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Modeling of the induced refractive index kinetics in photo-thermo-refractive glass

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Abstract: Photo-thermo-refractive (PTR) glass is a photosensitive multi-component silicate glass that exhibits refractive index change after successive UV-exposure and thermal treatment. The refractive index change was demonstrated to be associated with the precipitation of NaF nanocrystals in the glass matrix. This paper presents a systematic study of the dependence of the refractive index change on dosage of UV-exposure and thermal treatment duration and temperature in already UV-exposed and nucleated samples. It is shown using Avrami plots that the refractive index change in PTR glass is determined by a diffusion-controlled growth of particles from pre-existing nuclei while all coefficients have exponential dependence on temperature (Boltzmann law). The developed model, which includes both photo-chemistry and crystallization processes, allow describing the refractive index change dependence on dosage for a wide range of thermal treatment duration and temperature and an accuracy better than 10%.

OCIS codes: (160.4760) Optical properties, (160.5335) Photosensitive materials, (350.5130) Photochemistry.

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1. Introduction

Photo-thermo-refractive (PTR) glass is a class of glasses, which undergo photo-thermo-induced crystallization. It was invented by Stookey [1] many years ago and has been studied as a new material for hologram writing in the last 20 years [2-5]. Currently, PTR glass is sodium-potassium-zinc-aluminum-fluorine-bromine silicate glass doped with antimony, tin, cerium, and silver. It exhibits a localized refractive index decrement after UV-exposure and successive thermal treatment above the glass transition temperature, T_g , which results from the crystallization of about 0.5 wt.% sodium fluoride nano-crystals [6]. The possibility of recording phase holograms in this glass has potential for many high-tech applications, such as optical filtering [7] and spectral beam combining of high power lasers [8].

A description of the complex photo-thermo-induced crystallization mechanisms in this type of glass is given in reference [9]. The evolution of the material's nanostructure and optical properties after UV-exposure and thermal treatment are reported in several publications e.g. [6,10-14]. Actually, it was shown in ref. [6] that the photosensitivity of PTR glass results from the precipitation of nano-sized sodium fluoride crystals within the glass matrix in the UV-exposed regions after heat treatment. A simplified proposal for photo-thermal crystallization is the following: before any thermal development of the glass, sodium, fluorine and all other ions are dissolved in the matrix and the material is totally vitreous. When PTR glass is exposed to long wavelength UV radiation $\lambda > 250$ nm (e.g. a He-Cd laser at 325 nm), Ce^{3+} releases an electron and converts to hole-type Ce^{3++} center. The released electron is then trapped by intrinsic defects of the glass matrix or dopants in the highest valence state, including antimony and silver ions dispersed in the glass matrix. Then silver ions convert to

silver atoms. When a UV-exposed glass is nucleated at temperatures between 450 and 500°C, silver atoms agglomerate and form colloidal silver containing particles. It was also demonstrated that silver bromide clusters form [15]. The second part of the crystallization process consists in the heterogeneous precipitation and growth of sodium fluoride crystals on top of the silver (or silver bromide) clusters. NaF growth is then controlled by diffusion of sodium and fluorine from the glass matrix to the crystals [14].

It is seen that the induced refractive index change is obtained only after a very complex series of chemical and physical process. Moreover, refractive index change is controlled by three interconnected parameters: the dosage of UV-exposure, the thermal treatment temperature and duration. Controlling the final refractive index change in a refractive or diffractive optical element is a key point in order to obtain an optimized element. For example, in case of volume Bragg gratings, perfect control of the refractive index modulation would allow achieving an element with expected diffraction efficiency and bandwidth. To achieve the goal, physical models were developed for the description of the photoionization and the crystallization, and were combined to an integrated comprehensive model. This model finally allows describing the refractive index change after exposure to ionizing UV radiation and thermal development within wide ranges of temperature and duration. It is shown that this model predicts the refractive index change with an accuracy of about 10%.

2. Experimental

2.1 PTR glass preparation

The samples of a photosensitive PTR glass containing 15Na₂O–5ZnO–4Al₂O₃–70SiO₂–5NaF–1KBr–0.01Ag₂O–0.01CeO₂ (batch composition in mol.%) and minor amounts of Sn and Sb, which were used in this work, are similar to those described in previous studies [6,10-12]. Polished 25×25×5 mm³ samples were prepared for these experiments. The homogeneity of photosensitive glasses is a critical parameter affecting crystallization properties [16]. Optical homogeneity of the studied samples (refractive index fluctuations) was tested by the shadow method in a divergent beam of a He–Ne laser and was quantified by measurements using a Fizeau interferometer (GPI Zygo). The samples selected for this study had refractive index fluctuations of less than 40 ppm (4×10^{-5} peak-to-valley) across the aperture.

2.2 UV-exposure and heat-treatments

UV-exposure of samples was performed by a He–Cd laser (4 mW, 325 nm). A stripe with Gaussian distribution of dosage and maximum dosage about 1 J/cm² was recorded in each sample by scanning the laser beam over the sample's surface. Dosage was controlled with the scanning speed [10]. This maximum dosage was chosen because it provides induced refractive index close to saturation. The samples were then nucleated at 485°C for 100 minutes and heat-treated for different durations at temperatures between 485 and 535°C. For each thermal treatment, samples were heated from room temperature to the development temperature at a rate of about 20 K/min and then, at the end of the development, they were cooled down to room temperature, in the furnace following the natural decrease of the furnace temperature (about 2.5 K/min). Temperature was measured using a calibrated thermocouple.

2.3 Refractive index change measurements

Refractive index changes were measured in each sample using a shearing interferometer setup [10]. Its basic principle is to create an interferogram that converts the phase change at propagation through the glass to a fringe shift. A liquid cell with an index matching fluid was used to prevent thickness variations of the sample which would contribute to a fringe shift. Therefore the interferometer fringe distortions resulted only from refractive index variations. Precision on each measurement was demonstrated to be better than 10 ppm.

3. Modeling of the refractive index change

3.1 Refractive index change measurements versus time and dosage

PTR glass samples exposed with a Gaussian profile stripe with dosage at maximum (E_0) of 0.9 J/cm^2 were developed for different durations at different temperatures between 485 and 535°C . From the refractive index change measured on each of these samples, two sets of curves were obtained. First we plotted the dependence of the refractive index change on dosage for different thermal treatment durations and for different temperatures, as shown in Fig. 1. From these curves, the dependence of the refractive index change at maximum dosage on time of thermal treatment and for different temperatures was extracted (Fig. 2). From the curve in Fig. 1, one can see that the longer the thermal treatment duration, the higher the saturation level of the refractive index change.

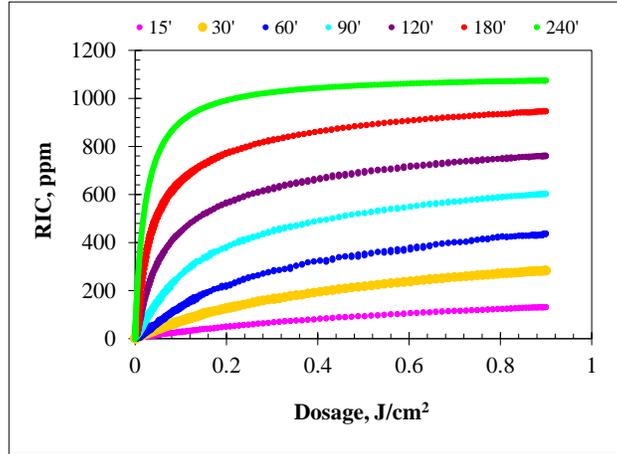


Fig. 1. Dependence of the refractive index change (RIC) on dosage of UV-exposure measured in PTR glass after nucleation and thermal treatment at $\sim 515^\circ\text{C}$ for different durations.

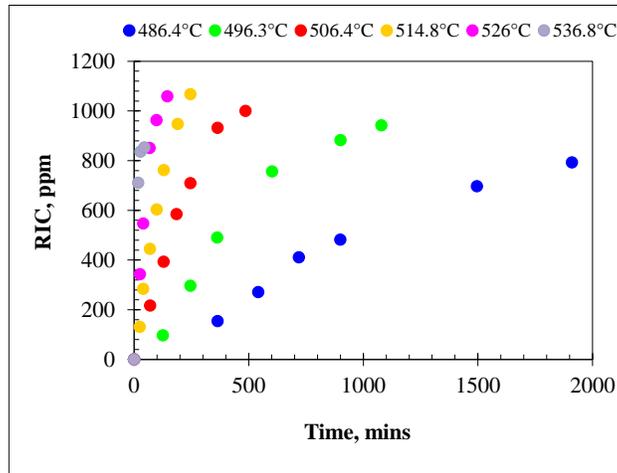


Fig. 2. Dependence of the maximum refractive index change (RIC) on thermal treatment duration measured in PTR glass UV-exposed with dosage E_0 of 0.9 J/cm^2 and developed at different temperatures.

From the curve of Fig. 2, we can justify the range of temperatures that was chosen for this experiment. At development temperatures of 485°C , the refractive index change becomes very slow as 40+ hours are required to reach refractive index change showing some approaching to

saturation; hence using temperatures lower than 485°C is out of any reasonable application. In contrary, when developing at 535°C, saturation is obtained after less than one hour, such as the precise control of the refractive index requires extremely precise control on the thermal treatment procedure; therefore using temperatures above than 535°C is also out of reasonable application. Thus, the range of temperatures that provides controllable regimes of thermal development is equal to only 50°C. The curves in Fig. 2 allow extracting a basic parameter defining the refractive index change kinetics, i.e. the slope at $t = 0$. The evolution of this slope (in ppm/hour) as a function of $1/T$ (in K^{-1}) is plotted in Fig. 3. One can see that the slope at $t = 0$ follows a Boltzmann law and that the induced refractive index kinetics is changed by 2 orders of magnitude within 50°C change of the development temperature. This result demonstrates high sensitivity of the thermal treatment in respect to temperature and justifies the usefulness of a model that can predict the refractive index change for any given dosage of UV-exposure and thermal treatment temperature and duration.

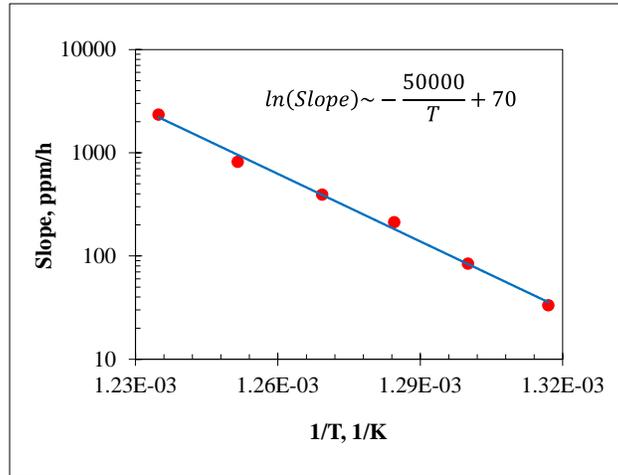


Fig. 3. Temperature dependence of the slope of the refractive index change versus thermal treatment duration at $t = 0$ (extracted from Fig. 2).

3.2 Modeling of the isothermal refractive index change versus time at constant dosage

The first part of modeling consisted in analyzing the isothermal refractive index change versus time at constant dosage E_0 of 0.9 J/cm^2 as measured in Fig. 2. We applied the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation [17-19] to model the refractive index change. This model is generally used to describe the crystallization kinetics (i.e. the evolution of the volume fraction of crystals versus time and temperature of thermal treatment) of ceramics [20]. As the refractive index change of PTR glass was shown to depend, in first approximation, on the volume fraction of NaF crystals [6,21], this model appears to be very attractive. However, the usage of this model generally requires taking some precautions as it is associated with some strong hypothesis on the crystallization process:

- First, nucleation must occur randomly and homogeneously over the entire untransformed portion of the material. And according to Ref. [22], this hypothesis should be respected.
- Second, the growth rate must not depend on the extent of transformation. This is the most dangerous hypothesis as we know that crystallization occurs in limited amount of fluorine and therefore rate is expected to decrease when the volume fraction of crystals is increasing. However, it was shown in Ref. [21] that within the regular thermal treatment used for producing refractive index change, only half of the concentration of the NaF available for creating NaF crystals is consumed and therefore, the rate can be considered as constant.

- The third hypothesis is that growth occurs at the same rate in all directions. In case of PTR glass, crystal growth is not expected to be anisotropic.

These considerations show an opportunity to use this JMAK equation for modeling the refractive index change kinetics of PTR glass. We therefore used the equation (1) to model the refractive index change dependence on temperature T and thermal treatment duration t for a fixed exposing dosage E_0 ($=0.9 \text{ J/cm}^2$):

$$\Delta n(E_0, t, T) = \Delta n_{\max}(E_0, T) \left(1 - \exp(-K(T)t^n) \right) \quad (1)$$

Where $\Delta n_{\max}(E_0, T)$ is refractive index at saturation, $K(T)$ is a thermodynamic parameter describing the slope at $t = 0$ versus temperature and n is the Avrami coefficient describing the type of crystallization. A common method for extracting each of the three unknown parameters consists in re-writing the equation (1) to linearize it:

$$\ln \left(-\ln \left(1 - \frac{\Delta n(E_0, t, T)}{\Delta n_{\max}(E_0, T)} \right) \right) = \ln(K(T)) + n \ln(t) \quad (2)$$

That way, by plotting the left term of the equation (2) as a function of $\ln(t)$, so-called Avrami plots were obtained. By fitting each curve with a linear function, the Avrami coefficient n was extracted from the slope while the intercept gives $\ln(K(t))$. Before performing such data processing, one can see that $\Delta n_{\max}(E_0, T)$ needs to be pre-determined and is temperature dependent. Based on the curve in Fig. 2, one can estimate an approximate value of $\Delta n_{\max}(E_0, T)$ that we plotted as a function of T in Fig. 4.

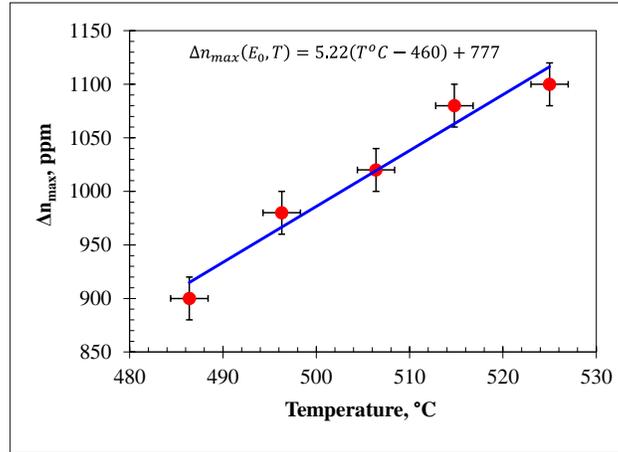


Fig. 4. Dependence of the maximum refractive index change (Δn_{\max}) at dosage E_0 versus thermal treatment temperature (extracted from Fig. 2).

One can see that, with good approximation, the maximum refractive index change appears to be, within our temperature range, almost a linearly dependent function of the thermal treatment temperature and can be described with the equation:

$$\Delta n_{\max}(E_0, T) = \Delta n(E_0, \infty, T) = 5.22(T^\circ\text{C} - 460) + 777 \quad (3)$$

One of the possible explanations of the increase of maximum refractive index change on temperature is related to the mechanisms of refractive index change in PTR glass. As stress is supposed to be one of the main effect causing the refractive index change [23], this linear dependence can be explained by the change of the stress level surrounding the crystal while cooling from thermal treatment temperature down to T_g . Actually, despite the fact that

thermal treatment is performed at a temperature above T_g (460°C), and that one would expect that only plastic deformation would occur, the situation is different. As shown in Ref. [22,24], due to the depletion of NaF, the glass surrounding crystal has a T_g higher than the development temperature resulting in an elastic deformation of the glass that generates larger stress in the crystal and larger refractive index change when larger temperature is used. Therefore the higher this stress, the higher the refractive index change. However, one must remember that refractive index change in PTR glass is the result of several interconnected processes (crystallization kinetics, diffusion processes, stresses...), such as the explanation given above is most probably only a partial one. Using the equation (3), we plotted in Fig. 5 the left term of the equation (2) as a function of $\ln(t)$.

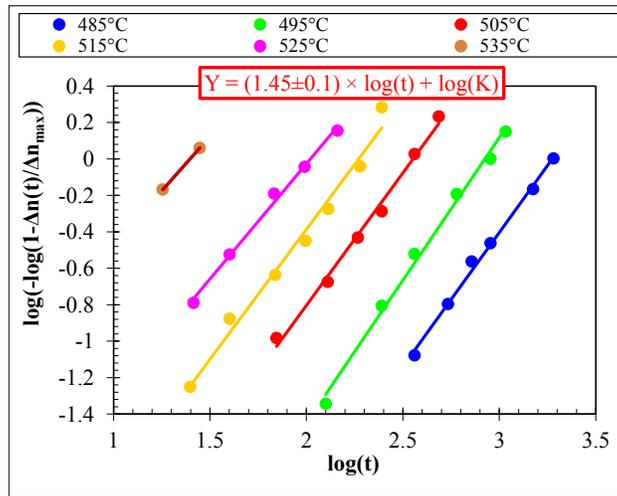


Fig. 5. Avrami plots calculated from the curves of Fig. 2 and using the data from Fig. 4.

One can see that we obtain parallel linear curves with slope equal to 1.5 ± 0.2 . The coefficient n is a parameter describing the crystallization mechanisms. When it equals to ~ 1.5 , it can be associated [19, 20], from the point of view of a crystallization process, with a diffusion-controlled growth of spherical particles from pre-existing nuclei. NaF crystals are expected to grow isotropically into cubic shape, which is close to the situation predicted by $n = 1.5$. The evolution of $\ln(K(T))$ as a function of $1/T$ is shown in Fig. 6.

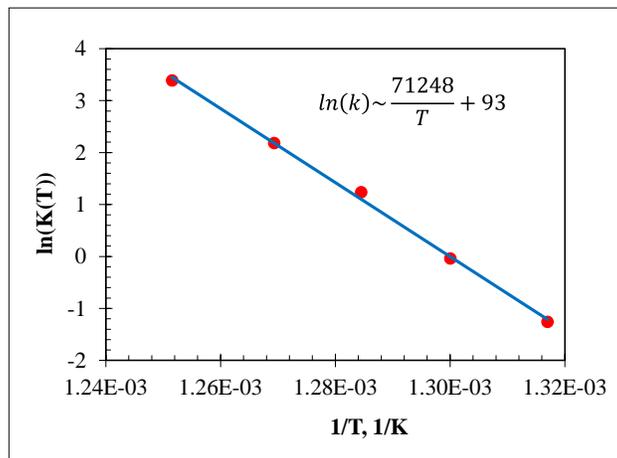


Fig. 6. Dependence of $\ln(K(T))$ on $1/T$.

A linear dependence can be observed proving that $K(T)$ is a thermodynamic parameter that follows a Boltzmann law:

$$K(T) = K_0 \times \exp\left(\frac{E_K}{RT}\right) \quad (4)$$

Where E_K is the activation energy and is equal to 592 kJ/mol. Thus, a combination of the equations (1), (2) and (4) allows predicting the refractive index change of this specific melt at a constant dosage E_0 and for any thermal treatment temperature and duration within the above determined range (Fig. 7).

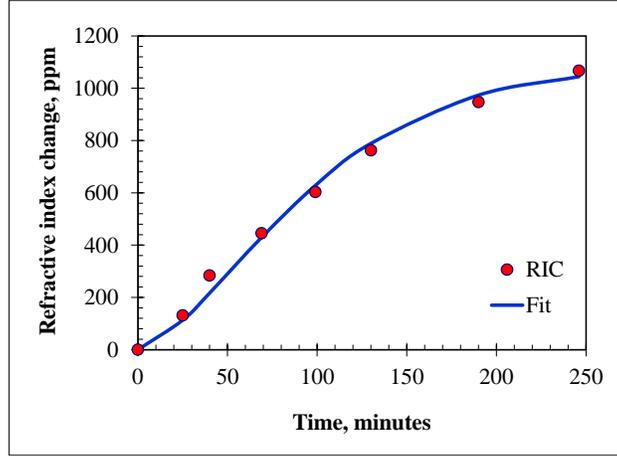


Fig. 7. Example of a fit of the dependence on thermal treatment duration of the refractive index change (RIC) measured in PTR glass UV-exposed with dosage E_0 of 0.9 J/cm² and thermally developed at ~515°C.

3.3 Modeling of the isothermal refractive index change versus dosage

Ref. [25], In order to model the refractive index change versus dosage for any thermal treatment duration and temperature as measured in Fig. 1, the results observed in ref. [25] were used. It was shown in [25] that by writing balance equations associated with the photoionization of PTR glass and supposing that trapping of electrons by silver and holes have comparable probability, the dependence of the refractive index change (Δn) on dosage (D) follows an hyperbolic function:

$$\Delta n(D) = \frac{n_s D}{D + \varepsilon} \quad (5)$$

where n_s is the refractive change at saturation and n_s/ε is the inverse of the slope at $D = 0$. Using the refractive index change at E_0 ($=0.9$ J/cm²) ($\Delta n(E_0, t, T)$) that can be predicted using JMAK theory (Equation (1)), the equation (5) becomes:

$$\Delta n(D, t, T) = \frac{\Delta n(E_0, t, T) (E_0 + \varepsilon(t, T)) D}{E_0 (D + \varepsilon(t, T))} \quad (6)$$

In our case $\varepsilon(t, T)$ is a thermodynamic parameter that needs to be determined for each thermal treatment temperature and duration. Combining the data of the section 3.2 with the equation (6) allows fitting each of the curves of the Fig. 1 with a precision better than 10% (Fig. 8) and to extract $\ln(1/\varepsilon(t, T))$ as a function of the thermal treatment duration t for each used temperature T (Fig. 9). It is seen that $\ln(1/\varepsilon(t, T))$ evolves almost linearly for any of the

temperature used in our study. Therefore an equation that accurately predicts $1/\varepsilon(t,T)$ is following:

$$\frac{1}{\varepsilon(t,T)} = \exp(\beta(T)t) \quad (7)$$

where $\beta(T)$ is a temperature dependent parameter. Despite the fact that physical meaning to this equation still requires additional study, it allows predicting the refractive index versus dosage for any thermal treatment at constant temperature.

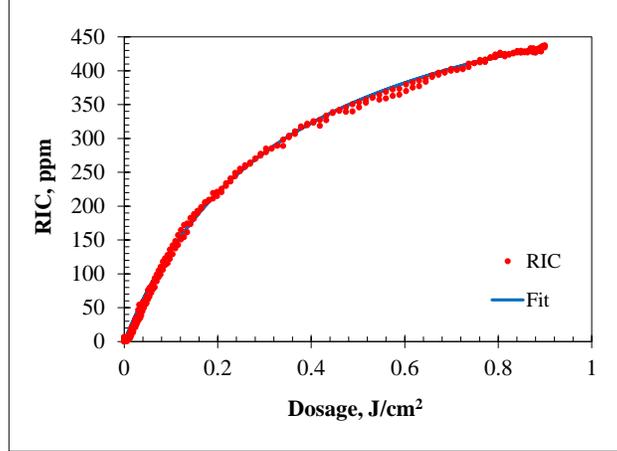


Fig. 8. Example of a fit of the dependence on the dosage of UV-exposure of the refractive index change (RIC) measured in PTR glass developed for ~60 minutes at ~515°C.

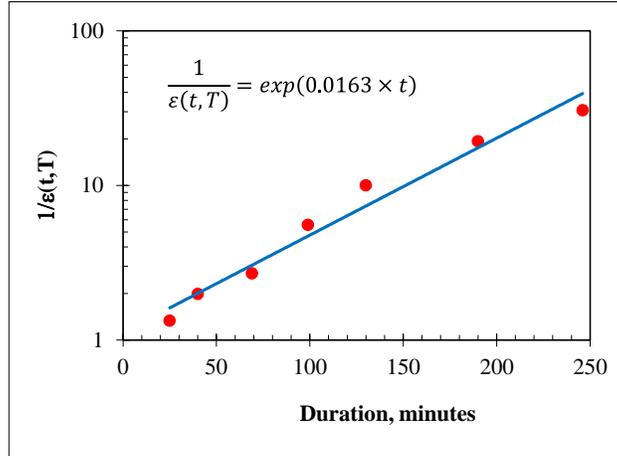


Fig. 9. Dependence of $1/\varepsilon(t)$ on the thermal treatment duration at ~515°C.

The evolution of $\ln(\beta(T))$ as a function of $1/T$ is shown in Fig. 10. A linear dependence is observed proving that $\beta(T)$ is a thermodynamic parameter that follows a Boltzmann law:

$$\beta(T) = \beta_0 \times \exp\left(\frac{E_\beta}{RT}\right) \quad (8)$$

Where E_β is the activation energy and is equal to 393 KJ/mol.

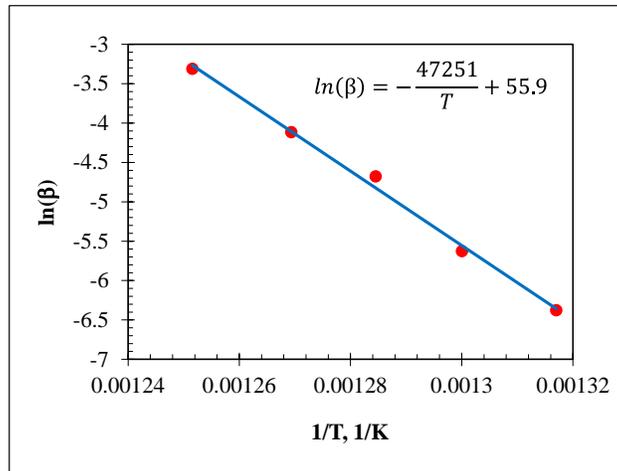


Fig. 10. Dependence of $\ln(\beta(T))$ on $1/T$.

4. Conclusion

The basic physical model that describes the refractive index change in PTR glass includes three independent parameters: the dosage of UV-exposure, the thermal treatment duration and the thermal treatment temperature. The use of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory permits to accurately predict the refractive index for a constant dosage at any of the thermal treatment procedure. The Avrami coefficient, describing the type of crystallization process, is equal to 1.5, demonstrating that the refractive index change is based on a diffusion-controlled growth of particles from pre-existing nuclei. The usage of hyperbolic functions permits to accurately predict dependence of refractive index on dosage of UV-radiation for fixed conditions of thermal development. Kinetic coefficients in these models show Boltzmann origin (exponential dependence on temperature).

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