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INVESTIGATION OF THE SYSTEM $\text{Al}_2\text{O}_3\text{-TeO}_2\text{-O}_2$

BY

VERA ZELENKOVA SESTAK, 1945 -

A

THESIS

submitted to the faculty of

UNIVERSITY OF MISSOURI - ROLLA

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Approved by

Charles Samuel (advisor)

Robert E. Moore

J. B. Clark

ABSTRACT

The system $\text{Al}_2\text{O}_3\text{-TeO}_2\text{-O}_2$ has been investigated by X-ray diffraction and differential thermal analysis in air and in sealed silica ampoules. The tellurate, Al_2TeO_6 , with tellurium in the +6 valence state, forms in air but not in vacuum at 1 mm pressure. A second phase, a tellurite, possibly $\text{Al}_2\text{Te}_2\text{O}_7$, forms in air or vacuum by devitrification. The glass-forming region is wider than previously stated and is more extensive in vacuum--from 50% to 98% TeO_2 . Tentative phase boundaries have been placed for the system in air and vacuum.

ACKNOWLEDGEMENT

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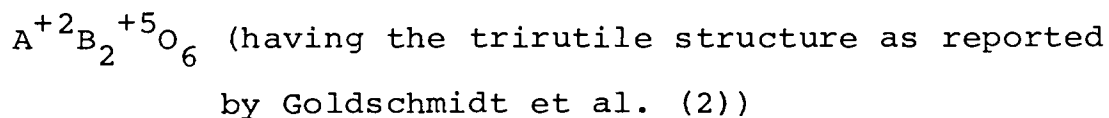
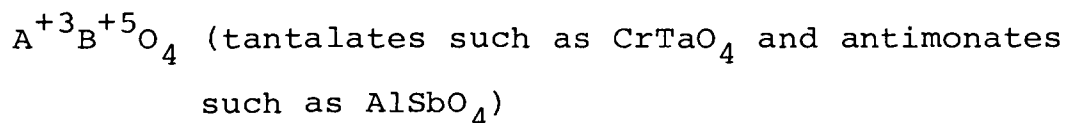
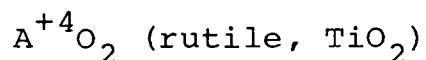
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I. INTRODUCTION

Little information regarding the system $\text{Al}_2\text{O}_3\text{-TeO}_2\text{-O}_2$ is available in the literature.

The first syntheses in the system were first reported by Bayer (1) who studied the reactions of TeO_2 with Al_2O_3 as well as with Cr_2O_3 and Ga_2O_3 . Single phases with compositions A_2TeO_6 , wherein A is Cr, Al, or Ga, were observed in these systems. A-atoms have a valence of +3 and the tellurium atoms have a valence of +6. The compounds were classified as rutile structures. Three variations of the rutile structure have been reported:



The rutile and trirutile structures are closely related. The unit cell of the trirutile structure corresponds to three unit cells of the monorutile structure except that the Ti^{+4} positions are occupied in an ordered array by A^{+2} and B^{+5} ions.

The metallic tellurates of the formula A_2TeO_6 have a general formula AB_2O_6 for a normal trirutile compound. The lattice positions of A and B ions are therefore interchanged and the structure can be interpreted as "inverse trirutile structure" as shown in Figure 1. The structure can be regarded as a

superlattice of rutile with regular distribution of the A^{+3} and Te^{+6} ions in the tripled unit cell.

Each of these compounds was prepared by Bayer by mixing of the respective A_2O_3 compounds with TeO_2 in a 1:1 molar ratio. After mixing they were pressed to a cohesive shape and fired in air at 650 - 700°C for about 20 hours. At this temperature and above, the compounds began to decompose by vaporization of TeO_2 after long heating. Each of the compounds was found to be insoluble in water and most acids.

The $TeO_2-Al_2O_3$ system was also investigated with regard to glass formation by Zlomanov et al. (3). Their tellurate glasses were based on tellurium dioxide and have a low melting temperature, a refractive index between 2.0 and 2.3, and high dielectric constants. These glasses are more transparent to infra-red radiation than silicate glasses. They are obtained by melting oxides of various metals with tellurium dioxide.

The most stable $TeO_2-Al_2O_3$ glass is obtained when a small quantity of Al_2O_3 is added. Accordingly, the authors investigated the formation of glass in the $TeO_2-Al_2O_3$ system with 1 - 15 wt.% Al_2O_3 . In the range from 4 wt.% to 12 wt.% Al_2O_3 these glasses may be obtained by quenching from 750°C. These glasses are insoluble in water and only slowly attacked by concentrated acids such as HCl , H_2SO_4 and HNO_3 .

This study was undertaken to investigate in more detail the mixed oxide system containing Al_2O_3 and TeO_2 . The only information available is the description of the tellurate by Bayer (1) and the glass formation region by Zlomanov et al. (2).

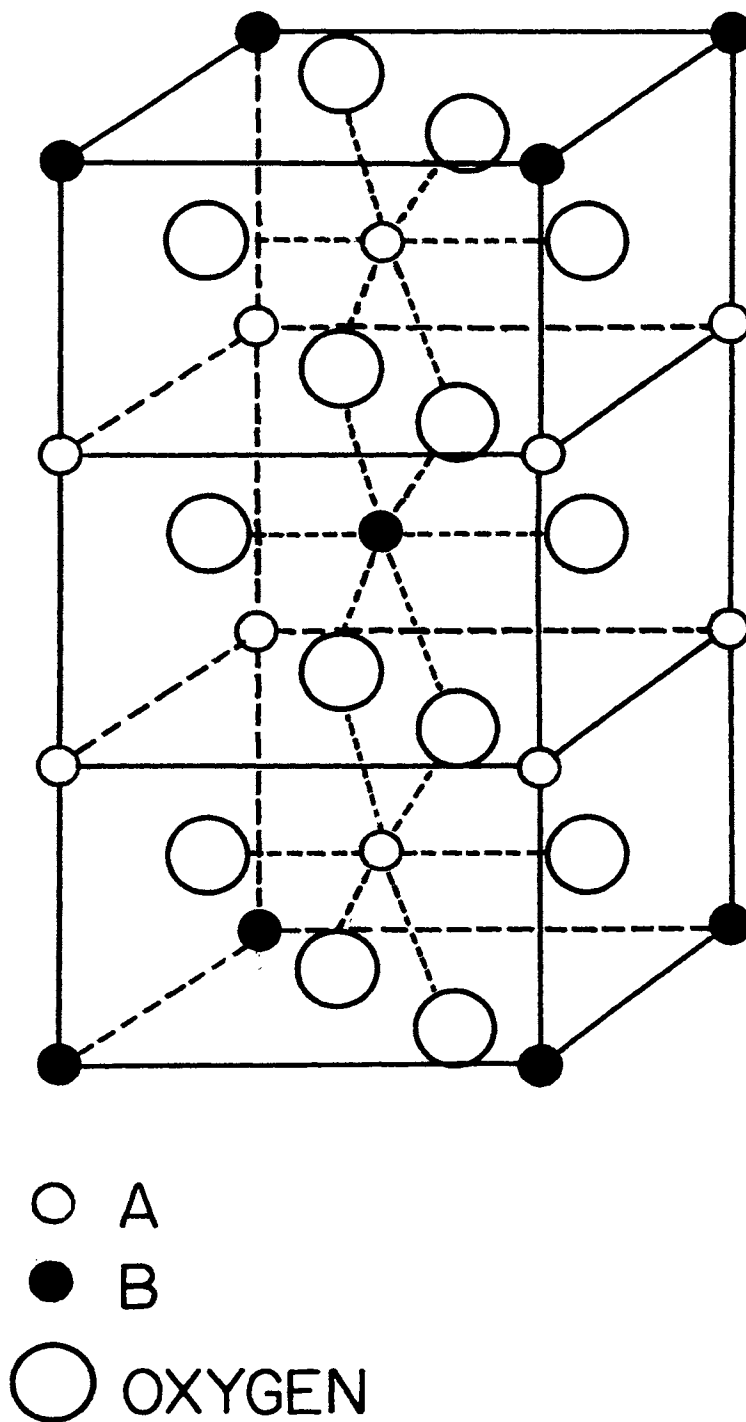


FIGURE 1. INVERSE TRIRUTILE STRUCTURE

The last data reported are, however, doubtful as those authors used alundum crucibles for melting, certainly increasing the Al_2O_3 content in their samples. The aim of the present work is to delineate the glass-forming region in the system and to provide preliminary information for phase diagram construction.

II. EXPERIMENTAL PROCEDURE

A. Sample Preparation

Fourteen samples with the compositions listed in Table I were prepared from TeO_2 (Alfa Inorganics, 99.5%) and Al_2O_3 (Fisher Reagent). Thirty-gram batches, with each component weighed to the nearest milligram, were prepared. The batches were mixed by grinding with mortar and pestle and stored in glass bottles.

B. Synthesis Methods

All heating experiments were conducted in a fume hood because of the toxicity of TeO_2 .

In air:

Approximately 2 gr of each sample was placed in a weighed platinum crucible, heated at 600°C for a few minutes to remove adsorbed water, and weighed. A set of 4 samples was then placed in a furnace controlled by an on-off set-point controller at each of 7 temperatures listed in Table II. Pt-Pt10Rh thermocouples were placed into the furnace adjacent to the crucibles and connected to a millivolt potentiometer. Observed temperature variation was $\pm 5^\circ\text{C}$. The samples were heated for 4 hours, removed, weighed, and examined by X-ray diffraction.

In vacuum:

A complete set of 14 samples was placed in silica tubes under vacuum no lower than 1 mm Hg and sealed. Then the samples were fired in set-point controlled furnaces at

TABLE I

Compositions investigated in the System $\text{Al}_2\text{O}_3\text{-TeO}_2\text{-O}_2$

Sample Number	Molar Composition	Weight %	
		TeO_2	Al_2O_3
1	A_9T	14.82	85.18
2	A_4T	28.13	71.87
3	A_7T_3	40.15	59.85
4	A_2T	43.90	56.10
5	A_3T	51.06	48.94
6	AT	61.02	38.98
7	A_2T_3	70.13	29.87
8	AT_2	75.79	24.21
9	A_3T_7	78.51	21.49
10	AT_4	86.23	13.77
11	AT_9	93.37	6.63
12	AT_{19}	96.75	3.25
13	AT_{49}	98.71	1.29
14	AT_{99}	99.36	0.64

A = Al_2O_3 T = TeO_2

TABLE II

Temperatures selected for sample synthesis

Air	Vacuum
600 °C	600 °C
635	-
666	666
730	750
790	-
850	850
900	-

temperatures listed in Table II for 5 hours, removed from the tubes, and examined by X-ray diffraction.

C. Vaporization Measurements

Weight losses were measured as functions of composition at all temperatures in air by weighing samples before and after firing.

D. X-Ray Investigation

All samples were examined by X-ray powder diffractometry using a General Electric recording diffractometer. Data were obtained using CuK_α radiation at a scanning rate of 2° 2θ /min. for phase identification and at 0.2 2θ /min., with Na_2WO_4 as an internal standard, for measurement of lattice parameters of several samples containing TeO_2 as the only crystalline phase.

E. DTA Measurements

A Stone differential thermal analysis apparatus, with fully automatic recording, was employed to study phase development. The measuring head is shown in Figure 2. As sample holders small platinum dishes were placed directly on the differential thermocouples. The weights of samples and Al_2O_3 standards were about 0.1 gr. Heating and cooling rates of $10^\circ\text{C}/\text{min}$ were used.

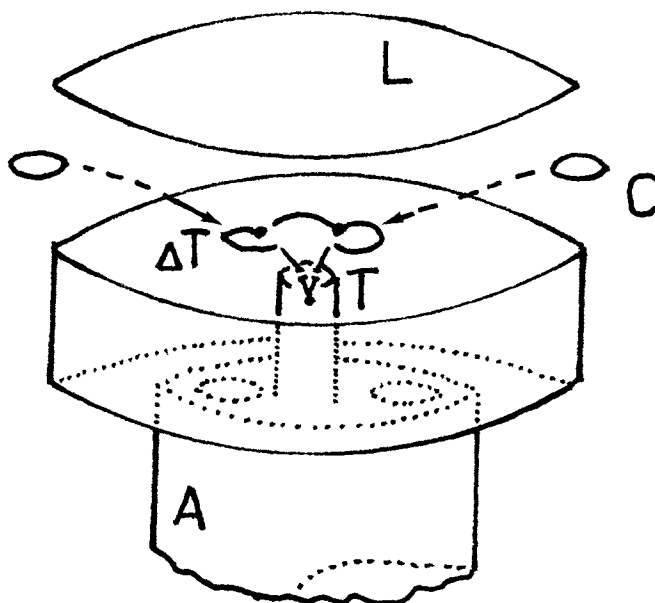


FIGURE 2. Head of DTA Apparatus

Metal chamber with removable lid (L) contains a ceramic thermocouple tube for temperature (T) and thermal difference (ΔT) measurements. Dishes (C) holding sample and standard are placed onto the wire loops.

F. Electron-microscope Measurements

A set of samples of different compositions, previously fired at 800°C , was investigated by scanning electron microscope for purposes of correlation with X-ray results. Samples were prepared by grinding on SiC papers of the following grit sizes: 120, 180, 240, 320, 400 and 600, and given a final polish with 1μ Al_2O_3 powder on microcloth. The samples were stored under distilled water to prevent surface corrosion. Each sample was etched with a solution of 1 HF + 10 H_2O for

8 sec. and washed by 3% solution of HCl and by distilled water. Immediately after drying the samples were gold-plated in a vacuum of 10^{-5} torr and investigated by scanning electron microscope.

III. RESULTS

A. Phase Identification

In air:

Each of 14 samples fired at each of seven different temperatures was analyzed by X-ray powder diffraction.

Phase assemblages are shown in Fig. 3.

The single phase TeO_2 is developed in TeO_2 -rich samples up to 10% Al_2O_3 . Whereas Al_2O_3 -rich samples up to 50% mol% TeO_2 , show two phases, Al_2O_3 and Al_2TeO_6 . However, the most interesting part of the system lies below the glass-forming region (temperature 660°C) between 50 and 70 mol% TeO_2 . In this region, three different phase mixtures were observed:

- (1) Al_2TeO_6 + Phase "Y" + rest of unreacted TeO_2
- (2) Phase "Y" + TeO_2
- (3) Unreacted mix of Al_2O_3 and TeO_2 with trace of Phase "Y"

Phase "Y" has a composition near $\text{Al}_2\text{Te}_2\text{O}_7$ but for a precise description more investigation is needed.

It was noted that, depending on the temperature, the glass forming range is comparatively wide: from about 95 to 65 mol% of TeO_2 . All glasses obtained were greenish-yellow in color.

In vacuum:

The phases produced in vacuum are much simpler than those in air because of the lack of oxygen (Figure 4). Al_2O_3 and

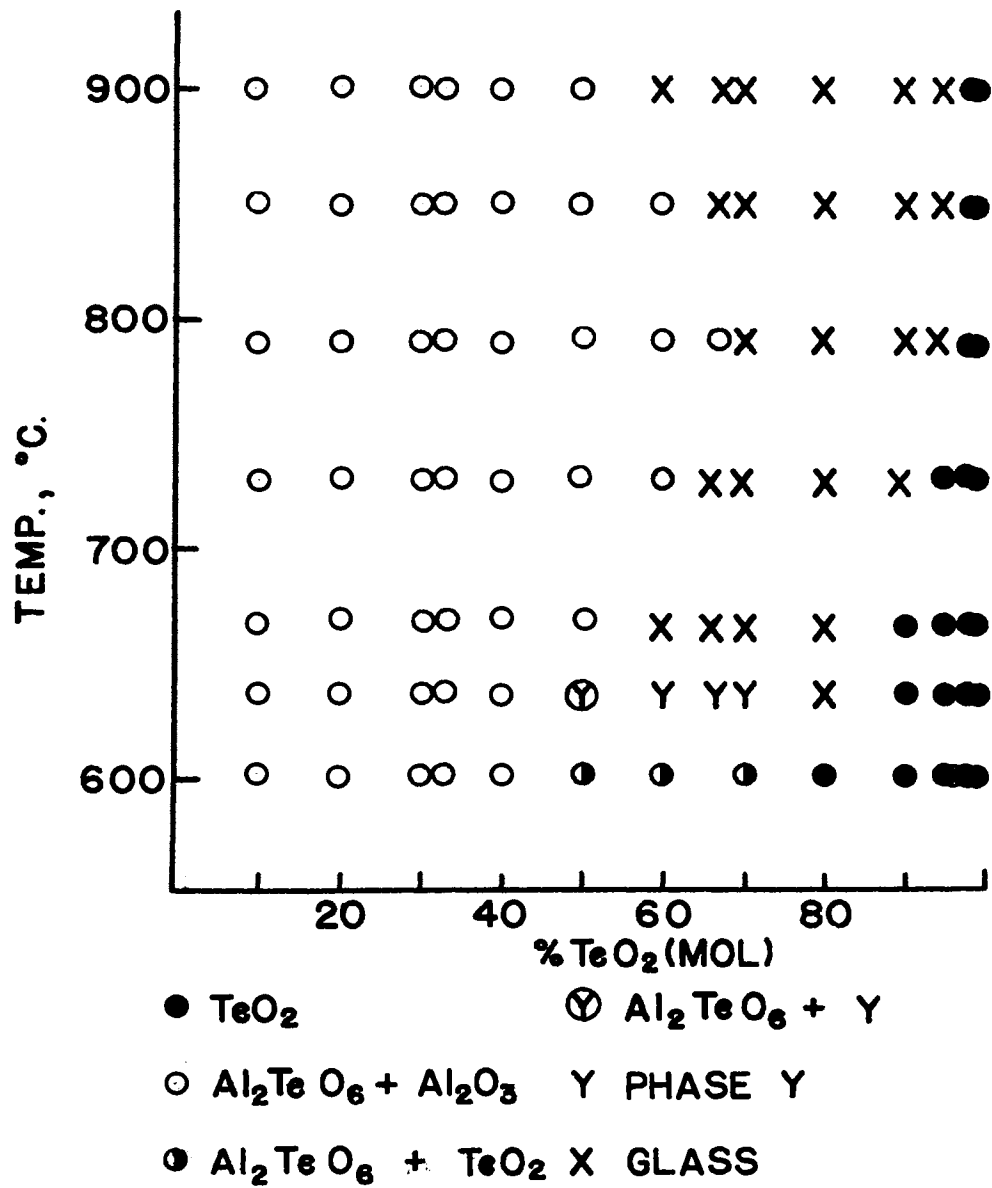


FIGURE 3. SAMPLES INVESTIGATED IN AIR

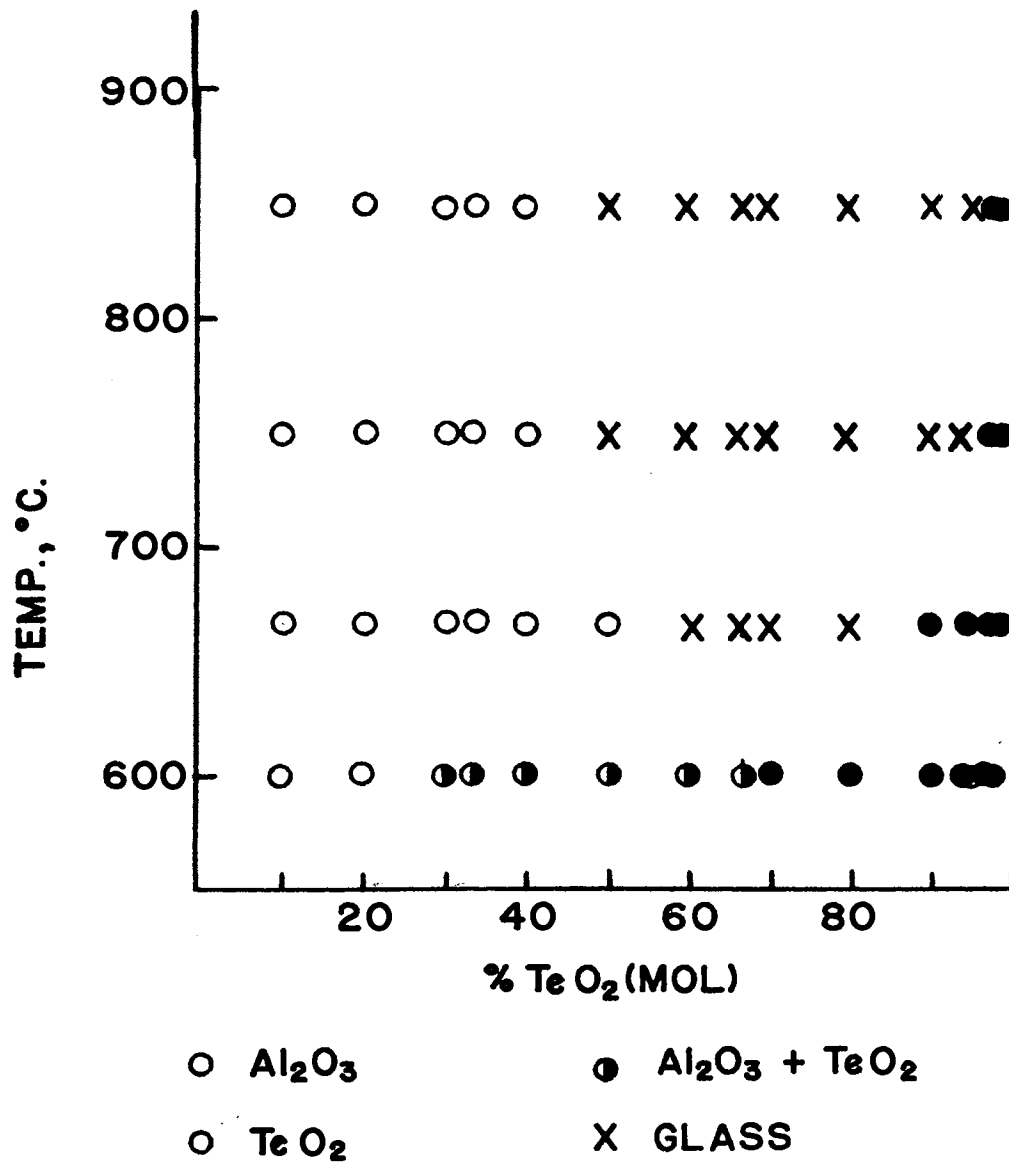


FIGURE 4. SAMPLES INVESTIGATED IN VACUUM

TeO_2 , therefore, are the only stable compounds because oxygen is not available at pressures necessary to oxidize tellurium to the +6 state. For Al_2O_3 and/or TeO_2 -rich regions, only the single phases Al_2O_3 and TeO_2 were found. The intermediate region showed only glass but that region is wider than that in air. At lower temperatures the time of synthesis was not sufficient to reach equilibrium. Typical diffractograms are shown in Figure 5.

B. Vaporization Characteristics

Owing to the high vapor pressure of solid TeO_2 vaporization is rapid at temperatures employed in this work. The vaporization process is assumed to be a simple dissociation. The vaporization-oxidation characteristics of Al_2O_3 - TeO_2 mixtures for different temperatures, calculated from a decrease and/or increase in weight of original samples, is shown in Figure 6.

The curves plotted can be compared with the theoretical one calculated from the assumption that Te is completely oxidized to the +6 state with no vaporization loss. The initial elevated slopes of experimental curves are due to tellurium oxidation in an agreement with the theoretical prediction. The maxima are shifted to the Al_2O_3 side of the theoretical maximum, indicating shift of composition by vaporization. Because of vaporization, therefore, the composition of the tellurate is difficult to verify.

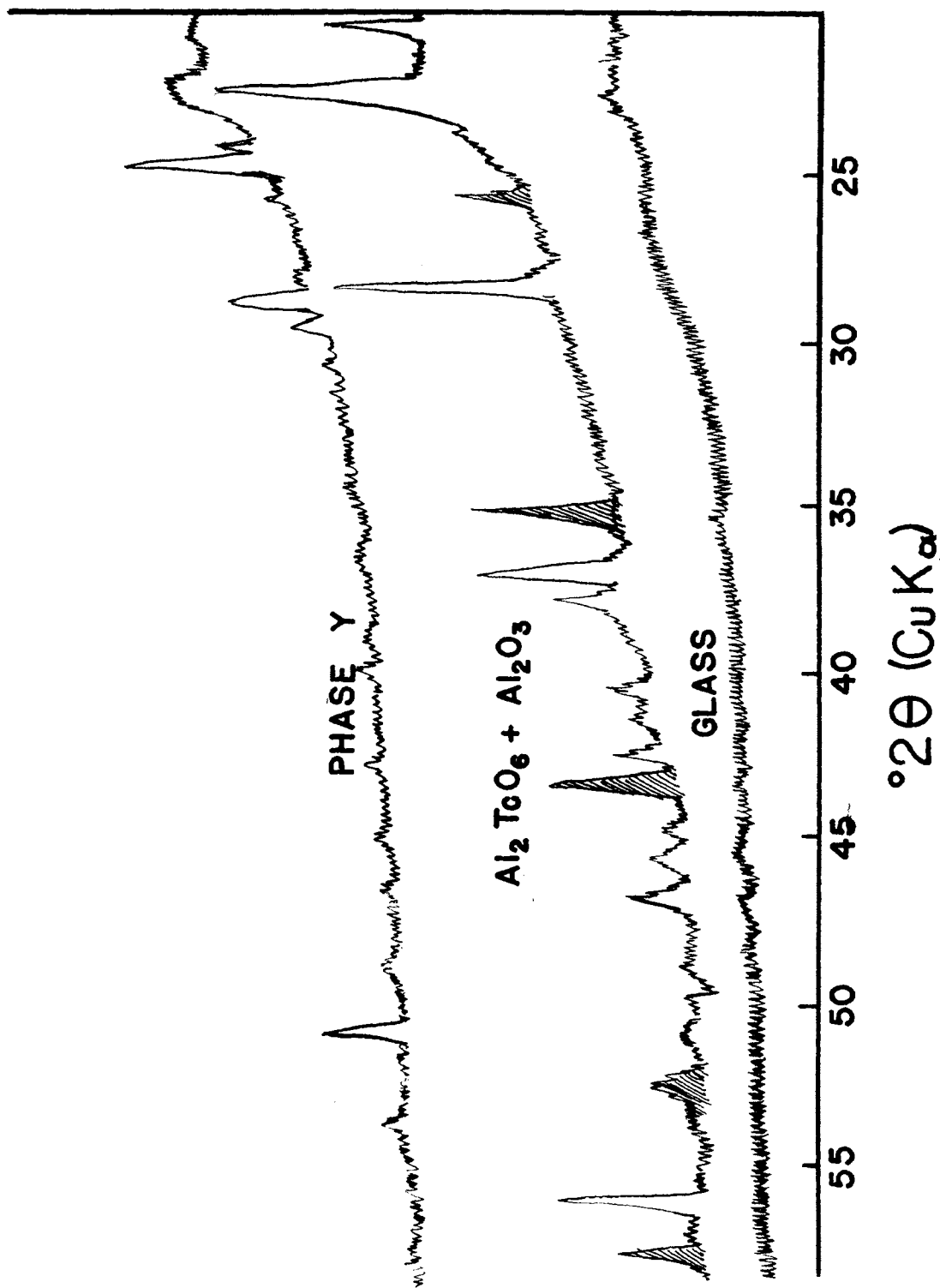


FIGURE 5. TYPICAL X-RAY PATTERNS

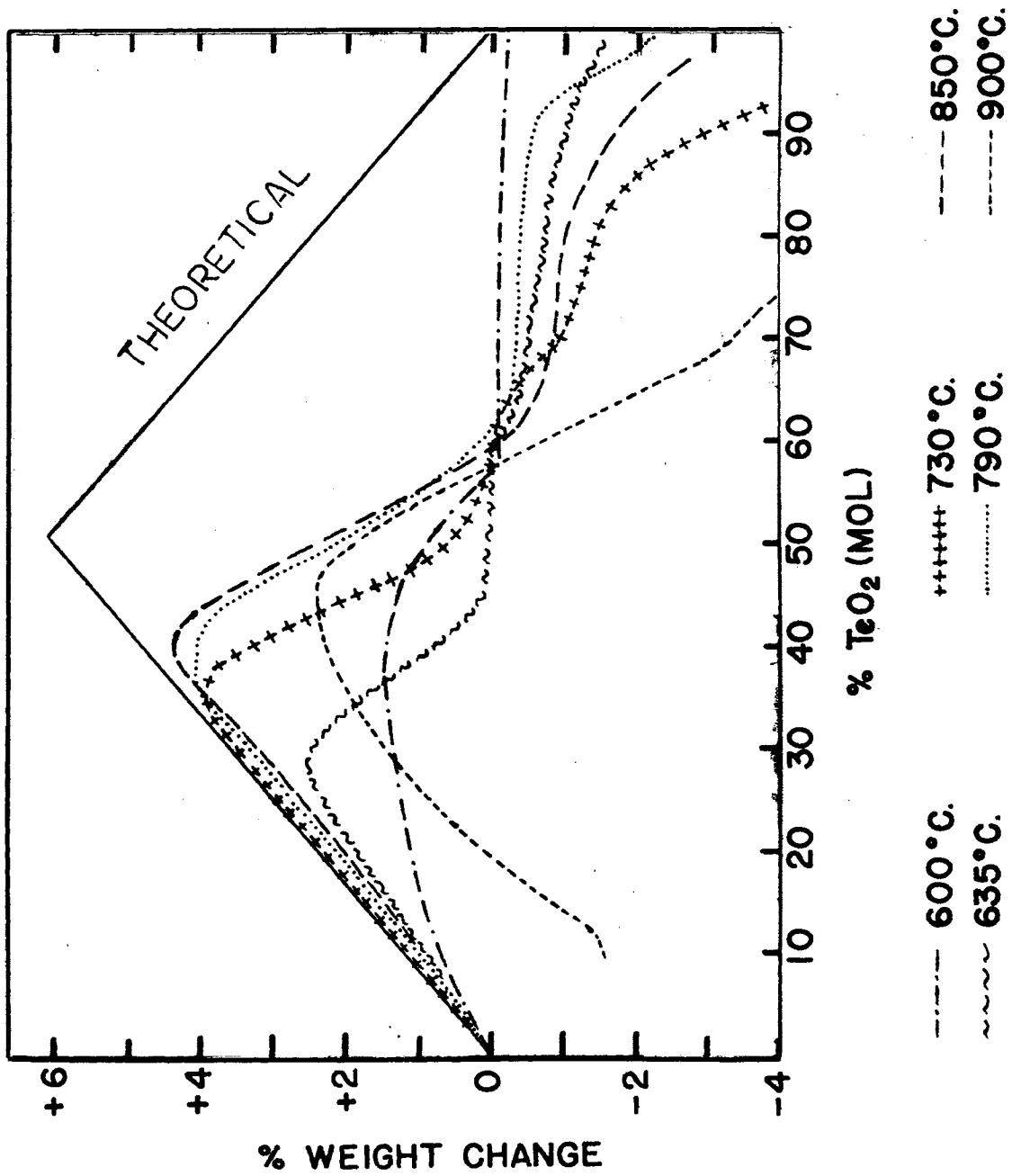


FIGURE 6. VAPORIZATION CHARACTERISTICS

C. Glass Devitrification

Some of the glassy samples were devitrified by a heat treatment at 500°C for 5 hours. The X-ray analysis showed a crystalline phase ("Y"), in the vicinity $\text{Al}_2\text{Te}_2\text{O}_7$, and TeO_2 .

D. DTA Measurements

All measurements were made under the same conditions in air for powdered samples. The traces obtained were very complex. For interpretation, it is necessary to assume a certain mechanism of the reaction taking place during heating. In Figure 7 a set of traces for one composition quenched from three different temperatures can be seen. In Figure 8 a set of curves experimentally obtained for different compositions of samples previously prepared at the same temperature is shown. To aid in the understanding of these traces, a simplified model for the curve is presented in Figure 9, together with two possible interpretations of the complex peaks between temperatures of 590-660°C.

The real DTA peaks presented in Figures 7 and 8 are composed of two oppositely directed major peaks as is shown on the idealized curve in Figure 9. The small experimentally obtained peaks in the temperature range 600-660°C are thus composed of the overlapping endothermic and exothermic effects, melting and oxidation. In certain parts of the complex process one of the two reactions may be more intense but it can be reversed by the onset of the opposite reaction, changing the direction instantly.

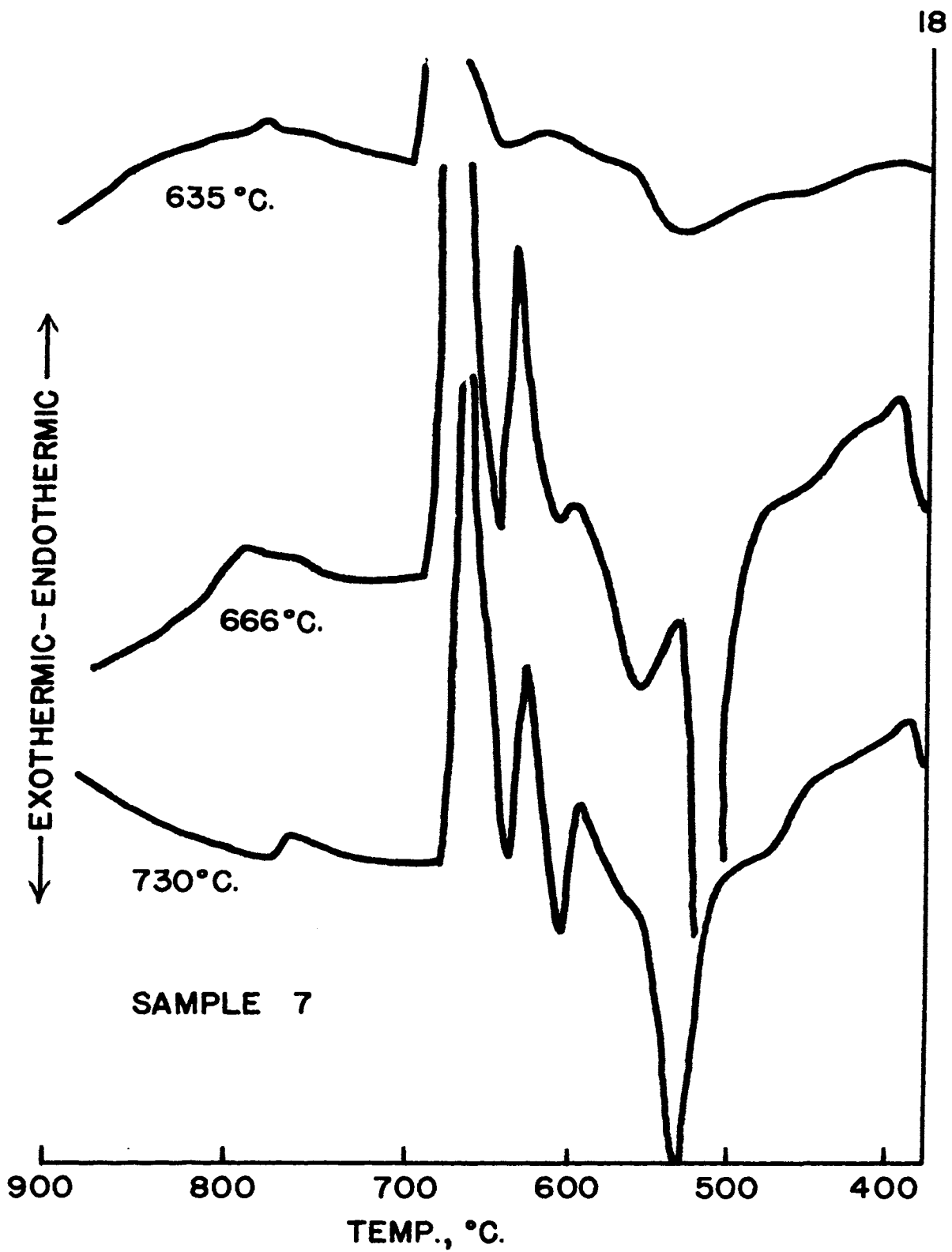


FIGURE 7. DTA CURVES

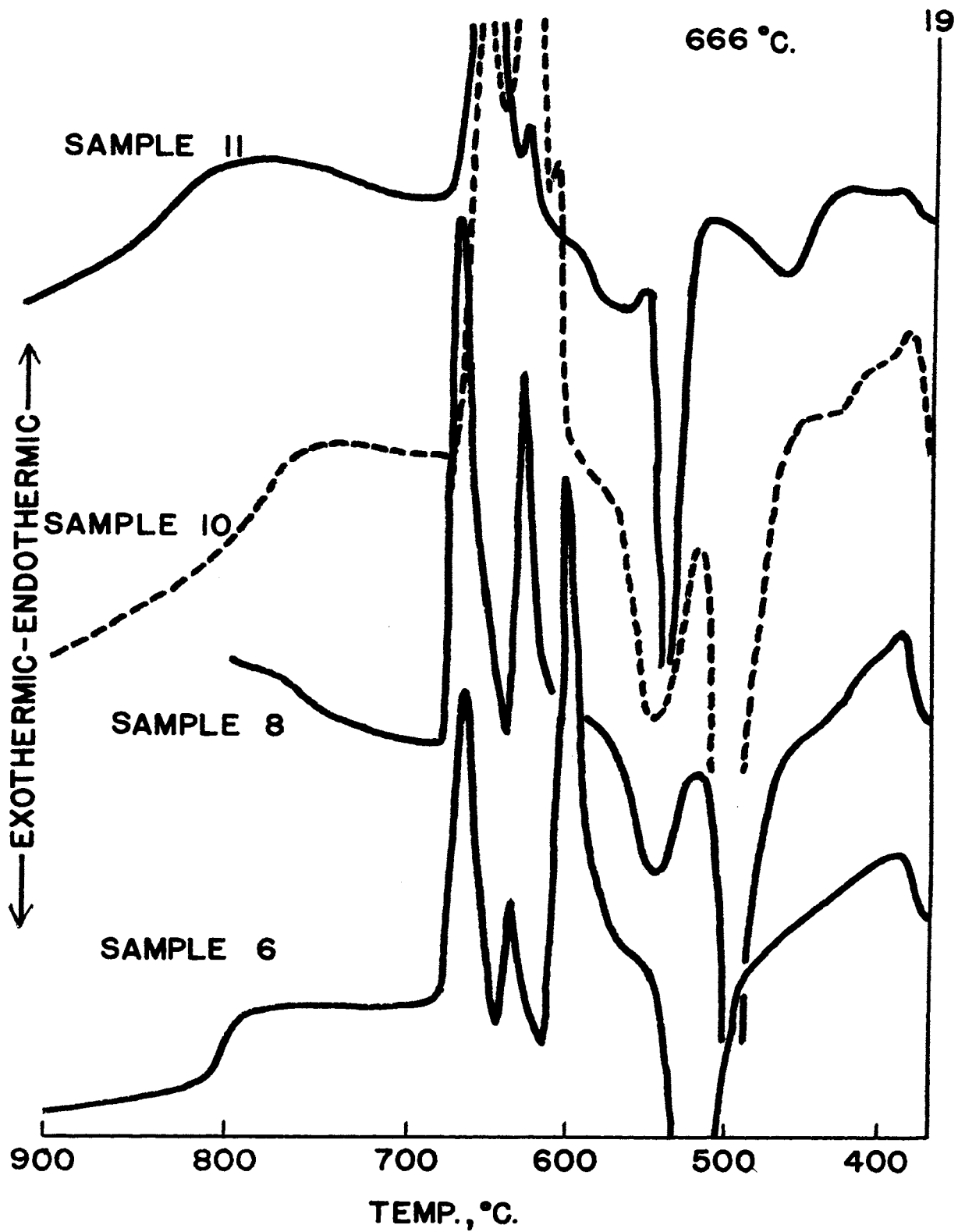


FIGURE 8. DTA CURVES

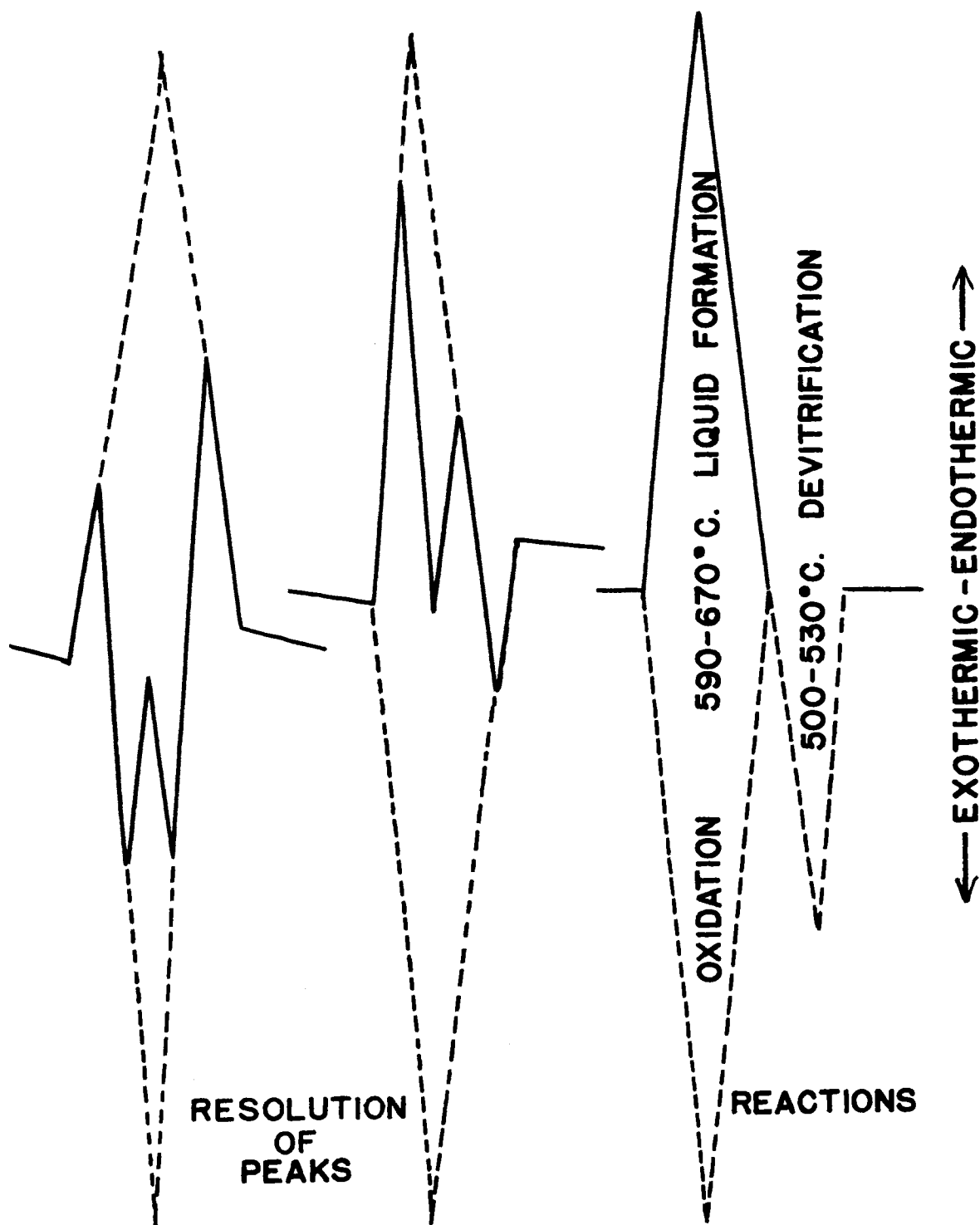


FIGURE 9. IDEALIZED DTA CURVE

IV. DISCUSSION

The results of synthesis experiments reported in this work, particularly the X-ray data for Al_2TeO_6 , are in essential agreement with those reported by Bayer (1). Al_2TeO_6 is the only stable intermediate phase in the system. The second phase detected by X-ray is designated "Y" because of uncertainty regarding its composition. It is assumed that the phase has a formula near $\text{Al}_2\text{Te}_2\text{O}_7$. The same X-ray lines were obtained for devitrified samples in the glassy region of the Al_2O_3 - TeO_2 system.

The glass forming region in air, as determined by X-ray analysis, is much wider than that reported by Zlomanov et al. (3). The Al_2O_3 -rich boundary of the region (about 65 mol% TeO_2) differs by more than 20% from the value published by the Russian investigators (90 mol% TeO_2 in alundum crucibles and about 80 mol% TeO_2 in porcelain). Obviously this difference can be explained by dissolution of the part of Al_2O_3 containers employed by Zlomanov et al. (3).

On the basis of 98 points determined in air a tentative phase diagram can be suggested (Figure 10). There is unfortunately little unequivocal information from the DTA measurements. For precise boundary determinations long time isothermal runs, with controlled TeO_2 contents, are necessary. Thus only a tentative phase diagram can be presented.

The most definite parts are the Al_2O_3 -rich portion of the diagram and the glass-forming region. The TeO_2 -rich portion of

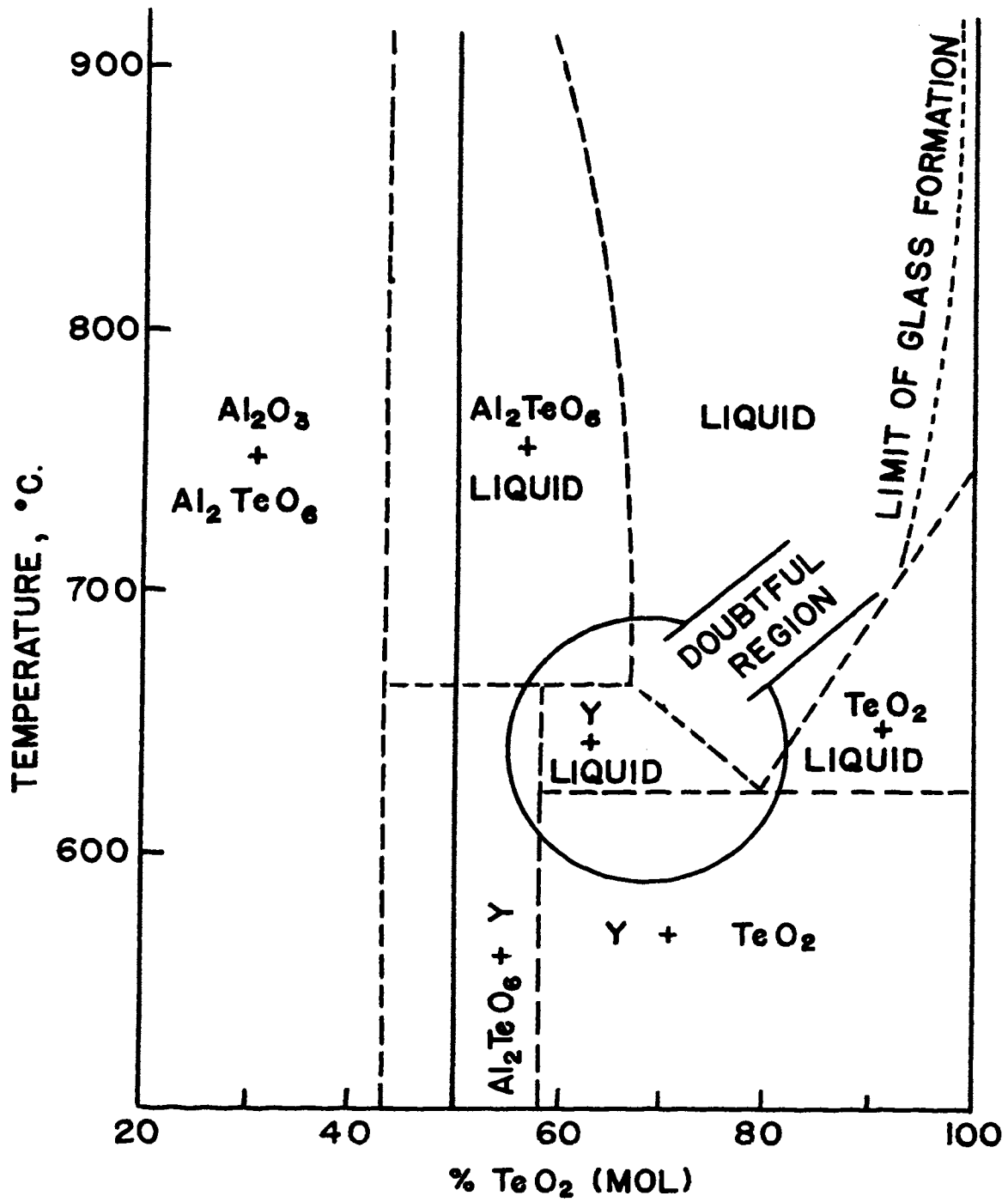


FIGURE 10. PSEUDOBINARY DIAGRAM, ISOBARIC IN AIR SYSTEM Al_2O_3 - TeO_2 - O_2

the diagram is a mix of TeO_2 and liquid up to the melting point of TeO_2 (734°C).

The uncertain region lies below the boundary between liquid and liquid + Al_2TeO_6 . The suggested incongruent melting point of phase "Y" in the vicinity of 660°C is not a true melting point but a rather more complex oxidation-melting temperature. Below 620°C phase "Y" still can be expected despite the fact that the samples showed unreacted oxides. The DTA traces of quenched samples (Figures 7 and 8) can provide some information. The first exothermic reaction indicates devitrification of glass at about 500°C to form phase "Y". The complex peak between 600° and 660°C indicates melting and oxidation and shows the field of phase "Y" + liquid existence to be very narrow. The sample of AT composition (No. 6) should lie at the phase boundary as reported by Bayer (1). But the DTA trace of that composition (Figure 8) shows an intense complex reaction that may be associated with liquid formation and phase "Y" oxidation. This suggests that the original phase boundary (full line in the phase diagram, Fig. 10) should be shifted to the left (dashed line). Using much longer reaction times one can eliminate the uncertainty, if the TeO_2 content of the sample is monitored continually. More information is needed both to find precise equilibria and to determine the compositions of phase "Y" and the tellurate.

The tentative phase diagram in vacuum has been constructed from a little more than half of the points determined in air. Assuming a certain similarity with the phase diagram in air a small field for phase "Y" may be expected. The Al_2O_3 -rich

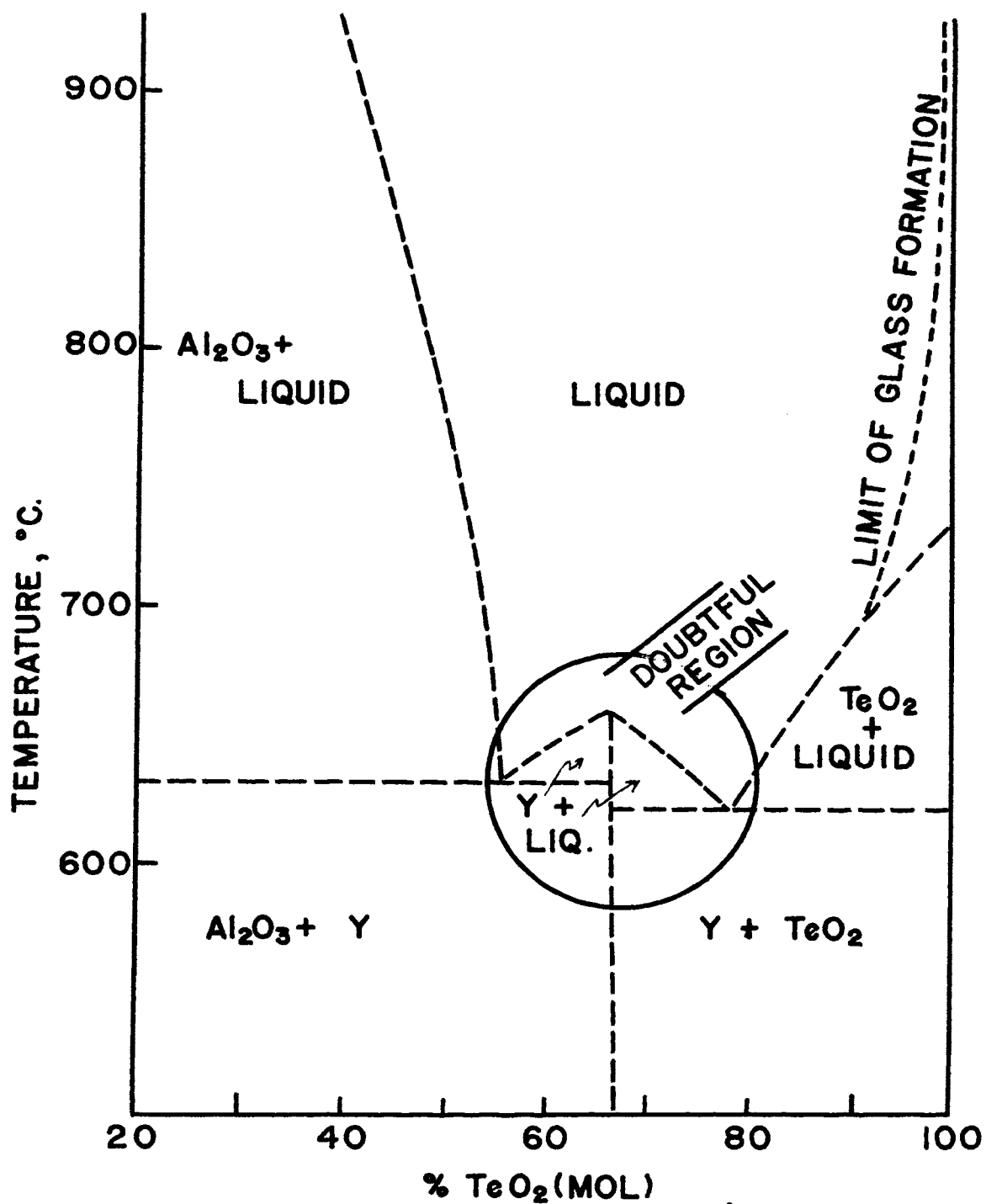


FIGURE II. PSEUDOBINARY SYSTEM IN VACUUM SYSTEM Al_2O_3 - TeO_2

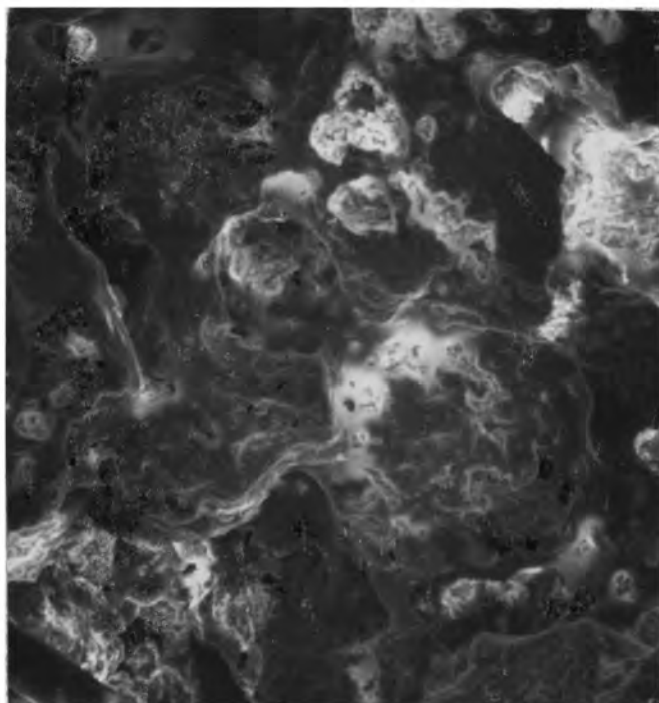
portion contains no Al_2TeO_6 because no oxidation of Te^{+4} took place. The eutectic compositions at approximately AT and AT_4 are excellent glass formers. The congruent melting point is suggested because of the absence of Al_2TeO_6 , resulting in a eutectic between phase "Y" and Al_2O_3 .

The scanning electron-microscope investigation made for a set of samples prepared at 800°C is basically in agreement with the X-ray results, but show more detail concerning the phases presented; see Figure 12a, b, c, d. The picture of AT composition (No. 6) shows a slightly amorphous appearance with no positive evidence of a glassy substance. The first two glassy samples AT_2 and A_3T_7 (Nos. 8 and 9) have a small number of crystals not detected by X-ray analysis. Crystals are absent in sample AT_4 (No. 10). The glassy sample AT_9 (No. 11), rich in TeO_2 , shows significant non-crystalline phase separation. Sample AT_{99} (No. 14) shows well formed TeO_2 crystals.

SAMPLE 6
AT

800 °C. 4 HRS.

100 μ



SAMPLE 8
AT₂

800 °C. 4 HRS.

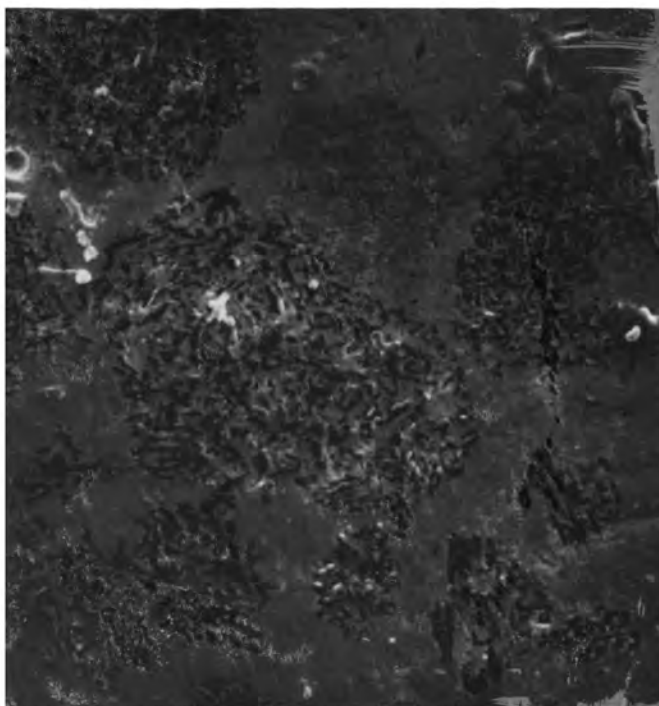


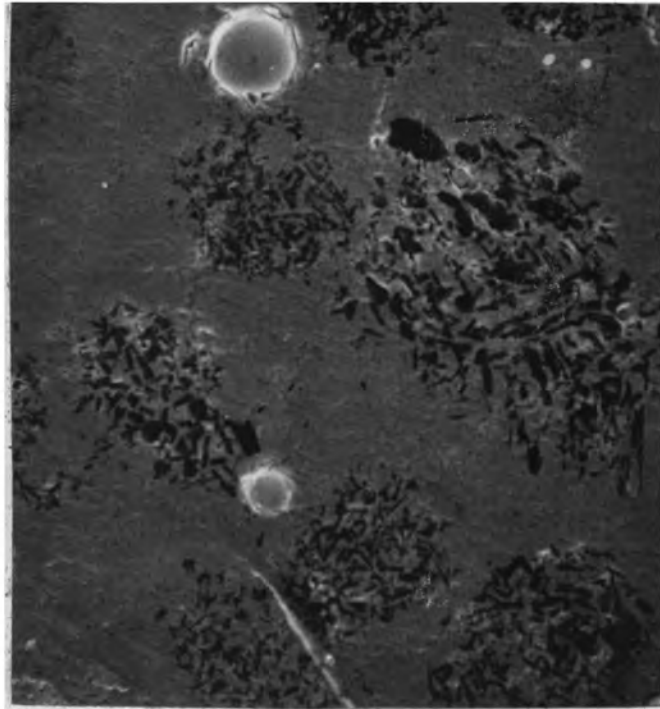
FIGURE 12(A) ELECTRON SCANNING MICROGRAPHS

SAMPLE 9

A_3T_7

800°C. 4 HRS.

—|—————|
100 μ



SAMPLE 10

AT_4

800°C. 4 HRS.

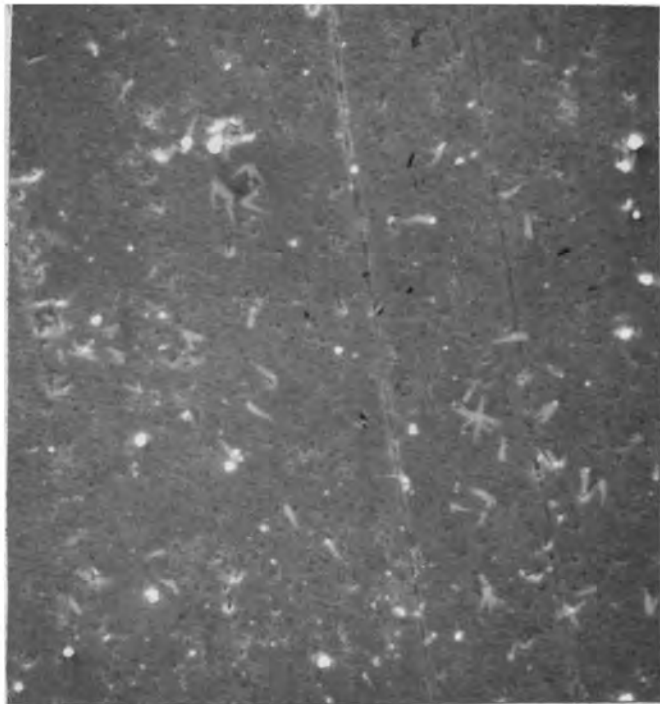
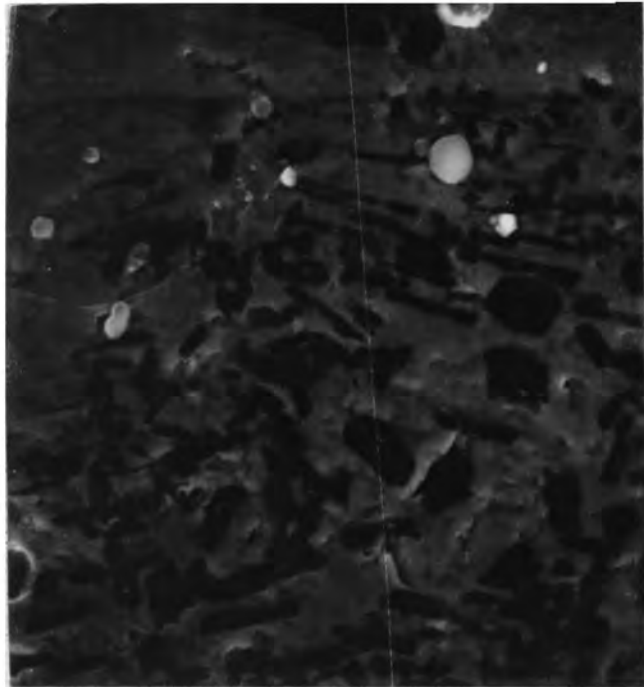
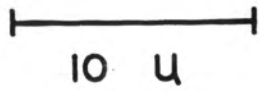


FIGURE 12 (B)

SAMPLE 8
AT₂
800°C. 4 HRS.



SAMPLE 11
AT₉
800°C. 4 HRS.

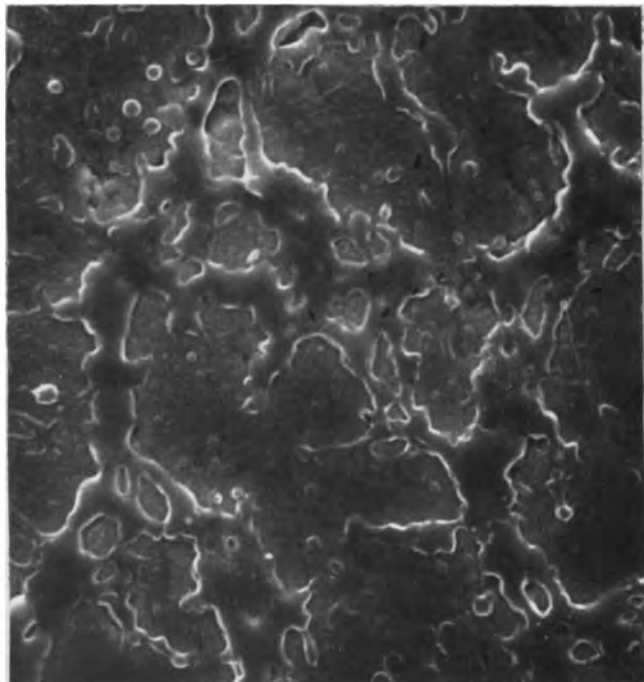


FIGURE 12 (D)

V. CONCLUSIONS

It has been demonstrated that the glass-forming region in the system $\text{Al}_2\text{O}_3\text{-TeO}_2$ is wider than reported previously. Oxidation of Te to the +6 state narrows the region of complete glass formation in air through formation of the tellurate Al_2TeO_6 . A new phase, possibly $\text{Al}_2\text{Te}_2\text{O}_7$, with Te in +4 state, has been identified but the composition and structure have not been established. The new phase, designated "Y", forms by devitrification of the glass and by direct precipitation in air or vacuum but the narrow "Y"-liquid stability field has not been satisfactorily delineated.

Complete description of phase compositions and equilibria will require much more detailed studies, with TeO_2 contents monitored as a function of time and temperature.

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VII. VITA

Vera Zelenkova Sestak was born April 17, 1945, in Prague, Czechoslovakia. She attended public school in Prague, graduating from high school in Prague in June 1963. She attended the University of Chemical Technology in Prague from September 1963 to June 1968. She received a Master of Science degree in Inorganic Technology from that institution in June 1968. From October 1969 until the present she has been enrolled in the Graduate School of the University of Missouri - Rolla studying for a Master of Science degree in Ceramic Engineering.