Kinetics modeling in photosensitive glass

Leonid B. Glebov *

School of Optics/CREOL, University of Central Florida, 4000 Central Florida, Optics and Lasers, Orlando, FL 32816-2700, USA

Abstract

Kinetics of photoinduced process is studied in a new photosensitive material for volume hologram recording which is a photo-thermo-refractive glass (PTRG). A system of balance equations is derived which describes the processes of generation of electrons in a conduction band of these glass matrix by photoionization of Ce^{3+} and trapping of electrons by both silver ions Ag^+ and hole centers $(Ce^{3+})^+$. The main approach for the system solution is a calculation of low quasistationary concentration of free electrons in a conduction band, while concentrations of generated electron and hole centers are expected to be variable. A general solution of a system is found as a combination of exponential and hyperbolic functions. It is shown that an exponential solution is the result of the absence of a re-trapping of electrons, while a pure hyperbolic solution occurs in the case of equal probability of trapping and re-trapping. The approach developed for the first stage of photo-thermo-refractive process which is photoionization and trapping, is applied for the modeling of the final result of the whole process of photo-thermo-induced refractive index transformation in glass. It is found that the refractive index increment in PTRG is better described by hyperbolic function compare to the exponential one. Kinetic parameters of induced refraction in PTRG are determined.
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1. Introduction

Photo-thermo-refractive glass (PTRG) is a new photosensitive material for phase volume hologram recording which is used last years for highly efficient holographic optical elements having very high thermal, optical, chemical, and mechanical stability [1,2]. PTRG is a multicomponent silicate glass doped with cerium, silver and fluorine which shows a refractive index decrement after UV exposure followed by a thermal development.

Description of different stages of the photo-thermo-refractive process one can find in the numerous papers published during last 50+ years [3–10, and references herein]. On the basis of those publications, refractive index variations in this glass can be described as a result of following photochemical and photo-physical reactions: UV radiation produces photoionization of Ce^{3+}, a released electron is captured by a silver ion which is converted to Ag^0, thermal treatment of an exposed glass causes diffusion of silver atoms and creation of silver nano-particles which serve as the nucleation centers controlling NaF crystalline phase precipitation. Further interaction of sodium

* Tel.: +1-407-823-6983; fax: +1-407-823-6880.
E-mail address: lbglebov@mail.ucf.edu (L.B. Glebov).

fluoride nanocrystals with glass matrix at elevated temperatures causes a refractive index modification. Difference of crystallization rates in exposed and unexposed areas results in a photo-controlled refractive index modulation. However, a comprehensive understanding of this process is still far from its completion. One of the important features of any photosensitive material is a nature of its photosensitivity which determines kinetic parameters of induced coloration or refraction. However, no special works were dedicated to such characterization of PTRG.

Kinetics of photoinduced processes in glasses is a subject of intensive discussion for a long time. This permanent interest to such an academic problem is determined by the practical necessity to describe such processes as induced absorption, scattering, and refraction that are widely used in photography, holography, and lithography. We will not provide the survey of the problem but refer to one of the books [11] which summarized experimental data and theoretical approaches for inorganic photochromic glasses. The most general approach for modeling is to write down one or several differential equations describing balance of different types of centers and defects interacting in the process and to solve the system with some appropriate simplifications. Reactions of the first and second orders with the rate of reaction proportional to the first and second power of concentration, respectively, are usually considered for such a description. The first order equation gives a solution with exponential functions, while the second order results in hyperbolic ones.

While almost no experimental data for photochromic materials could be described by an exponential function, the elementary reactions in theory were usually supposed to be the first order ones. To eliminate the discrepancy, several centers with different relaxation times, or centers with distributed parameters or distances between them were used. This modeling usually gives solutions in the form of sum of exponential functions or exponential functions with fractional power. Thus, for many materials, the basic law of relaxation for participating centers is not clear, and, consequently, effect of their parameters dispersion on relaxation law is not known.

It was mentioned in Ref. [11] that the best fitting with experimental data for photochromic glasses was achieved with the use of hyperbolic function but no theoretical justification of this formal approach was proposed.

Another approach was developed by Adirovich in Ref. [12] which was based on a supposition that no direct exchange of charge carriers between different local centers occurs in crystals under optical excitation, but some concentration of free electrons is generated in conduction band. The further relaxation to the final stage occurs by trapping the electrons at original and induced traps. This approach was successfully used in Ref. [13] for explanation of non-exponential decay of intrinsic color centers in sodium-silicate glass. The general goal of this paper is to derive an elementary law of photoinduced kinetics in a photosensitive glass by the use of this theoretical background and compare the modeling with experimental results. Unfortunately, a review of available experimental data for photosensitive glasses used for hologram recording [1–10] shows that induced refractive index measurements dominate while data on initial concentration changes of cerium and silver are absent. Such a situation resulted from both practical importance of refractometry for phase recording material and impossibility to separate absorption spectra or EPR signals of individual agents in a material including a number of ions with variable valence. This is why we decided to divide the problem to several stages. The first one is to examine applicability of functional dependence derived from the model with existing experimental data and in the case of success to use it as a tool for practical needs of hologram recording. This is the subject of the current publication. The second one is to synthesize PTRG-like glasses having only one and two dopants and study kinetics of carriers generating and trapping. This study is in progress and will be a subject of further publications.
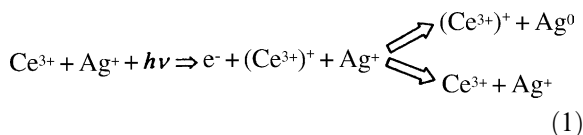
2. Derivation of a basic equation

It is clear from the previous section that the entity of photo and thermo-induced processes in

PTRG is rather complex. Let us make several suppositions and definitions which simplify deriving an elementary kinetic law which could be complicated in the further studies, if necessary:

- No other agents in glass except Ce^{3+} are excited by UV exposure. Ce^{3+} original concentration and specific absorption spectrum are C_{Ce3} and $A_{Ce3}(\lambda)$, correspondingly.
- Optical density D in the spectral region of photosensitivity is low enough to provide a uniform distribution of intensity in the volume because concentration of Ce^{3+} and thickness of the glass blank t are small $D = C_{Ce3}A_{Ce3}(\lambda_{exc})t \ll 1$. This condition corresponds to PTRG blanks with thickness below 2 mm [1,2] and can easily be satisfied.
- Quantum efficiency of cerium photo ionization after absorbing an ultraviolet photon is 100%. This means that each Ce^{3+} ion releases free electron in conduction band of glass matrix and converts to a hole center $p = (Ce^{3+})^+$ which is similar to Ce^{4+}. The hole center $p = (Ce^{3+})^+$ can trap electrons with probability T_p converting back to Ce^{3+}.
- Cerium in original glass is completely reduced, which means the absence of Ce^{4+} ions, thus no original electron traps except Ag^+ present in glass before UV exposure. Silver ions having concentration C_{Ag+} capture free electrons with probability of trapping T_n. Trapping of an electron by Ag^+ converts it to photoinduced electron center $n = (Ag^+)^-$ which is an atomic silver Ag^0.
- No atomic silver is in original glass, which means that no nucleation centers exist in PTRG except photoinduced silver atoms.
- No thermal and optical bleaching of any induced centers occurs in the process.

Thus, the reaction that we model is

$$Ce^{3+} + Ag^+ + h\nu \Rightarrow e^- + (Ce^{3+})^+ + Ag^+ \begin{cases} \nearrow (Ce^{3+})^+ + Ag^0 \\ \searrow Ce^{3+} + Ag^+ \end{cases} \tag{1}$$

An important feature of reaction (1) is an opportunity of two branches: the first one is electron trapping by silver ion, while the second one is re-trapping of electron by a cerium hole center. Let us write down the system of balance equations describing the photoinduced reaction (1). The balance of free electrons e in a conduction band is

$$\frac{de}{dt} = qA_{Ce3}(C_{Ce3} - p) - T_n(C_{Ag+} - n)e - T_p pe \tag{2}$$

where the first right term is the rate of photo-ionization resulted from absorption of exciting radiation by cerium ions Ce^{3+} which concentration is reduced by hole centers generation, the second term is the rate of electron trapping by silver ions, and the third term is the rate of electron trapping by hole centers. The balance of electron centers is

$$\frac{dn}{dt} = T_n(C_{Ag+} - n)e \tag{3}$$

where the term in brackets is the instant concentration of silver ions. Balance of hole centers is a linear combination of Eqs. (3) and (4) and should not be used in solution. The balance of electrical charges is

$$p = n + e \tag{4}$$

A system of Eqs. (2)–(4) should be solved to determine kinetics of electron centers accumulation in glass under UV exposure. Following Ref. [12], let us suppose that the lifetime of electrons in a conduction band is short enough to keep concentration of free electrons stationary and small compare to concentrations of electron and hole centers.

$$\frac{de}{dt} = 0, \quad n \approx p \tag{5}$$

This supposition actually corresponds duration of irradiation which significantly exceeds relaxation time for free electrons. This restriction can be a problem for photoionization by short-pulse lasers but it is automatically satisfied for all other sources of radiation. Substitution of (5) and (4) to (2) gives a stationary concentration of free electrons in conduction band

$$e = \frac{qA_{Ce3}(C_{Ce3} - n)}{T_n(C_{Ag+} - n) + T_p n} \tag{6}$$

Substitution of (6) to (3) results in a single equation for one variable which is a concentration of electron centers

$$\frac{dn}{dt} = \frac{qA_{Ce3}(C_{Ag+} - n)(C_{Ce3} - n)}{C_{Ag+} - (1 - R)n} \qquad (7)$$

where $R = T_p/T_n$ is a trapping ratio. $R = 0$ if $T_p = 0$, which means that no re-trapping by holes occurs. $R = 1$ if $T_p = T_n$, which means that probabilities of electron trapping by silver ions and holes are equal.

3. Modeling and discussion

Even after a number of simplifications, a general solution of (7) is rather cumbersome. Let us consider some particular cases which should show the main features of the natural kinetic law in a photosensitive medium undergoing photoionization. The simplest case is the absence of re-trapping when $R = 0$, and Eq. (7) has an exponential solution

$$n = C[1 - \exp(-qA_{Ce3}t)] \qquad (8)$$

where $C = C_{Ce3} = C_{Ag+}$ for the further simplification. This simplification can be done because we are looking for the basic kinetic law while precise comparison with some actual photoinduced center generation would be a goal of the future research. Another simple case is an equal rate of trapping and re-trapping $R = 1$, when Eq. (7) has a hyperbolic solution

$$n = \frac{CA_{Ce3}qt}{1 + A_{Ce3}qt} \qquad (9)$$

One can see that for the case of photo-transformations with intermediate relaxation of free electrons in a conduction band, there is no principal difference between recombination reactions of the first and second orders but only different proportions between probabilities of trapping electrons by original traps and re-trapping by photoinduced hole centers causes transformation of exponent-like kinetics to a hyperbola-like one. Integration of Eq. (7) gives a general solution for induced center concentration as an implicit function of time

$$\frac{Rn}{C - n} - (1 - R)\ln\frac{C - n}{C} = qA_{Ce3}t \qquad (10)$$

This function transforms to exponent (8) and hyperbola (9) at trapping ratio equal to zero and one, respectively. Kinetics of reduced concentration of electron centers $n_r = n/C$ versus reduced time $t_r = qA_{Ce3}t$ for different trapping ratios is shown in Fig. 1 for both linear and logarithmic time scales. One can see that increasing of probability of re-trapping causes dramatic deceleration of the rate of photoinduced centers generation, e.g. introducing re-trapping with probability equal to trapping by original trapping centers results in increasing of the period of 90% saturation by four times. The level of 100% saturation of photoinduced centers does not depend on the re-trapping
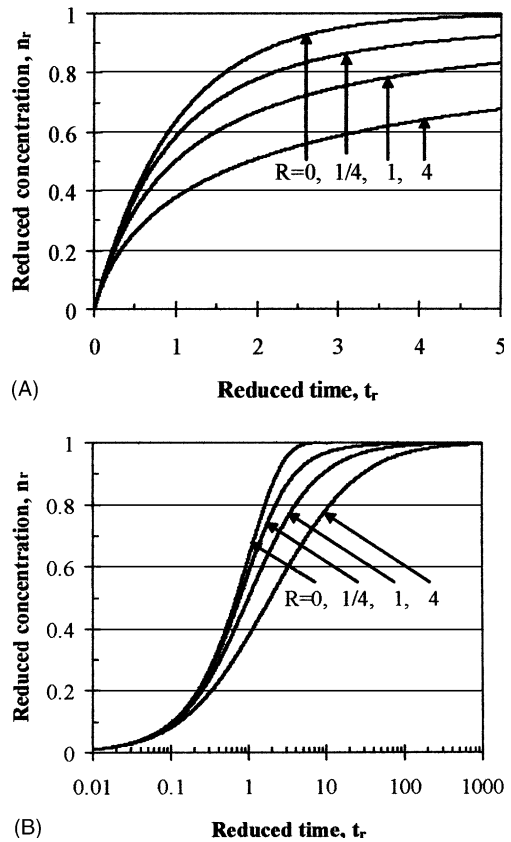

(A)

(B)

Fig. 1. Dependence of concentration of photoinduced silver atoms on time of UV exposure calculated with formula (10) for different rates of electron re-trapping. A and B—linear and logarithmic time scales, respectively.

because the total concentration of trapping sites cannot be changed by this process. One can see in Fig. 1 that basic shape of the kinetic curve depends significantly on the rate of re-trapping, so rescaling of the time axis cannot convert one curve to another.

4. Comparison with experimental data

Let us compare the basic shapes of kinetics at different level of re-trapping with experimental results observed in photosensitive glasses. Dependence of induced refractive index in PTRG measured by means of liquid-cell shearing interferometer [9] and presented in Ref. [1] is shown in Fig. 2. This curve where time derivative decreases in the process of exposure and system comes to a steady state is a typical for majority of photoinduced processes. It is clear that a refractive index variation in PTRG is the result of a number of consequent processes while the developed model considers the first stage only. However, it is possible to compare accuracy of experimental data treatment with formulae (8) and (9) and to find what the type of functional dependence with a minimal number of fitting parameters which should be used for practical modeling. The results of such comparison cannot be considered as a final proof of the whole concept, but they can give a

clue for the further study of photo-thermo-induced transformations in glass.

Write down empirical formulae similar to (8) and (9):

$$\Delta n = n_s \left[1 - \exp\left(-\frac{E}{\varepsilon} \right) \right] \qquad (11)$$

$$\Delta n = \frac{n_s E}{\varepsilon + E} \qquad (12)$$

where Δn—difference of refractive indices between exposed and unexposed areas, n_s—maximum value of refractive index increment in a saturation stage at infinite dosage, ε—rate of induced refraction which corresponds a dosage required for achieving a level of n_s/e or $n_s/2$ for exponential and hyperbolic fitting, respectively. Fig. 2 shows the best fitting by means of exponential and hyperbolic functions to experimental data on induced refraction. One can see that hyperbolic fitting gives significantly better results. Comparison of this fitting with other models shows that its accuracy corresponds to fitting by more complex functions, such as multiple exponents or fractional exponent. We will not assign physical meaning at microscopic level to parameters n_s and ε but will use them for a description of experimental data.

Fig. 3A shows dependence of induced refractive index in PTRG on dosage and time of thermal development [1]. One can see that the whole collection of data is described by function (12) with high accuracy. Fig. 3B shows dependence of maximum induced refraction n_s and half-maximum dosage ε on time of thermal development. One can see that maximum induced refraction comes to saturation level after about one hour of thermal treatment at 520 °C while half-max dosage continues decreasing at long-time development. Thus, determination of parameters in formula (12) allows precise modeling of induced refraction at all exposures and periods of thermal development for photosensitive glass and can serve a basis for modeling and design of holographic optical elments in PTRG. Successful comparison of the model and refractometric results paves a way for the further experimental and theoretical study of elementary processes in photosensitive glasses.
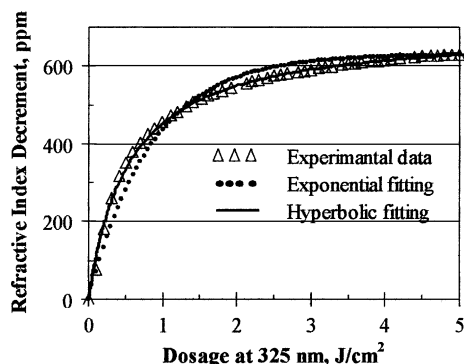

Fig. 2. Dependence of induced refractive index in photo-thermo-refractive glass on exposure at 325 nm from Ref. [1] and its modeling with exponential and hyperbolic functions.
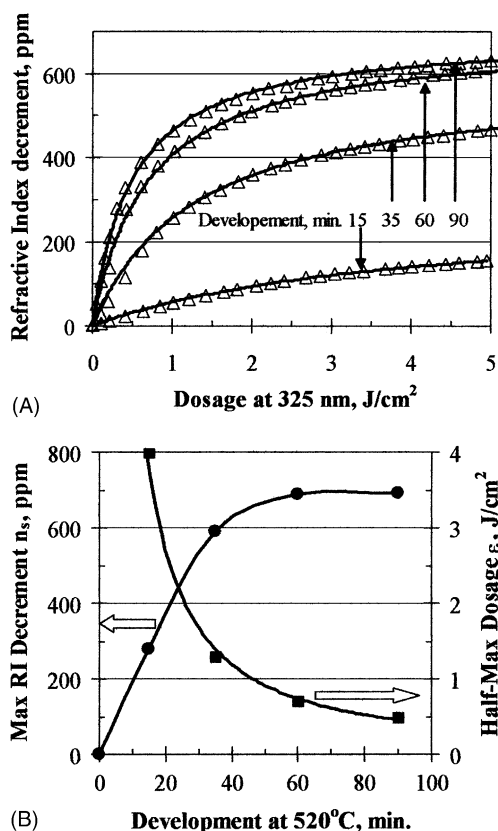
- Hyperbolic function describes variations of refractive index in a PTRG for a wide range of exposures and times of thermal development.
- Modeling of induced refraction with hyperbolic function having two fitting parameters provides accuracy similar to modeling with complex exponential functions having three and more fitting parameters.
- The developed model can be used for the study of elementary processes in photosensitive materials.

Fig. 3. Dependence of induced refractive index in photo-thermo-refractive glass on exposure at 325 nm after different times of thermal development at 520 °C (A). Experimental data ($\triangle$), modeling with hyperbolic function according to formula (12) (—). Dependence of parameters in this formula (maximal induced refraction and half-max dosage) on time of thermal development (B).

5. Conclusions

- A model of photoinduced valence transformation of dopants in glass matrix which takes into account generation of free electrons in conduction band and their re-trapping by photoinduced hole centers, gives an elementary law of relaxation as a combination of exponential and hyperbolic functions.
- The relaxation law degenerates to simple exponential and hyperbolic function when re-trapping is absent or rates of direct trapping and re-trapping are equal, respectively.

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