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# Kinetics of relaxation and crystallization of sodium metaphosphate glass

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## ABSTRACT

Kinetics of structural relaxation and crystallization of $NaPO_3$ glassforming melt is studied by means of thermal analyses. It is demonstrated that activation energy depends strongly on fictive temperature $T_f$. The dependence of the onset temperature $T_o$ of the glass transition interval on the heating rate $q^+$ is investigated for samples that were previously cooled down at a rate $q^-$ of about 850 K/min. The dimensionless fragility $F$ is a measure of the dependence of the activation energy for spatial rearrangement on the changes of structure. According to the present results $F$ is large for $NaPO_3$ (i.e. phosphates are 'fragile' substances).

## 1. Introduction

Glass-forming substances consist of units with nontrivial mutual interactions. Therefore, it is important to test which ions or 'molecular units' move collectively. The problem is whether motions of the same units are responsible for the shear viscosity, for the structural relaxation and for the crystallization processes. Most popular method to answer this question is to measure certain properties $A_i$ reflecting the activation energies $E_i$ of the corresponding process. Here subscript $i$ stands for one of the listed above processes. When plotted in Arrhenius coordinates (best is in coordinates log $A_i$ against $T_g/T$; here $T_g$ plays role of reference temperature) the corresponding slopes can be compared. Because of the properties of the logarithmic function, all slopes are dimensionless and should be equal, provided the processes are determined by the same activation energy. Moreover, if the experimental points lay along a straight line, it is likely that the value of the corresponding activation energy can be directly determined from the slope.

The goal of the present study is to study relaxation and crystallization of $NaPO_3$ by means of scanning calorimetry.

## 2. Theoretical considerations

Relaxation kinetics in glass transition region was a subject of many theoretical and experimental investigations [1–9]. Systems have glassy-like behavior when observation time is larger the relaxation time. The thermodynamic indication of this is the sharp change of the heat capacity $C_p$ from that of the melt $C_m$ to that of the glass $C_g$. The transition region shifts to higher temperatures when the measuring time decreases (or equivalently the applied temperature change rate increases). The problem gained a lot of interest [5–9] because it is particular case of treating a system in a process of failing out of equilibrium. As it was first recognized by de Donder and van Rysselberghe [10], the set of external parameters of state is not sufficient for the complete description of a non-equilibrium system: at least one additional internal parameter has to be added. For this reason, Tool and Eichlin [11] introduced the so-called 'fictive' or 'structural' temperature $T_f$. This is the temperature at which the system with a given structure will be in equilibrium. The system tends to relax when $T_f$ deviates from the actual temperature $T$. Kinetics of this process is controlled by the relaxation time $\tau$. Actually, in complex systems the relaxation proceeds as a number of more or less independent processes, each of them is controlled by particular characteristic time. The thermodynamic functions depend on

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the structure of the system in a different way. Therefore, $T_f$ depends on the measured macroscopic property of the system [12]. In general, more than one fictive temperature is needed to describe the relaxation of glasses and especially to describe the crossover experiments. Good illustrations of this give the experiments of Ritland [13]. Thus, if we measure the configuration enthalpy *H,* volume *V*, etc. the corresponding fictive temperatures are $T_{fH} \sim H$; $T_{fV} \sim V$, etc. Therefore, $T_f$ should refer to the particular property under investigation.

Considering non-isothermal experiments the key point is the assumption that the onset point of each process appears when its characteristic time $\tau$ is becoming equal to the observation time $\Delta t$.

$$\Delta t = \tau. \tag{1}$$

The scanning rate (heating or cooling) can be represented as a series of instantaneous temperature jumps $\Delta T$, followed by isothermal annealing steps of duration $\Delta t$.

$$q = \frac{dT}{dt} = \frac{\Delta T}{\Delta t}, \tag{2}$$

Combination of Eq. (1) and (2) leads to the important expression:

$$q\tau = \Delta T. \tag{3}$$

Although $\Delta T$ is to be considered as an unknown constant, Eq. (3) is widespread. Variants of Eq. (3) are popular to use because, in Arrhenius coordinates, the unknown constant belongs to intersect while the slope is completely determined by the activation energy. Indeed, under the assumption that the kinetics of the processes depend on the corresponding free activation energies *E* and the ideal gas constant *R* according to expression

$$\tau = \tau_o \exp\left(\frac{E}{RT}\right), \tag{4}$$

Eq. (3) transforms to

$$\ln q + \frac{E}{RT} = \text{Const}. \tag{5}$$

On the other hand, in logarithmic coordinates, the temperature dependence of viscosity $\eta$ is similar to Eq. (5).

$$\ln \eta = C + \frac{E_\eta}{RT}. \tag{6}$$

As soon as Eq. (1)–(5) were derived under the same basic assumption, they can be applied to crystallization kinetics just as successful as for the relaxation processes. It is seen that both ln *q* vs $T_g/T$ and −ln $\eta$ against $T_g/T$ will have equal slopes, provided that the corresponding processes are controlled by the same activation energy. Variants of Eq. (5) for specific experiments are shortly discussed.

It is useful to account for the temperature dependence of the activation energy in the following form [7,9,14,15]:

$$\frac{E(T)}{RT} \approx \varepsilon\left(\frac{T_g}{T}\right)^F, \tag{7}$$

where the 'fragility' parameter *F* accounts to what extent activation energy is temperature dependent. When *F = 1* viscosity gives a straight line in Arrhenian plot, indicating that glass is strong. The larger is *F* the more fragile is the glass. Note that there is a simple relation between the Angel's fragility parameter *m* and the present one $m \sim F$. In Eq. (7) $T_g$ is certain reference temperature at which the dimensionless activation energy for a system in equilibrium is

$$\varepsilon = \left.\frac{E(T)}{RT}\right|_{T=T_g}. \tag{8}$$

Generally, activation energies for molecular motions in glasses depend on both the fictive temperature $T_f$ and temperature *T*. Here, we adopt the expression derived in Refs. [14,15]

$$\frac{E(T_f, T)}{RT} = \varepsilon\left(\frac{T_g}{T_f}\right)^F \left(\frac{T_f}{T}\right)^\beta. \tag{9}$$

It is convenient to choose as reference the temperature at which viscosity is $\lg\eta = 12.5$ [Pa s], i.e. $T_g$ is well within the glass transition interval. Note that for systems in equilibrium $T_f = T$, so that Eq. (9) transforms to Eq. (7). The dimensionless *fragility* power *F* is proportional to the heat molar heat capacity $C_m$ of the melt, while $\beta = F\frac{C_g}{C_m}$ accounts for the molar heat capacity $C_g < C_m$ of non-equilibrium glass.

### 2.1. Analysis of relaxation kinetics

Gruener et al. [16] measured viscosity, electrical conductivity and the relaxation time for two calcium aluminosilicate systems. At high temperature, the relaxation times for the three processes are equal within experimental accuracy. Near the glass transition, decoupling takes place, so that $Ca^{2+}$ motion that controls conductivity is much higher the mobility, predicted from viscosity data.

When system is cooled at a constant rate $q^-$, Eq. (3) is the condition for the onset of non-equilibrium properties. In other words, at this point fictive temperature is fixed. Under this condition, Eq. (5) is known as the equation of Ritland–Bartenev [13,17]. Combination of Eqs. (5),(9) leads to

$$\ln q^- + \varepsilon\left(\frac{T_g}{T_f}\right)^F = \text{Const}. \tag{10}$$

On the other hand, when a glass is heated at a constant rate $q^+$ it starts to relax at a measurable rate at onset temperature $T_o$ so that combining Eqs. (5) and (7) one obtains

$$\ln q^+ + \varepsilon\left(\frac{T_g}{T_f}\right)^F \left(\frac{T_f}{T_o}\right)^\beta = \text{Const}'. \tag{11}$$

### 2.2. Analysis of non-isothermal crystallization kinetics

Generally, the activation energy for crystallization $E_c$ depends on temperature in a manner similar to Eq. (7). A suitable approximation is

$$\frac{E(T)}{RT} \approx \Xi\left(\frac{T_g}{T}\right)^\gamma, \tag{12}$$

where dimensionless power $\gamma$ accounts for the temperature dependence of the activation energy while $\Xi = \left.\frac{E_c(T)}{RT}\right|_{T=T_g}$ is dimensionless energy for crystallization at $T_g$. Although the assumptions that $\varepsilon = \Xi$ and/or $F = \gamma$ seem quite logical, these conditions are not a general rule, and there is no proof that they are always satisfied.

Eq. (12) relates the onset point $T_{co}$ at which crystallization begins and the constant heating rate as follows:

$$\ln q^+ + \Xi\left(\frac{T_g}{T_{co}}\right)^\gamma = \text{Const}''. \tag{13}$$

In general the rate at which the degree of crystallization $0 < x < 1$ increases depends on both *x* and time *t* according to the expression:

$$x = 1 - \exp\left(-\left(\frac{t}{\tau_{cr}}\right)^n\right). \tag{14}$$

For a constant heating rate *q*, starting at temperature well below the transformation interval, the temperature and time are related as $t \approx \frac{T}{q}$.