Optimization of light diffraction efficiency and its enhancement from a doped-PMMA volume holographic material

Mei-Li Hsieh [a,b,*], Wei-Cheng Chen [c], Hong-Yu Chen [a], Shawn-Yu Lin [b]

[a] Department of Photonics, National Chiao-Tung University, Hsinchu, Taiwan
[b] The Future-Chip Constellation, The Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180, USA
[c] Institute of Electro-Optical Science and Technology, National Taiwan Normal University, Taipei, Taiwan

ABSTRACT

In this paper, we study the diffraction efficiency from the volume gratings in holographic materials, PQ/PMMA, and their efficiency-enhancement in an optically dark environment (dark enhancement). We show that the diffraction efficiency is increased in real-time by light-exposure and then by a slow diffusion process in the dark after light-exposure. We observe strong correlations between the efficiency, the light-exposure energy and the dark-enhancement. Furthermore, we establish an optimum condition for light-exposure and dark-enhancement. Accordingly, we simultaneously achieve the best diffraction-efficiency of 82% for a 2 mm thick PQ/PMMA and an efficiency-enhancement of 3.1 times after exposure, approaching the theoretical limit of 4 times.

Published by Elsevier B.V.

1. Introduction

There is a great deal of current interest in holographic optical elements to improve the performance of optical systems. Examples are compact holographic lens, holographic grating for compact and integrated spectrometer and also holographic concentrator for solar energy harvesting [1–3]. One of the key issues for these holographic optical element concerns the optical properties of the recording materials. A good holographic recording material would typically need to have the following optical characteristics: high diffraction-efficiency, high optical quality, low shrinkage effect, simple fabrication procedures, and long-term stability. Among the current holographic recording materials, photopolymer materials [4–7] such as the PQ/PMMA, are among most popular ones for making holographic optical elements with high diffraction-efficiency and good stability. For example, Hsiao et al. reported a high efficiency of 90%, but for a thick PQ/PMMA material of 4 mm [8]. Liu et al. claimed a high efficiency-enhancement of 17 times in the dark (dark enhancement), yet reported a low efficiency of 35% [9]. So far, there is no comprehensive study of PQ/PMMA material that provides a clear correlation between the maximum diffraction-efficiency, light exposure-energy and the dark enhancement. There is also no simultaneous observation of a high diffraction-efficiency and high dark-enhancement in recording materials such as PQ/PMMA.

In this paper, we first synthesize holographic recording materials (PQ/PMMA), and then perform a comprehensive study of its diffraction-efficiency as a function of light exposure-energy, exposure-time and also dark-time after light-exposure. We show that the grating's diffraction-efficiency is determined by a fast process during light-exposure and a slow diffusion process in the dark. We further establish that there is an optimum condition for light exposure-energy to simultaneously achieve high diffraction-efficiency and dark-enhancement.

The synthesis of the phenanthrenequinone-doped poly methyl methacrylate (PQ-PMMA), recording material was described earlier [6]. Briefly, the preparation steps consist of dissolving PQ molecules with the weight ratio of 0.7 wt% in liquid methyl methacrylate (MMA) together with the azo-bis-isobutyrolnitrile (AIBN) molecules of 1 wt% [8]. The compound solution was stirred for 24 h under a constant temperature of 35 °C until the solution turned highly viscous. Finally, the solution was poured into a glass cell of a desired geometrical shape and baked for 3 days at 40 °C. This procedure ensures that most of the MMA molecules are polymerized and yields bulk samples with good optical quality and stability. The absorption spectra of PQ-PMMA had been studied before [8]. Its absorption is strong for $\lambda < 450$ nm and close to zero for $\lambda > 540$ nm. Particularly, its absorption-coefficient at $\lambda = 514.5$ nm and 632.8 nm before exposure is $\alpha = 2.7$ cm^{-1} and 0.048 cm^{-1}, respectively. Accordingly, in our experiments, we chose to use 514.5 nm as the recording wavelength and 632.8 nm as the reading wavelength. The corresponding transmittance at 632.8 nm for a 2 mm thick PQ/PMMA is 99.04%, nearly total-transparency. In addition, the shrinkage effect of this PQ/

* Corresponding author at: Department of Photonics, National Chiao-Tung University, Hsinchu, Taiwan. Tel.: +886 35712121.
E-mail address: mlh@cc.nctu.edu.tw (M.-L. Hsieh).
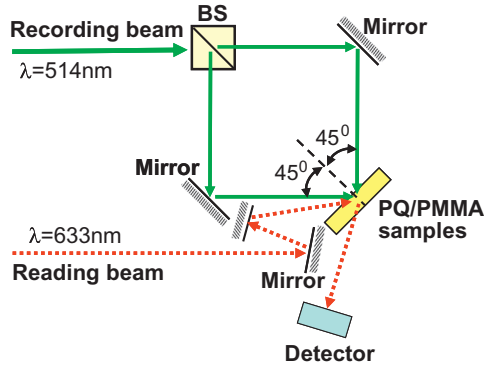
Fig. 1. A schematic diagram of the optical holographic recording and reading system. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
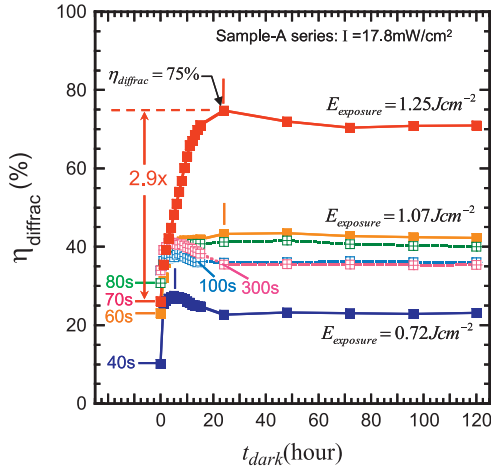

Fig. 2. The measured diffraction efficiency as a function of recoding time, or light exposure time. Sample-A and sample-B are nominally identical, 2 mm thick PQ/PMMA materials, having different incident intensities of the recording beams of $I=17.8$ and 32.1 mW/cm^2, respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

PMMA has been investigated [10], indicating that the shrinkage for a 5 mm thick bulk sample is smaller than 10^{-5}. In our experiment, we use a 2 mm thick material and the shrinkage effect for our sample may be ignored.

In Fig. 1, a schematic of our holographic recording and reading system is shown. An Argon laser with $\lambda=514$ nm is used as the "recording" beam (indicated as green lines in Fig. 1). The beam is first expanded to have a beam size of 2.5 cm × 2.5 cm and split into two with an equal intensity by a beam splitter (BS) cube. The two splitted beam are then reflected by mirrors and incident onto the PQ/PMMA sample at an incident angle of 45°. The grating period is $\Lambda=363$ nm for an incident angle of 45° and a refractive-index of $n=1.46$ for our PQ/PMMA material. The mutual interference of the two coherent beams creates a periodic, spatial modulation of light-field intensity (or light-field grating) in the photosensitive PQ/PMMA material. Simultaneously, this light-field is absorbed and initiates the attachment of free PQ-moleculars to MMA, leading to the creation of a periodic index-modulation (index-grating) in the PQ/PMMA material. Additionally, during the exposure process, a weak He–Ne laser of $\lambda=633$ nm is used as the "reading" beam (indicated as red lines in Fig. 1) to retrieve the diffracted beam from the PQ/PMMA sample. The reading beam is incident onto the sample at the Bragg matched angle to obtain the maximum diffraction. Finally, a photo-detector is used to capture and record the intensity of the diffracted beam in real time during the entire exposure procedure. The diffraction-efficiency is computed by rationing the intensity of the diffracted-beam through the volume-grating to that of the transmitted-beam before exposure.

In Fig. 2, we show the measured diffraction-efficiency as a function of recoding-time, or exposure-time, for two nominally identical PQ/PMMA samples (A and B). For sample-A, the total intensity of the recording beam is $I=17.8$ mW/cm^2 at $\theta_{incident}=45°$. The diffraction-efficiency (the red curve) shows a slow turn-on initially as the exposure-time is increased up to 40 s. It then follows a nearly linear dependence (the red dotted line) on $t_{exposure}$, reaches a maximum value of $\eta_{diffrac}=35.1\%$ at $t_{exposure}\cong95$ s and saturates at $\eta_{diffrac}=32\%$ at $t_{exposure}\cong300$ s. Because the diffraction-efficiency is retrieved by a weak laser at $\lambda=633$ nm, there is no significant absorption by the PQ/PMMA material. Therefore, the observed rise in diffraction-efficiency is due to the increase in exposure-energy ($E_{exposure}$) of the recording beams. To verify this conclusion, we perform measurements on sample-B using a higher incident intensity of $I=32.1$ mW/cm^2 at $\theta_{incident}=45°$. The diffraction-efficiency (the black curve in Fig. 2) shows a similar time-dependence as that for sample-A. Namely, it has a slow turn-on initially, is followed by a linear-dependence on $t_{exposure}$, reaches a maximum value of $\eta_{diffrac}=35.3\%$ and saturates at $\eta_{diffrac}=32\%$.
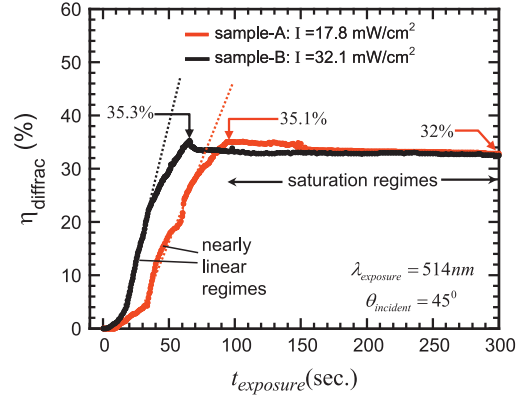
Three important points are worth noting. **First**, in the linear regime, the diffraction-efficiency of sample-B increases at a faster rate than that of sample-A. That is, when recording intensity is increased by 1.8 times (from $I=17.8$ to 32.1 mW/cm^2), the diffraction-efficiency is increased accordingly by 1.7 times (from slope=0.61% to 1.05% s). This correlation confirms that diffraction-efficiency scales linearly with exposure-time and, more importantly, with exposure-energy. Therefore, in the linear regime, the major contribution to diffraction-efficiency is index-modulation (or concentration $C_2(x,t)$) of the attached PQ-MMA molecules induced by the high-field region of the grating. **Second**, in the saturated regime, both samples exhibit the same efficiency of $\eta_{diffrac}=32\%$. The saturation occurs when free-PQ molecule is no longer available for further PQ-MMA attachment in the high-field regime. **Third**, the attachment of free PQ-molecules to MMA in the high-field grating region leaves an excess concentration of free PQ-molecules in the dark-field grating region. Therefore, a π phase-shift exists between the concentration gradients of the free PQ-molecules, $C_1(x,t)$, and the attached PQ-MMA, $C_2(x,t)$. This π phase-shift reduces the strength of the index-grating and, thus, the diffraction-efficiency. The two phase-grating and the modulation of the refractive index may be described by [11]

$$\Delta n(x,t)=\alpha_2 C_2(x,t)-\alpha_1 C_1(x,t) \tag{1}$$

where α_1 and α_2 are the polarizabilities of the free PQ and attached PQ-MMA, respectively. The minus sign in Eq. (1) reflects the π phase-shift between the two gratings. The diffraction-efficiency is proportional to the square of sine-function of Δn. To achieve a significantly greater diffraction-efficiency, $\eta_{diffrac}\geq35.3\%$, the π phase-shifted index-grating due to $C_1(x,t)$ must be significantly reduced. This may be done by removing $C_1(x,t)$ through the diffusion of free PQ-molecules in an optically dark environment.

To study the diffusion effect of free PQ-molecules, the sample is placed in the dark at room temperature and its diffraction-efficiency measured as a function of dark-time (t_{dark}). We study a sequence of samples, having different free PQ-molecule concentrations, $C_1(x,t)$. The six samples we study have an exposure-time ranging from $t_{exposure}=40,\ 60,\ 70,\ 80,\ 100$ and 300 s or exposure-energies $E_{exposure}=0.72,\ 1.06,\ 1.24,\ 1.42,\ 1.98$ and 5.36 J/cm^2, respectively. In Fig. 3, we plot the measured diffraction-efficiency as a function of t_{dark} for all six samples. For the $t_{exposure}=40$ s sample, its efficiency (the blue squares) increases from $\eta_{diffrac}=10\%$ to a maximum of 27% at $t_{dark}=5$ h. For the $t_{exposure}=60$ and 70 s samples (the orange and red squares, respectively), we observe higher initial-efficiencies of $\eta_{diffrac}=23\%$ and 26% and also higher maximum-efficiencies of 44% and 75% at $t_{dark}=24$ h. However, the trend of continuing increase of

Fig. 3. The measured diffraction-efficiency as a function of the dark-time (t_{dark}) for all six samples, having different exposure-times $t_{exposure} = 40, 60, 70, 80, 100$ and 300 s, respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
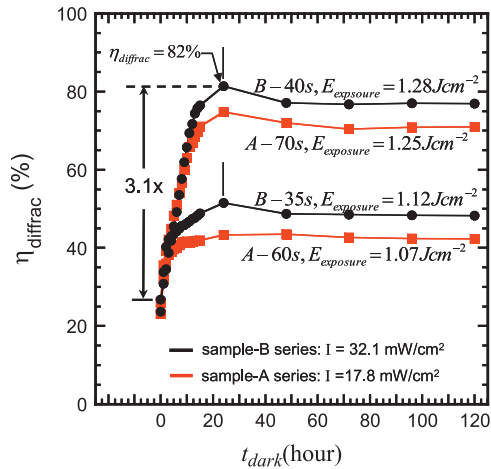
Fig. 4. The measured diffraction efficiency (the black dots) as a function of t_{dark} for sample-B with $t_{exposure} = 35$ s and 40 s or $E_{exposure} = 1.12$ and 1.28 J/cm², respectively. For comparison purpose, the diffraction-efficiencies for sample-A are also plotted (the red squares). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

maximum-efficiency does not hold for the $t_{exposure} = 80, 100$ and 100 s samples. The $t_{exposure} = 80$ s sample (the green cross squares) has an initial-efficiency $\eta_{diffrac} = 31\%$, but a maximum-efficiency of only 42% at $t_{dark} = 24$–48 h. For the $t_{exposure} = 100$ and 300 s samples, their respective maximum-efficiency values are 38% and 41% at $t_{dark} = 5$ h. We note that for those samples having higher maximum-efficiencies ($t_{exposure} = 60, 70$ and 80 s), the required dark-time is longer ($t_{dark} = 24$–48 h). We also note that, for the $t_{exposure} = 70$ s sample, a large efficiency enhancement of 2.9 times (from 26% to 75%) is observed in the dark, i.e. "dark-enhancement". To summarize the findings: we find that the dark-enhancement is (a) exposure-time dependent; (b) a slow process occurring within 5–48 h after light-exposure; and (c) more significant for those samples, requiring a longer dark-time to achieve its maximum efficiency. Next, we will study the exposure-time dependence of the dark-enhancement in more detail.

To search for the optimum light-exposure conditions, we will first repeat the same measurement for sample-B series with a higher incident light-intensity $I = 32.1$ mW/cm². We will then compare the dark-enhancement between sample-A and -B of similar exposure-energy, but different exposure-times. In Fig. 4,

we plot the measured diffraction-efficiency (the black dots) as a function of t_{dark} for sample-B with $t_{exposure} = 35$ s and 40 s or $E_{exposure} = 1.12$ and 1.28 J/cm² respectively. For comparison, diffraction-efficiencies for sample-A are also plotted (the red squares). The B-35s sample has a similar $E_{exposure}$ and initial-efficiency as that for the A-60s sample, but reaches a slightly higher maximum-efficiency of $\eta_{diffrac} = 51.5\%$ at $t_{dark} = 24$ h. The B-40s sample has a similar $E_{exposure}$ and initial-efficiency as that for the A-70s sample and reaches an even higher maximum-efficiency of $\eta_{diffrac} = 82\%$ at $t_{dark} = 24$ h. This data confirms our earlier observation that the maximum-efficiency occurs at a longer dark time of $t_{dark} = 24$ h. This data also shows that the primary factor for determining the maximum-efficiency is the total exposure-energy. Additionally, by keeping the exposure-time shorter (i.e. from 70 s for sample-A to 40 s for sample-B), the maximum-efficiency is further increased to 82% perhaps due to less scattering of light during exposure. This diffraction-efficiency is the best efficiency observed for a PQ/PMMA sample of only 2 mm thick.

It is noted that, during recording, the material is kept at room temperature and the rising time of the diffraction-efficiency will depend on the exposure-energy shown in Fig. 2. The exposure energy, to reach the maximum diffraction-efficiency, is ~1.7 J/cm² and is similar to that used in Ref. [8]. After exposure, the material is also kept in room temperature. The diffraction-efficiency continues to increase due to the dark enhancement and reaches the maximum after 24 h. The diffusion-coefficient for our PQ-PMMA is calculated to be $D_1 = 0.038$ nm²/s, which is a reasonable value for achieving diffusion over a distance of the $\Lambda = 363$ nm grating period [11,12]. According to the finding of Ref. [11], we believe that the efficiency-enhancement of the hologram after recording is due to the attachment of photoactivated PQ radicals to MMA.

In Fig. 5(a), we summarize the measured diffraction-efficiency as a function light exposure-energy for both sample-A and -B. The open-dots represent efficiency values measured right after light exposure (the fast process) and may be viewed as a combined plot of Fig. 2. The solid-dots represent the maximum efficiency achieved after dark-enhancement (the slow process). For both sample series, the maximum-efficiency is achieved at exposure-energy ranging from $E_{exposure} = 1.00$ to 1.40 J/cm², which is indicated as the pink region. In Fig. 5(b), we plot the corresponding dark-enhancement, which is obtained as the ratio of maximum-efficiency to initial-efficiency. Again, the maximum dark-enhancement falls within the exposure energy of $1.00 \leq E_{exposure} \leq 1.40$ J/cm². Another relevant factor for determining the maximum-efficiency is the length of dark-time. In Fig. 5(c), we plot the measured dark-time $t_{dark}(max)$ necessary for achieving the maximum-efficiency. We observe a strikingly strong correlation between a longer dark-time for free-PQ diffusion and a higher dark-enhancement. Note that at the high exposure regime, $E_{exposure} \geq 1.40$ J/cm², the free PQ-molecules concentration $C_1(x, t)$ is low due to an over-exposure. Because of a low $C_1(x, t)$, the modulation of refraction-index would not be altered as much by diffusion. So, the dark-time $t_{dark}(max)$ is short and the dark-enhancement weak (1.2 times). At the low exposure regime ($E_{exposure} \leq 1.00$ J/cm²), both $C_1(x, t)$ and $C_2(x, t)$ are low but compatible. Because they are both low, the dark-time $t_{dark}(max)$ is short. Because their magnitudes are compatible, the dark-enhancement is substantial (2.6 times). Finally, the optimum exposure condition is reached when both $C_1(x, t)$ and $C_2(x, t)$ are high. In this case, it takes a longer dark-time ($t_{dark}(max) \geq 24$ h) to reduce $C_1(x, t)$ to near zero by diffusion. The reduction or elimination of $C_1(x, t)$ also leads to a large dark-enhancement (3.1 times). This analysis provides, for the first time, the key to achieve simultaneously a high maximum-efficiency and a large dark-enhancement in a PQ/PMMA recording material.

Quantitatively, the maximum efficiency-enhancement may be predicted. The diffraction-efficiency is proportional to the square
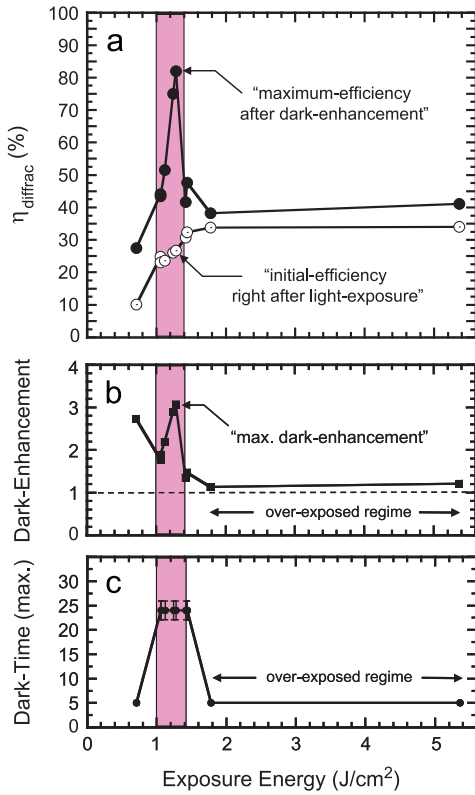
Fig. 5. (a). The measured diffraction-efficiency plotted as a function exposure-energy $E_{exposure}$ for both samples-A and -B. The open-dots represent efficiencies measured right after light exposure (the fast process) and the solid-dots the maximum efficiency achieved after dark-enhancement (the slow process). (b). The measured dark-enhancement, the ratio of maximum-efficiency to initial-efficiency, plotted as a function of $E_{exposure}$. (c) The measured dark-time $t_{dark}(max)$ necessary for achieving the maximum efficiency. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

of sine-function of modulation-depth of the refractive index [13]. And, the enhancement of diffraction-efficiency is given by

$$\eta_{enh} = \frac{\eta_{afterdark}}{\eta_{exposure}} = \frac{\sin^2(\pi d \Delta n_{dark}/\lambda \cos\theta)}{\sin^2(\pi d \Delta n_{expo}/\lambda \cos\theta)} \quad (2)$$

where d is the thickness of our material and λ and θ the wavelength and incident angle of the recording beam, respectively. Δn_{expo} and Δn_{dark} represent the modulation-depth of refractive-index right after exposure and after the completion of free PQ-molecules diffusion in the dark, respectively. Under the condition that the ratio of modulation-depth for the attached PQ-MMA and free-PQ is identical, the modulation-depth of refractive-index will become twice larger

after the completion of free-PQ diffusion. This was achieved, in our experiment, by varying the light exposure-energy. Furthermore, under the small modulation-depth limit ($\Delta n_{expo}/n \ll 1$), the maximum efficiency-enhancement is calculated to be 4 times. Experimentally, at $E_{exposure} = 1.28$ J/cm^2 and $t_{dark} = 24$ h, a maximum dark-enhancement of 3.1 times is demonstrated which approaches the theoretical limit.

In summary, we performed a comprehensive study the diffraction-efficiency of PQ/PMMA volume holographic materials. We show that the sample's diffraction-efficiency is increased initially by a fast process during light-exposure and then by a slow diffusion process in the dark. We observe strong correlations between the light exposure-energy, the maximum dark-enhancement and the maximum dark-time. This correlation allows us to optimize light exposure-energy and to achieve the best diffraction-efficiency of $\eta_{diffrac} = 82\%$ for a 2 mm thick PQ/PMMA. The observed efficiency-enhancement of 3.1 times after exposure also approaches the theoretical limit of 4 times.

Acknowledgments

References

[1] D.H. Close, Optical Engineering 14 (5) (1975) 408.
[2] J.N. Mait, Journal of the Optical Society of America A 12 (10) (1995) 2145.
[3] R. Kostuk, et al., High and low concentration for solar electric applications III, in: Proceedings of SPIE 7043, 2008, p. 704301.
[4] H. Franke, Applied Optics 23 (1984) 2729.
[5] S. Piazzolla, B.K. Jenkins, Optics Letters 21 (1996) 1075.
[6] S.H. Lin, K.Y. Hsu, W.Z. Chen, W.T. Whang, Optics Letters 25 (7) (2000) 451.
[7] A. Pu, D. Psaltis, Applied Optics 35 (14) (1996) 2389.
[8] Yi-Nan Hsiao, W.T. Whang, S.H. Lin, Optical Engineering 43 (9) (2004) 1993.
[9] H. Liu, D. Yu, X. Li, S. Luo, Y. Jiang, X. Sun, Optics Express 18 (7) (2010) 6447.
[10] Shiuan Huei Lin, June-Hua Lin, Po-Lin Chen, Yi-Nan Shiao, Ken Y. Hsu, Journal of Nonlinear Optical Physics and Materials 15 (2) (2006) 239.
[11] J. Mumbru, I. Solomatine, D. Psaltis, S.H. Lin, K.Y. Hsu, W.Z. Chen, W.T. Whang, Optics Communications 194 (13) (2001) 103.
[12] A. Veniaminov, E. Bartsch, Journal of Optics A: Pure and Applied Optics 4 (2002) 387.
[13] H. Kogelnik, Bell System Technical Journal 48 (1969) 2909.