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Thermal crystallization behavior of As-Te glasses

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Thermal crystallization behavior of As_xTe_{100-x} ($25 \leq x \leq 60$) glasses is studied by differential scanning calorimetry. As_xTe_{100-x} glasses with $x < 40$ are found to exhibit one glass transition and one crystallization reaction, during heating. On the other hand, glasses with $40 \leq x \leq 50$ show one glass transition and two crystallization reactions. Unlike other binary telluride glasses, the first crystallization reaction in As_xTe_{100-x} glasses does not correspond to the precipitation of hexagonal Te. It corresponds to the formation of a metastable intermediate crystalline phase, which transforms into the equilibrium As_2Te_3 phase at the second crystallization reaction. As a consequence of this difference in the crystallization behavior, As_xTe_{100-x} glasses with $40 \leq x \leq 50$ do not show the phenomenon of double glass transition. Further, the two crystallization reactions of these glasses are found to merge progressively, with the increase in arsenic content. As a result, As_xTe_{100-x} glasses with $50 < x \leq 60$ show only one crystallization reaction. An explanation for this interesting crystallization behavior of As_xTe_{100-x} glasses is provided with the help of x-ray diffraction, electron microscopy, and thermogravimetry studies.

I. INTRODUCTION

Chalcogenide glasses have been studied extensively in recent times because of their interesting physical properties, with many promising technological applications.[1,2] One of the interesting phenomena exhibited by these glasses is the electrical switching, observed by Ovshinsky.[3] The switching behavior of chalcogenide glasses is due to the partial crystallization of the samples during the application of a high current or a voltage across the material.[4] It is also known that glasses which exhibit a crystallization reaction on heating show memory-type switching and glasses which do not crystallize on heating show threshold-type switching.[5,6] Therefore a knowledge of crystallization behavior of chalcogenide glasses may be useful in identifying a suitable candidate for switching applications.

Further, it is well known from the earlier studies that Te-based chalcogenide glasses such as Si-Te,[7] Ge-Te,[8,9] Al-Te,[10,11] Ga-Te,[12] Pb-Ge-As-Se,[13] etc., exhibit the phenomenon of double glass transition and double stage crystallization. The double stage crystallization occurs in these glasses due to the primary crystallization of excess Te in an amorphous residual matrix. The second glass transition is a consequence of Te phase separation.

In this paper, an effort is made to understand the thermal crystallization behavior of As_xTe_{100-x} glasses by using differential scanning calorimetry (DSC) and to compare it with the behavior of other Te-based chalcogenide glasses. An attempt is also made in the present study to explain the crystallization behavior of As-Te glasses, using x-ray diffraction, electron microscopy, and thermogravimetry analyses.

II. EXPERIMENT

Bulk semiconducting As_xTe_{100-x} ($25 \leq x \leq 60$) glasses were prepared by the melt quenching method. High-purity As and Te samples (99.999% pure) were taken in desired proportions in quartz ampoules and the ampoules were evacuated to 10^{-5} Torr and then sealed. The sealed ampoules were heated in a horizontal furnace at a rate of 20 °C/h up to a temperature of 850 °C and the contents were agitated in the molten state for about 48 h for thorough homogenization. The ampoules containing the melt were subsequently quenched into ice water containing sodium hydroxide. The glassy nature of the samples was confirmed by x-ray diffraction studies.

Thermal crystallization studies were carried out on these glasses, using a Stanton Redcroft Differential Scanning Calorimeter. About 20–25 mg of samples were taken for each DSC run. Alumina (Al_2O_3) was used as the reference material in all the DSC experiments. X-ray structural investigations and electron microscopic studies were performed on the samples recovered after the crystallization reactions indicated in the DSC. Thermogravimetric analysis was also undertaken on the samples, to supplement the DSC studies.

III. RESULTS AND DISCUSSION

A. DSC studies

The differential scanning calorimetric thermograms of a few representative As_xTe_{100-x} glasses are shown in Figs. 1–4. As indicated in Fig. 1, glasses with $x < 40$ show an endothermic glass transition, followed by an ex-

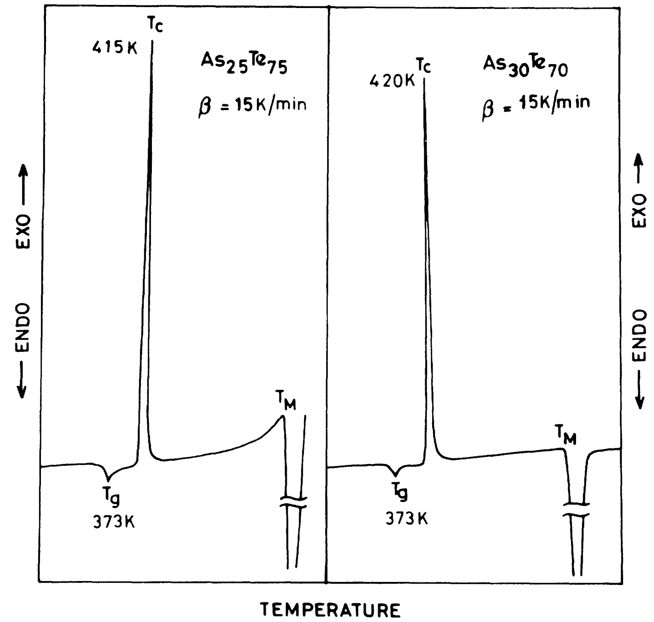


FIG. 1. DSC traces of $As_{25}Te_{75}$ and $As_{30}Te_{70}$ glasses (heating rate 15 K/min).

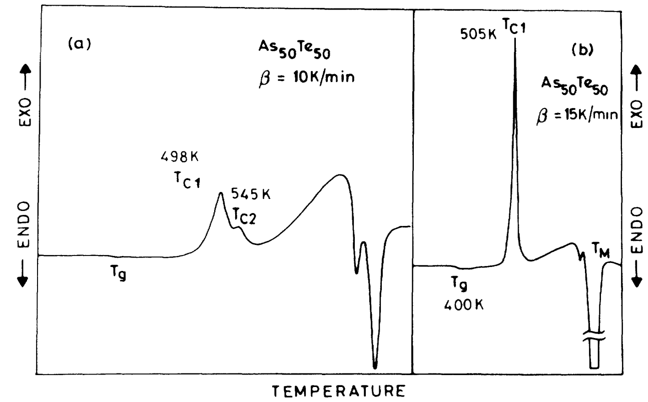


FIG. 3. The DSC thermogram of $As_{50}Te_{50}$ glass, at 10 and 15 K/min heating rates.

othermic crystallization reaction and an endothermic melting on heating. On the other hand, glasses with $x=40$, 45, and 50 exhibit an endothermic glass transition and two distinct exothermic crystallization processes as illustrated in Figs. 2 and 3. However, glasses with $x=55$ and 60 show one glass transition and one exothermic crystallization reaction only, as indicated in Fig. 4. Even though the thermal crystallization behavior of As-Te glasses with $x<40$ and $x\geq 55$ appear to be similar, the actual crystallization processes occurring in them are different. This difference in behavior can be easily visualized from Figs. 2 and 3. As the arsenic concentration is increased, the second crystallization reaction progressively approaches the first crystallization and they start merging at the composition $x=50$. In the case of $x=50$ glass, the second crystallization reaction is indicated only by a satellite peak at slower heating rates. However, at higher heating rates this reaction is not observed separately, as shown in Fig. 3. Therefore in the case of glasses with $x=55$ and 60 the crystallization reactions get superimposed, and they are not observed separately. This observation is consistent with earlier studies of Quinn.[14]

In tellurium-based binary and ternary glasses, the double stage crystallization is often associated with the phase separation occurring in these materials at higher temperatures.[11] Further, in many telluride glasses which exhibit phase separation and double stage crystallization, a double glass transition can also be observed, by following a

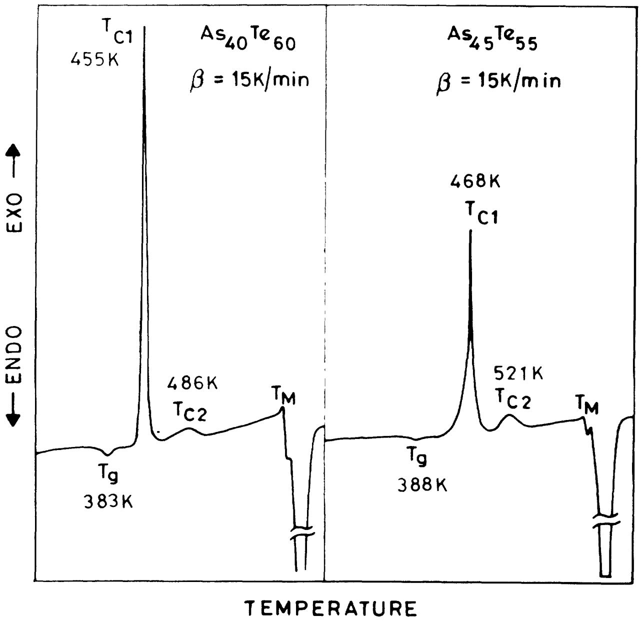


FIG. 2. DSC thermograms of $As_{40}Te_{60}$ and $As_{45}Te_{65}$ glasses (heating rate 15 K/min).

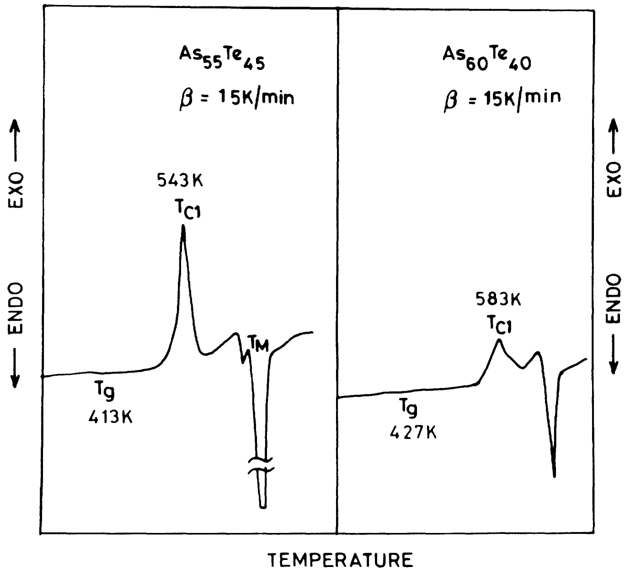


FIG. 4. DSC traces of $As_{55}Te_{45}$ and $As_{60}Te_{40}$ glasses (heating rate 15 K/min).

method proposed by Lasocka[15] and Chen.[16] In this method, glasses are heated up to the end of the first crystallization reaction and then quickly cooled down to the ambient temperature. If the same samples are reheated subsequently they exhibit the second glass transition reaction.[5–10]

The present studies indicate that even though $As_{40}Te_{60}$ and $As_{45}Te_{55}$ glasses exhibit a double stage crystallization, they do not show a double glass transition. Figure 5(a) shows the DSC traces of As_xTe_{100-x} glasses ($x=40,45$), heated up to the end of the first crystallization reaction. If the samples are quickly cooled back to the ambient temperature from the first crystallization reaction and reheated, the DSC traces shown in Fig. 5(b) are obtained. It can be seen from Fig. 5(b) that in $As_{40}Te_{60}$ and $As_{45}Te_{55}$ samples, quenched from T_{c1} and reheated, the second glass transition is not observed, only the second crystallization reaction is shown. This indicates clearly that though As-Te glasses exhibit a double stage crystallization, they do not exhibit the phenomenon of double glass transition, as seen in other binary telluride glasses such as Si-Te,[7] Ge-Te,[8] etc. X-ray diffraction and electron microscopic investigations are also carried out in the present study, to understand the difference in the thermal crystallization behavior of As-Te glasses.

B. X-ray diffraction analysis on thermally annealed As_xTe_{100-x} glasses

1. $25 \le x < 40$

X-ray diffraction studies have been performed on samples annealed at the first and second crystallization temperatures for about 15 min, to determine the structure of the crystalline phases. Figure 6 shows the x-ray diffraction patterns of the samples, with $x<40$, annealed in evacuated (10^{-3} Torr) ampoules above their crystallization temperature. It can be seen from these patterns that As_xTe_{100-x} glasses with $x<40$ exhibit a eutectic-type crystallization into monoclinic arsenic telluride and hexagonal tellurium phases.

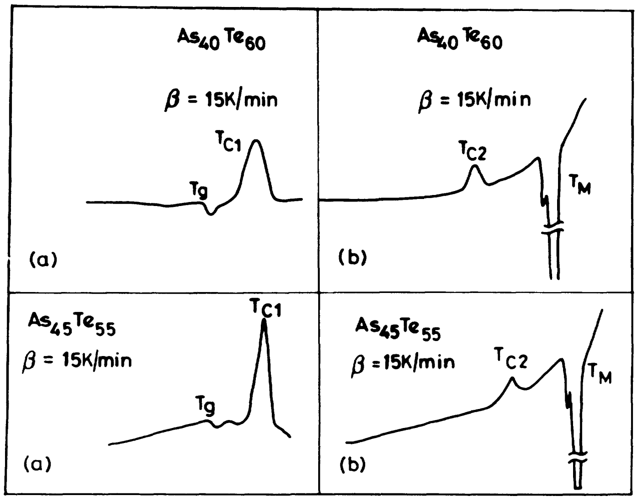


FIG. 5. DSC traces of $As_{40}Te_{60}$ and $As_{45}Te_{55}$ glasses. (a) The samples are heated up to the first crystallization reaction and cooled down to room temperature. (b) The samples which have been previously heated up to the first crystallization and cooled to room temperature are reheated until complete crystallization.

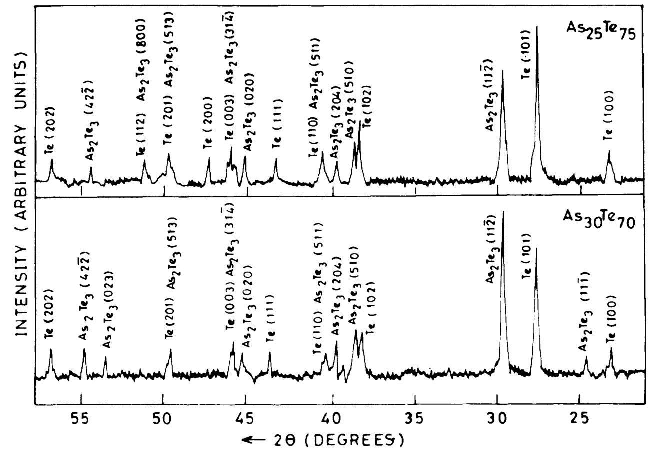


FIG. 6. X-ray diffraction patterns of two glasses, $As_{25}Te_{75}$ and $As_{30}Te_{70}$, representing the $25 \le x < 40$ region, annealed at T_{c1}.

2. $40 \le x \le 50$

Figures 7 and 8 illustrate the x-ray diffraction patterns of two representative glasses in this composition range, $As_{40}Te_{60}$ and $As_{45}Te_{55}$, annealed at the first crystallization temperature in evacuated quartz ampoules for about 5 min. It is interesting to note that these patterns do not correspond to crystalline Te, As, or As_2Te_3 phases. This indicates that in $As_{40}Te_{60}$ and $As_{45}Te_{55}$ glasses, which exhibit a double stage crystallization, the first crystallization reaction corresponds to the formation of a new intermediate crystalline phase. This behavior is in contrast with other binary telluride glasses such as Si-Te,[7] Ge-Te,[8] etc., which show phase separation and primary crystallization of Te at the first crystallization reaction. The for-

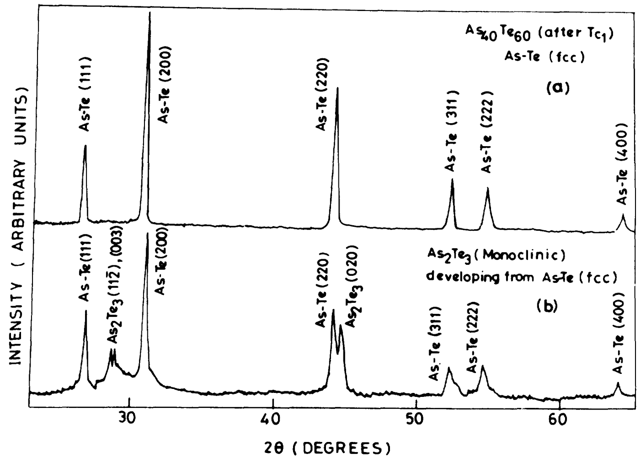


FIG. 7. X-ray diffraction patterns of $As_{40}Te_{60}$ glass annealed in a sealed evacuated (10^{-3} Torr) ampoule; (a) annealed at T_{c1} for 5 min, (b) prolonged annealing at T_{c1} for 10 min.

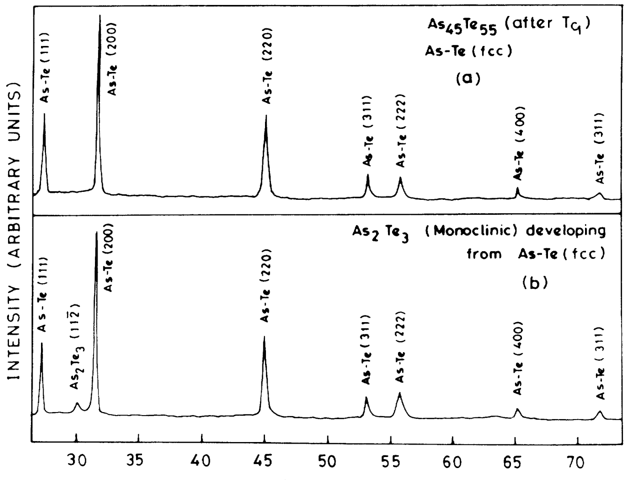


FIG. 8. X-ray diffraction patterns of $As_{45}Te_{55}$ glass annealed in a sealed evacuated (10^{-3} Torr) ampoule; (a) annealed at T_{c1} for 5 min, (b) prolonged annealing at T_{c1} for 10 min.

mation of an intermediate crystalline phase, while heating, in certain As-Te glasses, is also noted by other authors.[14,17–20] However, there are many discrepancies in the identification of the structure and composition of this intermediate phase.

Quinn has suggested that the intermediate phase which occurs in the crystallization of As-Te glasses probably has a NaCl-type structure. This author has also generated the intensity values for the permitted reflections and calculated the *d* values by computer simulation.[14] The *d* spacings estimated by Quinn are comparable with the *d* values observed in the present studies (Table I). It is also interesting to note that the intermediate phase formed during the first crystallization of $As_{40}Te_{60}$ and $As_{45}Te_{55}$ glasses is metastable. Prolonged annealing of these glasses at T_{c1} leads to the progressive transformation of this phase into the stable equilibrium monoclinic As_2Te_3 phase. Figures 7(b) and 8(b) show the x-ray diffraction pattern of $As_{40}Te_{60}$ and $As_{45}Te_{55}$ glasses annealed at T_{c1} for about 10 min, indicating the development of a monoclinic As_2Te_3 phase, from the intermediate As-Te phase with NaCl-type structure. The kinetics of transformation of the intermediate As-Te phase to monoclinic As_2Te_3 phase is not dealt with in the present study and it forms a basis for further investigation.

TABLE I. The *d* spacing for $As_{40}Te_{60}$ and $As_{45}Te_{55}$ samples annealed in sealed evacuated ampoules at T_{c1}.

Observed *d* ($As_{40}Te_{60}$)	Observed *d* ($As_{45}Te_{55}$)	Simulated *d*	Phase	Simulated (*hkl*)
3.34	3.33	3.33	As-Te(fcc)	(111)
2.90	2.88	2.88	As-Te(fcc)	(200)
2.05	2.03	2.03	As-Te(fcc)	(220)
1.75	1.73	1.74	As-Te(fcc)	(311)
1.67	1.65	1.67	As-Te(fcc)	(222)
1.45	1.43	1.44	As-Te(fcc)	(400)
	1.32	1.33	As-Te(fcc)	(331)

The x-ray diffraction patterns of $As_{40}Te_{60}$ and $As_{45}Te_{55}$ glasses, annealed at the second crystallization temperature in evacuated quartz ampoules for about 15 min, are shown in Fig. 9. It can be seen from the figure that in As_xTe_{100-x} glasses, with $40 \leq x \leq 50$, the second crystallization corresponds to the transformation of the intermediate As-Te phase into the equilibrium monoclinic As_2Te_3 phase. It is interesting to note that the diffraction patterns of As_xTe_{100-x} glasses ($40 \leq x \leq 50$), annealed in vacuum at T_{c2}, correspond only to the monoclinic As_2Te_3 phase (Fig. 9). It may be possible that the excess arsenic present in $As_{45}Te_{55}$ and $As_{50}Te_{50}$ glasses is accommodated in the As_2Te_3 lattice itself by random replacement of Te atoms. If the same samples are annealed in air, the excess arsenic combines with oxygen (because of greater affinity) and forms As_2O_3, which separates out. X-ray diffraction patterns of $As_{45}Te_{55}$ and $As_{50}Te_{50}$ glasses, annealed at T_{c2} in air for about 5 min are shown in Fig. 10, indicating clearly the formation of monoclinic As_2Te_3 and As_2O_3 phases.

3. $x=55,60$

As mentioned in Sec. III A, $As_{55}Te_{45}$ and $As_{60}Te_{40}$ glasses do not show two crystallization reactions, corresponding to the formation of an intermediate As-Te phase and its subsequent transformation into the equilibrium monoclinic As_2Te_3 phase. These glasses show only one crystallization reaction and the x-ray diffraction studies are performed on $As_{55}Te_{45}$ and $As_{60}Te_{40}$ samples, annealed at the crystallization temperature for about 15 min in vacuum and also in air. The x-ray diffraction pattern of $As_{55}Te_{45}$ glass, as a representative sample, annealed in vacuum, is shown in Fig. 11(a). It is clear from

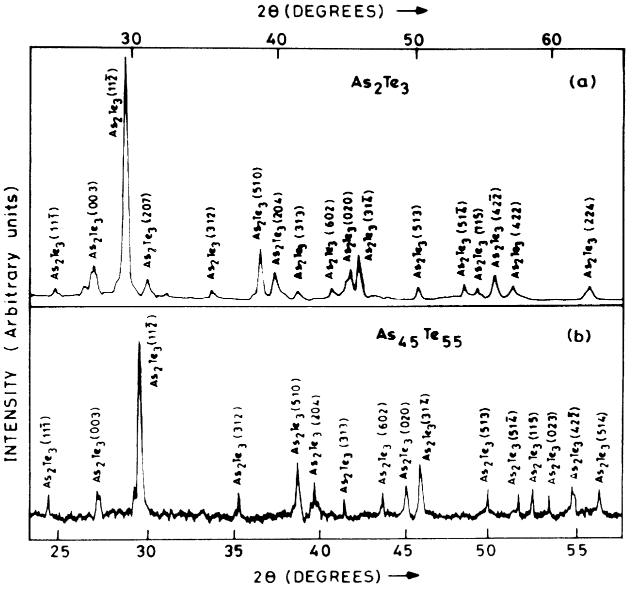


FIG. 9. X-ray diffraction patterns of $As_{40}Te_{60}$ and $As_{45}Te_{55}$ glasses annealed at the second crystallization reaction in a sealed evacuated ampoule.

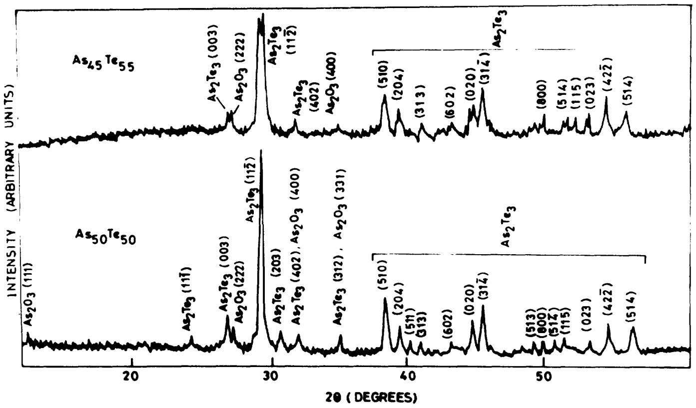


FIG. 10. X-ray diffraction patterns of $As_{45}Te_{55}$ and $As_{50}Te_{50}$ glasses annealed at the second crystallization reaction in air.

this figure that the sample crystallizes into the monoclinic As_2Te_3 phase, exhibiting only one crystallization reaction. It is interesting to note that in this case also, the excess arsenic is not shown in the x-ray pattern of these samples annealed in vacuum. However, $As_{55}Te_{45}$ and $As_{60}Te_{40}$ samples, annealed in air at the crystallization temperature, show diffraction peaks corresponding to As_2Te_3 and As_2O_3 phases. Figure 11(b) shows the x-ray diffraction pattern of the $As_{55}Te_{45}$ sample annealed in air, indicating As_2Te_3 and As_2O_3 peaks.

The lattice parameter of the intermediate fcc phase ($a_0 = 5.80$ Å) is related to the lattice parameters a, b, and c of the monoclinic phase by $a \approx \sqrt{6}a_0$; $b \approx a_0/\sqrt{2}$; $c \approx a_0\sqrt{3}$. It will be interesting to investigate the modality, thermodynamics, and kinetics of this transformation. This work will also be taken up in the future.

C. Crystallization schemes for As_xTe_{100-x} glasses

Based on the DSC and x-ray diffraction studies discussed above, the crystallization schemes for As_xTe_{100-x} glasses of different composition can be given as follows.

1. *For $25 \leq x < 40$ region*

$$\text{Virgin glass} \xrightarrow{T_g} \text{Super cooled melt} \xrightarrow{T_c} \text{Monoclinic } As_2Te_3 + \text{Hexagonal Te}$$

2. *For $40 \leq x \leq 50$ glasses*

$$\text{Virgin glass} \xrightarrow{T_g} \text{Super cooled melt} \xrightarrow{T_{c1}} \text{fcc As-Te} \xrightarrow{T_{c2}} \text{Monoclinic } As_2Te_3$$

If these samples are cooled down to ambient temperature after the first crystallization reaction and reheated, the following scheme is followed:

$$\text{Virgin glass} \xrightarrow{T_g} \text{Super cooled melt} \xrightarrow{T_{c1}} \text{fcc As-Te}$$

$$\xrightarrow{\text{cooled down to ambient temperature}} \text{Intermediate fcc (As-Te) crystalline phase} \xrightarrow{T_{c2}} \text{Monoclinic } As_2Te_3 \,.$$

The crystallization scheme for $As_{40}Te_{60}$, $As_{45}Te_{55}$, and $As_{50}Te_{50}$ glasses also explains why these glasses do not show the phenomenon of double glass transition. In glasses like Si_xTe_{100-x},[7] Ge_xTe_{100-x},[8,9] Al_xTe_{100-x},[10,11] etc., the crystalline Te precipitates out first at T_{c1}, leaving a glassy matrix behind. If the material is cooled back quickly from T_{c1} to ambient temperature, it becomes diphasic containing crystalline Te embedded in a glassy matrix. Hence the second glass transition in Si-Te, Ge-Te, and Al-Te glasses corresponds to the glass to supercooled liquid transformation of the glassy matrix. In As-Te glasses, on the other hand, there is no phase separation and partial crystallization at T_{c1}. The material cooled back from T_{c1}, in this case, is fully crystalline and it does not exhibit the second glass transition. As mentioned earlier, the material shows only the second crystallization reaction, corresponding to the transformation of the metastable intermediate phase into equilibrium crystalline phase.

3. *For $x = 55, 60$ glasses*

As seen in the DSC thermograms, the two crystallization reactions merge with the increase in As concentration. Hence the crystalline scheme for these glasses is as follows:

$$\text{Virgin glass} \xrightarrow{T_g} \text{Super cooled melt} \xrightarrow{T_c} \text{Monoclinic } As_2Te_3 \,.$$

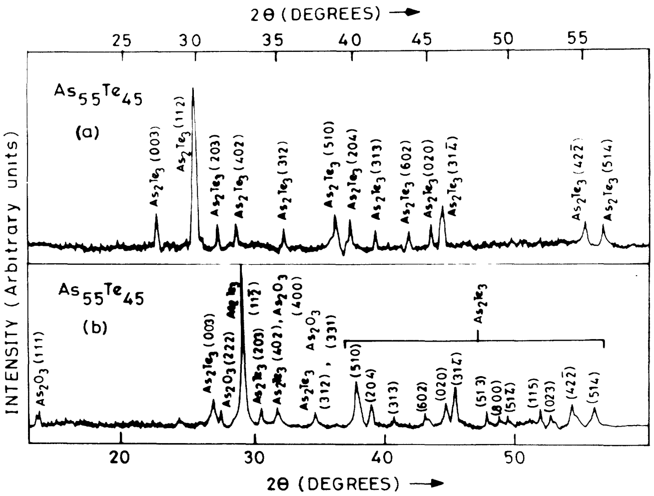


FIG. 11. X-ray diffraction patterns of $As_{55}Te_{45}$ glass annealed at the second crystallization reaction; (a) in an evacuated ampoule, (b) in air.

Further it can be suggested that the broad exothermic peak observed in the As-rich glasses may be due to the decomposition of the material at higher temperatures.

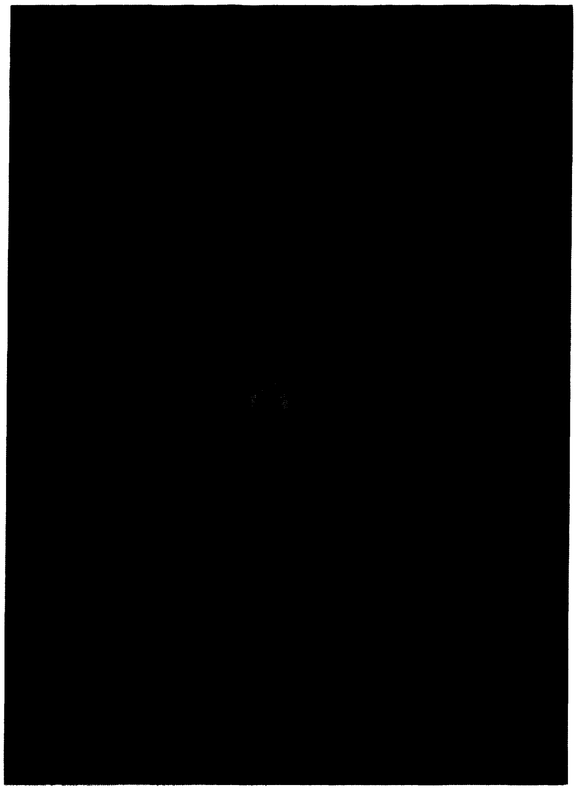
D. Electron diffraction studies on As_2Te_3 glasses

Since there are no detailed studies undertaken earlier to substantiate the structure and the composition of the intermediate metastable crystalline phase which forms during the first crystallization of the As-Te glasses, a representative $As_{40}Te_{60}$ glass has been taken for further investigations. This glass has been annealed up to the end of first and second crystallization reactions and electron diffraction and energy dispersive x-ray analysis (EDAX) studies are carried out to determine the structure and composition of the phases.

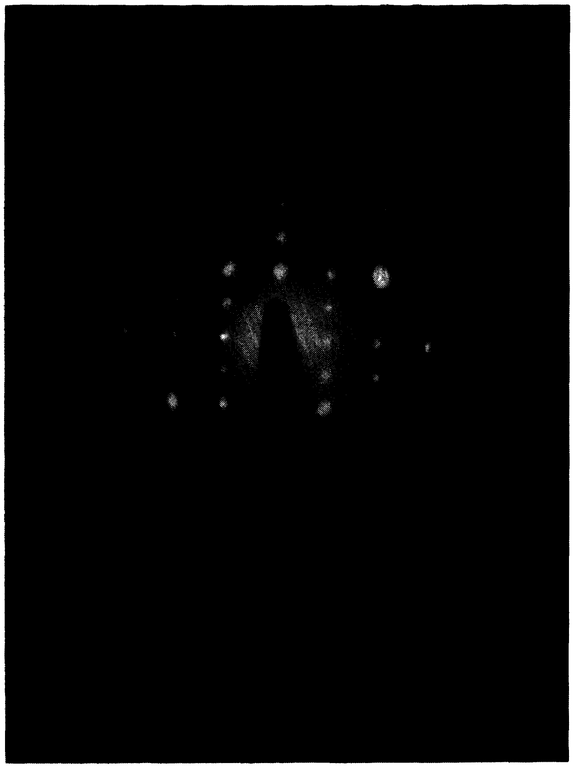
The electron diffraction patterns of $As_{40}Te_{60}$ samples annealed at the first crystallization reaction are depicted in Fig. 12. The patterns shown in Fig. 12(a) are found to have a zone axis $Z=[\bar{1}11]$. Afterwards the same particle has been tilted by about 19° and once again the diffraction pattern has been taken in a different orientation. The diffraction pattern obtained in this orientation is shown in Fig. 12(b), revealing a rectangle-type pattern. The zone axis of this diffraction pattern is identified to be $Z=[\bar{1}12]$. The calculated angle between these two axes is 19.5°, which is in agreement with the experimental value. It can be concluded from these observations that the intermediate metastable phase occurring in the arsenic telluride glasses is a fcc phase.

The electron diffraction pattern of the arsenic telluride samples recovered after the second crystallization reaction is given in Fig. 13. This pattern corresponds to the well-established monoclinic phase. It is confirmed from the above diffraction studies that the arsenic telluride glasses, on heating, form an intermediate fcc crystalline phase, which on further heating transforms into the monoclinic As_2Te_3 phase.

The scanning electron microscopy (SEM) and EDAX experiments performed on the samples recovered after



(a)



(b)

FIG. 12. The electron diffraction pattern of $As_{40}Te_{60}$ glass recovered after the first crystallization reaction; (a) a hexagonal-type pattern having $[\bar{1}11]$ zone axis; (b) a square-type pattern having $[\bar{1}12]$ zone axis.

FIG. 13. The electron diffraction pattern of $As_{40}Te_{60}$ glass recovered after the second crystallization reaction.

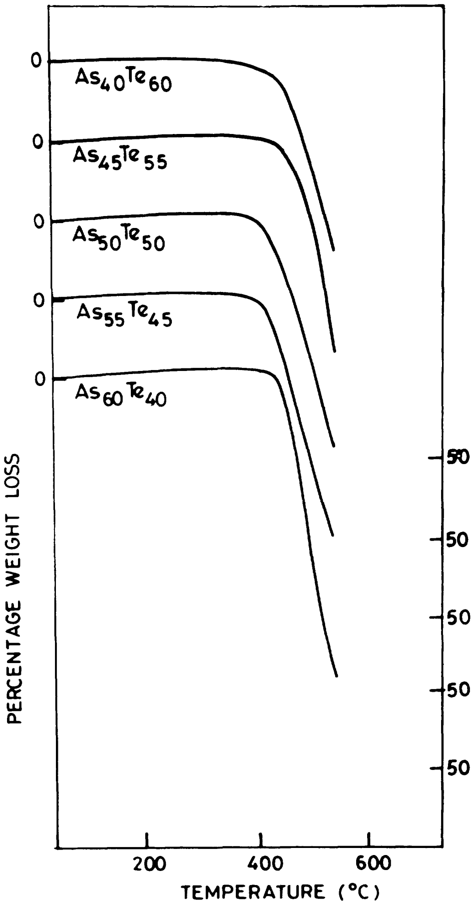


FIG. 14. The thermogravimetric traces of As_xTe_{100-x} glasses with $40 \leq x \leq 60$.

the first crystallization reaction indicate that the composition of the intermediate phase is around $As_{50}Te_{50}$.

E. Thermogravimetric analysis on arsenic-rich glasses

In addition to DSC and structural studies, thermogravimetric analysis has also been undertaken on As-rich As-Te glasses. Figure 14 shows the thermogravimetric analysis (TGA) traces of As_xTe_{100-x} glasses with $40 \leq x \leq 60$. It can be seen from Fig. 14 that at temperatures above the crystallization temperature, a considerable amount of weight loss occurs in the material. The weight loss increases with the increase in arsenic concentration. The weight loss observed in the TGA can be connected with the expulsion of excess arsenic as suggested in x-ray investigations (Sec. III C).

IV. CONCLUSIONS

The thermal studies on As_xTe_{100-x} glasses indicate that glasses with $x < 40$ exhibit only one glass transition and one crystallization reaction. On the other hand, glasses with $40 \leq x \leq 50$ show one glass transition and two crystallization reactions. The samples recovered after the first crystallization reaction are found to have a fcc structure, which in turn transforms into the equilibrium arsenic telluride with monoclinic structure. As a consequence of this, the phenomenon of double glass transition is not observed in these glasses as observed in the other chalcogenide glasses. Glasses with $x > 50$ exhibit single glass transition and single stage crystallization due to the overlapping of crystallization reactions with the increase in arsenic concentration. It is also suggested that the arsenic-rich glasses undergo decomposition into As_2O_3 at higher temperatures. In these glasses, the percentage of weight loss increases with the increase in the arsenic concentration, indicating the expulsion of excess arsenic present in the material.

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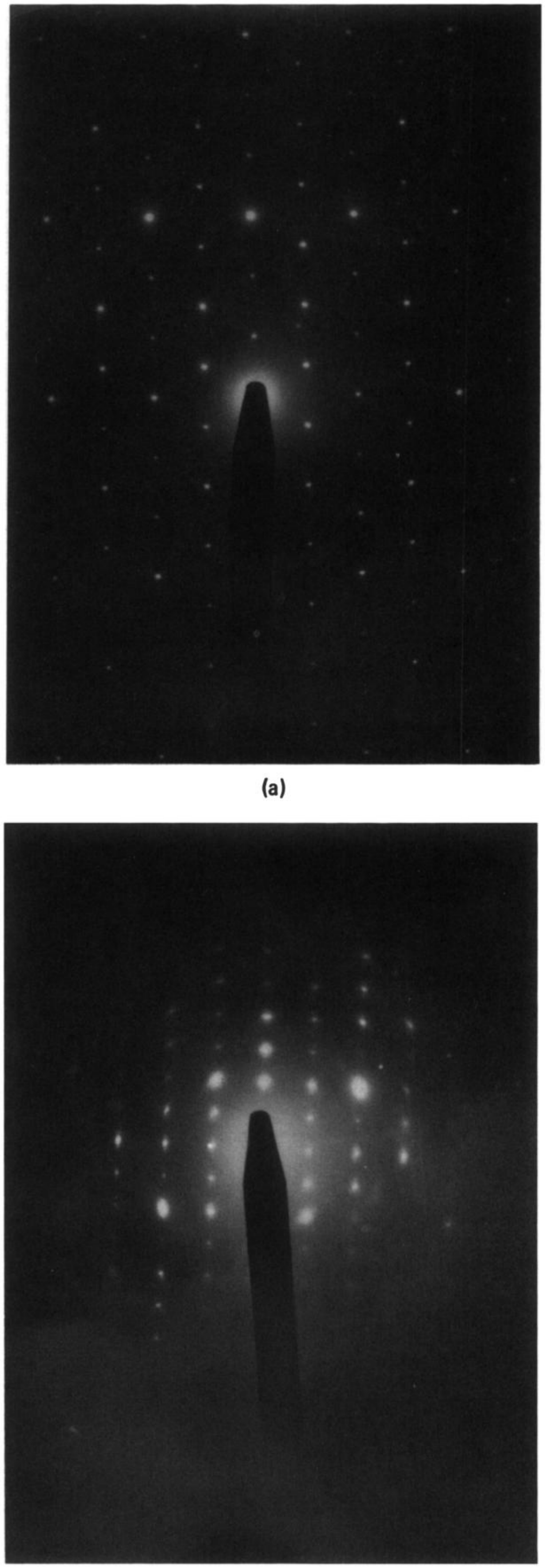

(a)

(b)

FIG. 12. The electron diffraction pattern of $As_{40}Te_{60}$ glass recovered after the first crystallization reaction; (a) a hexagonal-type pattern having [$\bar{1}11$] zone axis; (b) a square-type pattern having [$\bar{1}12$] zone axis.

FIG. 13. The electron diffraction pattern of $As_{40}Te_{60}$ glass recovered after the second crystallization reaction.