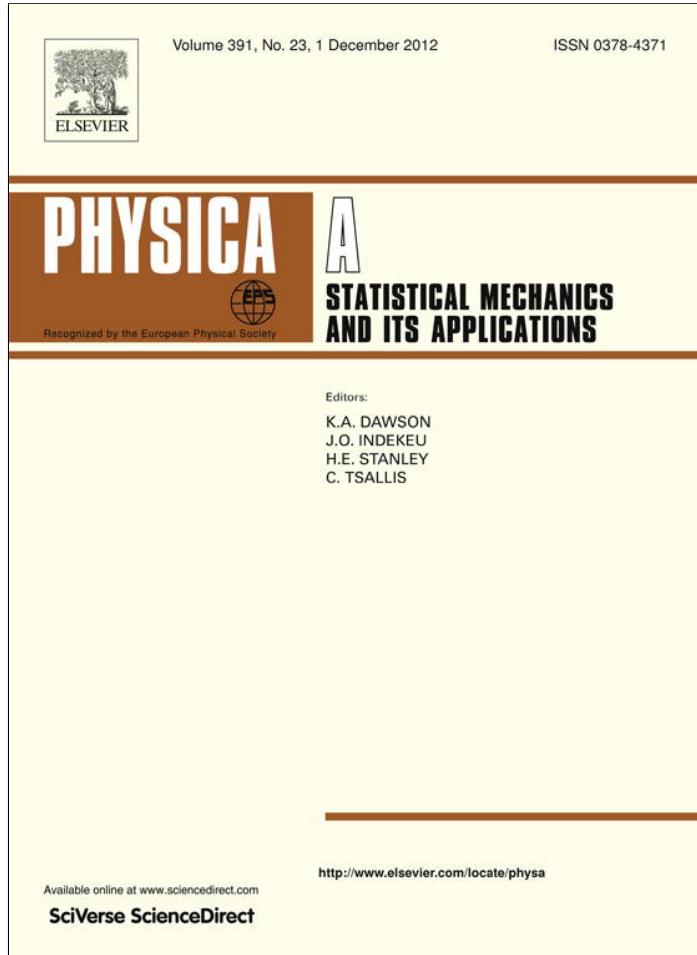


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Non-extensive treatment of surface nucleation on glass particles

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ABSTRACT

Experimental data of phase transformation kinetics was used to fit a new model based on a non-extensive formalism derived from Tsallis thermostatistics and another based on the Johnson–Mehl–Avrami–Yerofeyev–Kolmogorov (JMAYK) theory. For this we considered the same experimental parameters such as crystal geometric factor g , the density of nucleation sites, N_s and crystal growth rates U on glass powders. The kinetics of nucleation and growth of diopside crystals ($\text{MgO} \cdot \text{CaO} \cdot 2\text{SiO}_2$) on the glass surface at 825°C ($T_g \sim 727^\circ\text{C}$) were studied. Treatments for sinter-crystallization were performed in compacts of diopside glass particles by varying the treatment time. The crystallized fraction of the samples subjected to such treatments, which develop from the particles' surface toward their volume, was characterized by means of optical microscopy and X-ray diffraction. The two models were then fitted to the measured crystallized fraction data and compared to each other. It was found that surface nucleation occurs very rapidly from a random number of active sites. The JMAYK theory describes the case of fast heterogeneous nucleation from a constant number of sites on the glass surface. The Tsallis approach is better than the JMAYK model considering that the q factor equals 1.268 ± 0.062 and does not require taking into account the change in crystallization mode from three dimensional to one dimensional as JMAYK predicts, and this is advantageous. Furthermore, Tsallis thermostatistics contains the Austin–Rickett model as a special and limiting case study for this system. A generalized Avrami plot is also presented.

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1. Introduction

Overall crystallization from a melt is a complex process involving simultaneous nucleation and growth of separate crystallites [1]. While most types of glass display surface crystallization when properly heated, only a few show internal nucleation in the absence of nucleating agents [2]. The process can be described by determining the surface or volume fraction of the transformed phase, and this is an important goal when a correct description for a material fraction transformed at a given time in terms of nucleation and growth processes is required. The formal theory of crystallization kinetics under isothermal conditions was independently developed in the late 1930s–1940s by Kolmogorov [3], Johnson and Mehl [4], Avrami [5–7], and Yerofeyev [8], and it is well-known as the JMAYK theory. It is widely used to infer the mechanism of phase transformations in metals [9], polymers [10] and inorganic glass [11].

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The most universal form of the theory for the (extended) fraction transformed α as a function of the annealing time t in isothermal heat treatment conditions is:

$$\alpha(t) = 1 - \exp[-\alpha^*(t)] \quad (1)$$

where α^* is the extended or fictitious volume, which is calculated by neglecting impingement effects, allowing each crystal to nucleate and grow naturally. This quantity can be calculated if the nucleation, I , and growth rate, U , are known at the temperature T of interest.

Avrami proposed that [5–7], in general, the following relation should be used:

$$\alpha(t) = 1 - \exp(-Ct^n). \quad (2)$$

According to Kolmogorov [3] $\alpha(t)$ can be interpreted as the probability for crystallizing for example the glass until time t after the onset of the process. In typical applications the equation above is used in the form [6]:

$$\ln[-\ln(1-\alpha)] = \ln C + n \ln t. \quad (3)$$

The values of C and n can be obtained from experimental data by Eq. (2), and their specific values depend on the nature of nucleation and growth processes. The Avrami coefficient, n , depends on both the nucleation and growth mechanisms, and can be written for the case of three-dimensional growth as:

$$n = c + 3m \quad (4)$$

where c and m describe the variation in the crystal number with time ($N \approx t^c$) and the dependence of crystal size on time ($r \approx t^m$) [1,12].

A knowledge of the Avrami coefficient, n , is helpful to understand the mechanism of phase transformation at a given temperature [13]. When it is possible to independently measure the crystal growth rate, one can then calculate the nucleation rate from the coefficient C . This method is not as precise as direct measurements, but it can provide useful information about nucleation in the advanced stages of crystallization, when the application of other methods is hindered.

For the special case under study, i.e. fast nucleation of square shaped crystals from a fixed number of sites on the glass surface, N_S , the fictitious extended area, α^* , is:

$$\alpha^*(t) = gN_S r^2(t) \quad (5)$$

where r is the edge crystal size and g a shape factor (in this work, equal to four).

If the growth rate, U , is time independent, the crystal dimension can be related to the heat treatment time, t , by the simple relation:

$$r(t) = Ut. \quad (6)$$

Therefore, the actual crystallized fractional area is easily computed by the combination of the previous equations:

$$\alpha(t) = 1 - \exp[-4N_S U^2 t^2]. \quad (7)$$

For this particular glass system, nucleation occurs rapidly from a fixed number of (unknown) sites N_S in the very early stages of crystallization [14]. In the vast majority of types of glass, crystallization starts on athermal surface sites, such as scratches, solid impurities, etc. [15,16].

2. Nonextensive JMayK brief theory

According to Avrami, Eq. (1) comes from the differential equation [6]:

$$\frac{d\alpha(t)}{d\alpha^*} = 1 - \alpha(t). \quad (8)$$

Kayacan and Cetinel [17,18] proposed a similar equation, as described below:

$$\frac{d\alpha(t)}{d\alpha^*} = [1 - \alpha(t)]^q \quad (9)$$

based on Tsallis thermostatistics [19], where q is called the entropic index and measures the “nonextensivity” of the system. In the limit of $q \rightarrow 1$, Eq. (9) reduces to the JMayK equation.

The index q comes from the entropy definition [19]:

$$S_q = k \frac{1 - \sum_{i=1}^W p_i^q}{q-1} \quad (q \in \mathbb{R}, W \in \mathbb{N}) \quad (10)$$

where k is a constant, p_i is the probability of the system in the i microstate, W is the total number of configurations and q as previously defined. More details can be found in Ref. [20], in particular on deformed q -algebras [21] and possible new

expressions. It is important to note that Kayacan and Cetinel's proposal is not based on a rigorous physical model but on the physical meaning of the exponent q , which comes from the entropy definition, and seems reasonable.

Tsallis proposed Eq. (10) as an entropy definition in 1988 [19]. In the limit $q \rightarrow 1$, this equation is reduced to the Boltzmann–Gibbs (BG) entropy [19]. In other words, Eq. (10) contains Boltzmann–Gibbs statistics [1,12] as a special case [18]. BG statistics is a powerful and well known tool for the study of a variety of physical systems, as the present case. However, it fails for systems which (i) have long-range interactions (ii) have long-range memory effects and (iii) evolve in multi-fractal space–time [18]. Systems which have these properties are called “nonextensive” [20] and if a system does obey these restrictions, BG statistics seems to be inappropriate and a nonextensive formalism is needed to study the physical system [17].

The solution of Eq. (9) is [22]:

$$\alpha(t) = 1 - [1 - (1 - q) \alpha^*]^{\frac{1}{1-q}} \quad (11)$$

where we consider $\alpha^*(t) = 4N_S U^2 t^2$ in this work.

Eq. (11) can be also written as $\alpha(t) = 1 - \exp_q[-\alpha^*]$, following the q -exponential function definition [22] $\exp_q(x) = [1 + (1 - q)x]^{\frac{1}{1-q}}$, if $[1 + (1 - q)x] > 0$ and $\exp_q(x) = 0$ if $[1 + (1 - q)x] < 0$.

In this study, the adjustable parameter is the entropic index q and it comes from the definition of Tsallis entropy [19]. Moreover, Kayacan and Cetinel's kinetic proposal covers not only JMAXK (i.e. $q \rightarrow 1$), but also the Austin–Rickett (AR) model (i.e. $q = 2$) [23]. It is important to note that the Austin–Rickett proposal was drawn up at the same time as the Johnson and Mehl theory [4]. Thus it is very reasonable that the new equation containing the q parameter could give new insights into our understanding of the nucleation and growth processes in a glass system with heterogeneous nucleation such as diopside.

Based on the assumptions described above, our aim is thus to consider fixed N_S and U previously obtained for a powdered diopside glass [15,16]—to compare the JMAXK and Tsallis theories based on Kayacan and Cetinel's proposal. For this we have experimental volume fraction crystallized $\alpha(t)$ from null to almost 100% crystallized glass. As far the author is aware, this work is the first experimental verification of surface crystallization using Tsallis thermostatics.

3. Experimental

A glass with the stoichiometric composition of diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$) was prepared by mixing the correct proportion of high grade chemicals [15]. We use diopside as a suitable model glass, due to (i) the high confidence we have in the values of crystal growth rate (U) as a function of temperature for this system and the insensitivity of U to small compositional differences between different glass melts [24] (ii) the fact that only one crystal phase develops on heating and (iii) its high chemical durability, which prevents the formation of extra nucleation sites (by chemical attack) after sample preparation. Experimental data was obtained from previous work [15,16].

The chemicals were mixed in a Fritsch Pulverisette 6 high impact mill with Si_3N_4 jar and balls. The batch was then melted in a Pt crucible at 1500 °C for 4 h. The liquid was poured into a stainless steel mold and left to cool down in air. Minor devitrification patches formed on the surface of the glass plaque, which were ground off. The glass block was hammered and the ground pieces were further milled in the high impact mill for short time periods (30 s at 350 rpm) to keep the particle sizes in the desired range without introducing too many defects on the newly created surfaces. The glass powder was sieved through a 38–75 μm polymer mesh. The collected powder was washed in water to eliminate most of the fine particles that usually attach to the coarse ones [16].

To prepare compacts for sintering the collected powder was mixed with 20 wt% oleic acid. Details of sintering process in glass particles can be found elsewhere [15]. This powder was subsequently heated to 500 °C for some seconds to remove the excess acid, acquiring a gray color, which indicated that burning was only partial and that some residue remained. We proceeded in this way to enhance particle packing when pressing the powder into disks. Approximately 25 mg of powder was pressed under 2500 kgf in a stainless steel die into 1.5 mm thick disks of 10 mm in diameter. The acid was totally eliminated by subsequently heating of the samples at 500 °C for 1 h, resulting in white disks. Details of sintering process theory in glass particles can be found elsewhere [25].

It is important to note that the original glass grains considered in this work are not spherical and have a size distribution. The particle size distribution of the powder used was between 38 and 75 μm and was characterized in a Horiba LA-930 laser scattering particle size analyzer [15].

Two sets of samples for crystallization measurements were independently produced following the above procedure, and are indicated in the next figures as OM (*Optical Microscopy*) or XRD (i.e. *X-Ray Diffraction*) due to the experimental process. All these samples were heat treated at 825 °C, for 30 min to 8 h, for simultaneous sintering and crystallization. For each heat treatment experiment the samples were heated together.

The sintered disks were sectioned through half the diameter and one of the sectioned faces was polished for microscopy. We used a Leica DMRX optical microscope with digital image capture and Zeiss KS200 software for image analysis. Ten images of each section, randomly taken, were analyzed. Samples treated for time periods shorter than 2 h presented very thin surface crystallized layers, and it was difficult to analyze them in an optical microscope. Therefore these samples were only analyzed by XRD to estimate their crystallized volume fraction. For one batch we analyzed by means of atomic force

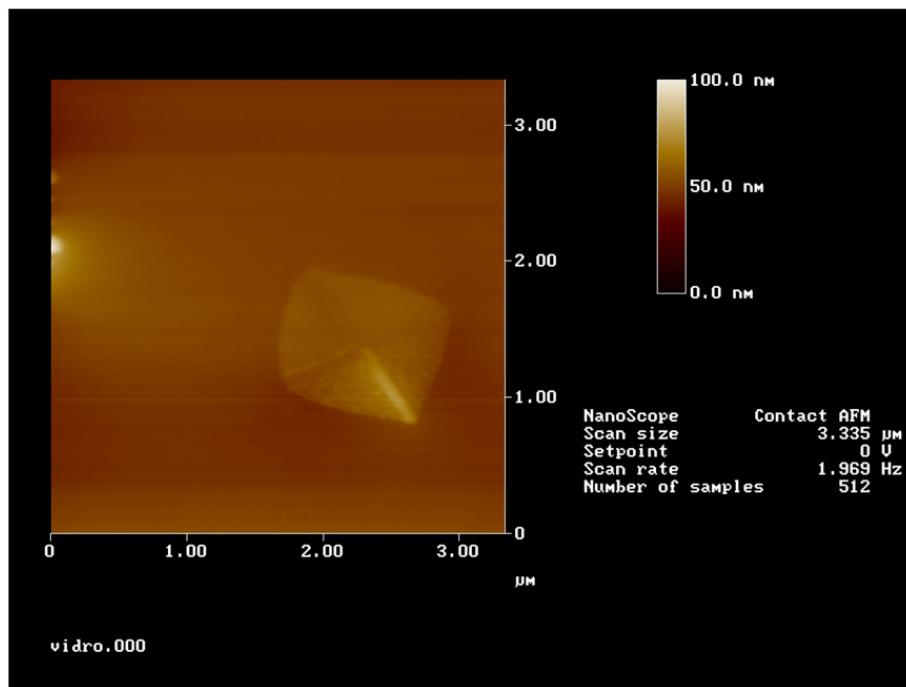


Fig. 1. Atomic force micrograph of polished (with cerium oxide) diopside crystal one micron length heat treated for 2 h at 820 °C. This glass is similar to another batch heat treated in equal conditions with $N_s \approx 8 \times 10^{10} \text{ m}^{-2}$ [26].

microscopy (Digital Nanoscope IIIa), contact mode, 1.969 Hz scan rate and 3.325 scan size growing crystals from a polished glass surface with CeO₂.

Although the microscopy method briefly explained above can give precise results, it requires several micrographs and is quite time consuming. Alternatively, X-ray diffraction has the advantage of sampling a large area in a single test, allowing the rapid determination of $\alpha(t)$. We used a Siemens D5005 XRD operated at 40 kV and 40 mA. More details on sample preparation can be found elsewhere [15].

4. Results and discussion

Fig. 1 shows an example of the crystal aspect ratio on the surface of a diopside glass mechanically polished with CeO₂, just to observe the squared crystal morphology. These crystals are similar to those obtained in Ref. [26], where the main goal was the study of concurrent sintering with crystallization process in this particular system. In this work we deal with jagged particles, as shown in Refs. [15,16], where it is possible to observe sectioned sintered grains whose centers are still glassy but whose surfaces have crystallized. The thickness of the crystallized surface layer increased with heat treatment time up to a point when the glass grains were completely consumed by the crystals.

Fig. 2 shows linear fits from Eq. (3) to experimental data, considering as variables the time t and the crystallized fraction α . According to this equation, plotting $\ln[-\ln(1-\alpha)]$ versus $\ln t$ for an isothermal experiment yields a linear dependence with the JMJAYK parameters C and n . According to Zanotto and Galhardi [27], it should be emphasized that the Avrami plots are insensitive to variations of α and t and that the value of the intercept C is seldom compared to the theoretical value.

The plot can be divided into two parts: the initial, ranging up to the time t^* , which depends on temperature and is around 4 h for isothermal heat treatment at 825 °C; and the next regime above t^* . A linear regression fit of the both regimes leads to the parameters which are indicated in Fig. 2. For $t < t^*$, n is of the order of 2 (a two dimensional growth, as explained by Avrami [6]) with parameter $\ln C \approx \ln gN_s U^2$ within the same order or magnitude found on the plot. However, for $t > t^*$ it is found that n is near 1, which indicates controlled diffusion or first-order kinetics or indicates athermal nuclei/needle-like crystals growing from the surface toward the volume of the particle. It is important to note that the coefficient $\ln C = \ln gN_s U^2$ does not match at high α values and with the linear regression plot in Fig. 2. As pointed out by Price [28] when linear Avrami plots (Eq. (3)) are obtained, n frequently differs from values expected, for example by that used in Eq. (7).

The number of crystals per unit area, N_s , and crystal growth rate, U , used are similar to previous results [14,29], i.e. within the same order of magnitude, even considering the difference in composition (1% Al₂O₃ addition in diopside for previous cases) or heat treatment temperatures. Zanotto [14] and Zanotto and Basso [29] found squared crystals growing from 1 to 4 h with $N_s = 7.874 \times 10^{10} \text{ m}^{-2}$ and linear behavior (following Eq. (6)) $U = 2.48 \times 10^{-10} \text{ m/s}$ with $15 < \alpha < 70\%$ at 820 °C by means of optical and scanning electron microscopies. In this work samples were heat treated at 825 °C, with parameters fixed as $N_s = 4 \times 10^{10} \text{ m}^{-2}$ and $U = 2 \times 10^{-10} \text{ m/s}$ [15]. Unfortunately, the optical determination of N_s is very difficult and not a practical task, especially in the case of small jagged particles prepared for sintering (as the present case). This is

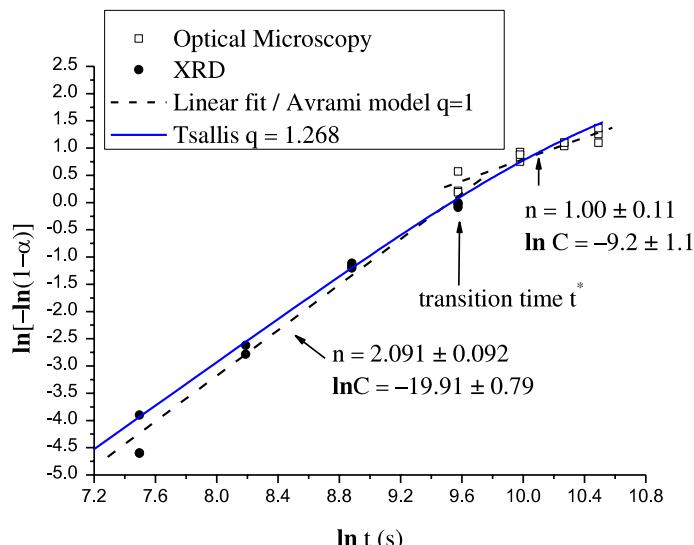


Fig. 2. Avrami plot for the formation of crystallized diopside samples from optical microscopy (OM) and X-ray diffraction (XRD) results for a fixed temperature 825 °C. Line fits of different crystallization behaviors are indicated ($n = 1$ and 2 , dashed line). Just for comparison, the best Tsallis fit using $q = 1.268$ (full line) as a continuous curve.

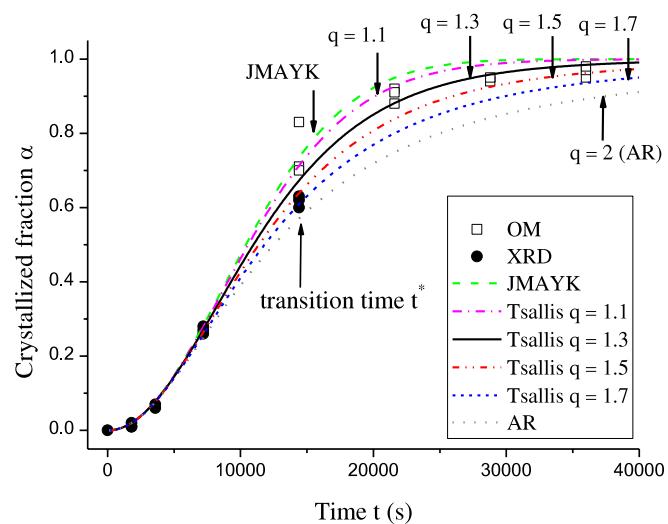


Fig. 3. Experimental volume fractions crystallized in sintered diopside glass compacts as a function of time at 825 °C, by means of optical microscopy (OM) and X-ray diffraction (XRD) results. Curve fits of different expressions to the experimental data (lines) considering geometric factor $g = 4$, crystal density $N_S = 4 \times 10^{10} \text{ m}^{-2}$ and growth rate $U = 2 \times 10^{-10} \text{ m/s}$. Best fits were found using the Tsallis approach with q between 1.1 and 1.3 .

the reason why we and other authors have used models that allow an indirect estimation of N_S (more details in Ref. [15]). Diopside crystal growth rates were analyzed in a broad temperature range [30].

Fig. 3 shows the experimental volume crystallized fraction in sintered diopside glass-ceramic compacts as a function of time at 825 °C. We omit the error bars for simplicity. Part of the potential experimental variation was eliminated by heat treating the samples together, but the results can be strongly affected by the surface condition of the particles, whose effect on N_S has been reported [31]. Despite the significant scatter, Fig. 3 shows that, on average, the experimental volume crystallized fraction increases with time at 825 °C and achieves about 100% after 10 h of heat treatment at this temperature. The validity of the JMAYK theory has been experimentally confirmed for heterogeneous surface nucleation for the limiting case of a large number of nucleation sites in diopside [14]. We verified this validity in a wide range of crystallization kinetics, from almost null to a completely crystallized sample comparing with the Tsallis and AR equations.

For comparative purposes Fig. 3 shows the JMAYK, Tsallis and AR curves calculated by the different models described in the introduction. The Tsallis approach best fits the experimental data with $q = 1.268 \pm 0.062$ considering a Levenberg–Marquardt non-linear fitting and using Origin™ software, with all other parameters fixed. In the figure we present curves between 1.1 and 1.3 to give a better idea of how the fitting procedure worked. Fig. 2 shows a comparison of a linear and the best Tsallis fit on an Avrami plot—as the curve is continuous though the crystallization range (similar to the JMAYK continuous curve in Fig. 3), no transition break was required from $n = 2$ to 1 . The small discrepancy with the experimental data can perhaps be explained if we recall that the glass particles have a relatively wide size distribution [15].

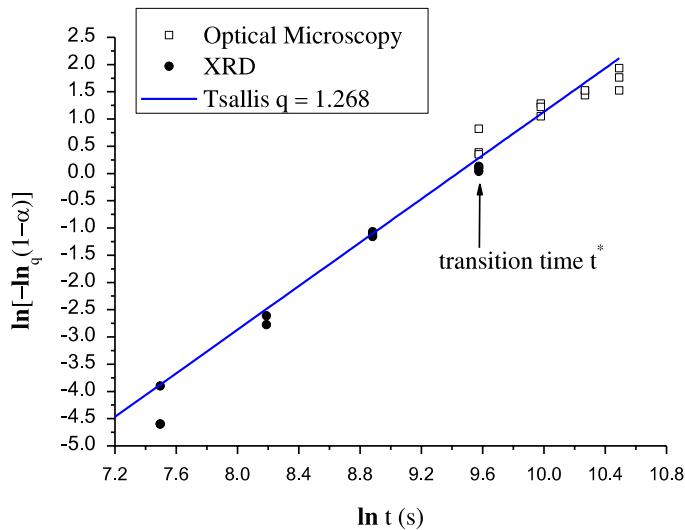


Fig. 4. Generalized Avrami plot considering in ordinate $\ln[-\ln_q(1-\alpha)]$, following the q -logarithm definition, where is possible to note a straight line for the proper value of $q = 1.268$.

Another important point is that one could argue that JMAYK is still valid for representing the overall crystallization process shown in Fig. 3, apart from some discrepancies from experimental data. The AR adjustment is shown for comparison with other models and because Tsallis thermostatistics contains the Austin–Rickett model [23] as a special and limiting case study for this system.

Fig. 4 shows another way to calculate q by means of q -logarithm definition. This generalized plot can also be used to choose the proper value of q : i.e. one that aligns the data to a straight line. It is important to note that, in the generalized Avrami plot, the ordinate uses both ordinary logarithm and q -logarithm, defined as $\ln_q x = \frac{x^{1-q}-1}{1-q}$, which is the inverse of the q -exponential function that appears in Eq. (11) [21]. Consequently, in the new generalized Avrami plot, the case $q = 1$ does not appear as a straight line.

Eq. (11) would be useful for lower N_S values due to the limitations of the JMAYK theory according to Todinov [32]. Weinberg [33] also pointed out that other practical limitations are due to transient/heterogeneous crystallization, non-spherical crystal growth, metastable crystallite formation, multiple phase formation, compositional change upon crystallization and combined surface and bulk crystallization. According to Weinberg, even for very large volume fractions (α) computer modeling using lower $N_S = 10^7 \text{ m}^{-2}$ and $U = 10^{-6} \text{ m/s}$ was in good agreement with JMAYK simulations, in the same way as Eq. (7) used in this work [33].

Conclusions

In this study we have presented a new generalized kinetic equation to study the nucleation and growth of a diopside glass system which nucleates heterogeneously. We have tested the kinetic equation based on a nonextensive formalism. In contrast to JMAYK and AR kinetic equations, we use an index q coming from the entropy definition of the physical system which measures the nonextensivity of the system. This generalized kinetic equation recovers both JMAYK and AR equations as special cases, for $q \rightarrow 1$ and 2, respectively.

In fact, Tsallis statistics, more precisely the Kayacan and Cetinel proposal, handles the kinetics of phase transformation with a q value close to unity (between 1.2 and 1.3), lower than 2 following the AR model, and besides such a small correction could improve the predictions of the JMAYK equation, mainly because it is simple and does not involve an exponential function. JMAYK still represents the temperature behavior of crystallization processes considering a high crystal density per unit area N_S and low crystal growth U . JMAYK was tested without any adjustable parameter, and the Tsallis approach works well considering one adjustable parameter q . In particular, the Avrami plot resulted in a parameter $\ln C = \ln g N_S U^2$ similar to expected values considering the range $t < t^*$. The surface nucleation occurs very rapidly from some random number of active (impurity) sites.

In fact, a test considering the generalized Avrami plot would be helpful to future analysis due to their facility on recognizing linear plots by means of reasonable q -values.

However, we must keep in mind that better agreement with experiment (or even simulation) obtained by employing the generalized JMAYK equation does not mean a validation of the generalized theory. To see whether it can be relied on or not, more studies are needed into its applications to the kinetics of phase transformation considering glass-forming systems. The Tsallis approach can possibly provide more insight into the open problems of Classical Nucleation Theory (CNT).

Acknowledgments

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