the negative Curie temperature associated with the linear high temperature relation. Isolated ions contribute increasingly to the total susceptibility at low temperatures and, hence, cause the downward curvature of the reciprocal susceptbility. The existence of "isolated" ferric ions in the 55 mole% glass has previously been reported.[14] Analyses of these data are continuing.

The ratio of the Curie temperature, Θ, to the temperature at which the reciprocal susceptibility appears to curve downward, T', gives an important contact between experimental results and theory. The fraction of interacting ions can be uniquely determined from experimentally observed values of Θ/T' since these have been shown to be essentially independent of the coordination number of the ions in an amorphous matrix.[15] At present susceptibility data is incomplete and exact values of T' have not been obtained. It is anticipated that a thesis containing a theoretical analysis of these glasses will be completed in the next report period.

It should be noted that no pronounced Néel temperature is observed in the susceptibility data for the iron glasses. Electron spin resonance data previously reported does indicate distinct onset of antiferromagnetic ordering however, these data clearly distinguish between Fe^{2+}-Fe^{2+}, Fe^{2+}-Fe^{3+}, and Fe^{3+}-Fe^{3+} coupling. The bulk susceptibility of the iron phosphate glasses is therefore not related to one specific crystalline phase but to possibly three. The principal value of the susceptibility data for these glasses clearly seems to be as another method to determine the numberof interacting ions.

Mössbauer effect spectroscopy of the 55 mole% FeO glass at 77^{o} and $300^{o}K$ has revealed that the interacting Fe^{2+} and Fe^{3+} ions are on octahedral sites. In addition, the Fe^{3+}/Fe^{TOT} ratio for this glass and for intentionally reduced

glasses are in good agreement with previously reported ESR data.[14] Figures 3, 4, and 5 show the spectra at 300°K for these glasses with known Fe^{3+} concentration. A spectrum is composed of two doublets, one from Fe^{3+} ions and one from the Fe^{2+}. The "stick diagram" below the actual spectrum is a computer analysis of the experimental data. The ratio of height of the integrated intensity line represents the Fe^{3+}/Fe^{TOT} ratio.

Figures 6, 7, and 8 are the spectral parameters of the 55 mole% FeO glass as a function of Fe^{3+}/Fe^{TOT}. An analysis of these data is currently being conducted and will be included in a M.S. thesis to be published during the next report period.[16]

Manganese-oxide phosphate

A study of the structural and magnetic properties of the manganese-phosphate glass system is currently in progress. As indicated in a preliminary study, the magnetic behavior of a phase separated 55-45 mole% MnO_2-P_2O_5 glass appears to be a superposition of the magnetic behavior of the phosphate-rich phase, which contains isolated, paramagnetic manganese ions, and the magnetic behavior of the manganese-rich phase, which contains exchange-coupled manganese ions. The magnetic behavior of the latter phase is remarkably similar to that of crystalline MnO.

In order to further investigate the interrelationship of composition, microstructure, and magnetic behavior, glasses over the range x MnO_2-(1-x) P_2O_5 with x = 20, 30, 40, 50, 55, and 60 have poured. The limit of the glass forming region of the manganese-phosphate system has been determined to be at x = 60; beyond this the melt spontaneously crystallizes into $Mn_2P_2O_7$. Crystalline $Mn_2P_2O_7$, was identified by vacuum Guinier-DeWolff x-ray techniques in glasses with x = 55 and x = 60.

At present, the low temperature magnetic susceptibility of the as-cast

gl ss melts is being investigated using a permeability bridge[17] and a nitrogen gas flow system. The bridge will be adapted for use with a hydrogen cryotip so that the magnetic susceptibility down to 20°K can be measured. It is anticipated that the results of these studies and variable temperature electron spin resonance studies on the as-cast samples will establish a relationship between the composition and magnetic behavior of the manganese-phosphate glass system. Further studies on heat treated samples will be conducted and a correlation between the magnetic behavior as observed in susceptibility and electron spin resonance experiments and the microstructure as determined by replication electron microscopy will be established.

Copper Oxide-Phosphate

Since the last report, attempts have been made to further characterize microstructural and electrical features of the $CuO-P_2O_5$ system. A glass of 55% CuO-45% P_2O_5 nominal composition was used in this investigation. D.C. electrical resistivity vs. time for varying applied potentials was studied using glasses of varying Cu^{2+}/Cu^{TOT} ratios and thermal histories. Direct replication techniques were used to study microstructural features of freshly fractured surfaces etched in 10% HCl for varying lengths of time.

As mentioned in the last report, high activation energies in the range of 0.80 to 1.0 ev/atom were observed for glasses of the same nominal composition as that used in this experiment, although Cu^{2+}/Cu^{TOT} ratios differed. These activation energies were higher than those observed for the $FeO-P_2O_5$ glasses (approximately 0.5 ev/atom). This fact, coupled with an observation of ionic conduction in a 50% CuO-50% P_2O_5 glass by Hansen,[18] led to suspicion of a more complex conduction mechanism than originally suspected, although Hansen's activation energies of conduction were higher (in the range of 1.4 ev/atom). Activation energies for electronic conduction in the same range as

our $CuO-P_2O_5$ glasses have been reported for other glass forming systems by Mackenzie.[8] To date, no significant time dependence of conduction has been observed for our specimens. Further experiments utilizing non-blocking electrodes and electromotive force measurements are being performed in order to further characterize the charge carrier. It should be pointed out that electronic conduction has been observed in a $CuO-CaO-P_2O_5$ glass.[19] It is felt on the basis of this evidence that the conduction mechanism changes from ionic to electronic depending upon thermal history of the specimens and the amount of glass former (i.e., CaO, Na_2O, etc.) added to the melt. The glass former constricts the structure, thereby decreasing considerably the mobility of the cations.

$As_2Te_3-As_2Se_3$ Glasses

Electrical: The bulk D.C. conductivity data for the $40As_2Te_3:60As_2Se_3$ to $80As_2Te_3:20As_2Se_3$ glasses are plotted in Figure 9 as log σ vs. 1/T. The activation energies derived from these plots are listed in Table 1. These data agree within experimental error with those of Roilos[20] but not with the Kolomiets[7] data.

Room temperature A.C. measurements from 0.2 kc to 2000 kc were taken on the series of glasses. Plots of tan δ vs. frequency show no dispersions, indicating that conditions for Maxwell-Wagner-Sillars heterogenous losses are not present in these glasses.

Behavior of both the D.C. conductivity and the tan δ factor of heat treated glasses should prove informative and this work is to be undertaken during the next report period.

Structural: Replica electron microscopy on the chalcogenides indicates that all the glasses studied are heterogenous and, thus their structure is sensi-

tive to thermal history.

An electron micrograph of a fresh fracture surface of arsenic triselinide, Figure 10, clearly shows the characteristic droplike structure of liquid-liquid phase separation. This phase separation in As_2Se_3 was surprising and, to our knowledge, has not been previously noted in the literature although this glass has been previously examined.

The other glass compositions examined also exhibit evidence of phase separation. This is evident with compositional changes and within different samples of the same composition. This is evidenced by the series of micrographs in Figures 11 through 15. Figure 11 shows large, well-formed drops, indicating well-separated phases. Figure 12 shows the glass in the beginning of the drop forming process with many small, irregular droplets. The glass in Figure 13 is in an advanced stage of phase separation as indicated by the droplets coalescence. Two coherent phases are shown in Figure 14, suggesting a spinodal process. Figure 15 shows an interesting structure which may be indicative of the formation of secondary segregations in the primary separated phases.

These E.M. studies indicate that these glasses are extremely structure sensitive to thermal history. The variations in droplet formation seen over a cross-section of an individual boule of glass shows that these diffusion controlled phase separation processes are sensitive to cooling rates. The different structures are noticeable between the rapidly cooled middle of the boule. The number and stages of phase separation processes occurring in these glasses conclusively point out the importance of control of melting variables such as maximum temperature, quench rate and subsequent heat treatment.

The variation on the stages of phase separation in the samples studied

makes accurately correlating the amount of phase separation, and therefore the structure, with composition difficult. The trend is to a larger degree of phase separation, i.e., more of the second phase, with increased tellurium content. Electron microscopic studies of glasses which have been heat treated under carefully controlled conditions are needed, and would be complimentary to the necessary electrical studies of heat treated samples.

Thus the next phase of our research on these glasses will be to study heat treated samples of the same composition. A report of these studies will be included in the next semi-annual report.

UHF and Microwave Dielectric Properties

The UHF and microwave dielectric properties of the arsenic-tellurium-selenium glasses have been determined at room temperature. The dielectric constant and loss tangent for a given glass composition were found to be essentially constant of the range 100-18,000 MHz. The dielectric constant varies from approximately 7 to 10 and increased with tellurium content. The loss tangent also increased with tellurium and had a maximum value of approximately 5.5×10^{-2}. The dielectric properties of these glasses compare favorably with those for other commonly used dielectrics for microwave integrated circuits, e.g., Y.I.G. and silicon. A paper on this phase of the program by Pearson, O'Reilly and Wilson is appended to this report.

Recommendations

1. Our principal recommendation is to continue the present program in its present direction to allow the synthesis of each of the results in a unified theory along the lines which are now clear in the chalcogenide system.

2. As in our previous recommendations, we continue to recommend the survey preparation of new glasses. We anticipate that the transition metal oxide-phosphate, silicate, borate and germanate survey presently in progress will be continued.

It is also anticipated that results on a new system Ag-As-S will be most helpful in developing switching models. A detailed ternary phase diagram was recently published (30) and our analyses should be simplified with this as a basis. It is further anticipated that Cu and Au substituted in the above system will be quite informative from an atomistic and microstructural model point of view.

3. The Mössbauer studies should be continued to examine 57 Fe and 127 Te in each of the systems presently under examination using other techniques. This will significantly aid in atomic structure model development in these systems as an addition to the present tools.

4. We recommend that the far infrared "conductivity spectra" be obtained to facilitate in theoretical analysis of the conductivity/loss spectra. This will allow the loss behavior to be explicitly attributed (31) to each mechanism thus reinforcing both atomic and microstructural analyses.

References

1. N. F. Mott, "Conduction in Non-Crystalline Systems I & II," Phil. Mag. 117, 1259-1284 (1968).
2. N. F. Mott and E. A. Davis, Electronic Processes in Non-Crystalline Solids, Oxford, London, 1971.
3. A. Gubanov, "Quantum Theory of Amorphous Semiconductors," Translated by A. Tubylewicz, Consultants Bureau, New York (1965).
4. A. D. Pearson, "The Hall Effect - Seebeck Effect Size Anomaly in Semiconducting Glasses," J. Electrochem. Soc. 111 (6) pp.753-755, (1964).
5. J. Volger, "Note on Hall Potential Across an Inhomogenous Conductor," Phys. Rev. 79, pp.1023-1024 (1950).
6. R. Bube, "Interpretation of Hall and Photo-Hall Effects in Inhomogenous Materials," Appl. Phys. Lett. 13 (4) pp.136-139 (1960).
7. B. N. Kolimets, X. Manontova and T. F. Nazarova, "The Structure of Glass," 11, Consultants Bureau, New York (1960).
8. J. D. Mackenzie, "Electronic Conduction in Non-Crystalline Solids," J. Non-Crystalline Solids 2 pp.16-26 (1970).
9. D. L. Kinser, L. L. Hench and A. E. Clark, "Effect of Heterogenities on the Electrical Behavior of a Semiconducting Glass," to be submitted to Journal of Electrochemical Society.
10. L. K. Wilson and D. L. Kinser, "Structure Dependence of Electrical and Magnetic Properties of Iron-Phosphate Semiconductor Glasses," Proc. Region III IEEE Conference, November, 1969.
11. E. J. Friebele, L. K. Wilson, A. W. Dozier and D. L. Kinser, "Antiferromagnetism in an Oxide Semiconducting Glass," Phys. Stat. Sol. (B) 45, 323- (1971).

References (Continued)

12. L. K. Wilson and D. L. Kinser, Bull. Am. Phys. Soc., Series II, 15, 1371 (1970).

13. A. W. Simpson, Physica Status Solidi, 40, 207 (1970).

14. E. J. Friebele, L. K. Wilson, A. W. Dozier and D. L. Kinser, Physica Status Solidi (B) 45 322 (1971).

15. J. M. Lucas, Ph.D. Thesis, University of Sussex, 1969.

16. H. L. Buchanan, M.S. Thesis, Vanderbilt University, 1972 (to be published).

17. S. T. Sekula, J. Appl. Phys. 42, 16 (1971).

18. K. Hansen, private communication.

19. C. F. Drake, F. F. Scanlan and A. Engel, Physica Status Solidi 32 193 (1969).

20. M. Roilos, "Conductivity and Hall Effect in Vitreous $As_2(Se,Te)_3$," J. of Non-Crystalline Solids 6 (1971) pp. 5-12.

Table 1. Summary of DC conductivity from low field DC results and switching results.

Composition		ΔE(ev)	ΔE(ev)
% As_2Te_3	% As_2Se_3	(low field)	switching analysis
80	20	0.43	0.47
70	30	0.52	0.40
60	40	0.55	0.45
50	50	0.59	0.52
40	60	0.62	—
0	100	0.73	—

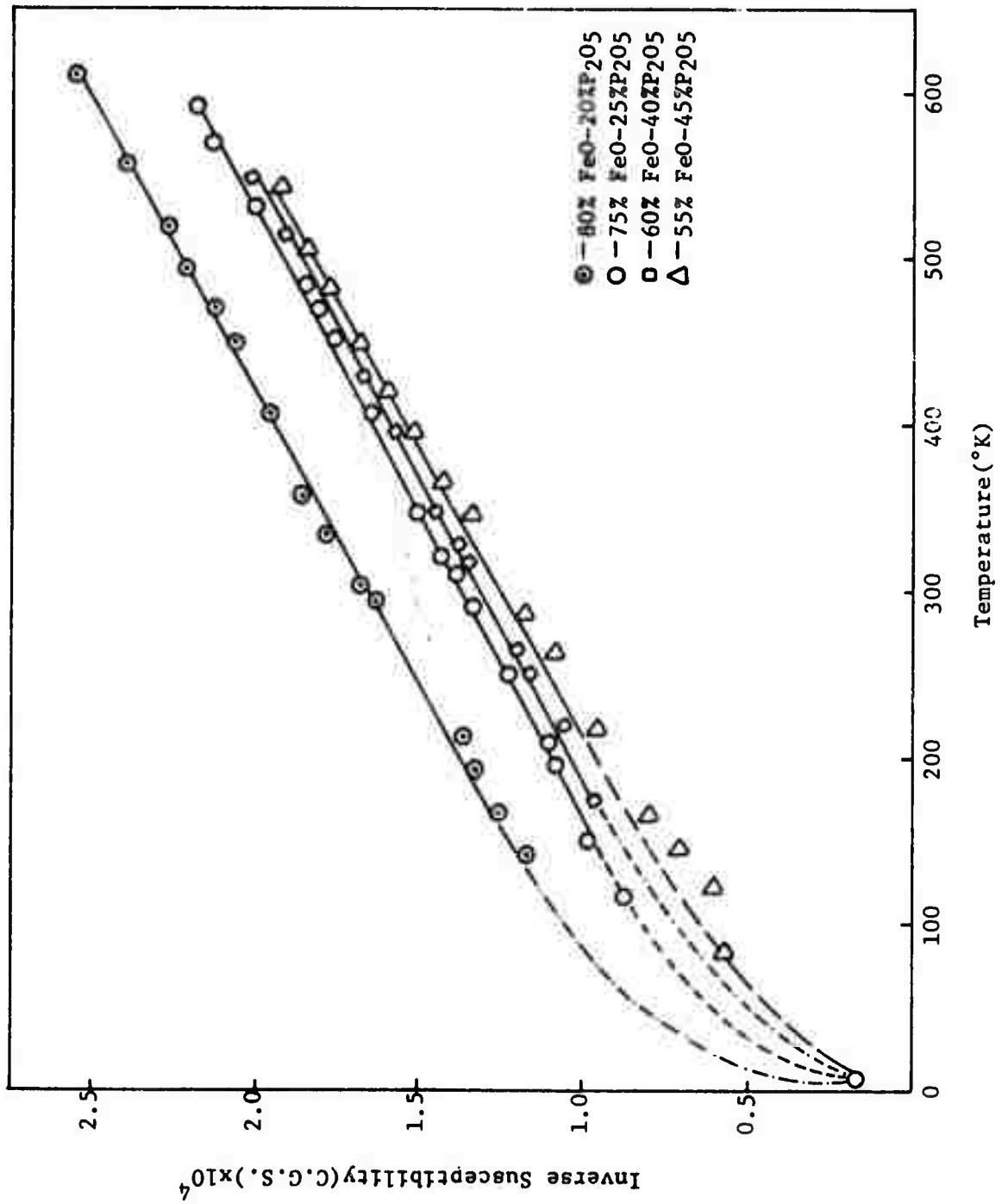

● —60% FeO-40%P2O5
○ —75% FeO-25%P2O5
□ —60% FeO-40%P2O5
△ —55% FeO-45%P2O5
Inverse Susceptibility(C.G.S.)x10⁴
2.5
2.0
1.5
1.0
0.5
0
100
200
300
400
500
600
Temperature(°K)

Figure 1.

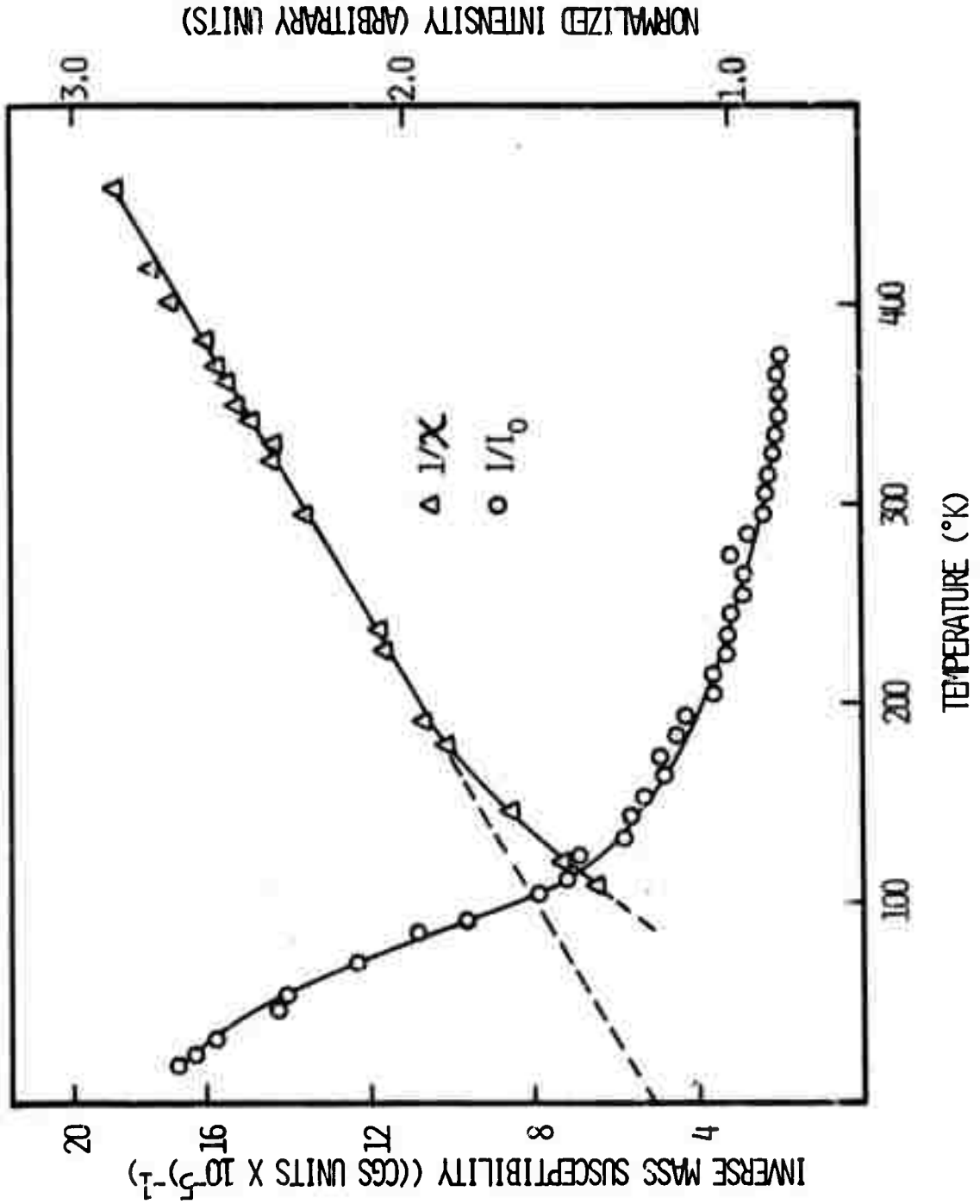

NORMALIZED INTENSITY (ARBITRARY UNITS)
3.0
2.0
1.0
INVERSE MASS SUSCEPTIBILITY ((CGS UNITS X 10^{-5})$^{-1}$)
20
16
12
8
4
100
200
300
400
TEMPERATURE (°K)
Δ 1/χ
o I/I_o

Figure 2.

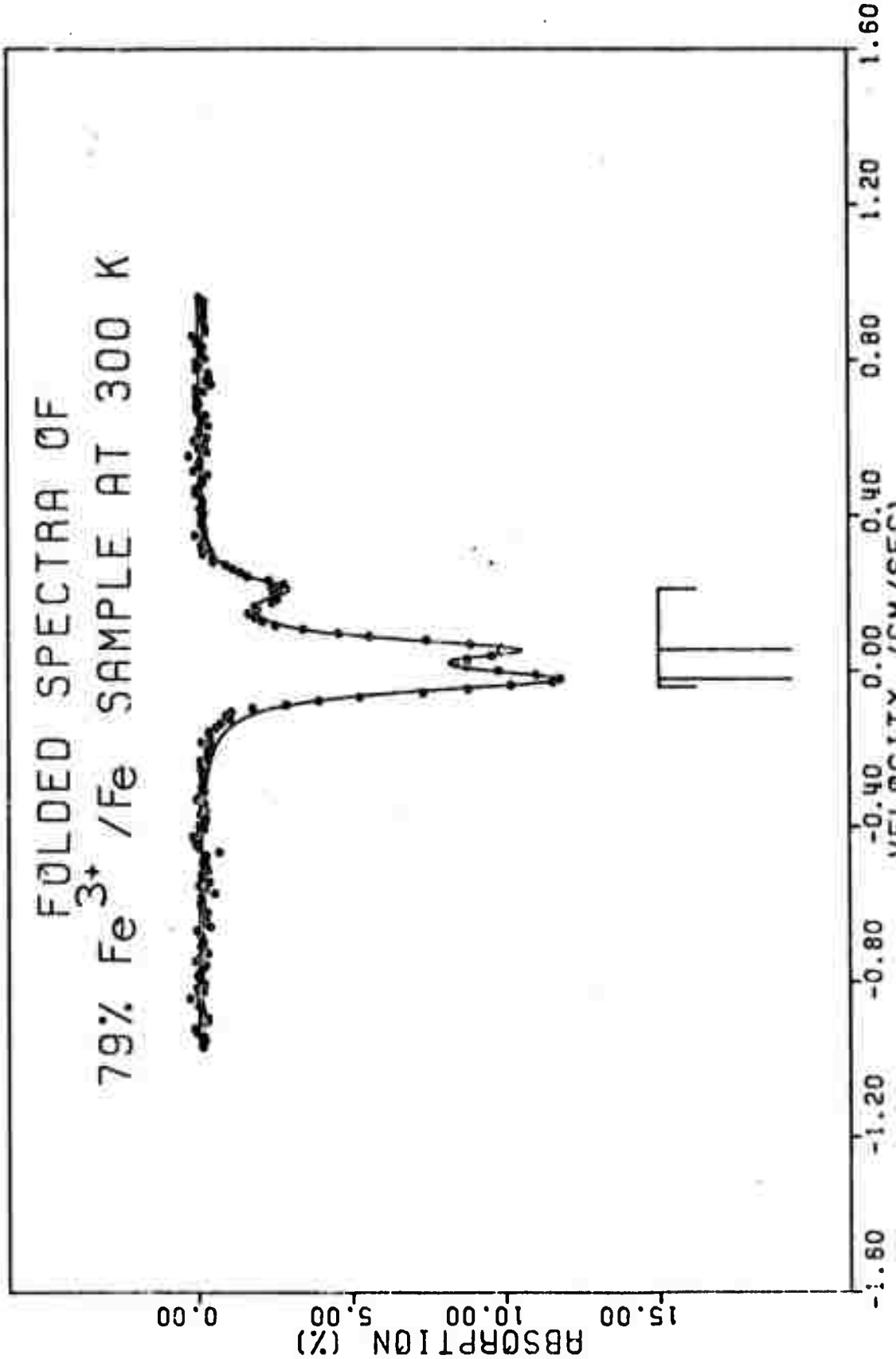

FOLDED SPECTRA OF
79% Fe^{3+} /Fe SAMPLE AT 300 K
ABSORPTION (%)
0.00
5.00
10.00
15.00
VELOCITY (CM/SEC)
-1.60
-1.20
-0.80
-0.40
0.00
0.40
0.80
1.20
1.60

Figure 3.

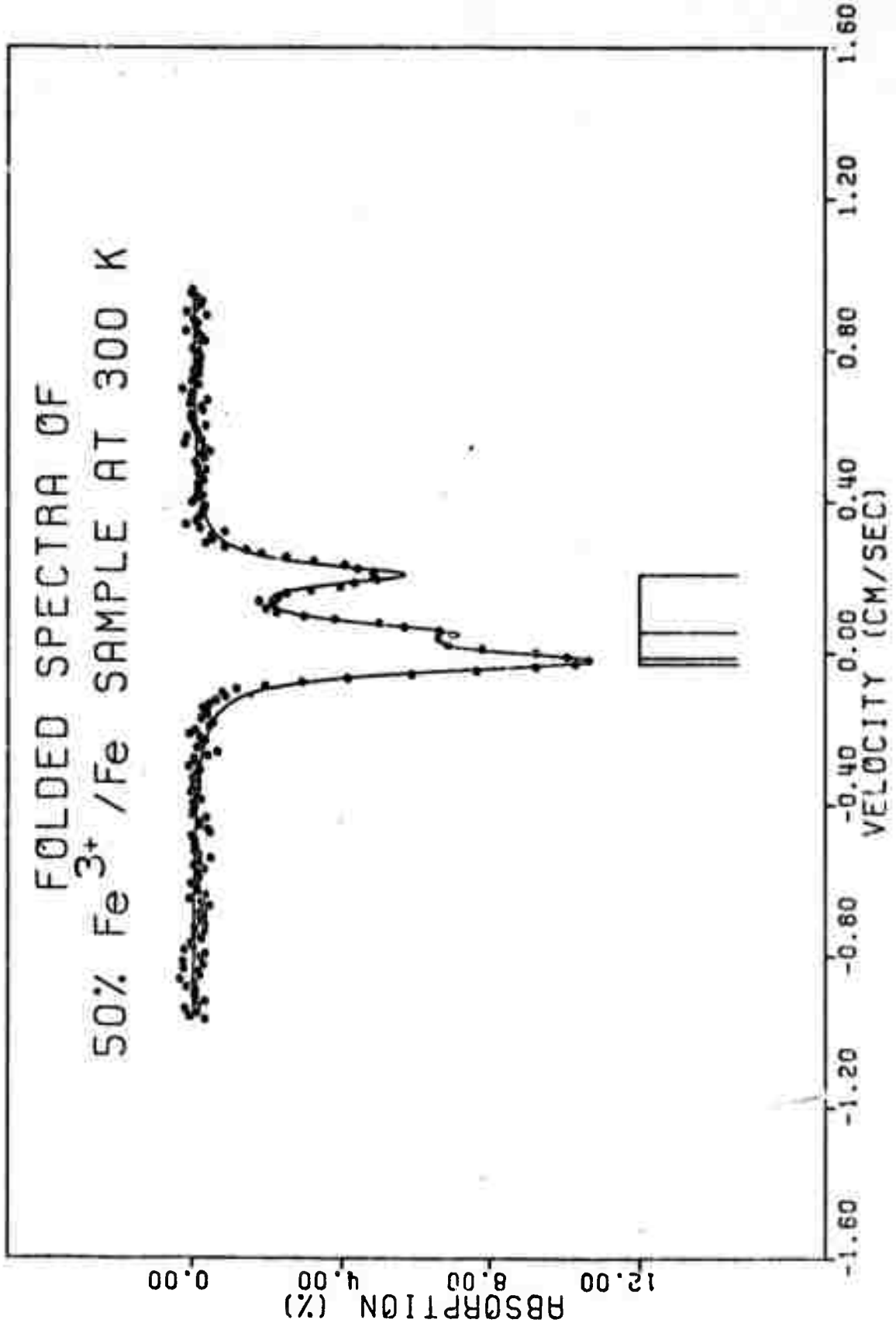

FOLDED SPECTRA OF
50% Fe3+ /Fe SAMPLE AT 300 K
ABSORPTION (%)
0.00
4.00
8.00
12.00
VELOCITY (CM/SEC)
-1.60
-1.20
-0.80
-0.40
0.00
0.40
0.80
1.20
1.60

Figure 4.

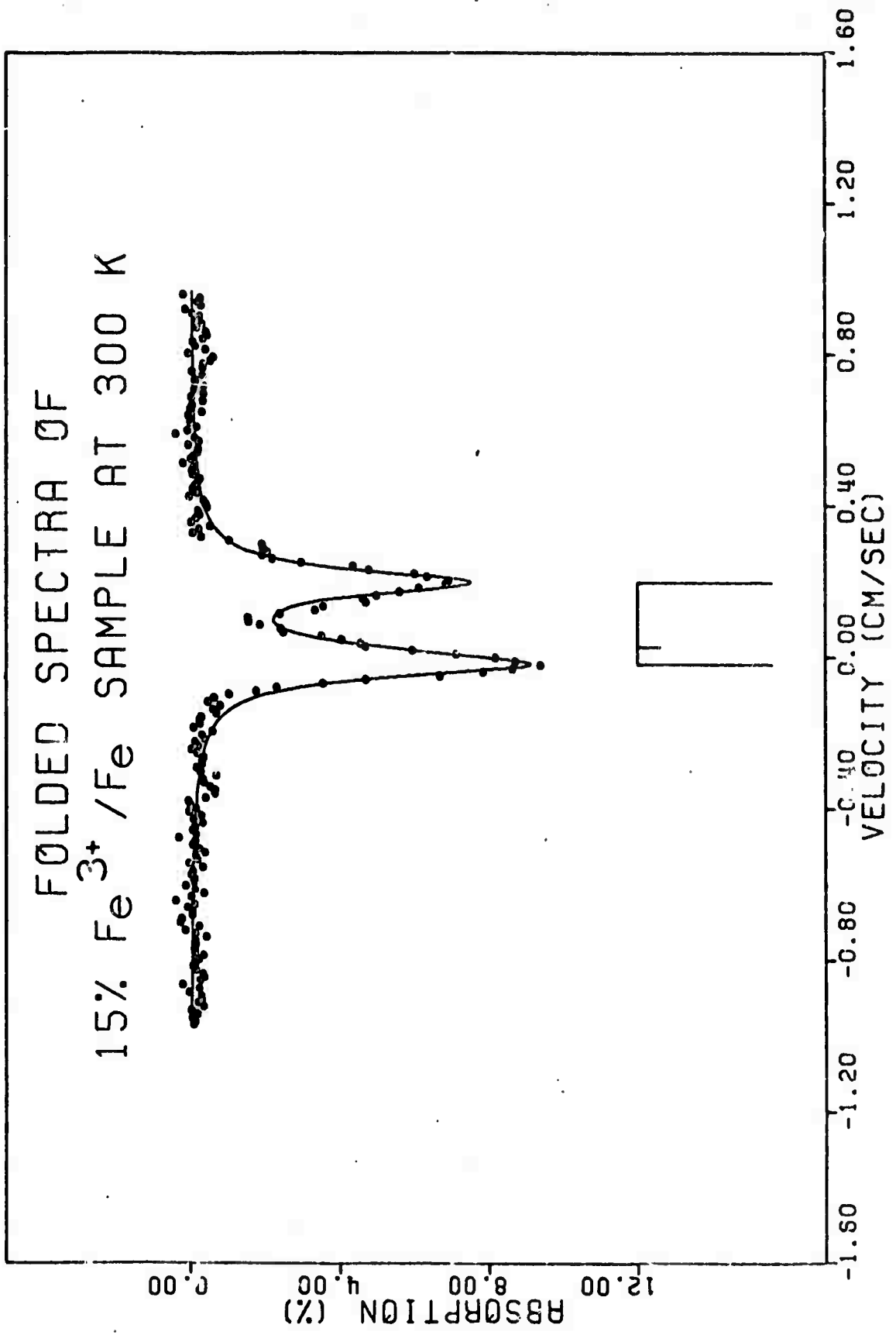

FOLDED SPECTRA OF
15% Fe^{3+} /Fe SAMPLE AT 300 K
ABSORPTION (%)
0.00
4.00
8.00
12.00
VELOCITY (CM/SEC)
-1.60
-1.20
-0.80
-0.40
0.00
0.40
0.80
1.20
1.60

Figure 5.

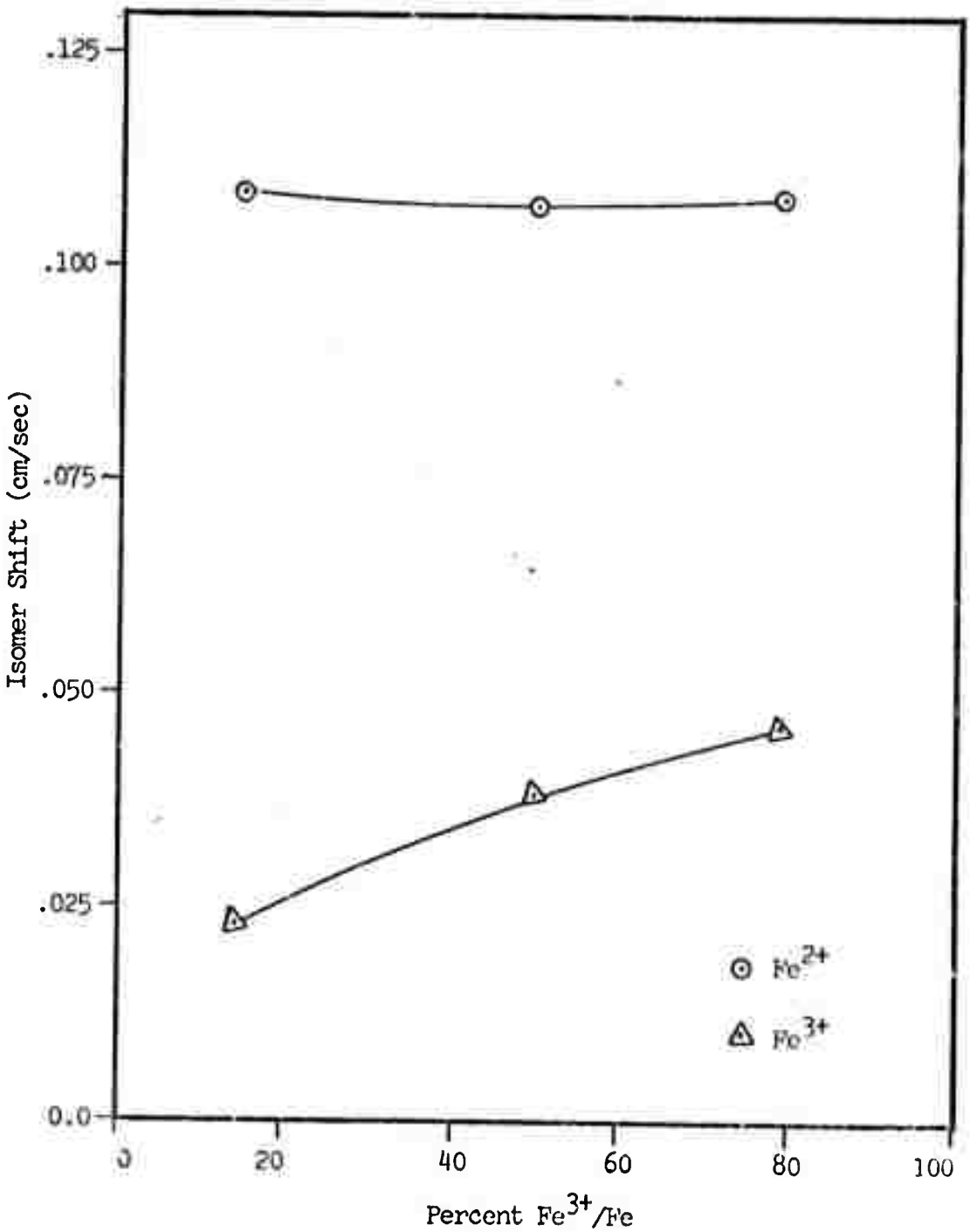


Fig. 6. Isomer shift of the Fe^{3+} and Fe^{2+} ion as a function of the concentration ratio, Fe^{3+}/Fe.

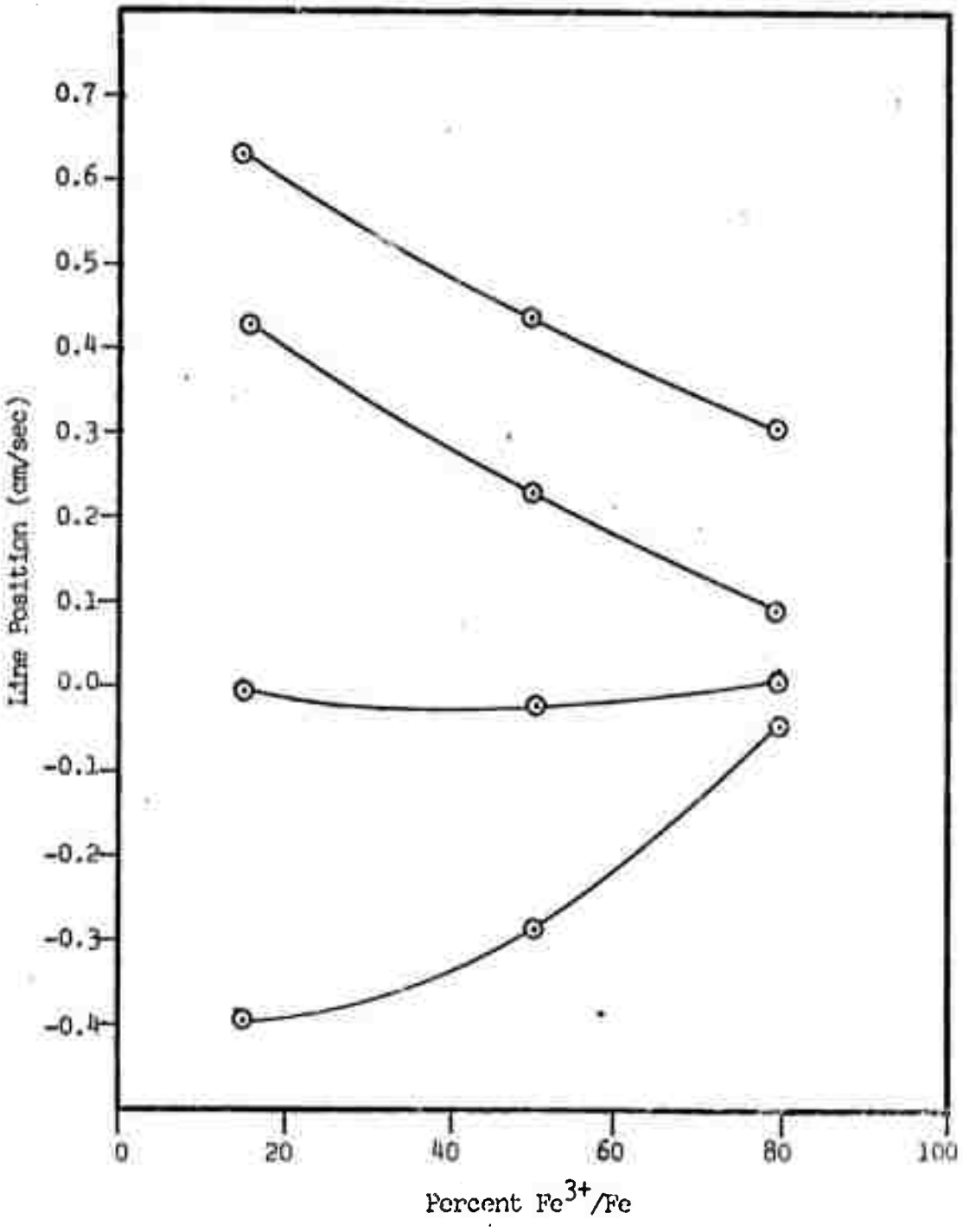


Fig. 7. Line positions as a function of the concentration ratio, Fe^{3+}/Fe, for the four lines of the 77° Kelvin sample.

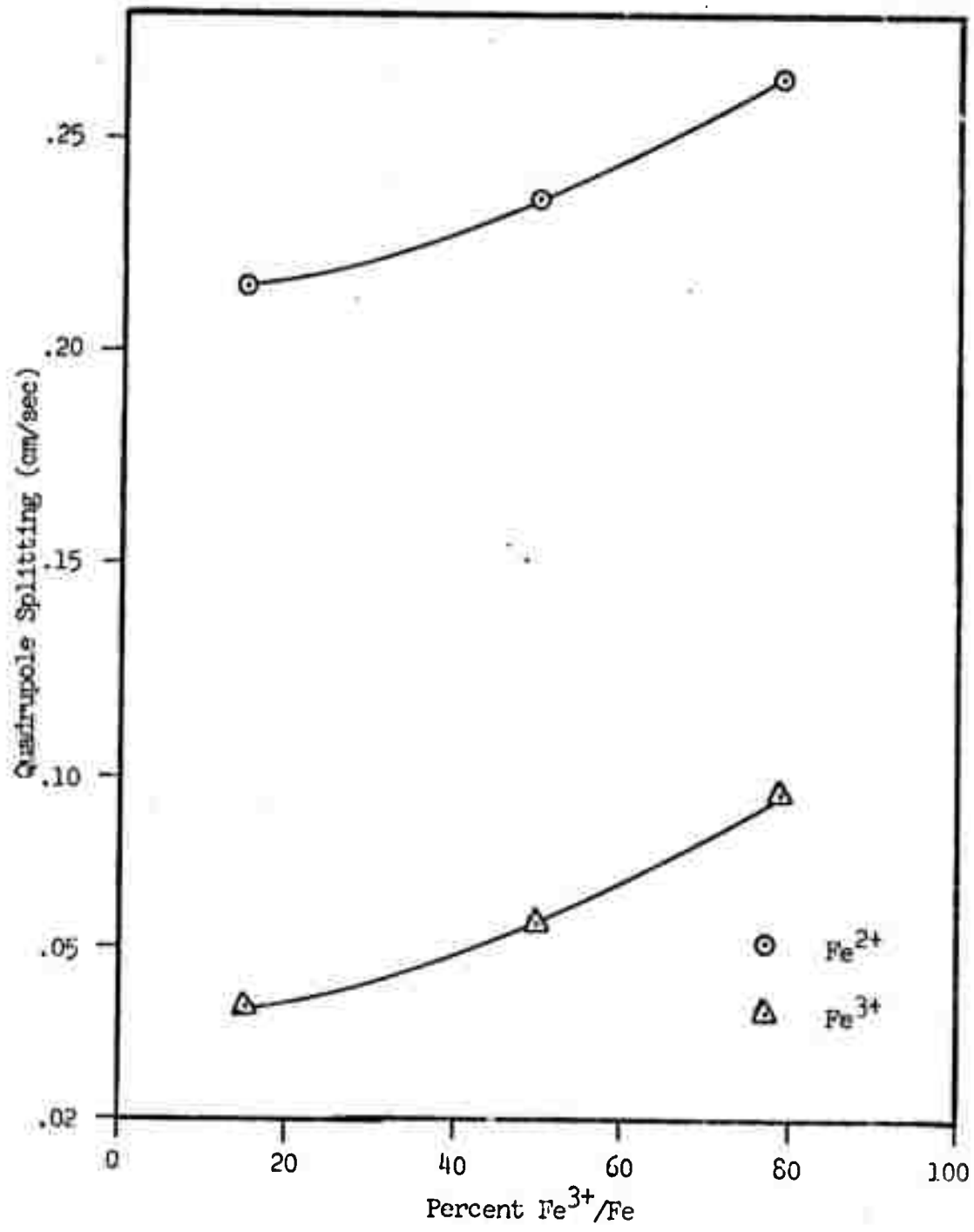


Fig. 8. Quadrupole splitting of the Fe^{3+} and Fe^{2+} ion as a function of the concentration ratio, Fe^{3+}/Fe.

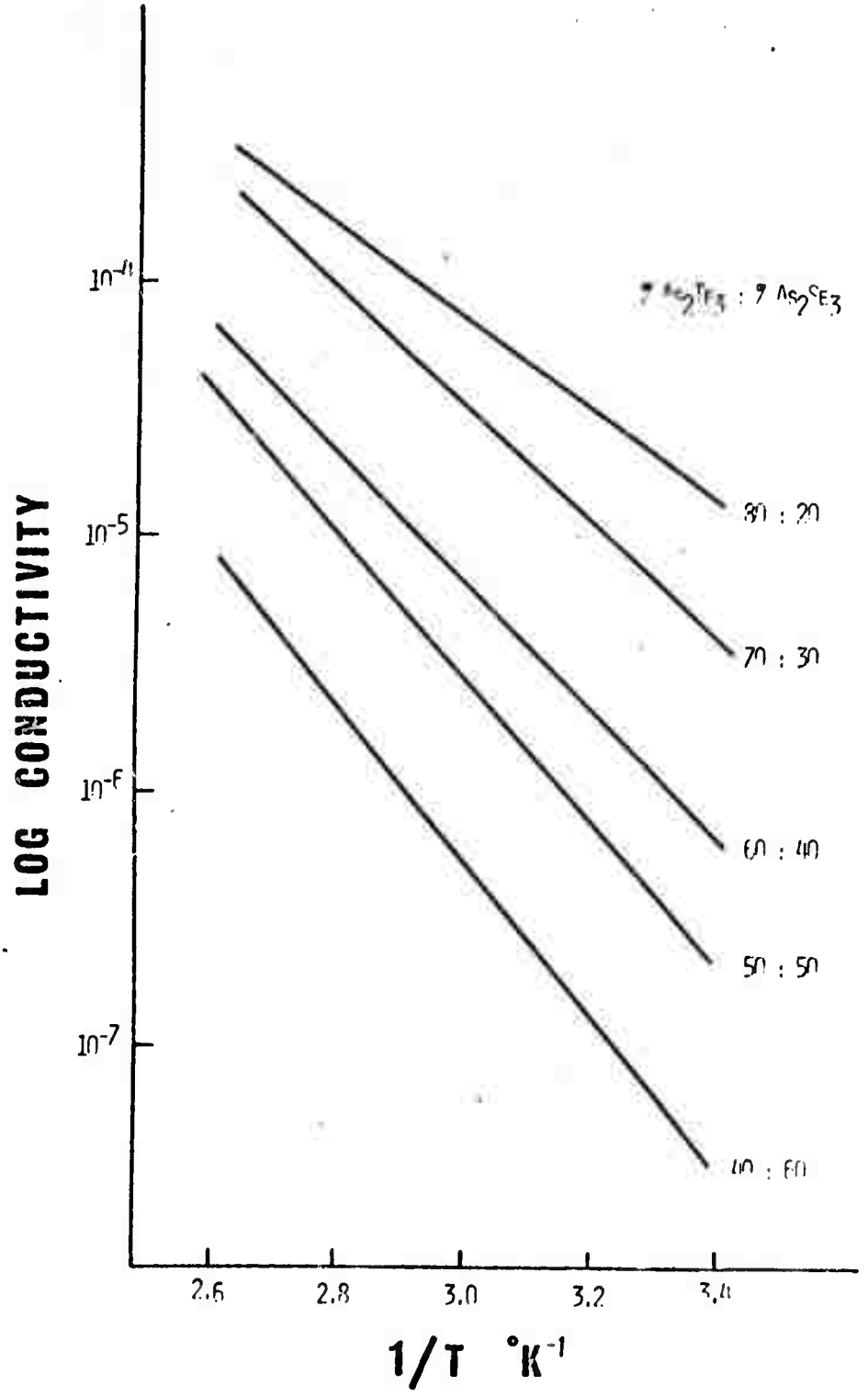

LOG CONDUCTIVITY
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
80 : 20
70 : 30
60 : 40
50 : 50
40 : 60
2.6
2.8
3.0
3.2
3.4
1/T °K⁻¹

Figure 9

Figure 10. As_2Se_3 Fracture Surface

Figure 11. 40 As_2Te_3 - 60 As_2Se_3
Fracture Surface from Center of Boule

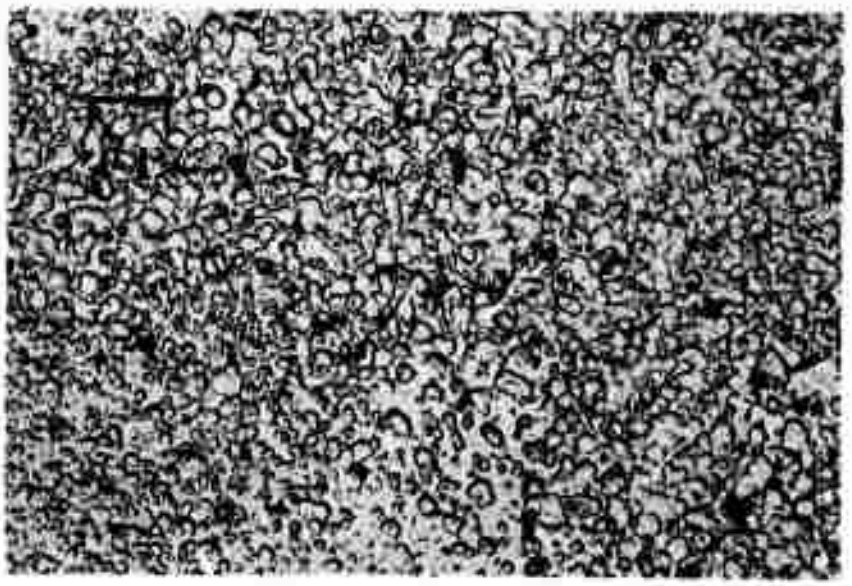


Figure 12. 40 As_2Te_3 - 60 As_2Se_3 KOH Etched Fracture Surface from Peripheral Region of Boule

Figure 13. 70 As_2Te_3- 30 As_2Se_3 KOH Etched Fracture Surface

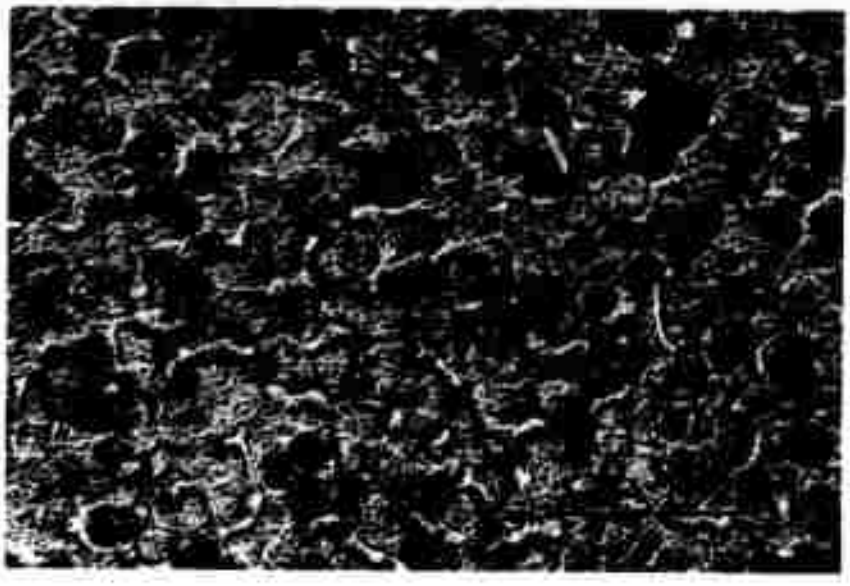


Figure 14. 80 As_2Te_3 - 20 As_2Se_3 KOH Etched Fracture Surface

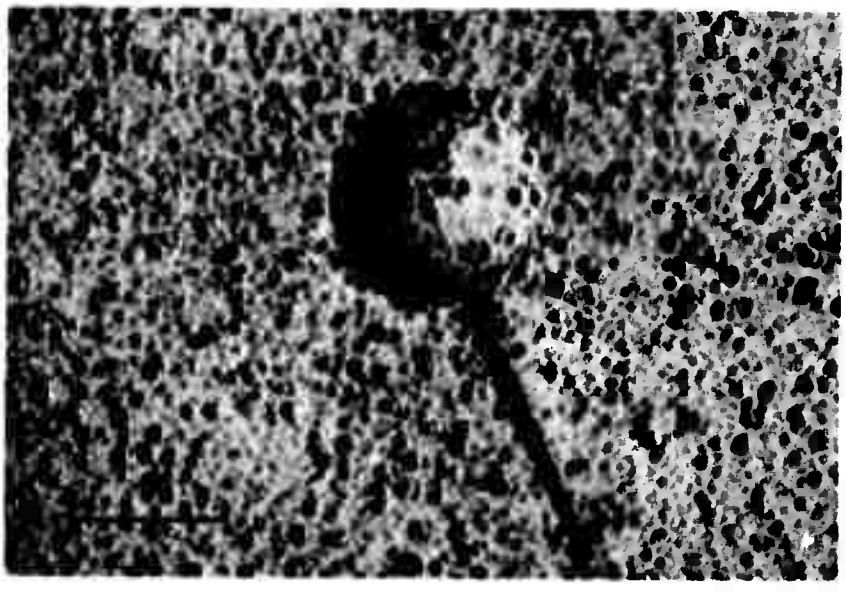


Figure 15. 40 As_2Te_3 - 60 As_2Se_3 Fracture Surface from same area as Figure 12.

Submitted to Journal of Non-Crystalline Solids

Electrical, Thermal & Structural Properties of As_2Te_3-As_2Se_3 Glasses

D. L. Kinser, L. K. Wilson, H. R. Sanders & D. J. Hill
Vanderbilt University, Nashville, Tennessee 37203

Electrical conductivity, switching, D.T.A., and electron microstructures are presented for a series of the chalcogenide glasses As_2Te_3-As_2Se_3. DTA observations were conducted on each of these glasses to determine the relative glass stability. Bulk threshold switching observations were conducted on a compositional series of glasses.

Replica electron microscopy observations indicate the presence of liquid-liquid immiscibility in the As-Te-Se ternary system. The evidence indicates that the As_2Te_3-As_2Se_3 join is not a quasi binary.

The immiscibility observed suggests that this system, like several analogous silicate ternary systems, is quite sensitive to thermal treatment.

I. INTRODUCTION

This paper reports results of electrical conductivity, switching, DTA and electron microstructural observations on a series of As_2Te_3-As_2Se_3 glasses. Roilos (1) and Kolomiets and Nazarova (2) have previously reported electrical conductivity in this system but their results are not in agreement. The present electrical conductivity results generally agree with the observations of Roilos although some disparities are present. The DTA observations indicate that the high As_2Se_3 glasses are more stable glasses. All of the glasses in this system exhibit bulk threshold memory switching with the critical voltage for switching increasing with As_2Se_3 content. The switching stability increases with As_2Se_3 content although the switching voltage rises to around 15 kilovolts in As_2Se_3. The microstructure exhibits a liquid-liquid separation in all glasses with a matrix structural change with composition. The more heterogenous microstructures occur in As_2Se_3 rich glasses in which better switching stability is observed. The switching process observed in these glasses appears to occur by a thermal mechanism as previously reported by Warren (3) in a single composition As_2Se_2Te. This conclusion is further substantiated by the compositional and microstructural trends noted above.

II. EXPERIMENTAL

All glasses examined in this study were prepared by fusing the appropriate materials in evacuated Vycor ampoules at 800°C in a rocking furnace. After heating for one hour the ampoules were rapidly quenched in water. Six compositions of the As_2Te_3-As_2Se_3 glass system were prepared with As_2Te_3/As_2Se_3 ratios of 0.8, 0.7, 0.6, 0.5, 0.4 and 0.0. Reagent grade raw materials were employed after an initial study revealed essentially no purity effects between reagent materials and 99.9999 materials. All samples were formed into small

platelets by briefly remelting on a graphite plate and quenching with a second plate. Samples for all observations had an area of about 1 cm^2 and a thickness of about 0.1 cm with similar thermal history. No samples were subjected to further thermal treatments.

Conductivity measurements were conducted using silver electrodes in a guard ring configuration with applied fields of approximately 5 volts/cm. Switching observations were conducted using a special fixture with spring loaded electrodes with appropriate external current limiting circuitry (4). DTA observations were conducted on powdered samples in a Modified Fisher Model 260 thermal analyzer.

Electron microscopy observations were conducted on freshly fractured and on etched fracture surfaces utilizing platinum/rhodium shadowed indirect carbon replicas. The etchant used was a dilute aqueous KOH solution.

III. RESULTS

The DC conductivity at 21°C as a function of composition is plotted in Figure 1 with previous data of Roilos and Kolomiets. The general compositional trends are similar although pronounced differences exist between the Roilos/present work and Kolomiets results. An example of the conductivity versus inverse temperature behavior for a 50/50 glass is given in Figure 2 along with Roilos' data. It is clear that the temperature dependence of both samples is different although the room temperature conductivity is similar in this case. Results of the threshold switching behavior as a function of composition are given in Fiugre 3. These data indicate an increasing breakdown voltage at higher As_2Se_3 content with somewhat larger scatter from sample to sample in the higher As_2Se_3 glasses. Observations on a single sample of the higher As_2Se_3 glasses do not exhibit changes in switching voltage through numerous switching cycles; hence the stability of this material as a switch is considerably higher than glasses with high As_2Te_3 content.

The DTA observations, summarized in Table 1, indicate that the crystallization temperature of these glasses increases with As_2Se_3 content. As one might predict, the selenium is a much stronger glass former, thus, the high selenium glasses crystallize at higher temperatures, if in fact they crystallize at all.

Electron microstructures of five representative glasses presented in Figures 4-8 exhibit a primary liquid-liquid drop-like separation. The drop size and volume fraction is sensibly unchanged throughout the composition range including the As_2Se_3 glass. The drop phase in the 70/30 glass exhibits a peculiar structure unlike any known to the authors. A pronounced change in the matrix phase with composition is apparent, and the 60/40 matrix exhibits a structure similar to that previously attributed to a spinodal decomposition process. (5)

IV. DISCUSSION

The disagreement between the present work and Roilos' versus the early Kolomiets work is surprising and no rationalization of this disparity is advanced. The more subtle differences between Roilos and the present work are probably the result of differing thermal histories leading to microstructural differences. The difference in activation energy for the 50/50 glass is undoubtedly a consequence of compositional differences in the matrix phase resulting from different degrees of compositional segregation between the two laboratories.

The switching behavior exhibits first a smooth compositional trend along with an opposite trend in switching stability. The increase in switching voltage with selenium is a consequence of combined Joule heating/thermal conductivity trends with composition. The change in switch stability appears to be a consequence of increased microstructural heterogenity with higher selenium content.

The phase separation observed in the As_2Se_3 glass indicates that a metastable immiscibility gap is present in the binary As-Se system and similar observations in tellerium containing glasses indicate that the immiscibility extends into the ternary system. Since the lines connecting phases in metastable equilibria do not lie in the As_2Se_3-As_2Te_3 join the system under examination is not a true quasibinary. This appears to be the only conclusion that can be reached from observations of constant phase fractions over the compositional range examined.

It thus appears that the As-Se-Te ternary system exhibits metastable immiscibility similar to the Na_2O-B_2O_3-SiO_1 system (6) and that the physical properties are similarly sensitive to thermal history.

CONCLUSIONS

1. Disagreement in electrical conduction observations among various investigators can be partially rationalized by the microstructure.

2. Switching stability in this system is enhanced by the presence of a more heterogenous microstructure.

3. The As-Se-Te ternary system exhibits metastable immiscibility on the join As_2Te_3-As_2Se_3.

ACKNOWLEDGEMENT

This work was supported by the U.S. Advanced Research Projects Agency monitored by ARO-D under Contract DAHC04-70-C-0046.

BIBLIOGRAPHY

1. M. N. Rollos, J. Non-Crystalline Solids 6 (1971) 5.

2. B. T. Kolomiets and T. F. Nazarova, Soviet Phys.-Solid State 2 (1960) 369.

3. A. C. Warren, J. Non-Crystalline Solids 4 (1970) 613.

4. H. R. Sanders, D. L. Kinser and L. K. Wilson, Proc. Region III IEEE Meeting (1971) 429.

5. For example J. W. Cahn and R. J. Charles, Physics & Chem. of Glasses 6 (1965) 181.

6. W. Haller, D. H. Blackburn, F. E. Wagstaff and R. J. Charles, J. Am. Ceram. Soc. 53 (1970) 34.

Figure Captions

1. DC conductivity as a function of composition with data from Roilos (1) and Kolomiets and Nazarova (2).
2. DC conductivity as a function of inverse temperature with data from Roilos (1).
3. Threshold switching voltage as a function of composition. Large error bars are result of numerous samples - single samples exhibit smaller scatter in higher As_2Se_3 glasses.
4. Replica electron micrograph of stoichiometric As_2Se_3. Unetched fracture surface.
5. Replica electron micrograph of 40 As_2Te_3-60 As_2Se_3 glass. Unetched fracture surface.
6. Replica electron micrograph of matrix region of 60 As_2Te_3-40 As_2Se_3 glass. KOH etched fracture surface.
7. Replica electron micrograph of 70 As_2Te_3-30 As_2Se_3 glass. KOH etched fracture surface.
8. Replica electron micrograph of droplet/matrix interface region in 80 As_2Te_3-20 As_2Se_3 glass. KOH etched fracture surface.

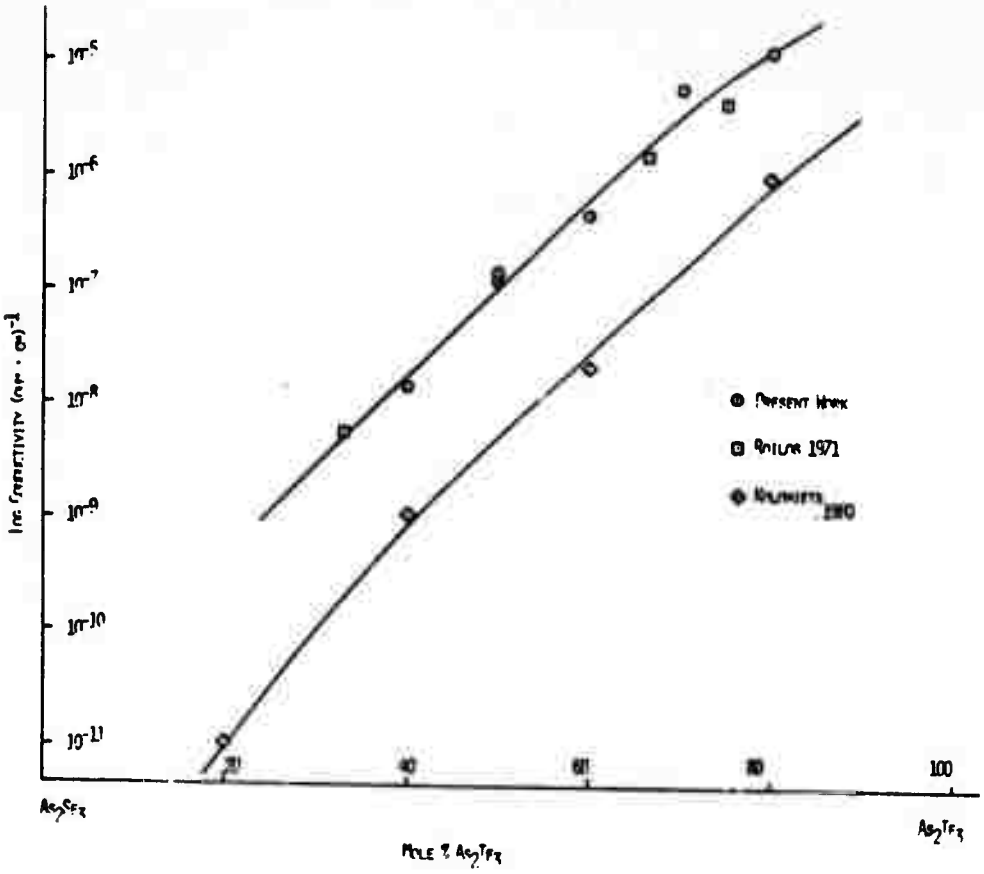


Figure 1
Kinsel et al

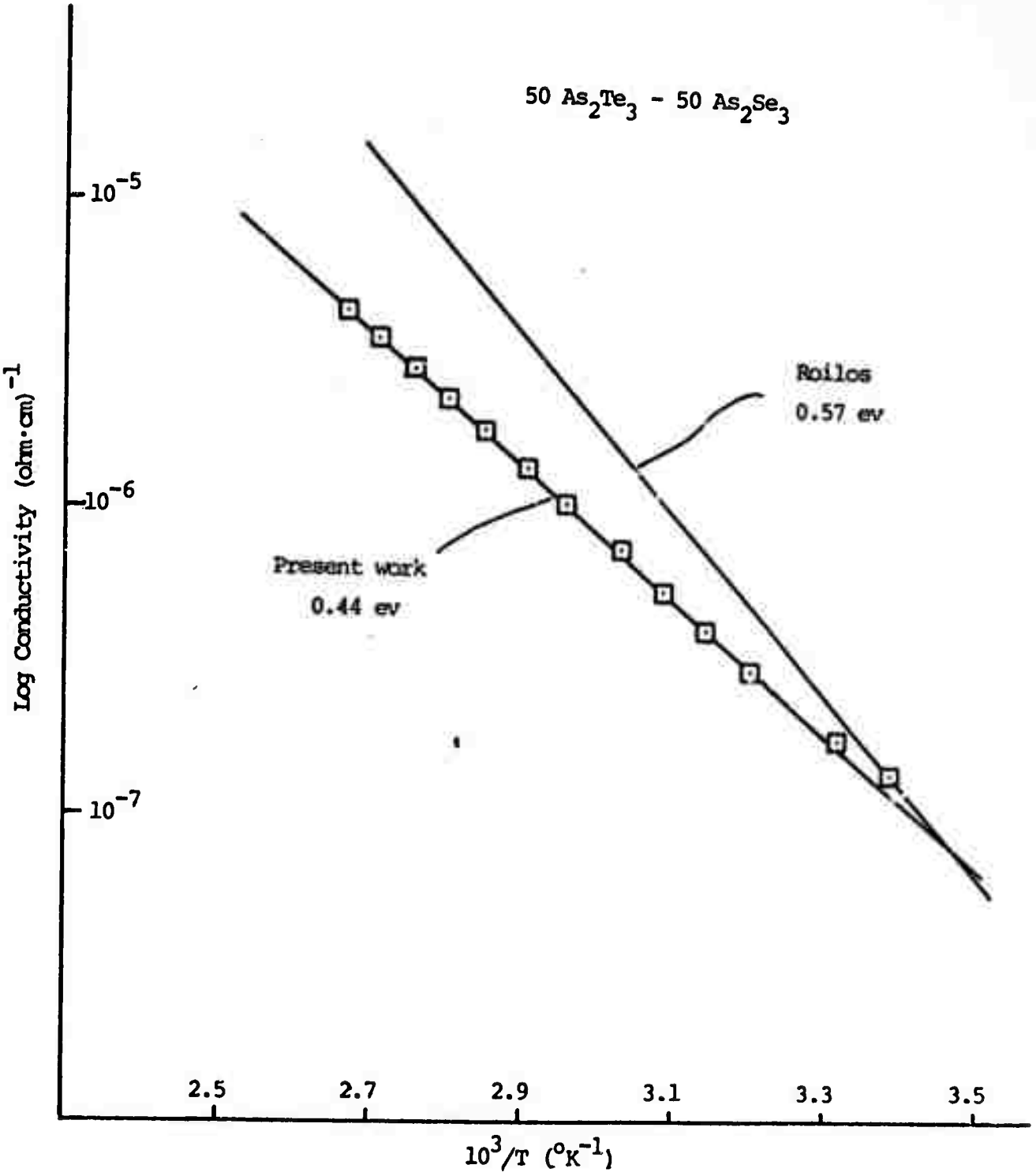
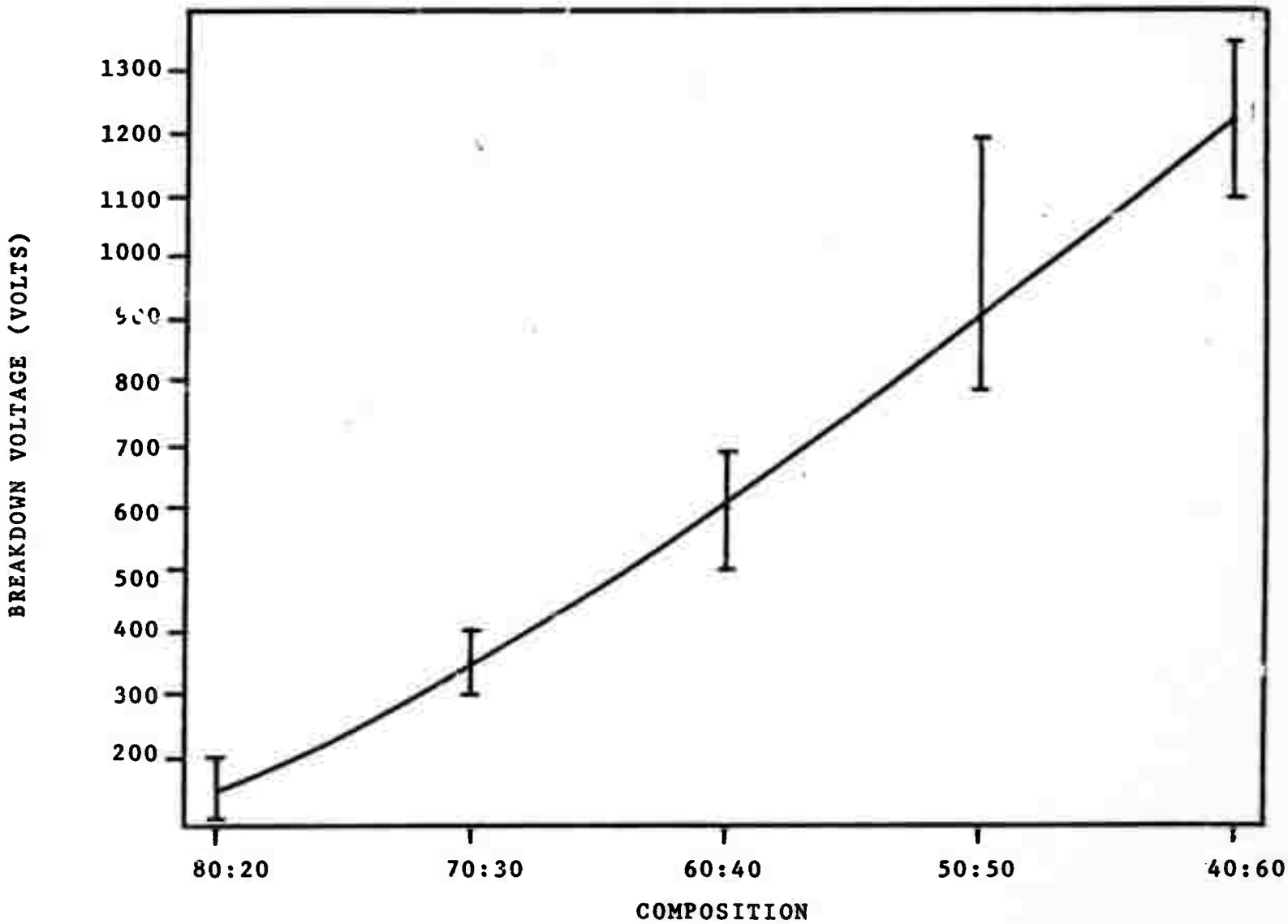

50 As2Te3 - 50 As2Se3
Roilos
0.57 ev
Present work
0.44 ev
Log Conductivity (ohm·cm)-1
10-5
10-6
10-7
2.5
2.7
2.9
3.1
3.3
3.5
10³/T (°K-1)

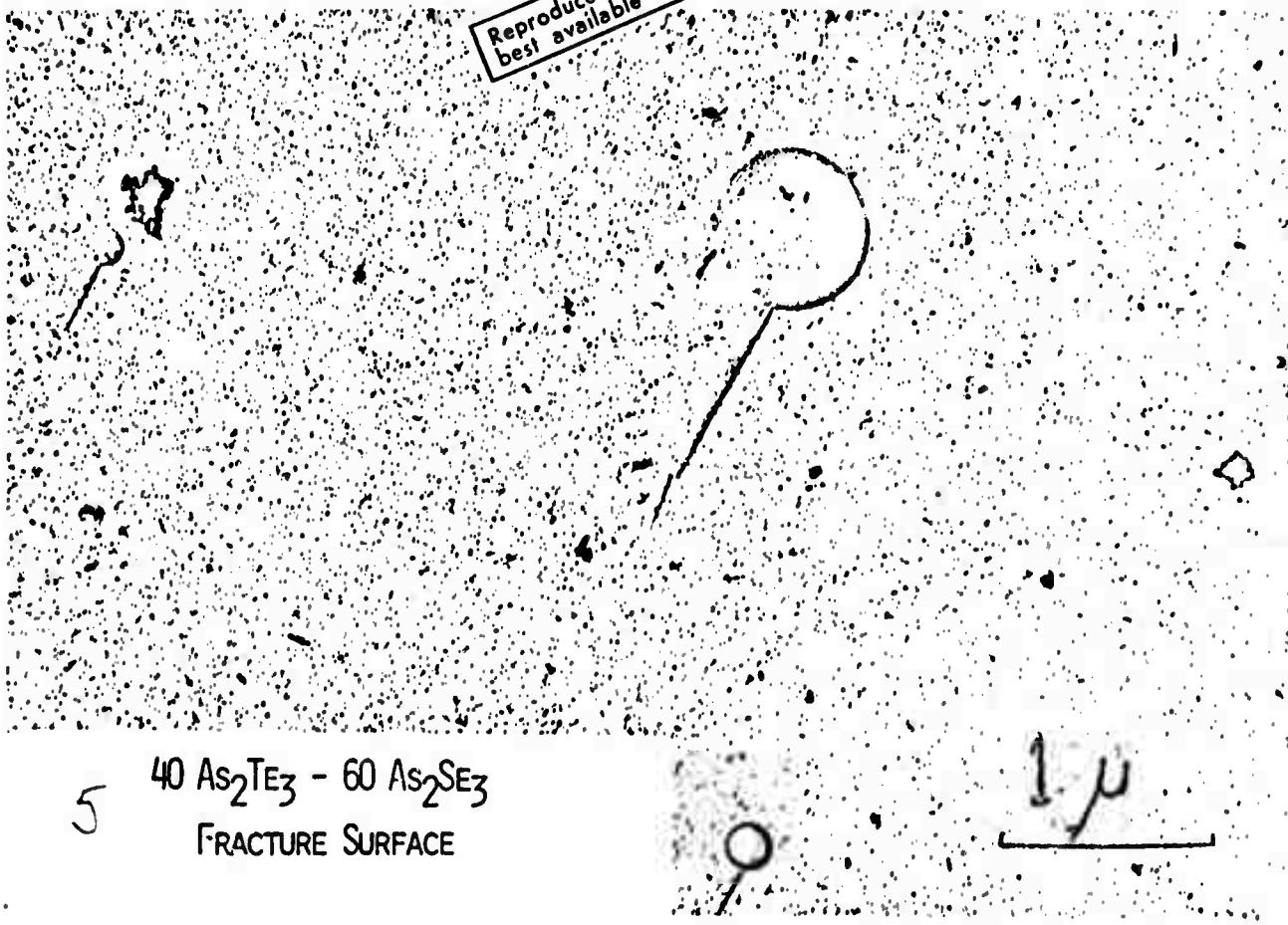
Figure 2



Breakdown voltage vs. composition for the As_2Te_3:As_2Se_3 system. (Error bars indicate results of measurement of several samples. Single sample observations show little scatter.

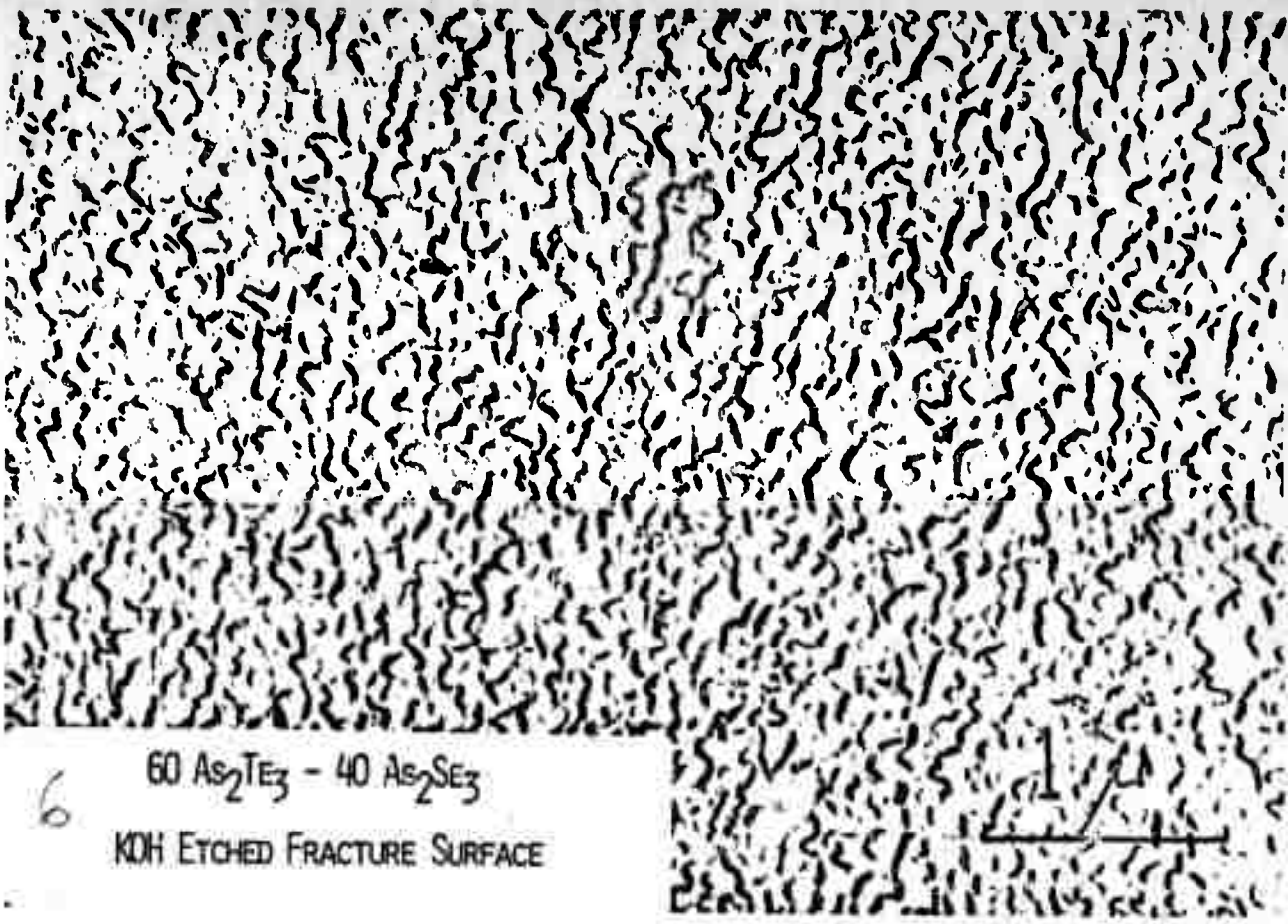
4 As_2Se_3

FRACTURE SURFACE



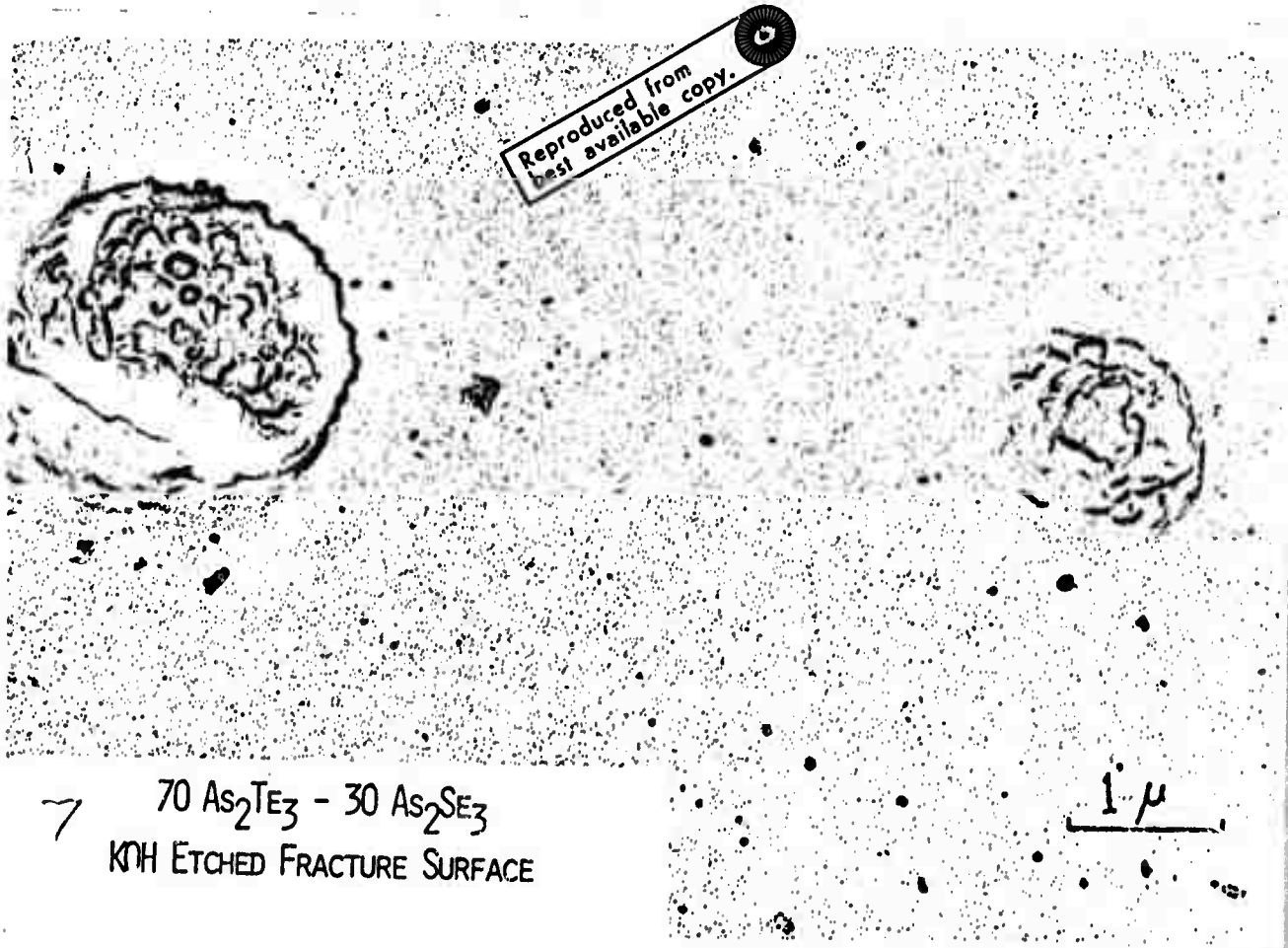
5 40 As_2Te_3 - 60 As_2Se_3

FRACTURE SURFACE



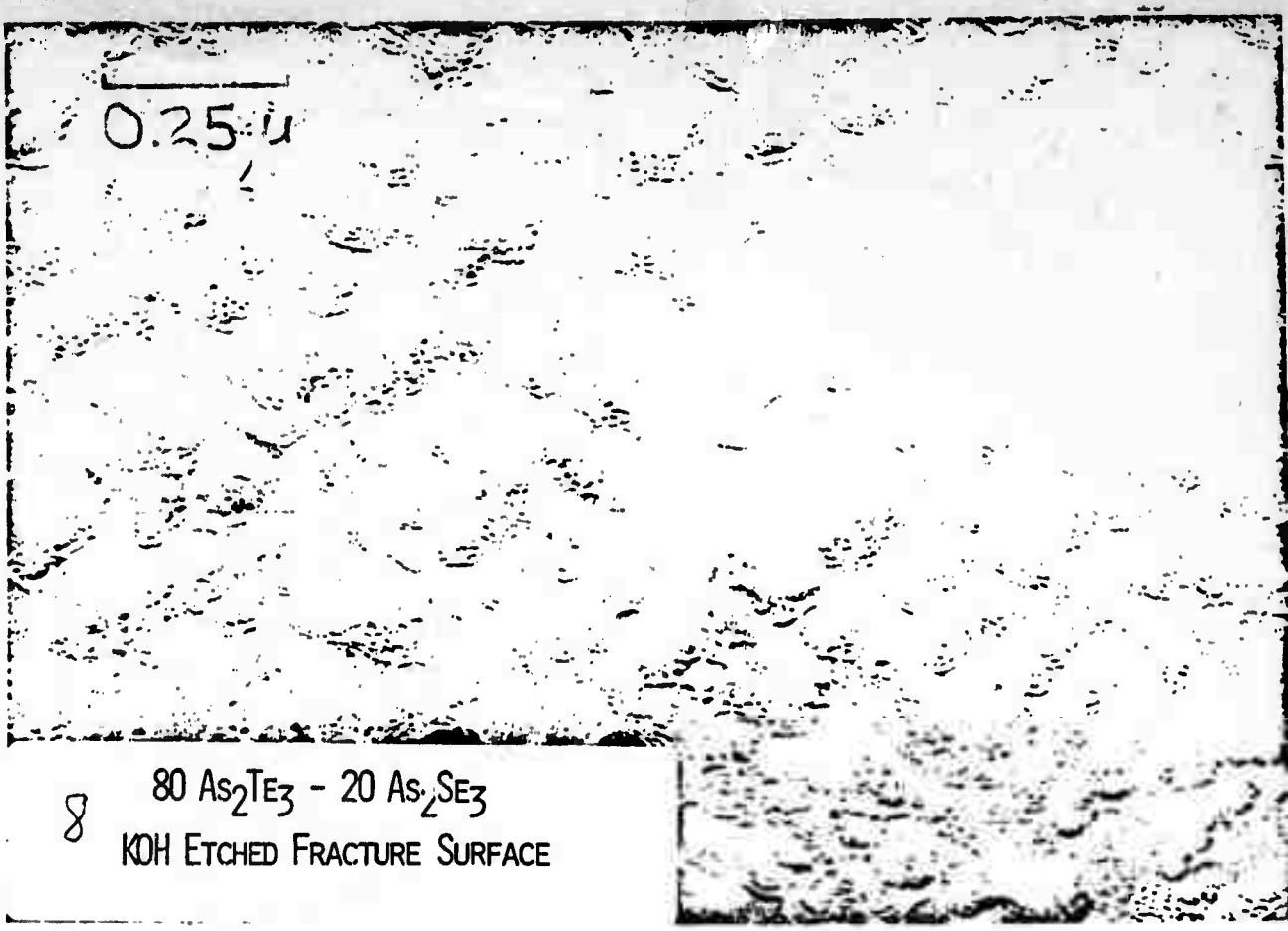
6 60 As_2Te_3 - 40 As_2Se_3

KOH Etched Fracture Surface



7 70 As_2Te_3 - 30 As_2Se_3

KOH Etched Fracture Surface



8 80 As_2Te_3 - 20 As_2Se_3
KOH ETCHED FRACTURE SURFACE

U. H. F. AND MICROWAVE DIELECTRIC PROPERTIES OF AN AMORPHOUS SEMICONDUCTOR

J. D. Pearson, G. T. O'Reilly, and L. K. Wilson
Vanderbilt University
Nashville, Tennessee

Summary

This paper considers the Ultra High Frequency and microwave dielectric properties of a class of amorphous semiconductors at room temperature. Complex permittivity measurements are presented for the glass system $(x)As_2Te_3(1-x)As_2Se_3$ for x = 0.4,0.5,0.6,0.7 and 0.8, over the frequency range 100-18,000 Mhz. The dielectric constant was found to be essentially frequency independent over the frequency range studied, and was found to decrease with decreasing Te content. The loss tangents observed compare favorably with values encountered for commonly used microwave substrates such as YIG or silicon.

Introduction

The last several years has evidenced an increase in research concerning the electrical and physical properties of amorphous semiconductors. In an attempt to test various density-of-state models for the amorphous materials, considerable experimental study has been conducted on the temperature dependence of the d.c. conductivity, the frequency dependence of the conductivity in the audio and high frequency range, and the optical absorption spectrum.[1] The switching[2] and electrical, thermal, and structural[3] properties of the system $(x)As_2Te_3(1-x)As_2Se_3$ has been extensively investigated at Vanderbilt University. However, there has been no published research characterizing the high frequency dielectric properties of this glass system.

[redacted]

relations[4] used for 100-500 Mhz, to yield the complex permittivity of the sample.

10,000 Mhz-18,000 Mhz. For this frequency range, a K_u-band slotted waveguide, terminated with the sample and a variable short circuit was used. The rectangular sample, slightly smaller than waveguide dimensions, was placed just inside the variable waveguide short. A tightly fitting styrofoam spacer held the sample erect in the guide. Sample thickness was approximately 0.22". Measurements taken for this method were wavelength, position of the voltage minimum, and VSWR. The two-point method was again used to obtain the VSWR. A graphical technique given by Von Hippel[5,7] was used to solve the equation for the wave impedance in the sample.

This latter method could also have been applied to X-band frequencies, but data was not taken in this range because samples of sufficient height and thickness were not available at the time of testing. Errors involved in the experimental setups include errors in slotted line null measurements, VSWR, and sample height and position. These led to a statistical error of about ± ten per cent.

[redacted]

Experimental

Preparation of Samples

The materials were prepared by fusing a mixture of As_2Te_3 and As_2Se_3 in evacuated Vycor ampoules at 800°C in a rocking furnace. After heating for one hour the molton material was quenched in water. The samples were then shaped and polished according to the experimental requirements.

Permittivity Measurements

100 Mhz-500 Mhz. For this frequency range the materials were shaped into circular disks approximately 0.24" in diameter and 0.03" thick and placed at the end of a shorted air-filled coaxial line. A Thurston Bridge (G. R. Model 1602-B) was used to determine the complex admittance of the sample. The sample arrangement was considered as a parallel plate capacitor and the corresponding field equations[4] were used to calculate the complex permittivity from the measured admittance

500 Mhz-2000 Mhz. In this frequency range a slotted coaxial line, terminated in the sample and a variable short, was used to measure null shift and VSWR. The VSWR was obtained by the two point method,[5] since high VSWR values were encountered. The frequency was measured using a transfer oscillator and a 10 Mhz Electronic Counter. The same disk-shaped samples used in the frequency range 100-500 Mhz were used in this range. The null shift and VSWR data were substituted into the transmission line equations for input admittance[6] to yield the sample admittance. The sample admittance was then used with the same capacitance

Conclusions

Figures 1 and 2 show the compositional and frequency variation of the dielectric constant and loss tangent of the glass system.

The permittivities of the samples were found to be essentially frequency independent over the frequency range studied, with slight variations attributed to differences in experimental techniques. By increasing the Te composition, it was found that the dielectric constant can be varied from approximately 7.0 to 10.0, for the compositions studied. The values for dielectric constant found here compare favorably with data recently given for As_2Se_3 by Taylor, et al.[8] The loss tangent was found to also increase with increasing Te content, and varied between approximately 0.02 and 0.07. Crevecoeur and de Wit[9] have presented the dielectric properties of As_2Se_3 glass over the frequency range 10^2 to 10^{10} Hz. In the U. H. F. and microwave regions, they give an average loss tangent of 10^{-4}. This value may be considered as a low limit to the data given in the present paper, since it represents glass having no Te content. The dielectric properties of this glass system compares favorably with those for dielectric materials used for microwave substrates, such as YIG or silicon.

Acknowledgment

This work was supported in part by the U. S. Advanced Research Projects Agency monitored by ARO-D under Contract DAHC04-70-C-0046.

References

1. See for example Proceedings of the 4th International Amorphous Semiconductor Conference, Ann Arbor, Michigan, August, 1971 (to be published).

2. H. R. Sanders, D. L. Kinser, and L. K. Wilson, "Low-Field Switching and Memory Phenomena in an Amorphous Semiconductor," Proceedings of the 9th Annual (1971) IEEE Region III Convention, Charlottesville, Virginia, April, 1971, pp. 429-433.

3. D. L. Kinser, L. K. Wilson, H. R. Sanders, and D. J. Hill, "Electrical, Thermal & Structural Properties of $As_2Te_3As_2Se_3$ Glasses," to be published in Journal of Non-Crystalline Solids.

4. Roger F. Harrington, Time-Harmonic Electromagnetic Fields (New York: McGraw-Hill, 1961), pp. 30-31.

5. Arthur R. Von Hippel, ed., Dielectric Materials and Applications (New York: Technology Press of M.I.T., 1954), pp. 67 88-101.

6. Robert E. Collin, Foundations for Microwave Engineering (New York: McGraw-Hill, 1966), p. 93.

7. S. Roberts and A. Von Hippel, "A New Method for Measuring Dielectric Constant and Loss in the Range of Centimeter Waves," Journal of Applied Physics, Vol. 17, pp. 610-616, July, 1946.

8. P. C. Taylor, S. G. Bishop and D. L. Mitchell, "Far Infrared and Microwave Optical Properties of Vitreous As_2Se_3," Solid State Communications, Vol. 8, No. 21, pp. 1783-1787, (1970).

9. C. Crevecoeur and H. J. de Wit, "Dielectric Losses in As_2Se_3 Glass," Solid State Communications, Vol. 9, No. 8, pp. 445-449, (1971).

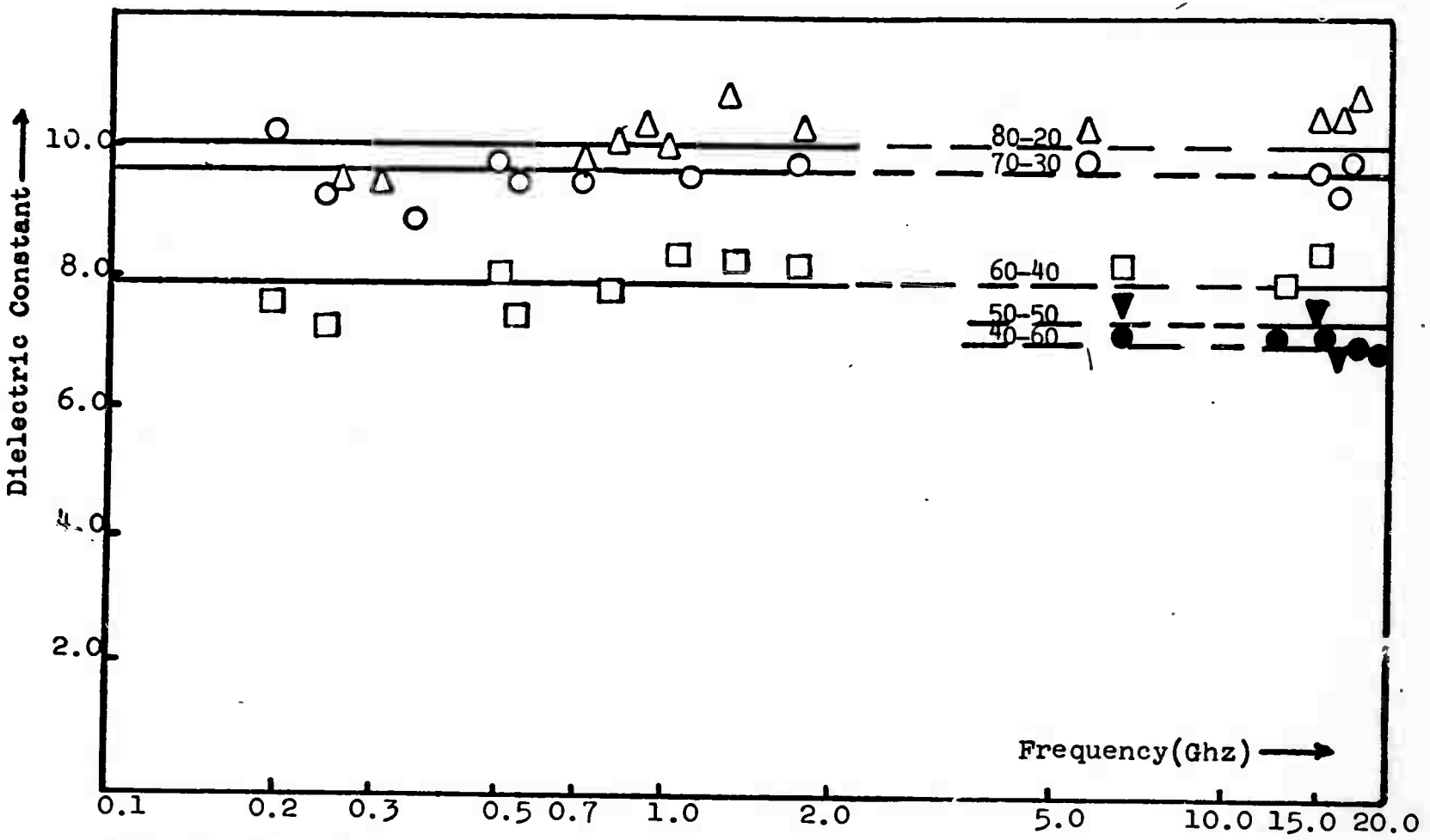


FIG. 1. The frequency dependence of the dielectric constant for $(x)As_2Te_3(1-x)As_2Se_3$ for x=0.4,0.5,0.6,0.7, and 0.8.

0.1 . 0.2 0.3 0.5 0.7 1.0 . . 2.0 5.0 10.0 15.0 20.0

FIG. 1. The frequency dependence of the dielectric constant for $(x)As_2Te_3(1-x)As_2Se_3$ for x=0.4,0.5,0.6,0.7, and 0.8.

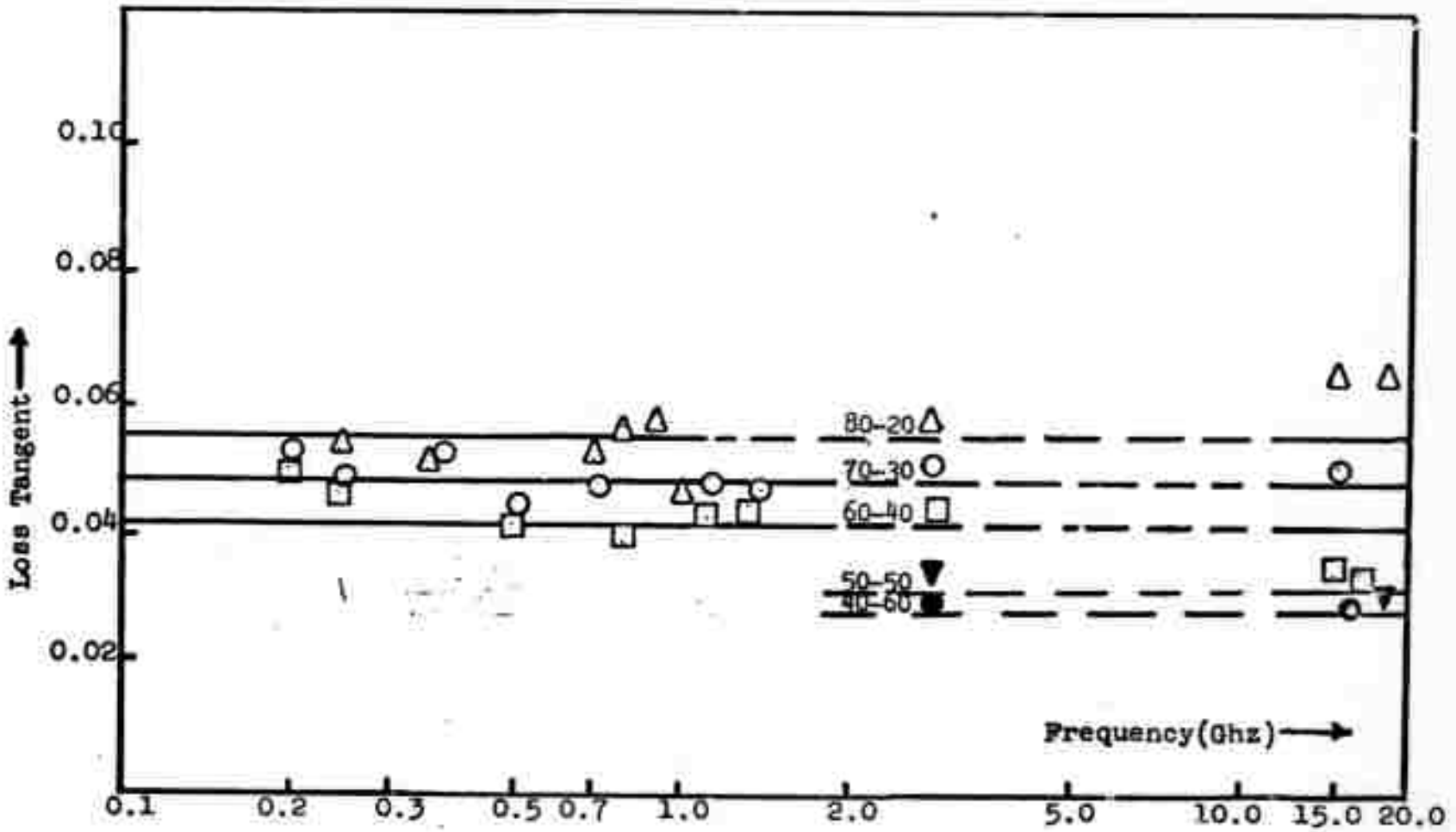


FIG. 2. The frequency dependence of the loss tangent for $(x)As_2Te_3(1-x)As_2Se_3$ for x=0.4,0.5,0.6,0.7, and 0.8.

Abstract presented to
The Tenth Annual (1972) IEEE Region 3 Conference
University of Tennessee
Knoxville, Tennessee

U. H. F. AND MICROWAVE DIELECTRIC PROPERTIES OF AMORPHOUS SEMICONDUCTORS

J. D. Pearson*, G. T. O'Reilly*, and L. K. Wilson**
Vanderbilt University
Nashville, Tennessee 37203

This paper considers the Ultra High Frequency and microwave dielectric properties of some amorphous semiconductors at room temperature. Complex permittivity measurements are presented for the glass system $(x)As_2Te_3(1-x)As_2Se_3$ for x=0.4, 0.5, 0.6, 0.7 and 0.8, over the frequency range 100-18,000 Mhz. The dielectric constant was found to vary slightly with frequency and to decrease with decreasing As_2Te_3 content. This research was sponsored by the U. S. Army Research Office-Durham.

* Student Member, IEEE
** Member, IEEE

Summary presented to
The Tenth Annual (1972) IEEE Region 3 Conference
University of Tennessee
Knoxville, Tennessee

U. H. F. AND MICROWAVE DIELECTRIC PROPERTIES OF AMORPHOUS SEMICONDUCTORS

J. D. Pearson*, G. T. O'Reilly*, and L. K. Wilson**
Vanderbilt University
Nashville, Tennessee 37203

Recent interest in amorphous semiconductors has focused primarily on the electrical switching behavior of these materials.(1) Considerable experimental study has been conducted on the temperature dependence of the d.c. conductivity, the frequency dependence of the conductivity in the audio and high frequency range, and the optical absorption spectrum, in an attempt to test various density-of-states models for the amorphous materials. Very little work has been directed, however, toward characterizing the dielectric properties of these materials in the U. H. F. and microwave range.

This paper considers the compositional variation in the dielectric properties of the glass system $(x)As_2Te_3(1-x)As_2Se_3$ (x=0.4,0.5,0.6,0.7 and 0.8) over the frequency range 100-18,000 Mhz, at room temperature (25°C).

The materials were prepared by fusing a mixture of As_2Te_3 and As_2Se_3 in a rocking furnace. After heating for several hours, the molton material was quenched in ice water.

Complex permittivity measurements were made by three techniques. For the frequency range 100-500 Mhz, the materials were shaped into circular disks and placed in an air-filled coaxial line. A Thurston Bridge (G.R. Model 1602-B) was used to determine the complex impedance of the sample, which was then used to determine ϵ' and ϵ''. In the frequency range 500 Mhz-2 Ghz, a slotted coaxial line was used for measurement of null shift and VSWR. For 2-6 Ghz this procedure was repeated using a greater precision coaxial slotted line. In the range 12-18 Ghz, retangular shaped samples were used in conjunction with a Ku-band slotted waveguide. Permittivity was obtained by measuring VSWR, wavelength, and position of voltage minimum and calculating the proper order solution to a complex transcendental equation.(2)

* Student Member, IEEE
**Member, IEEE

The average complex permittivities measured over the entire frequency band are given in Table I.

TABLE I. Average Complex Permittivity Variation with Composition.

Composition	Permittivity
80% As_2Te_3-20% As_2Se_3	10.0-j0.4
70% As_2Te_3-30% As_2Se_3	9.1-j0.3
60% As_2Te_3-40% As_2Se_3	8.7-j0.25
50% As_2Te_3-50% As_2Se_3	8.4-j0.2
40% As_2Te_3-60% As_2Se_3	7.2-j0.4

Slight variations of permittivity with frequency were noted and the dielectric constant decreased as the As_2Te_3 content decreased. The values for dielectric constant found here compare favorably with data recently given for As_2Se_3 by Taylor et al.(3)

Variations of permittivity with frequency can be attributed to variations in experimental techniques. Errors involved in the experimental setup include errors in slotted line null measurements, VSWR, and sample height and position. These lead to a statistical error of ± 10%. All measurements were within this statistical error.

References

1. See for example PROCEEDINGS OF THE 4TH INTERNATIONAL AMORPHOUS SEMICONDUCTOR CONFERENCE, Ann Arbor, Michigan, August 1971 (to be published).

2. S. Roberts and A. Von Hippel, "A New Method for Measuring Dielectric Constant and Loss in the Range of Centimeter Waves," JOURNAL OF APPLIED PHYSICS, vol. 17, pp. 610-616, July 1946.

3. P. C. Taylor, S. G. Bishop and D. L. Mitchell, "Far Infrared and Microwave Optical Properties of Vitreous As_2Se_3," SOLID STATE COMMUNICATION, vol. 8, pp. 1783-1787, 1970.