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Effect of topological thresholds on thermal behaviour of germanium telluride glasses containing metallic additive

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Abstract. Differential Scanning Calorimetric (DSC) studies on $Ag_xGe_{15}Te_{85-x}$ glasses have been undertaken over a wide range of compositions, to understand the effect of topological thresholds on thermal properties. It is found that the compositional dependence of glass transition temperature (T_g), crystallization temperature (T_c), activation energy for crystallization (ΔE) and thermal stability (ΔT) show anomalies at the rigidity percolation threshold. Unusual variations also observed in different thermal properties at the composition $x = 20$, clearly establishes the occurrence of chemical threshold in these glasses.

PACS. 61.43.-j Disordered solids – 61.43.Fs Glasses – 65.90.+i Other topics in thermal properties of condensed matter

1 Introduction

Chalcogenide glasses exhibit unusual variations in physical properties at two topological thresholds known as rigidity percolation threshold [1,2] and chemical threshold [3] respectively. Investigations on composition dependence of various properties of glassy chalcogenides help us in identifying these two thresholds and also to understand the nature of anomaly seen in a particular property. Normally chemical threshold occurs at higher coordination numbers. Very few systems (Ge–As–Te and Ge–Se–Te) in Ge–Te based glasses can form glasses in a wide range which cover both mechanical and chemical threshold compositions. Glasses in the Ag–Ge–Te system can be formed in a wide range of composition to cover both mechanical and chemical thresholds.

In the present work, DSC studies have been undertaken on $Ag_xGe_{15}Te_{85-x}$ glasses, to know the effect of Ag on the thermal crystallization behaviour of Ge–Te glasses. A large number of glasses with compositions, covering the rigidity percolation as well as chemical thresholds, have been studied to understand the influence of both the topological threshold on the thermal properties. Earlier studies [4] on these glasses indicate that the bonds between the atoms are predominantly covalent and differ from other metal doped chalcogenide glasses such as Ag–Ge–Se and Ag–As–Se which are partly ionic. Hence, Ag–Ge–Te system, with a wide range of glass forming region may be suitable for studying topological effects as the covalency of the constituents play major role in these effects.

2 Experimental

Bulk $Ag_xGe_{15}Te_{85-x}$ glasses have been prepared in the composition range $2.5 \leq x \leq 20$ (atom%) by melt quenching technique. The required amounts of constituent elements in quartz ampoules are sealed in evacuated (10^{-5} torr), flattened quartz ampoules. These ampoules are heated to 1000 °C in a horizontal rotary furnace for 48 hours. The ampoules containing the melt are rotated at 10 rpm to homogenize the melt and are subsequently quenched in a bath containing NaOH + ice-water mixture. Figure 1 shows the X-ray diffraction patterns of $Ag_xGe_{15}Te_{85-x}$ glasses which confirms the amorphous nature of the samples.

DSC runs at different heating rates have been performed on all compositions, with alumina as the reference material. Kissinger's method [5] is used to evaluate the activation energy for thermal crystallization. These glasses are annealed at their crystallization temperature for 48 hours and X-ray diffraction studies are carried out to identify the devitrified phases.

3 Results and discussion

3.1 DSC studies

DSC traces taken at 10 °C/min, are shown in Figure 2. It is seen from the figure that the $Ag_xGe_{15}Te_{85-x}$ glasses ($2 \leq x \leq 21.5$) undergo a single glass transition and single stage crystallization on heating. Binary Ge_xTe_{100-x} glasses exhibit double glass transition and double stage crystallization on heating upto $x \leq 20$. Ge_xTe_{100-x} glasses

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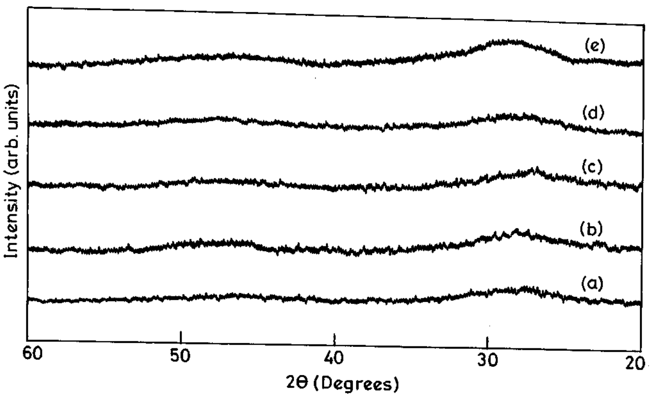

Fig. 1. X-Ray diffraction patterns indicating the amorphous nature of the as prepared $Ag_xGe_{15}Te_{85-x}$ glasses. (a) $Ag_{2.5}Ge_{15}Te_{82.5}$, (b) $Ag_5Ge_{15}Te_{80}$, (c) $Ag_{10}Ge_{15}Te_{75}$, (d) $Ag_{15}Ge_{15}Te_{80}$, (e) $Ag_{20}Ge_{15}Te_{65}$.

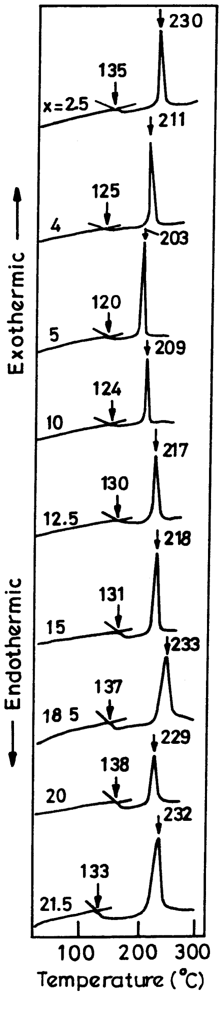

Fig. 2. DSC thermograms of $Ag_xGe_{15}Te_{85-x}$ glasses recorded at the heating rate of 10 °C/min.

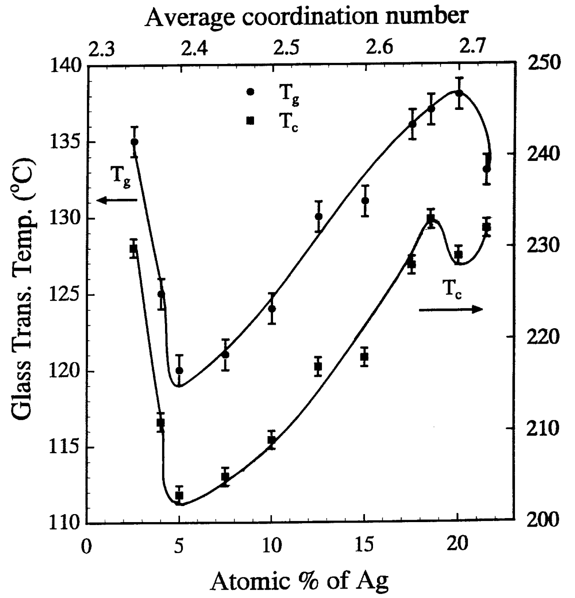

Fig. 3. The variation of glass transition and crystallization temperatures of $Ag_xGe_{15}Te_{85-x}$ glasses with composition and average coordination number.

with $x > 20$, show single T_g and single T_c [6]. The present results indicate that the addition of Ag, changes the thermal behaviour of Ge–Te system from double T_g and double T_c to single T_g and single T_c. Microscopic phase separation has been attributed to the occurrence of double T_g and double T_c in chalcogenide glasses. It has been suggested that the addition of third components such as Cu, Ag, I, *etc.*, may improve the phase mixing in Ge–Te glasses at microscopic level [7], which can result in single glass transition and single stage crystallization.

Figure 3 shows the composition dependence of glass transition temperature and crystallization temperature of $Ag_xGe_{15}Te_{85-x}$ glasses, which indicates that both T_g and T_c exhibit a minimum at the composition $x = 5$. Thereafter, T_g increases continuously and shows a maximum at $x = 20$. On the other hand, T_c shows a reversal in trend around the composition $x = 18.5$ and exhibits a local minimum at $x = 20$.

Heating rate dependence of crystallization reaction has been studied to evaluate the activation energy for crystallization. DSC traces taken at various heating rates are shown in Figure 4 for a representative $Ag_5Ge_{15}Te_{80}$ glass. Figure 5 shows the Kissinger's plot of the variation of $\log(\beta/T_c^2)$ *versus* $(1000/T_c)$, for $Ag_5Ge_{15}Te_{80}$ from which the activation energies have been determined. The variation of activation energy (ΔE) of $Ag_xGe_{15}Te_{85-x}$ glasses with composition is shown in Figure 6. It can be seen that ΔE exhibits minima at both $x = 5$ and 20.

The difference between the crystallization temperature and glass transition temperature (ΔT) gives the tendency of the system towards crystallization [8]. Greater the difference smaller the tendency towards crystallization. In a chalcogenide glassy system, the glass forming ability

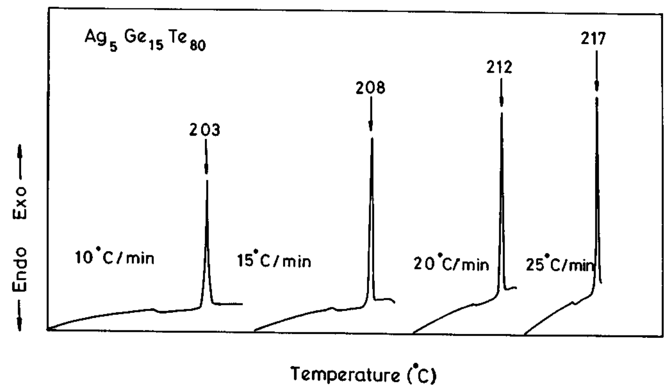

Fig. 4. DSC traces of $Ag_5Ge_{15}Te_{80}$ glass at different heating rates.

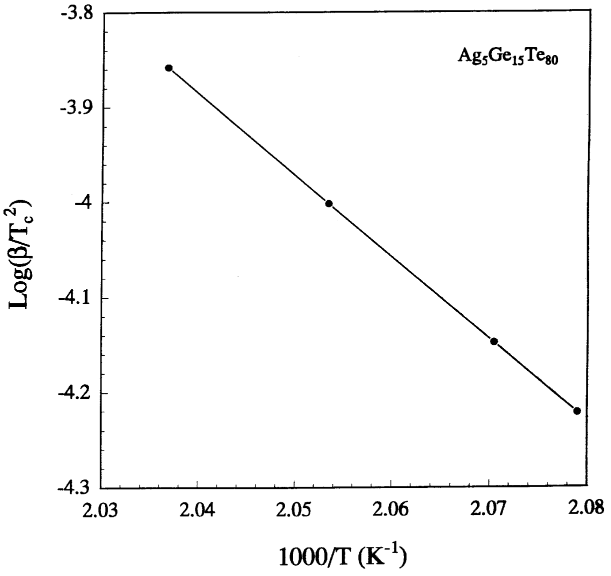

Fig. 5. Kissinger's plot showing the variation of log (β/T_c^2) *versus* $(1000/T_c)$ for $Ag_5Ge_{15}Te_{80}$ glass.

(GFA) is also found to be directly proportional to the separation between T_c and T_g. The present results show that the ΔT of $Ag_xGe_{15}Te_{85-x}$ glasses decreases with composition and exhibits a minimum around $x = 5$ (Fig. 6). In the range of $5 \leq x \leq 18.5$, ΔT increases and after that there is a decrease in ΔT, with a minimum seen at $x = 20$.

Table 1 consolidates the various thermal parameters namely T_g, T_c, E_c and ΔT of Ag–Ge–Te glasses of different compositions. In Table 1, peak temperatures are indicated for T_c and the tangent of the baseline and the endotherm is taken as T_g. The error involved in determining the T_g and T_c values is within ± 1 °C.

3.2 Mechanical threshold and chemical threshold in network glasses

3.2.1 Mechanical threshold

It has been proposed by Phillips and Thorpe [1,2] that the rigidity of the structural network in a chalcogenide glass is composition dependent. The network becomes rigid, when the number of topological constraints, equals the number of degrees of freedom. With composition, the network rigidity percolates in a chalcogenide glass and the material undergoes a transformation from a floppy polymeric glass to rigid amorphous solid, at an average coordination number $Z_{av} = 2.4$ (known as the percolation or mechanical threshold). Tanaka [9] has suggested that in systems in which medium range interactions are dominant, the rigidity percolation threshold may shift to $Z_{av} = 2.67$. In many binary glassy systems such as Ge–Te [10], Si–Te [11], Ge–Se [12], Ge–S [10], Si–Se [10] and As–Te [13], the mechanical threshold is fond to occur at $Z_{av} = 2.4$. Several ternary

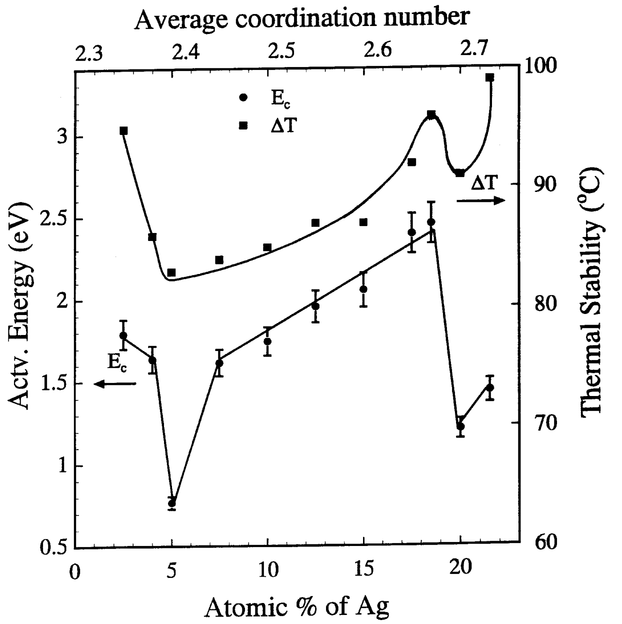

Fig. 6. The variation of crystallization activation energy for $Ag_xGe_{15}Te_{85-x}$ glasses with composition and average coordination number.

Table 1. Thermal parameters of $Ag_xGe_{15}Te_{85-x}$ glasses.

Ag (at%)	Z_{av}	T_g (°C)	T_c (°C)	ΔE (eV)	ΔT (°C)
2.5	2.34	135	230	1.79	95
4.0	2.38	125	211	1.64	86
5.0	2.40	120	203	0.76	83
7.5	2.45	121	205	1.61	84
10.0	2.50	124	209	1.74	85
12.5	2.55	130	217	1.95	87
15.0	2.60	131	218	2.05	87
17.5	2.65	136	228	2.39	92
18.5	2.67	137	233	2.45	96
20.0	2.70	138	227	1.21	89
21.5	2.73	133	232	1.44	96

glassy systems like As–Se–Te [14] and Al–As–Te [15], Ge–Se–Te [16], Ge–As–Se [17,18], Ge–Sb–Se [19] and Ge–In–Se [20], Ge–As–Te [21], *etc.*, show rigidity transformation at $Z_{av} = 2.4$. In all the above glassy systems, unusual variations in different properties have been found at the mechanical threshold composition.

In most of the chalcogenide glassy systems, Ge is 4-fold coordinated and Te is 2-fold coordinated. Structural investigations on Ag–Ge–Te glasses by Ferhat *et al.* using EXAFS, reveal that the coordination of Ag in Ag–Ge–Te glasses is 4. EXAFS measurement of Ge environment indicate that Ge is also four fold coordinated [4]. The tetrahedral coordination for Ag and covalent bonding is specific to Te based glasses only. It should be mentioned that Ag in Ge–Se–Ag and As–Se–Ag glasses have a coordination of 2 and the bonding in these glasses is more ionic [4].

Using the coordination numbers 4, 4 and 2 for Ag, Ge and Te respectively as mentioned above, the average coordination for a particular composition can be calculated for $\mathrm{Ag}_x\mathrm{Ge}_{15}\mathrm{Te}_{85-x}$ glasses, from the formula [22]

$$Z_{av} = \frac{Z_{\mathrm{Ag}}(x) + Z_{\mathrm{Ge}}(15) + Z_{\mathrm{Te}}(85-x)}{100} - - - - . \qquad (1)$$

It is interesting to note that the average coordination number (Z_{av}) for $\mathrm{Ag}_5\mathrm{Ge}_{15}\mathrm{Ag}_{80}$ glass, estimated using equation 1, comes to be 2.40. Hence, the minima exhibited in T_g, T_c, ΔE and ΔT at this composition, clearly show that the rigidity percolation occurs at $Z_{av} = 2.40$, in the Ag–Ge–Te system.

Though an anomaly in a property is generally expected at the percolation threshold, the exact nature of the anomaly (slope change/maxima/minima) depends on the property studied and also it varies from one system to another. For example, most of the telluride glasses such as Ge–Te [10], Si–Te [23], *etc.*, show a minimum in T_g at the percolation threshold, whereas the glassy selenides such as Ge–Se [12], Ge–In–Se [24], Ge–Ga–Se [19], *etc.*, show only a slope change. The present results indicate that T_g of Ag–Ge–Te glasses show a minimum at the mechanical threshold and in that way the behaviour is consistent with other tellurides.

As seen from Figures 3 and 6, T_g, T_c, ΔE and ΔT of Ag–Ge–Te samples show a minimum at the rigidity percolation threshold. Even though a similar behaviour is seen in Ge–Te [10] and Si–Te [23] glasses, Cu–Ge–Te [25] glasses have been found to exhibit a local maximum in T_c and GFA at the percolation point. In this context, it should be pointed out that the exact nature of anomaly observed in a particular property at the rigidity percolation threshold, will be modulated by other aspects such as relative covalency of the constituents, atomic size, metallicity of the additive, *etc.* This aspect is very important and needs to be investigated in more detail.

3.2.2 Chemical threshold

According to the Chemically Ordered Random Network (COCRN) [3] model, in a chalcogenide glassy system, there exists a critical composition at which only heteroploar bonds are favoured. The glass is expected to be maximally chemically ordered and anomalous variations have also been observed in several glassy systems at this composition (known as chemical threshold) [10].

The composition $x = 20$, in $\mathrm{Ag}_x\mathrm{Ge}_{15}\mathrm{Te}_{85-x}$ glasses at which a maximum in T_g and a minimum in T_c, ΔE and ΔT have been observed, is likely to be the chemical threshold of this system.

Unlike in rigidity percolation threshold, the anomalies in the chemical threshold seem to be universal. For, example, a maximum in T_g has been observed at the chemical threshold in a variety of glasses such as Ge–Se [12], Ge–Sb–Se [20], Ge–In–Se [24], *etc.*, including the present Ag–Ge–Te glasses.

The minimum observed in T_c, ΔE and ΔT of Ag–Ge–Te samples, at the chemical threshold is expected. It is known that the glass at the chemical threshold is maximally ordered and hence closest to the crystalline state. Also, at the chemical threshold, the molar density is minimum in most of the systems, implying that the network is least constrained for any structural reorganisation. Hence, the energy barrier and the driving force required for crystallization of the ordered glass are the lowest. Consequently, the crystallization temperature, the thermal stability and the activation energy for crystallization of Ag–Ge–Te glasses, exhibit a minimum at the chemical threshold. This conjecture is consistent with earlier experimental results which show a minimum in glassy semiconductor to crystalline metal transition pressure [10] and the memory switching fields [21] of chalcogenide glasses. It also supports the theoretical predictions which propose a minimum in GFA at the chemical threshold [26].

3.3 Devitrified phases in $\mathrm{Ag_xGe_{15}Te_{85-x}}$ glasses

$\mathrm{Ag}_x\mathrm{Ge}_{15}\mathrm{Te}_{85-x}$ glasses have been annealed at their crystallization temperatures for 48 hours to study the devitrified phases. X-ray diffraction patterns of $\mathrm{Ag}_5\mathrm{Ge}_{15}\mathrm{Te}_{80}$ and $\mathrm{Ag}_{20}\mathrm{Ge}_{15}\mathrm{Te}_{65}$ are shown in Figure 7. The diffraction peaks of the crystallized samples can be indexed with cubic $\mathrm{Ag}_8\mathrm{GeTe}_6$ [27], cubic GeTe_4 [28] and hexagonal Te [29] phases.

It is interesting to note that the Te phase peak intensity is decreasing as Ag is increased. At the chemical threshold ($x = 20$), the Te peak intensity is considerably reduced. The increase in Ag increases the ternary $\mathrm{Ag}_8\mathrm{GeTe}_6$ phase and at the same time GeTe_4 and Te phase decrease. Considering that $\mathrm{Ag}_8\mathrm{GeTe}_6$, GeTe_4 and Te phases are present in annealed $\mathrm{Ag}_x\mathrm{Ge}_{15}\mathrm{Te}_{85-x}$ samples, the composition analysis reveals that at $x = 20$,

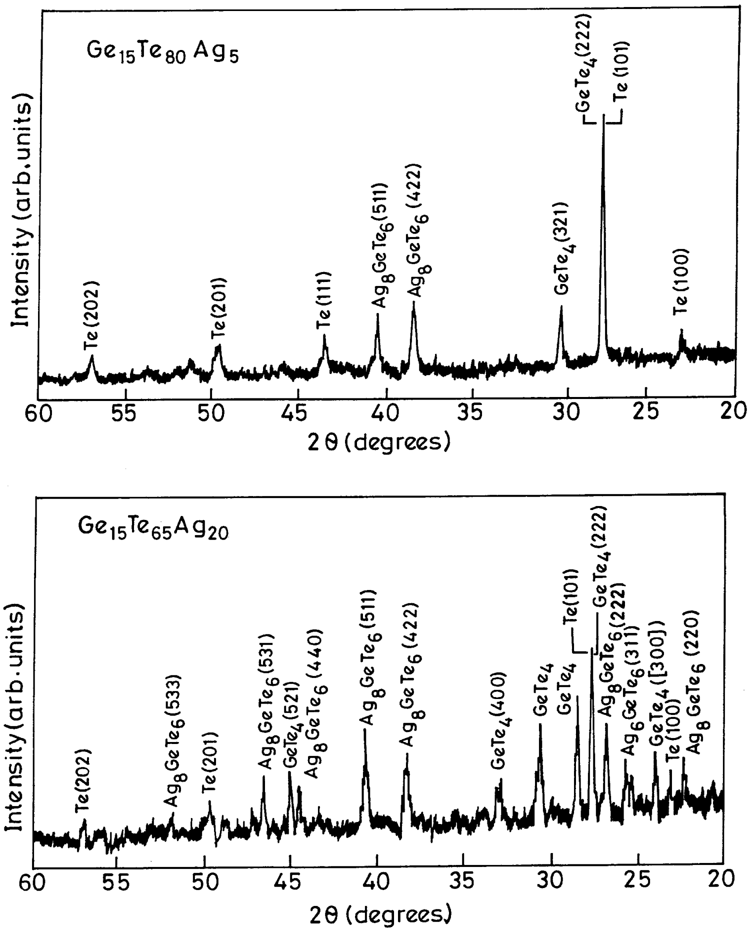

Fig. 7. The X-Ray diffraction pattern of $Ag_5Ge_{15}Te_{80}$ and $Ag_{20}Ge_{15}Te_{65}$ glasses annealed at the crystallization temperature for 48 hours.

only Ag_8GeTe_6 and $GeTe_4$ phases present:

$$\begin{aligned} Ag_5Ge_{15}Te_{80} &= 0.63\ (Ag_8GeTe_6) + 14.4\ (GeTe_4) \\ &\quad + 18.7\ Te \\ Ag_{10}Ge_{15}Te_{75} &= 1.25\ (Ag_8GeTe_6) + 13.8\ (GeTe_4) \\ &\quad + 12.5\ Te \\ Ag_{15}Ge_{15}Te_{70} &= 1.88\ (Ag_8GeTe_6) + 13.1\ (GeTe_4) \\ &\quad + 6.2\ Te \\ Ag_{20}Ge_{15}Te_{65} &= 2.5\ (Ag_8GeTe_6) + 12.5\ (GeTe_4). \end{aligned}$$

The above composition analysis also supports the idea that $x = 20$, corresponds to the chemical threshold in $Ag_xGe_{15}Te_{85-x}$ glasses.

4 Conclusions

Bulk, melt quenched Ag–Ge–Te glasses are found to exhibit single T_g and single T_c. Anomalous variations observed in different thermal parameters such as T_g, T_c, ΔE and ΔT at the average coordination numbers $Z_{av} = 2.4$ ($x = 5$) and $Z_{av} = 2.7$ ($x = 20$) which correspond to the rigidity percolation and chemical threshold respectively. Devitrification of these glasses results in the formation of cubic Ag_8GeTe_6, cubic $GeTe_4$ and hexagonal Te phases.

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