

Crystallization of glasses: the Avrami theory revisited

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Although dynamics of crystallization under isothermal conditions in glassy materials is fairly well described by the Kolmogorov-Johnson-Mehl-Avrami (KJMA) formalism, there are still unsolved problems with the KJMA equation. By introducing a fractal structural concepts and the Meyer-Neldel rule on thermally activated processes, an extended KJMA model is proposed that allows one to get a better insight into the phase changes in glasses. The phase changes of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) system in steady and nanosecond-scale pulse-heating conditions are also discussed.

1. Introduction

Phase transitions are one of the most important topics in material science, since they are usually encountered in the production cycle of materials. During the last decade, there has been great interest in amorphous chalcogenides such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) for applications in optical data storage [1]. Random nucleation and isotropic growth in an infinite specimen is well described by the Kolmogorov [2], Johnson and Mehl [3], and Avrami [4] models (KJMA model). The KJMA model gives the macroscopic evolution of the transformed phase under isothermal conditions [5-7].

Dynamics of crystallization in GST materials has been fairly well interpreted in terms of the KJMA model [8,9]. At the same time, while its applicability is criticized by Senkader and Write [10]. The KJMA formalism may have some difficulties, which have not been well understood so far; e.g. the Avrami exponent and the reaction rate [10]. On the other hand, crystallization kinetics under pulse-heating conditions has been discussed in GST [11,12]. It is also unclear whether or not the KJMA model can be applied to the phase transitions under pulse-heating conditions.

In the present study, we concentrate a *macroscopic* property which is based on the KJMA model. The unclear growth kinetics (the Avrami exponent and reaction rate) of phase changes will be discussed by introducing a fractal structural concept [13] and by the Meyer-Neldel rule [14] for the growth rate. A modified, or extended KJMA equation proposed here may be useful to get proper understandings of phase changes in GST and other glassy systems, without losing simplicity of the KJMA formalism. It should be also noted that *microscopic* view is still a matter of debate [1,15-17], which will be not discussed in the present paper.

2. KJMA formalism

We briefly discuss the KJMA theory. This theory requires that the nucleation sites should be randomly distributed over the volume V . In Fig.1, three particles have grown together and growth ceases where the particles impinge, as indicated by the heavy lines [6]. The particle-overlap in the absence of impingement is shown as well (extended volume V^{ex}).

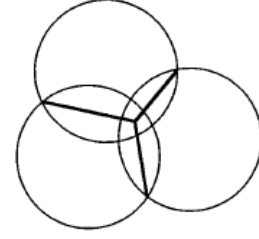


Fig.1 Particle growth

The actual (transformed) volume V^{tr} is given as

$$dV^{\text{tr}} = \left[1 - \left(\frac{V^{\text{tr}}}{V} \right) \right] dV^{\text{ex}}. \quad (1)$$

Note that the extended volume V^{ex} is a virtual volume. Equation (1) is written as

$$f = 1 - \exp(-f^{\text{ex}}), \quad (2)$$

where $f = V^{\text{tr}}/V$, $f^{\text{ex}} = V^{\text{ex}}/V$. Here, f is the transformed volume fraction. In the case of instantaneous nucleation of spherical grains with number density N , the volume growth rate with radius r for an interface-controlled reaction can be expressed as

$$\frac{dV^{\text{ex}}}{dt} = 4\pi r^2 N V \frac{dr}{dt}. \quad (3)$$

Here the effective growth rate is given by $G = dr/dt$ and then f^{ex} at time t is expressed by

$$f^{\text{ex}} = \frac{4\pi}{3} N r^3 = \frac{4\pi}{3} N (Gt)^3. \quad (4)$$

We then get well known KJMA equation

$$1 - f = \exp[-(kt)^n], \quad (5)$$

with $n = 3$. Here, n is called the Avrami exponent (coefficient), and k is an effective rate constant (growth rate). The Avrami exponent should be an integer providing information on the dimensionality of the crystallization process. Actually, however, the values of n in the range from 1 to 5.8 in GST [10]. The effective rate constant k is temperature-dependent and is given by

$$k(T) = \nu \exp\left(-\frac{E_A}{kT}\right), \quad (6)$$

where ν is the frequency factor and E_A the activation energy. Note that ν takes unreasonably large values (10^{17} - 10^{24} s⁻¹) [10]. These will be discussed in the following section together with non-integer Avrami coefficient.

3. Extended KJMA model

The KJMA formalism is a very simple and is useful to understand the time evolution of crystallization of glasses. However, at least, two problems on the KJMA should be overcome without losing its simplicity. The first problem is the Avrami exponent n . The theory predicts that n represents the Euclid dimensions ($n = 1, 2, 3$). However, the values of n are reported to be non-integer and sometimes n is bigger than 3 as already stated. Non-integer values of n can be attributed to violation of the fundamental assumptions (strict conditions) of KJMA formula which requires (i) a random distribution of potential site of nucleation, (ii) instantaneous nucleation, (iii) interface-controlled grain growth, and time (or grain size) independent growth rate k [10,12].

Here, we introduce a fractal concept on space dimension, which may be useful for discussing the phase changes, since the surfaces of most materials are expected to be fractals [13,18]. The volume growth rate, eq.(3), can then be modified as

$$\frac{dV^{\text{ex}}}{dt} = Cr^D NV \frac{dr}{dt}, \quad (7)$$

where C is a constant and D the fractal dimension of the *surface* of grains. Finally, we get f as

$$1 - f = \exp\left[-(kt)^{D+1}\right]. \quad (8)$$

It is therefore suggested that various values of the Avrami exponent n observed can be attributed to complex shape of the crystalline grain surfaces with fractal structure. This fractal-surface-controlled (FSC) crystallization may be supported by the following reports, e.g., that D -value takes ~ 3.0 for silica gels [19] and 2.6-2.9 for sandstones[20].

Turn to the second problem: We discuss the temperature-dependent rate constant $k(T)$ [eq.(6)]. The reported activation energies E_A are around 2 eV (1-3 eV) in GST alloys [10], which are deduced also from the other thermal analysis such as the Differential Scanning Calorimetry (DSC) [21]. The problem is that unreasonably large frequency factor ν (10^{17} - 10^{24} s⁻¹) is deduced [10,22]. It is known that thermally activated phenomena, such as electronic and ionic transports, and structural relaxation in disordered matters, obey the Meyer-Neldel compensation rule [14,23]. For example $k(T)$ in eq.(6) is modified to

$$k(T) = \nu_0 \exp\left(\frac{E_A}{E_{MN}}\right) \exp\left(-\frac{E_A}{kT}\right), \quad (9)$$

where the frequency factor ν experimentally deduced is

$$\nu \equiv \nu_0 \exp\left(\frac{E_A}{E_{MN}}\right), \quad (10)$$

and E_{MN} is called the Meyer-Neldel energy and ν_0 is a constant. Equation (9) is called the Meyer-Neldel (MN) rule or compensation law [23]. In temperature-activated electronic transport in amorphous chalcogenides, the conductivity pre-factor also involves the term of $\exp(E_A/E_{MN})$ with $E_{MA}=25\text{-}60$ meV [24].

Recent reports on structural relaxation and phase change in GST also follow the MN rule, as shown in Fig. 2 [22]. Open circles show the structural relaxation (SR), i.e. the conductivity change under thermal annealing, and other symbols are for the crystallization in GST. The both phenomena fall into similar MN rule. E_{MN} and ν_0 here are estimated to be 66 meV and $10^6\text{-}10^7$ s⁻¹, respectively. Thus the experimentally deduced unphysical frequency factor ν can be explained in the frame work of The MN rule. The Origin of the MN rule is still not clear [22], although many-body thermal excitation in activated processes is suggested [22,23].

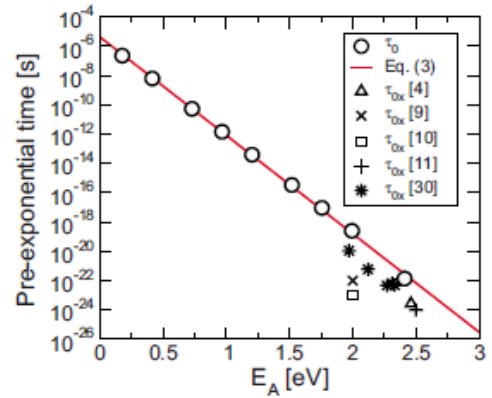


Fig.2 Correlation between E_A and ν in GST.

4. Phase changes under pulse-heating (non-isothermal condition)

The KJMA theory is applied to the phase changes under isothermal conditions. It is of interest to examine whether or not the KJMA formalism applies to the phase changes under pulse heating (non-isothermal conditions). Weidenhof *et al.* [12] have reported the phase changes, f vs. t , in GST under isothermal and non-isothermal (pulse heating) conditions. Results are shown in Fig. 3 (a) and (b). The Avrami exponent n is reported to be 2.5 under isothermal condition. n under the pulse-heating condition (several hundreds nanoseconds) has two components, 2.2 for short time and 1.3 for longer time ranges. The buckling of the KJMA plot after approximately 220 ns is suggested to be due to saturation of the growth in vertical direction [12]. These results suggest that the isothermal conditions may be hold if the phase changes proceed during pulse heating. Finally, it should be noted that the phase change processes in nano- and pico-seconds time scales have been reported [25,26]. It is not clear whether or not the KJMA works for such short time scale.

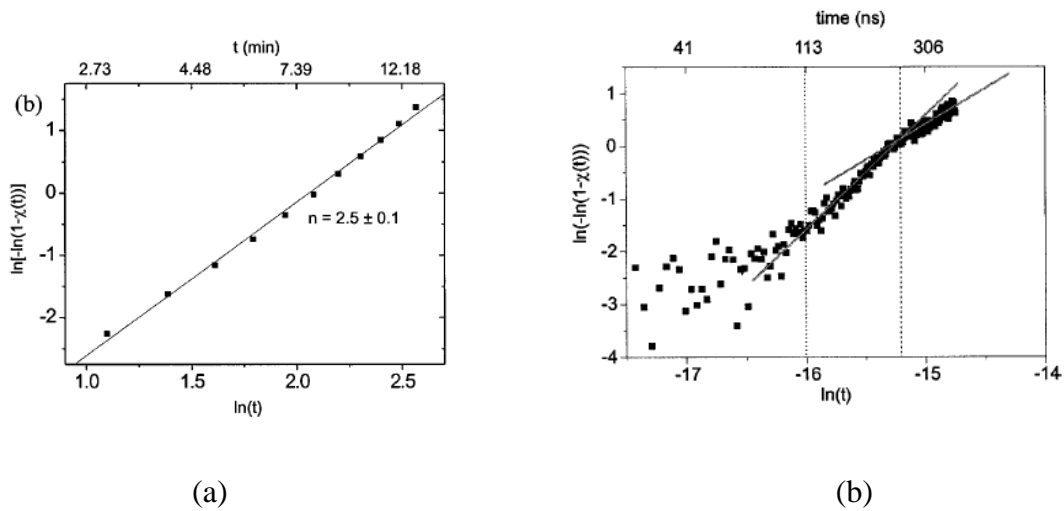


Fig. 3 The KJMA plots in GST. (a) under isothermal condition, (b) pulse-heating condition [12].

5. Summary

An extended KJMA theory has been proposed. The classical KJMA theory with some modifications (extended KJMA theory) can be applied to explain the dynamics of crystallization in GST. Some difficulties underlying the KJMA formalism were overcome by introducing fractal structural concept on crystal growth. Unphysical frequency factor in the KJMA can also be explained in the frame work of the Meyer-Neldel rule. It is still not clear whether or not the extended KJMA applies to the phase change processes in nano- and pico- seconds regions.

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