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Iso-conversional study of crystallization activation energy of amorphous-crystallization transformation for $Se_{79}Te_{20}Pb_1$ glass using non-isothermal differential scanning calorimetry technique

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The ternary $Se_{79}Te_{20}Pb_1$ chalcogenide glass is prepared using melt quenching technique. Differential scanning calorimetry technique (DSC) is used to investigate the kinetics of crystallization of amorphous-crystallization (a-c) phase transformation under non-isothermal conditions at three different heating rates; 5, 10 and 15° C min^{-1}. The variation of crystallized activation energy (E_c) with crystallized fraction (χ) and hence, with temperature (T) is investigated using five iso-conversional methods namely KAS, OFW, Friedman, Tang and Chen and Starink. It is found that E_c is not constant but vary with χ as well as T. Thus, the iso-conversional analysis of investigated glass indicates that the assumption of constant E_c is not appropriate.

Keywords: Chalcogenide glass, Differential scanning calorimetry, Non-isothermal methods, Iso-conversional analysis

1 Introduction

Chalcogenide glasses have received attention of researchers because of their important properties like wide transmission range, high refractive index, good chemical durability, optical switching, and amorphous to crystalline phase transition[1-3]. Thermal analysis is an important quantitative analysis that provides an insight into the structural arrangement, thermal stability, phase transitions, phase separations and their effect on the various transport mechanism, thermo-mechanical, optical and electrical properties. Therefore, the study of thermodynamical properties of chalcogenide glasses is an important area of materials science which gives a deeper understanding of the elementary process of transformation of amorphous system to stable crystalline system. Out of all the standard thermal analysis techniques, differential scanning calorimetry (DSC) is the most widely used technique because it is easy to carry out, very sensitive, non-destructive and requires small amount of sample. The kinetics of glass transformation can be studied by isothermal[4] and non-isothermal measurements[5-13]. The thermal stability of glasses against crystallization is a critical issue for potential technological applications and it enables us to determine the range of operating temperatures.

Se based chalcogenide glasses have wide range of properties such as high transparency in broad middle and far infrared regions, reversible transformations and have strong non-linear properties[14]. The doping of tellurium helps to overcome the problems like short lifetime and low sensitivity of amorphous Se. The addition of third element to Se-Te glassy system creates compositional and configurational disorder with respect to the binary system[15]. Addition of metallic impurity like Pb not only increases conductivity and thermal stability of the system but also leads to transition in conduction from p type to n type[16-19] which makes them ideal materials for replacing the conventional p-n junction. Pb additive chalcogenide materials are being considered to be used for high resolution spectroscopy, optical fiber analysis, optical communication, detecting atmospheric pollutants such as hydrocarbons and fast automotive exhaust analysis which makes them an attractive area for further research[20, 21].

The dielectric study[22] of $Se_{80-x}Te_{20}Pb_x$ ($0 \leq x \leq 2$) has been done in our lab. The dielectric parameters

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viz dielectric constant, dielectric loss and AC conductivity in frequency range 10 Hz to 500 kHz and temperature 300-320 K have been evaluated. It is found that for dielectric constant, dielectric loss and AC conductivity the glassy system show unique trends at x=1 at % for same temperature and frequency. Hence, it has been concluded that $Se_{79}Te_{20}Pb_1$ is critical composition and thus, it is further investigated for various studies. Further, in our previous work[23], various kinetic parameters including glass transition activation energy, activation energy for crystallization and Avrami exponent have been deduced using different empirical approaches. From the values of the kinetic parameters, it has been revealed that crystallization mechanism has one dimensional growth. It was also concluded that $Se_{79}Te_{20}Pb_1$ is made from good glass forming liquids.

According to JMA model, the Avrami exponent (n) and the activation energy of crystallization (E_c) should be constant during the transformation process[4]. However, recently researchers have shown that n and E_c values are not necessarily constant but vary during the amorphous-crystallization (a-c) transformation[5-7]. Therefore in continuation of our previous work[23], the present study aims to substantiate the variation of E_c for amorphous to crystallization transformation in $Se_{79}Te_{20}Pb_1$ glass. This variation with degree of crystallization and temperature has been reported and discussed in detail by employing different five different iso-conversional methods.

2 Experimental Details

The investigated $Se_{79}Te_{20}Pb_1$ chalcogenide alloy was prepared by melt quenching technique. 5N high purity (99.999 %) Se, Te and Pb, procured from Sigma Aldrich, were weighed in appropriate atomic weight percentage with accuracy of 10^{-4} g and sealed in a quartz ampoule (length ~ 8 cm, diameter ~ 10 mm) under high vacuum of $\sim 2\times10^{-5}$ mbar. The sealed ampoule was heated in a muffle furnace for 10 h with the rate of 3 °C/min up to 900 °C. The ampoule was rocked frequently to maintain homogeneity. The heated ampoule was quenched rapidly in ice cooled water. The ingot of the sample was taken out by breaking the quartz ampoule and then it was crushed into a fine powder using mortar and pestle. The structural characterization was carried out using PANalyticalX`Pert Pro x-ray diffractometer in the range $5° < 2\theta < 90°$ at the scanning rate of 1°/min equipped with a Ni filter using Cu K_α (λ = 1.5406 Å) radiation as x-ray. No prominent peak was observed in the x-ray diffraction pattern of the investigated glass which confirms the amorphous nature of the material[22].

The glassy nature of the material was confirmed through DSC technique (NETZSCHSTA 4491 DSC). The temperature precision of this instrument is ±0.1 K in the measured values. 3-5 mg of sample was sealed in standard aluminum pan and heated under non-isothermal conditions in dry nitrogen atmosphere at the flow rate of 40 mL min^{-1} at three different heating rates 5, 10 and 15 °C min^{-1} in the range 300-575 K to investigate thermal transformation region. The DSC thermograms at 5, 10 and 15 °C min^{-1} are shown in our previous work[23].

3 Results and Discussion

In the present study, the non-isothermal a-c transformation data obtained from DSC has been analyzed using different iso-conversional methods of kinetic analysis. The degree of crystallization χ has been determined using partial area technique. The crystallized fraction χ at any temperature T; $\chi = A_T/A$. Here A is the total area of the exothermic peak between temperature T_i (on which the crystallization just begins) and T_f (at which the material is completely crystallized) and A_T is the area of the peak between temperatures T_i and T. The temperature dependence of crystallized fraction χ is observed to be a sigmoid curve as shown in Fig. 1. The experimental data of the plot displayed in Fig. 1 has been used to calculate activation energy of crystallization using five iso-conversional methods. The iso-conversional methods namely KAS, OFW, Tang and Chen and Starink, use approximations for the evaluation of the integral appearing in the rate equation whereas

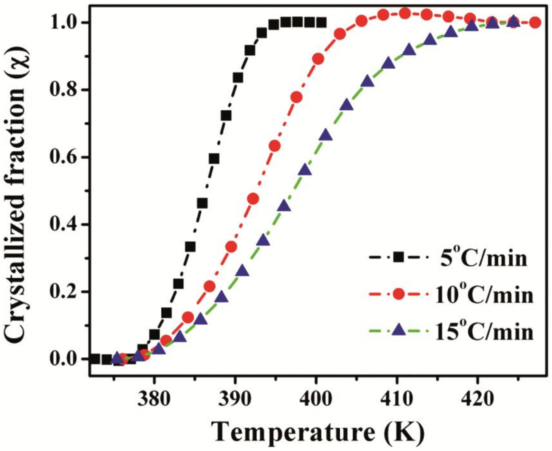

Fig. 1 — Variation of crystallized fraction as a function of temperature for ternary $Se_{79}Te_{20}Pb_1$ glass.

Friedman method uses a differential form of the rate equation which leads to the simple linear equations for evaluating the activation energy.

3.1 Iso-conversional analysis

The crystallized fraction χ can be expressed in terms of time (t), is provided by Johnson-Mehl-Avrami (JMA)[24-26], in which the volume crystallized $\chi(t) = 1 - exp[-(Kt)^n]$ where $\chi(t)$ is the crystallized fraction or the fraction of the first phase which has transformed into the second phase in time t, n is Avrami exponent that depends upon the growth mechanism and the dimensionality of the glassy alloy, K is defined as the effective overall reaction rate constant and it usually has an Arrhenian temperature dependence as $K = K_o exp(-E_c/RT)$ where K_o is the pre-exponential frequency factor, E_c is the activation energy for crystallization and R is universal gas constant.

The isothermal a-c transformation rate can be given as:

$$\frac{d\chi}{dt} = nK(1-\chi)[-\ln(1-\chi)]^{(n-1)/n} \qquad ...(1)$$

Using the assumptions of isothermal condition, the isothermal transformation rate can be written as:

$$\frac{d\chi}{dt} = K(T)f(\chi) \qquad ...(2)$$

Where, $f(\chi)$ is the reaction model, χ is the conversion fraction that represents the volume of the crystallized fraction.

Substituting expression for K, the transformation rate can be rewritten as:

$$\frac{d\chi}{dt} = K_o \exp\left(-\frac{E_c}{RT}\right) f(\chi) \qquad ...(3)$$

Under non-isothermal conditions with a constant heating rate of $\alpha = dT/dt$, Eq. (3) can be modified as:

$$\frac{d\chi}{dT} = \frac{d\chi}{\alpha dt} = \frac{K_o}{\alpha} \exp\left(-\frac{E_c}{RT}\right) f(\chi) \qquad ...(4)$$

The integral form of the reaction model can be obtained by integrating Eq. (4) using the method of separation of variables as follows:

$$g(\chi) = \int_0 \frac{d\chi}{f(\chi)} = \frac{K_o}{\alpha} \int_{T_o}^{T} exp\left(-\frac{E_c}{RT}\right) dT \qquad ...(5)$$

In the present work, the variation of activation energy for amorphous-crystallization transformation in $Se_{79}Te_{20}Pb_1$ chalcogenide glass using five iso-conversional methods is deduced and discussed. These methods are as follows:

3.2 Kissinger-akahira-sunose (KAS) method

The KAS method[27-29] or generalized Kissinger method may be obtained applying logarithm and rearranging Eq. (5) as:

$$\ln\left(\frac{\alpha_i}{T_{\chi i}^2}\right) = \ln\left[\left|\frac{df(\chi)}{d\chi}\right|\left(\frac{K_o R}{E_\chi}\right)\right] - \frac{E_{\chi i}}{RT_{\chi i}} \qquad ...(6)$$

The subscript i denotes different heating rates. For each degree of conversion χ (0.1 - 0.9), a corresponding temperature $T_{\chi i}$ and heating rate α_i are used to plot $\ln(\alpha_i/T_{\chi i}^2)$. As shown in Fig. 2, the plot obtained is straight lines which were desired from Eq. (6) and the slopes of these lines are used to calculate the activation energy $E_{\chi i}$ as listed in Table 1. It is observed that $E_{\chi i}$ decrease with crystallized fractionχ.

3.3 Ozawa-Flynn-Wall (OFW) method

In OFW method[30,31], the temperature T_χ corresponding to a fixed value of fraction crystallized χ is measured from the experiments at different heating rates α. The OFW method is based on the following equation:

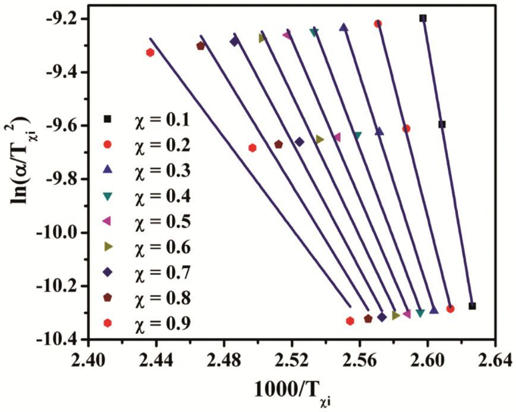

Fig. 2 — Plot of $\ln(\alpha_i/T_{\chi i}^2)$ versus$1000/T_{\chi i}$ for$Se_{79}Te_{20}Pb_1$ glassy alloy obtained using KAS method.

Table 1 — Local activation energy at different extent of conversion using different iso-conversional methods for $Se_{79}Te_{20}Pb_1$ chalcogenide glass.

χ	E_c (kJ mol^{-1})				
	KAS	OFW	Friedman	Tang & Chen	Starink method
0.1	308.51	299.42	320.00	308.39	308.52
0.2	208.17	204.05	229.15	208.20	208.26
0.3	164.74	163.75	174.52	165.84	165.87
0.4	140.20	139.48	137.55	140.34	140.35
0.5	123.16	123.31	121.12	123.32	123.32
0.6	110.53	111.33	105.47	110.71	110.70
0.7	99.01	100.41	85.43	99.72	99.20
0.8	86.32	88.37	71.47	86.55	86.52
0.9	70.69	73.56	34.70	70.94	70.90

$$\ln(\alpha) = -\frac{1.0516\, E_{\chi}}{RT_{\chi}} + constant \qquad \ldots(7)$$

The plot of ln(α) versus 1000/T_χ (Fig. 3) gives the slope -1.0516 E_χ/R from which the activation energy is calculated and deduced values of E_χ are reported in table 1.

3.4 Friedman method

The differential iso-conversional method suggested by Friedman[32] can be used directly from the Eq. (5) for the various heating rates α_i at a specific crystallization fractionχ as:

$$\ln\left(\frac{d\chi}{dt}\right)_{\chi i} = \ln\big(K_\chi f(\chi)\big) - \frac{E_{\chi i}}{RT_{\chi i}} \qquad \ldots(8)$$

The activation energy $E_{\chi i}$ at the specific value of χ is estimated from the plot of ln(dχ/dt)$_{\chi i}$ versus 1/ $T_{\chi i}$ for different heating rates and repeated for all values of χ giving continuous function of χ for E_c as shown in Fig. 4. The values of E_c calculated from Friedman method are different from those obtained by other methods (Table 1) as unlike others this method involves differentiation of crystallized fractionχ.

3.5 Tang and Chen method

In Tang and Chen method[33], the relation between the temperature $T_{\chi i}$ and heating rate α_i is given by:

$$\ln\left(\frac{\alpha_i}{T_{\chi i}^{1.895}}\right) = -\frac{1.00145 E_\chi}{RT_{\chi i}} + constant \qquad \ldots(9)$$

The graphs of $\ln\left(\frac{\alpha_i}{T_{\chi i}^{1.895}}\right)$ versus 1000/ $T_{\chi i}$ for $Se_{79}Te_{20}Pb_1$ chalcogenide glass is plotted as displayed in Fig. 5. From the slope of straight lines obtained in the graph, E_χ is evaluated and tabulated in Table 1.

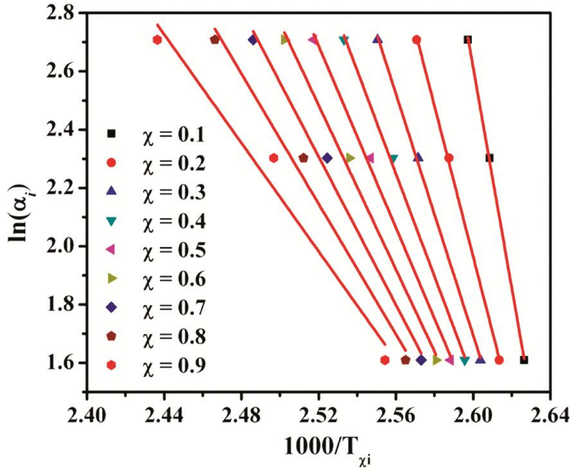

Fig. 3 — Plot of ln(α_i) versus 1000/$T_{\chi i}$ for $Se_{79}Te_{20}Pb_1$ obtained by OFW method.

3.6 Starink method

In Starink method[34], the relation between the temperatures $T_{\chi i}$ and heating rate α_i is given by:

$$\ln\left(\frac{\alpha_i}{T_{\chi i}^{1.92}}\right) = -\frac{1.0008\, E_\chi}{RT_{\chi i}} + constant \qquad \ldots(10)$$

The graphs of ln($\alpha_i/T_{\chi i}^{1.92}$) versus 1000/$T_{\chi i}$ for $Se_{79}Te_{20}Pb_1$ are drawn as presented in Fig. 6. The values of activation energy E_χ are calculated from the slopes of the straight lines thus obtained and recorded in Table 1.

The estimation of activation energy at degree of conversion χ = 0.5 using the five iso-conversional methods for the crystallization peak of $Se_{79}Te_{20}Pb_1$ alloy is given in Fig. 7. Figure 8 displays the dependence of activation energy with both the extent of crystallization and temperature for investigated

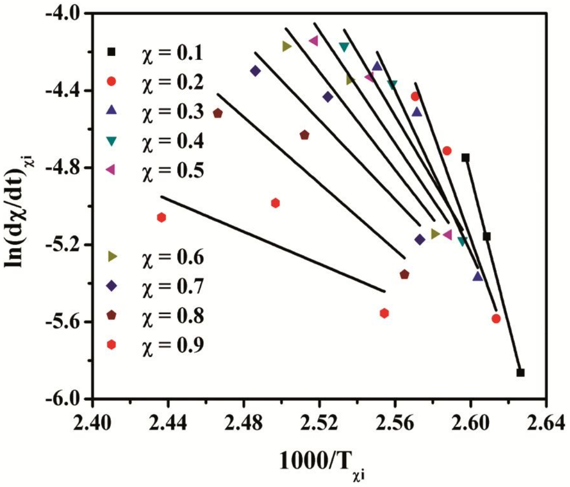

Fig. 4 — Plot of ln(dχ/dt)$_{\chi i}$ versus 1000/$T_{\chi i}$ for $Se_{79}Te_{20}Pb_1$ obtained using Friedman method.

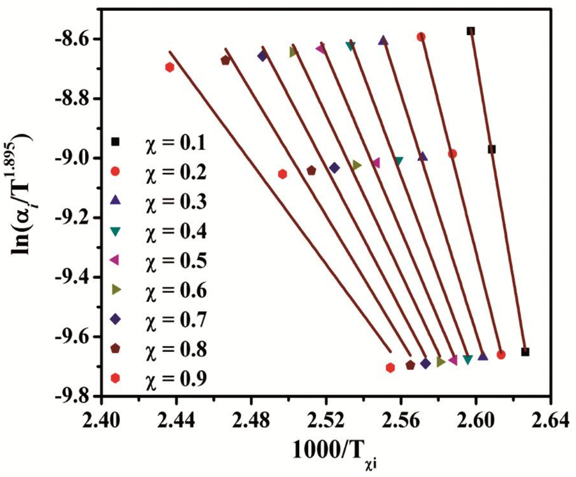

Fig. 5 — Graphs of ln($\alpha_i/T_{\chi i}^{1.895}$) versus 1000/$T_{\chi i}$ for $Se_{79}Te_{20}Pb_1$ glass obtained using Tang and Chen method.

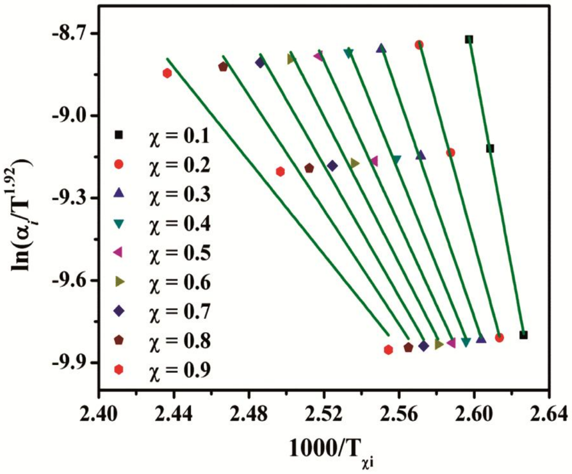

Fig. 6 — Plot of ln($\alpha_i/T_{\chi i}^{1.92}$) versus 1000/T$_{\chi i}$ for $Se_{79}Te_{20}Pb_1$ chalcogenide glass obtained by Starink method.

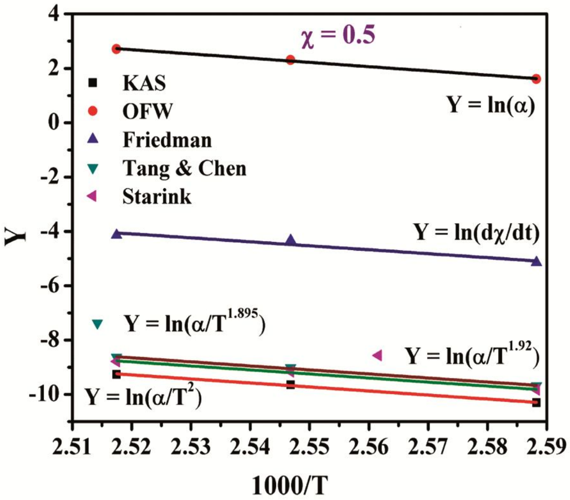

Fig. 7 — KAS, OFW, Friedman, Tang and Chen and Starink plots for $Se_{79}Te_{20}Pb_1$ alloy.

glass. The purpose of applying these various iso-conversional methods is to check their validity. It is observed that all the iso-conversional methods show decrease in E_c with increase in temperature which implies that the amorphous-crystallization transformation rate increases with the increase in temperature. It is also worth to note that the values obtained from KAS, OFW, Tang and Chen and Starink methods, are in good agreement except those of Friedman method (Table 1). A similar observation was also reported for $Ge_{22.5}Te_{77.5}$ using KAS, Tang, Starink and OFW methods[35]. The values of activation energy evaluated by KAS and OFW methods are different from those obtained by the Friedman method[36]. Friedman method employs instantaneous heating rate values due to which it is sensitive to experimental noise and tends to be numerically unstable especially when rate is estimated by numerical differentiation of experimental data[37].

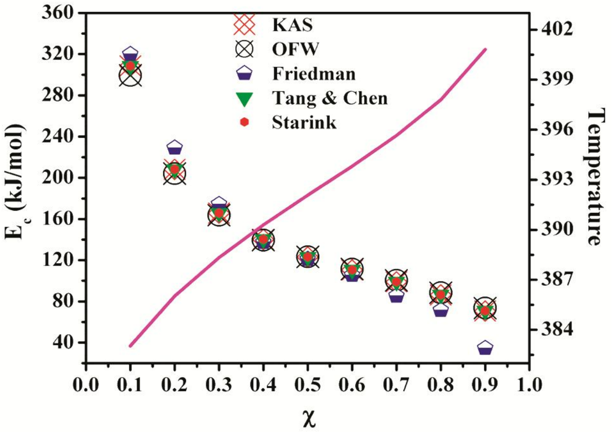

Fig. 8 — The variation of local activation energy as a function of χas well as temperature as determined by different iso-conversional methods.

It is evident from the temperature dependence of the activation energy observed in the present investigated system that a-c transformation must be described by complex multi-step reactions involving several processes of growth with different activation energies and mechanisms rather than a single-step mechanism. The observed decrease of activation energy with temperature validates the fact that the two processes of nucleation and growth determines the rate constant of crystallization. These two mechanisms tend to have different activation energies as a consequence the effective activation energy of a-c transformation will vary with temperature[38]. This interpretation is based on the nucleation theory suggested by Fisher and Turnbull[39]. According to this theory, the temperature dependence of the crystallization rate r as $r = r_0 \exp\left(\frac{-E_D}{k_B T}\right) exp\left(\frac{-\Delta F}{k_B T}\right)$ where r_0 is the pre-exponential factor, k_B is the Boltzmann constant, E_D is the activation energy for diffusion and ΔF is the maximum free energy necessary for the nucleus formation.

4 Conclusions

In the present work, investigated $Se_{79}Te_{20}Pb_1$ chalcogenide glass is prepared using melt quenching technique. The thermal behaviour of the glass is investigated using differential scanning calorimetry (DSC) under non-isothermal conditions. Amorphous to crystallization transformation has been analyzed using five iso-conversional methods viz. KAS, OFW, Friedman, Tang and Chen and Starink. There is agreement in the values of activation energy of crystallization E_c and similar variation of E_c is observed with degree of conversion χ and temperature in all iso-conversional methods. When the amorphous material is reheated, a new complex phase is obtained as the nuclei come together, i.e., nucleation takes place. Simultaneously, growth of the new phase takes place. Because the two processes, nucleation and growth are likely to have different activation energies of a-c transformation, the effective crystallized activation energy will vary with temperature according to the theory of Turnbull and Fisher. Hence, it is concluded by iso-conversional analysis that the assumption of constant E_c is not appropriate. The values of crystallization activation energy E_c as calculated by the five iso-conversional methods are not constant but vary with crystallized fraction and hence, with temperature.

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