



Determination of diffusion activation energy from self-similarity of concentration profiles in glasses



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ABSTRACT

Technique for analysis of diffusion processes, where temperature dependence of the diffusivity is assumed to obey the Arrhenius law, is developed. It is shown that in this case verification of self-similarity of concentration profiles in glasses can be performed by comparison of refractive index profiles resulted from diffusion under different temperatures. The proposed technique enables evaluating the diffusion activation energy directly in the procedure of self-similarity verification. This technique requires twice less number of analyzed samples treated under different time–temperature conditions in comparison to traditional techniques.

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1. Introduction

Diffusion processes are the base of fabrication techniques in the production of gradient structures in optical materials (GRIN lenses, optical waveguides, etc.). Progress in operating performances of gradient optical elements and development of new devices often require application of new materials, including specially synthesized. However, reliability of *a priori* predictions of material diffusive properties is not high enough nowadays, particularly in cases of multicomponent materials. Therefore, experimental study of diffusion characteristics and simulation of diffusion processes are usually performed in order to determine the treatment conditions which could provide gradient structures with the required optical parameters when designing the composition of new material. If necessary, composition of the material is corrected, and new trial samples are produced and studied that means repeating the whole cycle of treatments, measurements and simulations.

One of the most important characteristics is the diffusion activation energy. Evaluation of this parameter is usually based on determination of diffusion coefficients at different temperatures. Mostly, dependence of the diffusion coefficient D on the temperature T obeys the Arrhenius law. However, in some cases this law is not valid [1–5]. Deviations from linear dependence $\ln D(1/T)$ can occur in cases of polycrystalline samples or phase transformations in the material in the examined temperature

range, under simultaneous realization of different diffusion mechanisms, and also in some other cases, including the ones considering peculiarities of formation and interaction of vacancies in the material matrix. Often appearance of the factors leading to deviation from the Arrhenius law can be predicted in advance. If manifestation of these factors is not expected within the examined temperature range, diffusion activation energy is determined by the standard method where this value is calculated by the slope of the dependence $\ln D(1/T)$ (for example, [1–4]). When diffusion is concentration-dependent, this logarithmic dependence is built for the same levels of concentration in the examined samples. Concentration dependence of the diffusivity is preliminary estimated by means of the Boltzmann–Matano method (described, for example, in [1–3,6–8]) using the measured concentration profiles. Applicability of this method is usually determined through verifying fulfillment of self-similarity condition for diffusion profiles obtained at the same temperature during different times. Hence, at least two series of samples are required for mentioned procedures of diffusion process studying: the first series must be treated during various times at the same temperature while the second one – under various temperatures of the process.

Here we present the technique that allows combining these procedures and performs the analysis based on examination of only one series of samples treated under different temperatures. As fabrication of the additional series (often time-consuming) is not required, application of the method enables significant time reducing in investigations.

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2. Basis of the developed technique

By verifying a self-similarity of concentration profiles, one determines applicability of the Boltzmann substitution to the second Fick's law that allows writing this law as an ordinary differential equation. It is known that this transformation is valid if concentration is a function of the reduced coordinate $x/t^{1/2}$, that is $C = C(x/t^{1/2})$, where C – the concentration, x – the depth, t – the diffusion time. This dependence can be rewritten also in the following way: $x = At^{1/2}$, where A – the function of concentration C only [7]. Just these conditions are the basis of the traditional criterion of self-similarity: concentration profiles in the samples meet the condition of self-similarity if they coincide when plotted via the reduced variable $x/t^{1/2}$. In order to eliminate temperature influence, this verification is performed usually by analyzing the profiles obtained at one temperature during different times. However, here we show that in case of fulfillment of the Arrhenius law the mentioned procedure can be performed for concentration profiles obtained at different temperatures.

According to [9], general expression for the diffusivity can be represented through the dependence $D(C, T) = D_m(T)\phi(C, T)$, where $D_m(T)$ – the temperature dependence of the diffusion coefficient which corresponds to the minimum level of concentration C_m in the studied sample. Then the function $\Phi(C_m, T) = 1$ for concentration C_m . As fulfillment of the Arrhenius law is suggested, we can write: $D(C_m, T) = D_m(T) = D_0 \exp(-H/kT)$, where H – the diffusion activation energy, k – the Boltzmann constant, D_0 – some constant. Substitution of this expression to the general form of diffusivity for $D_m(T)$ leads to following: $D(C, T) = D_0 \exp(-H/kT)\phi(C, T)$. Since the temperature-dependent exponential factor is already present in the obtained expression, we must assume that $\Phi(C, T) \equiv f(C)$ in order to provide fulfillment of the Arrhenius law for the whole profile. Hence, in this case the diffusion coefficient can be represented as the product of independent factors showing its concentration $f(C)$ and temperature $g(T)$ dependences

$$D(C, T) = D_0 g(T) f(C) \quad (1)$$

Consideration of more often applied general form of the diffusivity $D(C, T) = D_0 F(C, T)$ results in the same conclusion. Indeed, as verification of meeting the self-similarity condition is performed for the same levels of concentration in the samples, we should write the following for the certain concentration C_0 considering fulfillment of the Arrhenius law: $D(C_0, T) = D_0 F(C_0, T) = D_0 B \exp(-H/kT)$, where B – some numerical factor that is constant for the chosen concentration level C_0 and does not depend on the temperature. Since there are no restrictions on C_0 value, the obtained formula is valid for any concentration level in the sample. So, here we also obtain that the diffusion coefficient can be expressed through the product of temperature and concentration factors as in (1).

Considering (1), the second Fick's law for concentration-dependent one-dimensional diffusion in plane samples with the use of Boltzmann transformation (for example, [6–8]), is as follows:

$$-(\lambda/2)(dC/d\lambda) = d[D_0 g(T) f(C) dC/d\lambda]/d\lambda$$

where $\lambda = x/t^{1/2}$ – the reduced coordinate. Let there be concentration profiles $C(x)$ and $C(x')$ resulted from some diffusion process performed at temperatures T_1 and T_2 and diffusion times t_1 and t_2 respectively. Let us assume that verification of self-similarity was performed by the traditional method at each temperature resulting in positive conclusion. Then the profiles $C(x)$ and $C(x')$ are the solutions of the following equations:

$$-(\lambda/2)(dC/d\lambda) = K_1 d[f(C) dC/d\lambda]/d\lambda \quad (2)$$

$$-(\mu/2)(dC/d\mu) = K_2 d[f(C) dC/d\mu]/d\mu, \quad (3)$$

where $\mu = x'/t'^{1/2}$ – the reduced coordinate, $K_1 = D_0 g(T_1) = D_0 \exp(-H/kT_1)$, $K_2 = D_0 g(T_2) = D_0 \exp(-H/kT_2)$. Here K_1 and K_2 are constant factors, and factor $f(C)$ is common for (2) and (3). Using the substitution of $\mu' = (K_1/K_2)^{1/2} \mu$ in (3), we obtain the equation similar to (2):

$$-(\mu'/2)(dC/d\mu') = K_1 d[f(C) dC/d\mu']/d\mu' \quad (4)$$

It is obvious that the solutions of Eqs. (2) and (4) are of the same form, that is: $C(\mu') = C(\lambda)$. Hence $\mu'(C) = \lambda(C)$ and $\mu(C) = (K_2/K_1)^{1/2} \lambda(C)$. Then the expression for linear coordinates can be written as:

$$x'(C) = P \cdot x(C), \quad (5)$$

where $P = [(K_2 t_2)/(K_1 t_1)]^{1/2}$. Thus we can conclude that, in case of the Arrhenius law validity, self-similar concentration profiles obtained at different temperatures are proportional both by the reduced (λ and μ) and by absolute (x and x') depths. Just this feature is proposed to be used in verification of self-similarity of the profiles.

To perform this verification, one must choose some concentration level C_0 and determine corresponding depths $x_i(C_0)$ in the considered profiles (these profiles can be numerated, and i – their assigned numbers). Let us consider the profile with $i = 1$ as the basic one in the comparison procedure and define temperature and time conditions of corresponding diffusion process as T_1 and t_1 , respectively, in terms of the designations above. Then factors $P_i = x_i/x_1 = x'(C_0)/x(C_0)$ should be calculated for other profiles, and all studied profiles must be plotted via the variable $P_i \cdot x$ (instead of x). Coincidence of the obtained curves $C_i(P_i \cdot x)$ means proportionality of the profiles by depth and hence proves self-similarity of the profiles. Contrary, divergence of these curves indicates violation of self-similarity condition (and then Boltzmann transformation cannot be applied to the Fick's equation) or breaking the Arrhenius law in the examined temperature range (and then activation energy cannot be evaluated assuming $\ln D(1/T)$ as linear dependence). Therefore, if mismatch of the curves occurs, additional detailed study of the diffusion process is needed within the used temperature range.

When studying diffusion processes in optical materials, profile of normalized refractive index increment $\delta N = \Delta N/\Delta N_{max}$ is often considered instead of normalized concentration profile C/C_{max} in assumption of proportionality of these profiles (see examples in [9–11]). If refractive index (RI) increases due to diffusion, it is convenient to use a waveguide effect for determination of RI profiles in thin layers (less than 100 μm). In these cases RI profiles are usually reconstructed following the techniques [12,13] based on the results of mode index measurements. It should be noted that some difficulties can occur if general type of the obtained RI profile is unknown in advance, and also in analysis of few-mode waveguides often obtained at temperatures near the lower limit of the examined temperature range. In these cases reasonable choice between above-mentioned reconstruction techniques cannot be made while computing of RI profiles according to the methods [12] and [13] with the same initial data results in different maximum RI values into the same gradient layer [14]. Such difference reach up to 10–15% of maximum RI increment ΔN_{max} obtained in the sample due to diffusion (and sometimes even more). This circumstance leads to distinction between RI profiles at shallower depths (along 1/4–1/3 of each profile) reconstructed by the mentioned methods. However, analysis of experimental samples shows that the rest parts of these RI profiles (from about the middle of the profile curve) demonstrate good coincidence. One can see the same in the results of the study [14]. So we can consider these deeper parts of RI profiles as properly reconstructed. Therefore, the profile depth corresponding to $\delta N = 1/2$ can be chosen for determination of

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