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Thermal Study and Crystallization Kinetics of $In_x(Te_{10}\ Se_{90})_{100-x}$ Glassy Chalcogenides

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Abstract: results of differential scanning calorimetry (DSC) at different heating rates ($2.5 \leq \alpha \leq 40$ K/min.) $In_x\ (Te_{10}\ Se_{90})_{100-x}$ (where $0\leq x \leq 10$ at. %) glassy system were studied. The heating rate (α) are found to affect the characteristic temperatures (the temperature of glass transition (T_g), the onset temperature of crystallization (T_c) and the temperature of crystallized peak (T_p)) which in turn helps one in the determining of the the kinetic exponent (*n*) and the activation energies for the glass transition (E_g) and crystallization (E_c). The obtained results were discussed in terms of the approach of chemical bond, the cohesive energy (CE) and the average heats of atomization (H_s). The X- ray diffractograms confirmed the amorphous nature of the prepared glasses while the annealed glasses at temperature ($T = T_c$) shows some crystallites such as Se–Te and In–Se.

Keywords: Chalcogenides; DSC; XRD.

1 Introduction

Chalcogenides have great of interest because of their wide range of scientific and technological applications. Binary glasses such as Se-Te and In-Se have several advantages in comparison with a-Se [1,2]. Binary glasses of In-Se are attractive due to their used in solar cells [3,4]. On the other side Se-Te glasses are characterized by their high temperature of crystallization, great hardness, high photosensitivity and small ageing effects than a-Se [1]. But, these glasses are characterized by low thermos mechanically properties, therefore increasing their softening temperature and mechanical strength enlarge their applications. Adding indium as a third element not only enlarge their glass forming region but, also creates composition and configuration disorder in the system, modifying the structure and improved the electrical and thermal properties of the Se-Te system [5-10].

In the literature many papers [11-16] deals with studying electrical and photoelectrical properties and thermal analysis of In-Se-Te glasses. From an application point of view it is necessary to study the thermal analysis of such glasses. The current paper deals with the effect of In content thermal analysis of different compositions of $In_x(Te_{10}\ Se_{90})_{100-x}$ ($0.0 \leq x \leq 10$ at.%) chalcogenide glasses.

2 Theoretical Base

Explaining results of DTA and DSC is retired by the formal theory of kinetic transformations in terms of the crystallized volume fraction (χ) through a period of time (t) by using the Johnson, Mehl and Avrami's relationship [17]

$$\chi = 1 - e^{-(k.t)^n} \tag{1}$$

where n is the kinetic exponent and have an integer or half integer depending on the mechanisms of growth and the crystal dimension, k is the effective reaction rate, that is have an Arrhenius dependence of temperature.

$$k = k_0 . e^{-E_c/RT} \tag{2}$$

Where E_c is the crystallization activation energy.

2.1 Afify's Method

In accordance with Afify condition [18,19] at $\chi = 0.63205$ one can find that $\ln(1-\chi) = -1$ and equation 1 take the following:

$$\ln(1-\chi) = -1 = -(k_{0.63}\ t_{0.63})^n \tag{3}$$

i.e.

$$k_{0.63} = t_{0.63}^{-1} \tag{4}$$

Based on the above equation (4) the $k_{0.63}$ at $\chi = 0.63205$

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is easily determined at each heating rate. Then the reaction rate $k_{0.63}$ in the logarithmic form can be written:

$$\ln(k_{0.63}) = \ln(k_0) - E_c/RT_{0.63} \qquad (5)$$

The E_c and k_0 values can be deduced without any dependence on the kinetic exponent (n) from the slope and intercept of the relation between $\ln(k_{0.63})$ and $1000/T_{0.63}$. Furthermore, eq.5 successfully apply on iso- and noniso- thermal techniques [20].

The kinetic exponent (n) can be determined by rewrite Eq. 3 in the logarithmic form as

$$\ln(\ln(1-\chi)) = n.\ln(k) + n.ln(t) \qquad (6)$$

k is constant at constant temperature, when $\ln(\ln(1-\chi))$ was plotted versus $ln(t)$ the slope is equal to n. In isothermal technique, Eq. 6 is carried out for only one DSC curve while, in nonisothermal technique, Eq. 6 is carried out, at constant temperature for different DSC curves i.e. different heating rates.

2.2 Bansal's method

The details of Bansal's method is quoted approximation that may introduced an error of a 3% in E_c/R value in the worst cases [21] and the final equation take the following form:

$$\ln(T_p^2/\alpha) = -E_c/RT_p - \ln(K_0R/E_c) \qquad (7)$$

Based on Bansal's analysis the kinetic exponent is easily determined using the following relationship:

$$\dot{\chi}_p = n(0.37\alpha E_c)/(RT_p^2) \qquad (8)$$

and exponent which depends on the dimensionality of the crystal growth (m) also can be determined from:

$$\left[\frac{d\chi}{dt}\right]_p = mE\alpha(1-\chi_p)/RT_p^2 \qquad (9)$$

At study the kinetics of crystallization in the glass, $n = m$ when the formation of nuclei take place during any previously heating treatment prior to DSC or DTA scan. But in the case of the nuclei are already formed during the heating at constant rate α are dominant, the kinetic exponent, *n*, is equal to *m+1* [31, 32].

3 Experimental

$In_x(Te_{10}Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at.%) glasses were prepared starting with highly purity In, Te and Se (99.999 %) using the well known melt quench technique. The amorphousity of the as-prepared glasses was checked using a Philips (1710) X-ray diffract meter. The elemental composition was measured using energy dispersive X-ray spectroscopy (Link analytical EDS) indicating that as-prepared glasses as well as that calculated according to their ratios and atomic percentage with small deviation only ± 0.4 at %. 15 mg in powder form for each sample was sealed in Al boat and scanned through the temperature range 300-450 K at different heating rates (α = 2.5, 5, 10, 20 and 40 K min^{-1}) using Shimadzu 50 DSC. The characteristic temperatures T_g, T_c, and T_p, are investigated with ±1 K accuracy using the microprocessor of the thermal analyser. T_g, T_c, and T_p, are the temperature of glass transition, the onset of the crystallization peak, and the temperature of the crystallized peak, respectively.

The crystallized fraction, χ, at any temperature, T, lies between T_i where crystallization is just beginning and T_f where the crystallization is completed is given by $\chi = A_T/A$, where A is the whole area of the exothermal peak (between T_i and T_f) of the DSC curve between the temperature and A_T is the area between T_i and T, as investigated in figure 1.

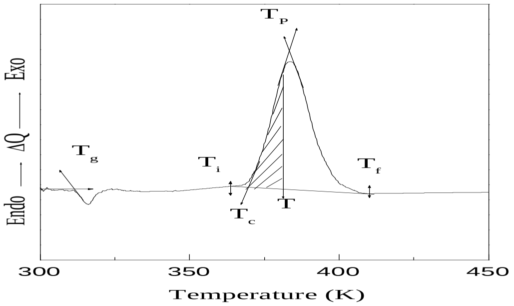

Figure. 1 DSC curve for $Te_{10}Se_{90}$ glass measured at α = 5 K min^{-1}. The area between T_i and T investigate A_T (shaded area).

4 Results and Discussion

Figure 2 shows the DSC curves for $In_x(Te_{10}Se_{90})_{100-x}$ different compositions of the (where x = 0, 2.5, 5, 7.5 and 10 at.%) glasses measured at heating rate 10 $K.min^{-1}$. The characteristic temperatures, T_g, T_c and T_p are increases with the increase of In content.

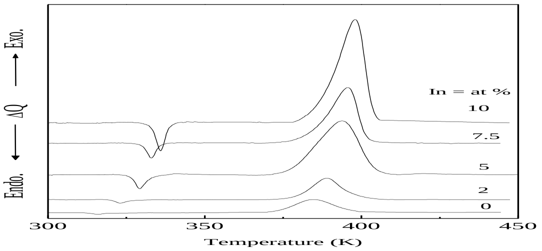

Figure. 2 DSC curves for powdered $In_x(Te_{10}Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at.%) chalcogenides scanned α = 10 K/ min.

Table 1: The glass transition parameters for $In_x(Te_{10} Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at.%) chalcogenides.

In at. %.	A	B	E_g (Eq.22)	E_g Eq.23)(	$<E_g>$	CE	H_s
			kcal mol^{-1}				(kcal g $atom^{-1}$)
0	324.09	6.23	30.00	31.25	30.625	44.12	28.60
2.5	328.22	5.44	35.83	37.10	36.465	45.17	28.78
5	336.61	4.69	44.31	45.62	44.965	47.29	28.96
7.5	338.96	4.51	47.00	48.31	47.655	48.34	29.08
10	342.81	4.28	49.54	50.87	50.205	49.40	29.14

4.1 Glass transition

The heating rate (α) dependence of the glass transition temperature can be described by the following empirical relationship:

$$T_g = A + B\ln(\propto) \qquad (10)$$

Where A and B with the same meaning written here [35].The deduced values of A and B for $In_x(Te_{10} Se_{90})_{100-x}$ glasses satisfies the above equation (10) and are given in Table 1 .

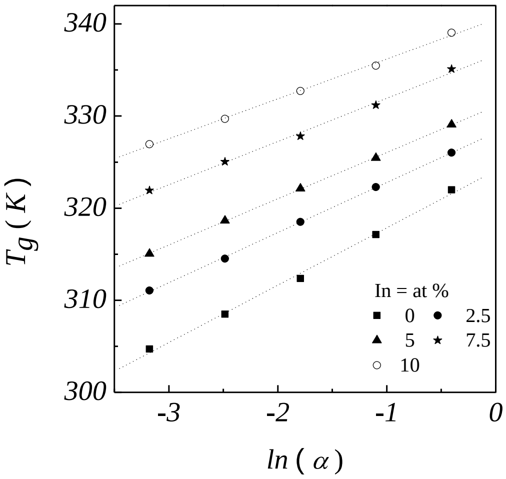

Figure. 3 the T_g values versus ln(α) for $In_x(Te_{10}Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at.%) cchalcogenides**.**

On the other side, Eq.7 can be rewritten for the glass transition temperature, T_g as [27]:

$$\ln(T_g^2/\alpha) = E_g/RT_g + const. \qquad (11)$$

By plotting $\ln(T_g^2/\alpha)$ versus 1000/T_g, the slope can be used to determine the E_g value as well as demonstrated in Figure 4. Keeping in mind that, the changes of $\ln(T_g^2)$ with α can be cancelled behind the changes of $\ln(\alpha)$ therefore, Eq.27 take the following form [35, 36]:

$$\ln(\alpha) = -E_g/RT_g + Con. \qquad (12)$$

When the value of $\ln(\alpha)$ were plotted against $1000/T_g$ for $In_x(Te_{10}Se_{90})_{100-x}$ as shown in Figure 5. The deduced E_g values based on equations 11 and 12 and their averaged $<E_g>$ are listed in Table 1.

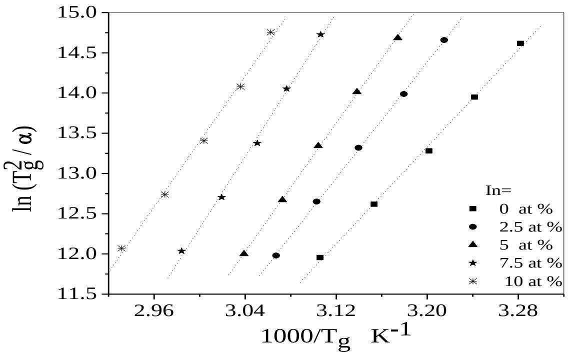

Figure. 4: the values of $\ln(T_g^2/\alpha)$ against 1000/T_g, for $In_x(Te_{10} Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at. %) chalcogenide glasses

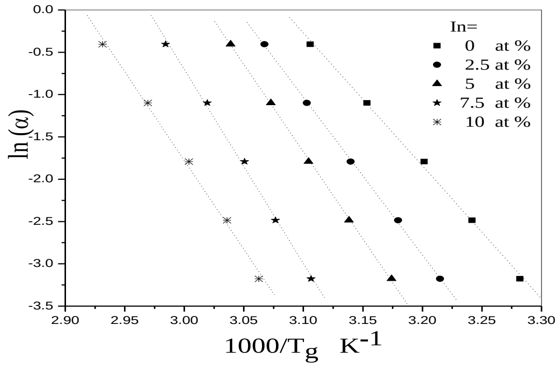

Figure. 5 the $\ln(\alpha)$ values versus 1000/T_g for $In_x(Te_{10} Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at.%) chalcogenide glasses**.**

The deduced values of E_g are in good agreement with that was observe for chalcogenides [36-38]. The E_g values increases with the increase of In content which can be considered as a result of increasing the T_g values consequentially the glass rigidity also are increased. The glass transition temperature is strongly affected by many

Table 2: The E_c, n and m values for $In_x(Te_{10}\ Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at.%) glasses.

In at. %.	E_c Eq.6)(	E_c (Eq.14)	< n > Eq.7)(	< n > Eq.16)(	< m > Eq.20)(
	$Kcal.mol^{-1}$				
0	20.10	20.62	2.77	2.78	1.63
2.5	23.52	21.78	2.65	2.64	1.64
5	26.93	25.58	2.63	2.63	1.54
7.5	27.85	28.32	2.61	2.61	1.54
10	29.07	29.66	2.56	2.56	1.50

independent parameters for example the effective molecular weight, the optical, bonding energy, the fraction and type for different structural units formed, the average heats of atomization, cohesive energy, the mean coordination number [39, 41]. For heteronuclear bonds the bonding energy between to different atoms $D(C-E)$ can be estimated using Pauling's relationship [42]:

$$D(C-E)=[D(C-C).D(E-E)]^{1/2}+30(\chi_C-\chi_E)^2 \quad (13)$$

where $D(C-C)$ and $D(E-E)$ are the homonuclear bond energies in units kcal mol^{-1} [43], χ_C and χ_E are the electronegativity values for C and E atoms [44]. Bond formation tack place in sequence of decreasing bond energy up to the available atom valences are satisfied [45]. For In-Se-Te glasses, bonds of In-Se are expected to occur firstly because of their highly possible energy (54.321 kcal mol^{-1}) then, Se-Te bonds (44.19 kcal mol^{-1}) in try to saturate all available Se valences but, the Te atoms isn't enough to do this. Therefore, Se-Se defect homopolar bonds are formed. In accordance with approach of chemical bond, the bond energies are assumed to be additive. Therefore, the summation of bond energies over all the bonds expected in glass gives cohesive energy (CE). The calculated values of CE for the glasses under study are listed in Table 1 and it were increases with the increase of indium content.

Extending Pauling's idea to the ternary glasses (In-Se-Te in the present study) in accordance with Sadagopan et al. [47] and neglecting formation heat. Hence, the average heat of atomization can be estimated by substituting the H_S values for In, Se, and Te into the following relationship [46].

$H_s(In-Se-Te)$ is given by:

$$H_S\,(In-Se-Te)=\frac{1}{2}\,(H_S^{In}+H_S^{Se}+H_S^{Te}) \quad (14)$$

The deduced values of H_s for $In_x(Te_{10}\ Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at.%) glasses were shown in Table 1,

4.2 Crystallization

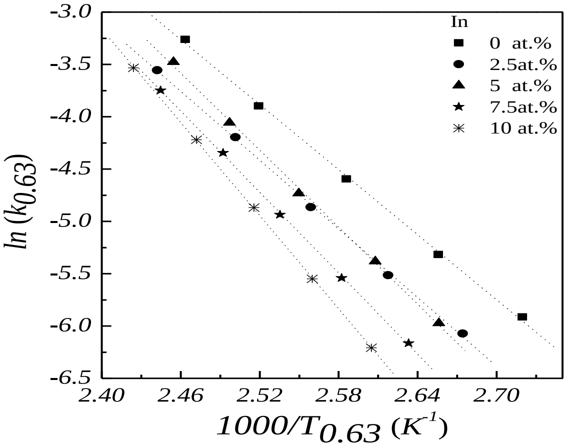

Figure. 6 The $\ln(k_{0.63})$ vs. $1000/T_{0.63}$ for $In_x(Te_{10}\ Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at.%) chalcogenide glasses.

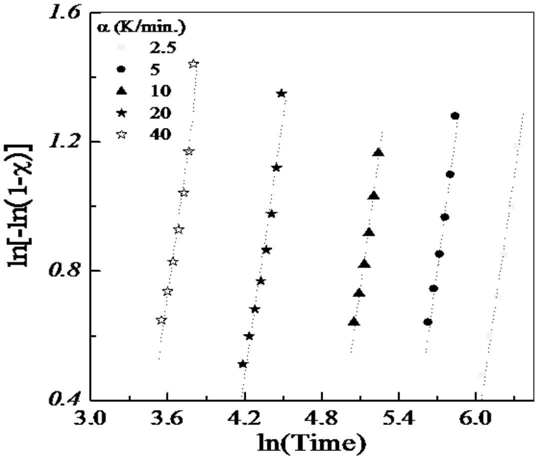

Figure. 7 $\ln[-\ln(1-\chi)]$ vs. ln(t) at different heating rates for$Te_{10}\ Se_{90}$ glass.

Based on Eq.6 the crystallization activation energy (E_c) can be estimated by plotting the values of $\ln(k_{0.63})$ as a function of $10^3/T_{0.63}$ for $In_x\ (Te_{10}\ Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at.%) glasses as shown in Fig. 6. The deduced values of E_c were listed in Table 2.

The Avrami's exponent, n which is the slope of the linear relation between $\ln[-\ln(1-\chi)]$ and $\ln(t)$ at different heating rates for as represented in figure 7.

On the other hand, according to Bansal's equation using the slope and intercept of the linear relation between $\ln[T_p^2/\alpha]$ and $10^3/T_p$, both the K_0 and E_c values can be deduced. Figure 8 shows this plots for $In_x(Te_{10}\ Se_{90})_{100-x}$ glasses.

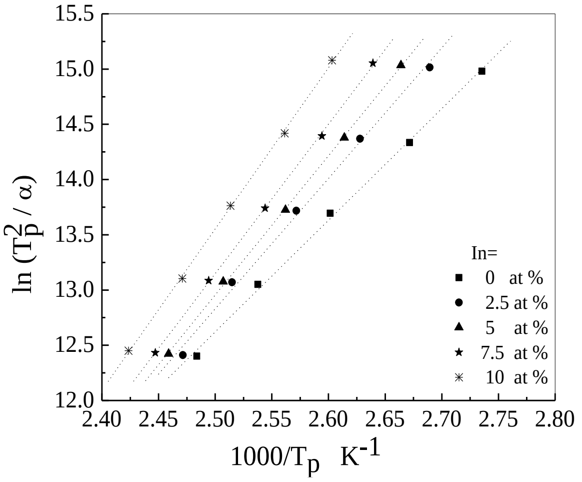

Figure. 8 $\ln[T_p^2/\alpha]$ vs. $1/T_p$ for $In_x(Te_{10}\ Se_{90})_{100-x}$ (where x = 0, 2.5, 5, 7.5 and 10 at.%) glasses.

The total amount of the alloy crystallized is directly proportional to area under DSC curve. The corresponding crystallization rates $(d\chi/dt)_p$ is the ratio between the ordinates and the total area of the peak therefore, it is possible to plot the exothermic peak as investigated in figure 9 for $Te_{10}Se_{90}$ as an example. It might be noted that, the $(d\chi/dt)_p$ values is directly proportional the heating rate as well as previously discussed [50].

In accordance the preceding theory, the sample was reheated up to a temperature slight larger than T_g for 1 hour to forming a large number of nuclei. Using XRD measurements it was confirmed that, some crystalline peaks are detected after heating treatment. Some crystallites of Se Te and In Se indicated with d and I, respectively are observed in the XRD diffractograms of the treated samples as represented Figs.10 and 11.

Based on the experimentally results, It was shown that, the correlation coefficients of the corresponding straight regression lines show a maximum value for a given temperature, which is the most suitable to calculate the n using Eq.(8).

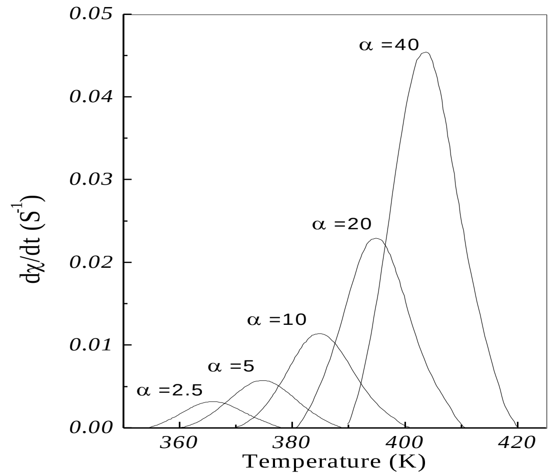

Figure. 9 The rate of crystallization as a function of temperature of the exothermic peaks for $Te_{10}\ Se_{90}$ glass at different values of α.

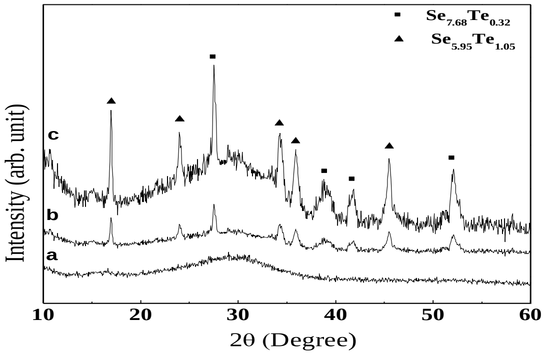

Figure. 10 XRD patterns for as prepared $Te_{10}\ Se_{90}$ (a), annealed glass at 370 K for 1 hr (b) and for 2 hr (c).

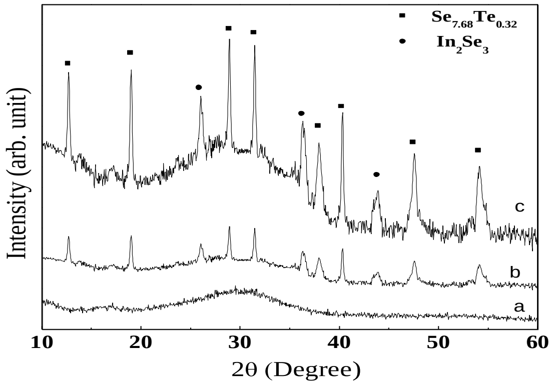

Figure. 11 XRD patterns for as prepared $In_{10}(Te_{10}\ Se_{90})_{90}$ glass (a), annealed glass at 380 K for 1 hr (b) and for 2 hr (c).

The value of n for the as-prepared glass isn't equal to that for the treated glass. This confirms that, the as prepared glass is free from any nuclei thus, $n = m+1$ for $In_x(Te_{10}\ Se_{90})_{100-x}$ glasses. The kinetic parameters n and m are calculated depending on the crystallization mechanism. The n value decreases from 3 to 2 with increasing the content of indium. The value of n *=2* for the as prepared glass corresponding to the mechanism of volume nucleation with one dimensional growth and *n= 3* corresponding to volume nucleation mechanism with two dimensional growth. At the final it was worth mentioned that, Eq. 9 gives m values which confirm the rule of *n=m+1* for $In_x(Te_{10}\ Se_{90})_{100-x}$.

5 Conclusions

Adding the In content into $Se_{10}Te_{90}$ glass results in: Increasing the T_g, T_c, and T_p with the increase of indium content leading to the increase of both the activation energy of glass transition, E_g, and crystallization, E_c. The observed results well explained in terms of the approach of chemical bonds, the mean heats of atomization and cohesive energies (CE). Successful applied of Afify's method gives accurate values of E_c, and *n*. Identification of the crystalline phases confirms formation of some Se-Te and In-Se crystallites in the remaining amorphous matrix.

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