

## Avrami exponent of crystallization in tellurite glasses

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**Abstract** Nucleation process and crystal growth for three samples of the  $(20-x)\text{Li}_2\text{O}-80\text{TeO}_2-x\text{WO}_3$  glass system were studied using X-ray diffraction and differential scanning calorimetry techniques. X-ray diffraction data confirmed the amorphous characteristic of the *as-quenched* samples and indicated the growth of crystalline phases formed due to the thermal treatment for annealed samples. These results reveal the presence of three distinct  $\gamma\text{-TeO}_2$ ,  $\alpha\text{-TeO}_2$  and  $\alpha\text{-Li}_2\text{Te}_2\text{O}_5$  crystalline phases in the TL sample, and two distinct  $\alpha\text{-TeO}_2$  and  $\gamma\text{-TeO}_2$  crystalline phases in the TLW5 and TLW10 samples. The activation energy and the Avrami exponent were determined from DSC measurements. The activation energy values X-ray diffraction data of the TLW10 glass sample suggest that  $\gamma\text{-TeO}_2$  phase occur before the  $\alpha\text{-TeO}_2$ . The results obtained for the Avrami exponent point to that the nucleation process is volumetric and that the crystal growth is two or three-dimensional.

**Keywords** Tellurite glasses · Nucleation · Crystallization · Activation energy · XRD · DSC

### Introduction

With the advent of the lasers, mainly the pulsed lasers, vitreous materials have attracted considerable interest for

applications in the communication and in the photonics devices, especially in the non-linear optics. Currently, the objective of the research is to substitute electronic systems by optical devices with objective to use the light in the transmission, modulation, amplification, and information storage [1, 2]. Vitreous matrices based on tellurite glasses ( $\text{TeO}_2$ ) [3, 4] present a third harmonic generation ( $\chi^3$ ) with approximately one order of magnitude higher than silicates and borates glasses.

Study of the thermal and structural properties [5, 6] of tellurite glasses is important to understand the nucleation and crystal growth mechanism which is essential to obtain high quality glasses for technological applications. Many works have reported the glass thermal properties studied by isothermal and non-isothermal methods [7, 8]. The non-isothermal method offers some advantages when compared to isothermal method. One of them is that the non-isothermal experiments can be performed in shorter time period and in a wider temperature range. In addition, most phase transformations occur too rapidly to be measured under isothermal conditions because of the inherent transients associated with the experimental apparatus [9, 10].

Structural properties studies reveal two stable crystalline forms for  $\text{TeO}_2$ :  $\alpha\text{-TeO}_2$  (paratellurite) [11] and  $\beta\text{-TeO}_2$  (tellurite) [12]. The basic structure is constituted by the trigonal bipyramid ( $\text{TeO}_4$ ), linked for vertexes in the  $\alpha\text{-TeO}_2$  phase and for the edges in the  $\beta\text{-TeO}_2$  phase. In addition, new crystalline polymorphic phases,  $\delta\text{-TeO}_2$  and  $\gamma\text{-TeO}_2$ , were discovered [13, 14]. The  $\gamma\text{-TeO}_2$  structure is constituted by a distorted  $\text{TeO}_4\text{E}$  bi-pyramid with one of the vertexes occupied for a pair of free electrons.

The purpose of this study was to study the nucleation and crystallization kinetic of the  $\text{Li}_2\text{O}-\text{TeO}_2-\text{WO}_3$  glass system determining the activation energy and the Avrami

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exponent from the formed crystalline phases due to heating treatment of the samples.

## Materials and methods

The glasses of the  $(20-x)\text{Li}_2\text{O}-80\text{TeO}_2-x\text{WO}_3$  system were prepared by the conventional melt-quenching method. The obtained samples are referred in the text as TL ( $x = 0$  mol%), TLW5 ( $x = 5$  mol%), and TLW10 ( $x = 10$  mol%). The samples were obtained from the commercial reagents  $\text{Li}_2\text{CO}_3$  (Aldrich, 99+%),  $\text{TeO}_2$  (Aldrich, 99+%) and  $\text{WO}_3$  (Aldrich, 99+%). These reagents in appropriated ratios were mixed to give 5 g batches. The mixture was melted in a platinum crucible using an electric furnace at 800 °C for TL glass and at 850 °C to the other two glasses for 30 min. The molten material was poured onto pre-heated brass mold and was immediately placed in other furnace for annealing. The samples were annealed at 200 °C for TL and 250 °C for TLW5 and TLW10 glasses during 2 h. These samples will be cited in the text *as-quenched*.

Thermal properties were studied by differential scanning calorimetry (DSC) technique carried out in a DSC 2920 equipment (TA Instruments). The DSC thermograms were obtained using 10 mg of sample enclosed in aluminum pan under dry nitrogen atmosphere for five different heating rates (2.5, 5.0, 7.5, 10.0, and 12.5  $\text{K min}^{-1}$ ). The crystallized glasses were analyzed by X-ray diffraction (XRD) technique using Cu  $K\alpha$  radiation of a RU200B Rigaku equipment. Powder samples with particle size of 45–63  $\mu\text{m}$  were used for DSC and XRD measurements.

The Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory was used to determine the Avrami exponent ( $n$ ) [15–17]. This theory describes the evolution in the time ( $t$ ), or temperature ( $T$ ), of the crystallized volume fraction ( $x$ ) for non-isothermal process [18–21]. The  $n$  parameter was determined from the DSC data considering the following equation [9, 22]:

$$n = \left( \frac{dx}{dt} \right)_p \frac{RT_p^2}{0.37 \phi E} \quad (1)$$

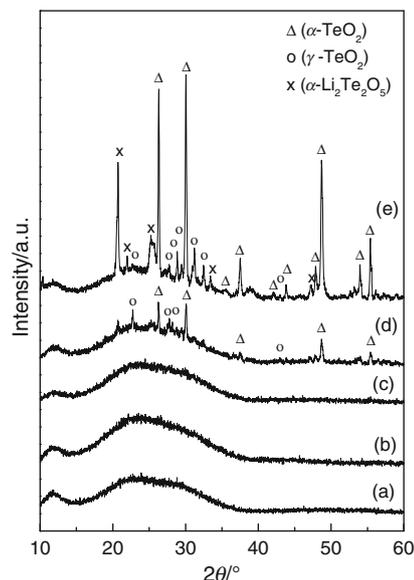
where  $E$  is activation energy for the crystallization,  $T_p$  the temperature corresponding to the maximum of the DSC crystallization peak,  $R$  the gas constant,  $\phi$  the heating rate, and  $(dx/dt)_p$  the maximum crystallization rate. All thermograms were fitted using Gaussian functions to determine the crystallization peak temperature ( $T_p$ ) corresponding to the phases observed in each glass sample. The  $E$  values were determined through the Kissinger relation [23, 24],  $\ln(T_p^2/\phi) = E/RT_p$ , considering the slope of the  $\ln(T_p^2/\phi)$  versus  $(1/T_p)$  curve.

The  $n$  value matches the nucleation type, if it is homogeneous or heterogeneous, and also the dimensionality of crystal growth. The  $n = 1$  and  $n > 1$  values indicate that the nucleation is superficial and volumetric, respectively. On the other hand, the crystal growth can be three- ( $n = 4$ ), two- ( $n = 3$ ), or one-dimensional ( $n = 2$ ) [16, 17, 25–28].

There are others theoretical models to evaluate the crystallization mechanism of glasses such as Ozawa [29], Augis and Bennett [30], Vázquez et al. [31], Ray and Day [32], and Matusita et al. [25, 26]. In this work, the results obtained using the JMAK theories were compared with the Matusita model.

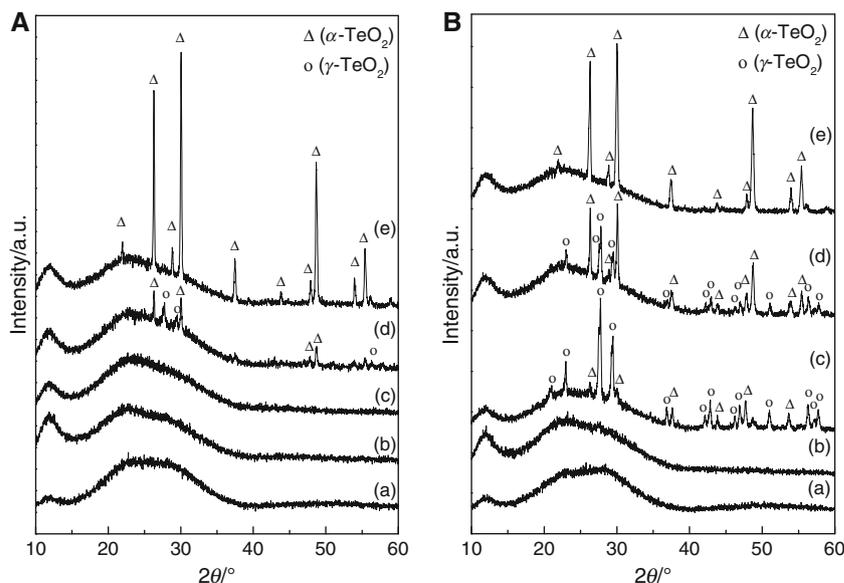
## Results

Figure 1 shows XRD patterns of TL glass as-quenched (Fig. 1a) and heat annealed at different temperatures (Fig. 1b–e). In the Fig. 1a shows a typical amorphous characteristic which was maintained with also heat treatment at 548 and 597 K for 5 min, Fig. 1b and c, respectively. However, XRD pattern of the sample treated at 608 K for 5 min (Fig. 1d) shows a typical glass–ceramic XRD pattern where the indexed peaks were attribute to  $\alpha\text{-TeO}_2$  and  $\gamma\text{-TeO}_2$  crystalline phases. Finally, the XRD pattern of glass heat annealed at 634 K for 5 min (Fig. 1e) shows the presence of the  $\alpha\text{-Li}_2\text{Te}_2\text{O}_5$  crystalline phase in coexistence with the  $\alpha\text{-TeO}_2$  and  $\gamma\text{-TeO}_2$  phases. The structure of the  $\alpha\text{-TeO}_2$  phase is formed by a three-dimensional net of  $\text{TeO}_4$  connected by asymmetric bridges of  $\text{Te-O-Te}$  and the structure of the  $\gamma\text{-TeO}_2$  phase is



**Fig. 1** X-ray diffraction patterns of the TL glass: (a) as-quenched and heat treated at (b) 548 K, (c) 597 K, (d) 608 K, and (e) 634 K for 5 min

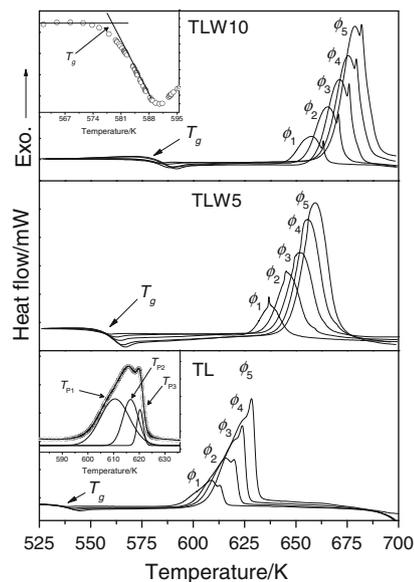
**Fig. 2** X-ray diffraction patterns. **A** TLW5 glass: (a) as-quenched and heat treated at (b) 553 K, (c) 643 K, (d) 653 K, and (e) 663 K; and **B** TLW10 glass: (a) as-quenched and heat treated at (b) 658 K, (c) 681 K, (d) 689 K, and (e) 713 K



formed by unities of  $\text{TeO}_4$  alternately linked by almost symmetrical and highly asymmetric bridges of  $\text{Te-O-Te}$  [13, 14, 33].

XRD measurements also were performed for the TLW5 and TLW10 glasses and the results are showed in Fig. 2A and B, respectively. The XRD patterns of the as-quenched and heat treated samples at 553 and 643 K (Fig. 2A) and at 658 K (Fig. 2B) are typical of amorphous materials. On the other hand, the patterns of the treated samples at 653 K (Fig. 2A-d) and 663 K (Fig. 2A-e) for the TLW5 glass, and at 681 K (Fig. 2B-c), 689 K (Fig. 2B-d), and 713 K (Fig. 2B-e) for the TLW10 glass are characteristic of a vitro-ceramic and are associated the formation of the  $\alpha\text{-TeO}_2$  and  $\gamma\text{-TeO}_2$  crystalline phases. It is observed only the  $\alpha\text{-TeO}_2$  crystalline phase for the TLW5 and TLW10 glasses heating treated at 663 and 713 K, respectively, suggesting a transition [12, 34, 35] from the  $\gamma\text{-TeO}_2$  to the  $\alpha\text{-TeO}_2$  crystalline phase. Furthermore, the XRD data of the TLW5 and TLW10 glasses indicate that the addition of  $\text{WO}_3$  in the composition of the glass not allow the formation of the  $\alpha\text{-Li}_2\text{Te}_2\text{O}_5$  crystalline phase.

Figure 3 shows DSC curves for heat flow versus temperature recorded at different heating rates. The  $T_g$  of all glasses were determined as indicated in the top insert of Fig. 3. The curves show the presence of exothermic peaks for each sample in different heating rates. The asymmetry observed in the crystallization peaks suggests the formation of different crystalline phases during the crystallization process. This is in agreement with XRD data. As mentioned above, were observed three crystalline phases ( $\alpha\text{-TeO}_2$ ,  $\gamma\text{-TeO}_2$ , and  $\alpha\text{-Li}_2\text{Te}_2\text{O}_5$ ) for the TL sample and of two crystalline phases ( $\alpha\text{-TeO}_2$  and  $\gamma\text{-TeO}_2$ ) for TLW5 and TLW10 samples. The crystallization peaks were fitted



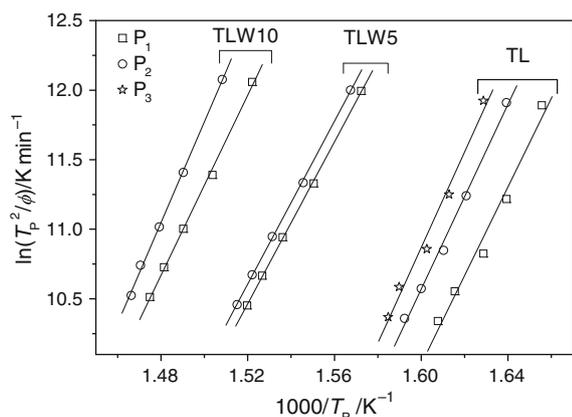
**Fig. 3** DSC curves of the TL, TLW5, and TLW10 glasses recorded at different heating rates ( $\phi$ )

using Gaussian functions considering the superposition of the crystalline phases. Thus, the maximum temperatures associated with the crystalline phases were obtained. As example, the bottom insert of Fig. 3 shows the three maximum temperatures ( $T_{P1}$ ,  $T_{P2}$ , and  $T_{P3}$ ) associated the three crystalline phases observed in the TL glass.

Table 1 summarizes the values of the  $T_g$  and  $T_P$  of the TL, TLW5, and TLW10 glasses for different heating rates. As can be observed, occurs a significant increase in the  $T_g$  value for the samples with  $\text{WO}_3$ . This increase may be associated with decreasing of mobility in the glasses.

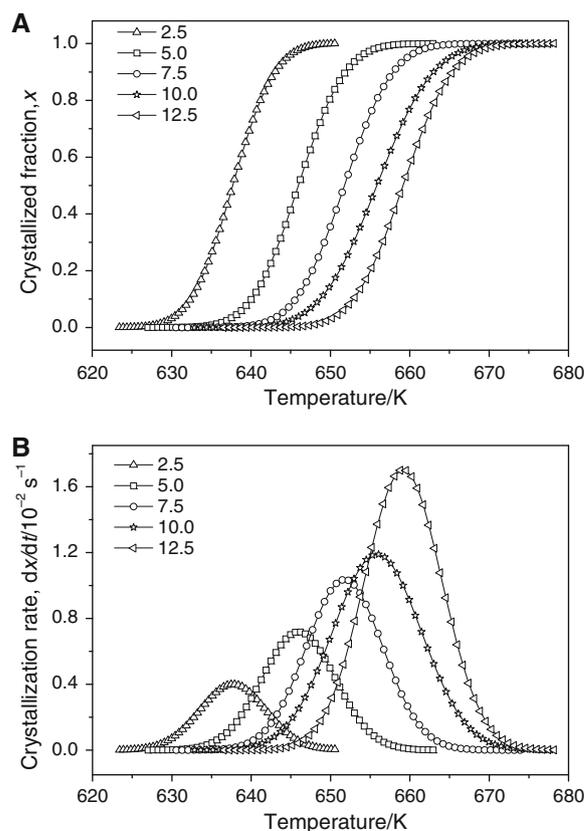
**Table 1** Summary for temperature of crystallization peak from DSC curves recorded for TL, TLW5, and TLW10 glasses of 45–63  $\mu\text{m}$  particles size at different heating rates

Heating rate $\phi/\text{K min}^{-1}$	TL glass				TLW5 glass			TLW10 glass		
	$T_g/\text{K}$	Peak temperature/K			$T_g/\text{K}$	Peak temperature/K		$T_g/\text{K}$	Peak temperature/K	
		$T_{P1}$	$T_{P2}$	$T_{P3}$		$T_{P1}$	$T_{P2}$		$T_{P1}$	$T_{P2}$
2.5	526	604	610	614	548	636	638	570	657	663
5.0	530	610	617	620	550	645	647	574	665	671
7.5	532	614	621	624	552	651	653	576	671	676
10.0	533	619	625	629	554	655	657	578	675	680
12.5	534	622	628	631	555	658	660	579	678	682

**Fig. 4** Kissinger plots for the crystallization peaks of the TL, TLW5, and TLW10 glasses

To obtain  $n$  values it is necessary calculate the activation energy ( $E$ ) and maximum of crystallization rate curve  $(dx/dt)_p$ . First, the activation energies of the crystalline phases of each sample were determined from slope of the  $\ln(T_p/\phi)$  versus  $1/T_p$  curves (Fig. 4). On the other hand, the crystallization rate  $(dx/dt)$  it was determined from the crystallized volume fraction ( $x$ ) as function of the temperature for the DSC crystallization peaks in different heating rates. The crystallized fraction at generic temperature  $T$  is given by  $x = A/A_0$ , where  $A_0$  is total area between the  $T_i$  and  $T_f$  temperatures.  $T_i$  is the temperature where the crystallization is just beginning and  $T_f$  is the temperature where the crystallization is completed. The  $A$  is the partial area between  $T_i$  and  $T$  temperatures [7, 36]. The Fig. 5A shows the crystallized fraction in function of the temperature for the second crystallization peak of the TLW5 glass. The sigmoid form of the obtained curves is characteristic of volumetric crystallization. The curves of Fig. 5B represent the slope of crystallized fraction curves (Fig. 5A) with respect to the temperature and the maximum of these curves correspond to the  $(dx/dt)_p$  values.

Therefore, the values  $(dx/dt)_p$ ,  $T_p$ ,  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $\phi$ , and  $E$  were used to determine the  $n$  parameter using the

**Fig. 5** **A** Crystallized fraction ( $x$ ) and **B** Crystallization rate  $(dx/dt)$  as function of the temperature ( $T$ ) for second crystallization peak of the TLW5 glass at different heating rates

Eq. 1. The  $n$  and  $E$  values are summarized in the Table 2. The  $n$  values are the average between the values obtained for different heating rates. The  $n$  values indicate that the nucleation and the crystals growth take place through more than one mechanism. Thus, the results obtained by JMAK and Matusita models are in agreement and point to a volumetric nucleation with crystals growth occurring in two-dimensional ( $\bar{n}_1 \approx 3$ ) followed by three-dimensional ( $\bar{n}_2$  and  $\bar{n}_3 > 4$ ) for TL glass, two-dimensional ( $\bar{n}_1$  and  $\bar{n}_2 \approx 3$ ) for

**Table 2**  $E$  and  $n$  values associated to the crystallization peaks for three studied glasses

Glass	Activation energy, $E/\text{kJ mol}^{-1}$			Avrami exponent, $n$					
	$E_1$	$E_2$	$E_3$	JMAK			Matusita		
				$\bar{n}_1$	$\bar{n}_2$	$\bar{n}_3$	$\bar{n}_1$	$\bar{n}_2$	$\bar{n}_3$
TL	$265 \pm 9$	$276 \pm 5$	$285 \pm 8$	2.8	3.8	5.3	2.8	3.7	5.8
TLW5	$242 \pm 1$	$243 \pm 1$	–	2.8	3.3	–	2.6	3.6	–
TLW10	$269 \pm 3$	$302 \pm 3$	–	2.8	4.0	–	2.4	4.3	–

TLW5 glass, and two-dimensional ( $\bar{n}_1 \approx 3$ ) followed by three-dimensional ( $\bar{n}_2 = 4$ ) for TLW10.

As in our previous work [37], the XRD data of the TL glass it not allow to know between  $\gamma\text{-TeO}_2$  and  $\alpha\text{-TeO}_2$  phases what of them takes place first. It is possible only to affirm that the  $\alpha\text{-Li}_2\text{Te}_2\text{O}_5$  crystalline phase occurs after the  $\gamma\text{-TeO}_2$  and  $\alpha\text{-TeO}_2$  phases. The same occur with the TLW5 glass. For these two glasses no significant difference was observed in the activation energy. On the other hand, though it is not possible to affirm but the tendency observed in the XRD patterns and the  $E$  values obtained for TLW10 glass suggest that the  $\gamma\text{-TeO}_2$  phase occur before than  $\alpha\text{-TeO}_2$  phase.

## Conclusions

The  $(20-x)\text{Li}_2\text{O}-80\text{TeO}_2-x\text{WO}_3$  glasses were studied by XRD and DSC techniques to understand the nucleation and crystals growth process on these glasses. The results obtained with TL glass suggest that the  $\text{Li}_2\text{Te}_2\text{O}_5$  crystallization occur after the  $\gamma\text{-TeO}_2$  and  $\alpha\text{-TeO}_2$ . Furthermore, from XRD data and the  $E$  values obtained for TL and TLW5 glasses it does not allow to know what is the phase between  $\gamma\text{-TeO}_2$  and  $\alpha\text{-TeO}_2$  that crystallized first. On the other hand, the  $E$  values and XRD data for TLW10 glass suggest that the  $\gamma\text{-TeO}_2$  occur before the  $\alpha\text{-TeO}_2$ . Finally, the Avrami exponents point to a volumetric nucleation with two-dimensional crystal growth followed by three-dimensional for TL and TLW10 glasses and only two-dimensional for TLW5 glass.

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