

The Synthesis and Application of Pb-doped GLYMO/Chelated-Zirconium Complex Coating Materials for UV-Light Absorption

Meltem Asiltürk,¹ Funda Sayılkan,² Hikmet Sayılkan,² Galip İçduygu¹

¹İnönü University, Faculty of Arts and Science, Department of Chemistry, 44289, Malatya, Turkey

²İnönü University, Faculty of Education, Department of Science, 44289, Malatya, Turkey

Received 8 July 2004; accepted 13 April 2005

DOI 10.1002/app.22583

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: New glass coating materials containing γ -glycidoxypropyltrimethoxy-silane/zirconium(IV)-*n*-propoxide(2-methoxyethylacetoacetate)/lead(II) nitrate were developed for UV-light absorption by sol-gel process. The effect of agitation time, temperature, and Zr complex and Pb²⁺ ion concentrations on UV light absorption were investigated. Zr complex was characterized by using ¹H-NMR, ¹³C-NMR, and FTIR spectroscopy. Ultraviolet visible spectroscopy was utilized to determine the optical properties of coating materials. Results

showed that coated glass has very low transmission in the UV region (300–400 nm) relative to uncoated glass, especially at 150°C for 15 h agitation. UV light transmission of coated glasses treated at 80, 100, 450, or 500°C was not different from uncoated glass. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1175–1179, 2006

Key words: coatings; UV-Vis spectroscopy; sol-gel process; hybrids

INTRODUCTION

The sol-gel process is a low temperature method that has been successfully utilized to prepare optical materials by incorporating different cations or molecules in a silica host.^{1,2} The advantages of the sol-gel process for preparation of optical materials come from the uniformity of chemical compositions and the low contamination caused by its preparation process. The relatively low temperature allows the incorporation of large numbers of inorganic and organic additives during the process of glass formation yielding materials with interesting optical properties.³ Metal alkoxides and their organic derivatives play an important role in synthesis of glasses, ceramics, and organic-inorganic hybrid materials by using the sol-gel process.^{4–8} In the last few years, hybrid organic-inorganic coatings have been developed to improve mechanical, thermal, optical, and abrasion properties.^{9–11} In recent years, silica-titania, silica-zirconia, or metal ion doped silica-titania-based organic-inorganic materials were studied as a promising system for photonic applications^{12,13} and low-loss waveguides based on organically modified metal alkoxides have been synthesized by a sol-gel process.^{14–16} It is known that sunburn and premature skin aging are caused by prolonged and cumulative skin aging exposure to the highest energy

radiation levels emitted by the sun that reaches the surface of the Earth, the UV radiation. The relevant wavelength of this UV radiation in terms of greatest damage are subdivided into UV-B (290–320 nm) and UV-A (320–400 nm) designations. Recent work^{17,18} has demonstrated that both UV-B and UV-A exposure play a role in initiating skin cancer by damaging DNA and suppressing immune surveillance, respectively. It is also known that ordinary glasses are not universally suited for optical applications since they have low flexibility, high brightness, and high process temperatures. In addition, these glasses transmit an important part of the UV light (300–400 nm), which causes damages in the human system. However, the application of some suitable thin films obtained from organic-inorganic hybrids on glass alters the UV light transmission property of glass. Addition of soluble transition metal salts into the starting solution to obtain organic-inorganic network-containing metal ions and entrapment of these ions by sol-gel process were found very effective for the glass in UV-B and UV-A regions.^{3,19} Transition metal ions (such as Cr³⁺, Pb²⁺, and Ce⁴⁺) were incorporated in the SiO₂ network following a sol-gel process and several optical spectroscopic studies have been reported.^{20–23} The UV absorption properties of inorganic-organic hybrid material coated glass were affected from heat treatment, the type and concentration of metal ions, and/or organic-modified silanes. Inorganic-organic hybrid materials prepared from γ -glycidoxypropyltrimethoxysilane (GLYMO) as SiO₂ source and organic

Correspondence to: H. Sayılkan (hsayilkan@inonu.edu.tr).

modified or unmodified metal alkoxides via sol-gel process find manifold interest (e.g., for scratch and abrasion-resistant coating on polymers,^{24–26} for contact lenses,²⁷ photochromic,²⁸ antifogging,²⁹ and colored layers on glass).³⁰ GLYMO has also been used as a binder in the colloidal silica coatings, leading to increased density, higher film thickness, and improved adhesion to polymer substrates.³¹

In this work, the primrose yellow and dark yellow colored coating solutions were synthesized by adding Pb^{2+} ion to prehydrolyzed GLYMO/Zr complex mixtures and incorporated onto microscope slide glass surfaces by dip-coating method. The effects of Pb^{2+} and Zr complex concentrations, the agitation time, and thermal treatment temperature on the UV light absorption properties of coated glass surfaces were investigated.

EXPERIMENTAL

Materials

GLYMO (Fluka, Germany), zirconium(IV)-*n*-propoxide [$\text{Zr}(\text{OPr}^n)_4$, Fluka, Germany], 2-methoxyethylacetate (2-MEAA, Aldrich) were used as received. *n*-Propyl alcohol (Riedel, Germany) was used as solvent after drying over the molecular sieves (Fluka, Germany, 3ÅXL8) for a day. Microscope slide glass (2.5×7.5 cm) was cleaned with acetone and dried at 80°C before coating.

Apparatus

Optical properties of coated and heat treated (80–500°C) glass surfaces were determined by using a Shimadzu 1601 model ultraviolet–visible (UV–Vis) spectrophotometer at wavelengths between 200 and 800 nm. $^1\text{H-NMR}$ (in CDCl_3), $^{13}\text{C-NMR}$ (in CDCl_3), and FTIR (on KBr pellet) spectra of chelated-Zr complex were recorded on a Bruker Advances model 300 MHz NMR spectrophotometer and a Perkin–Elmer 283 model FTIR spectrophotometer, respectively.

Preparation of coating materials

Coating materials were synthesized as described below: GLYMO was hydrolyzed without solvent and catalyst, and by adding dropwise 3 mol of water/mol of GLYMO. The mixture was stirred at ambient temperature until a clear and homogeneous solution formed. The alcohol formed with the reaction of hydroxyl group of water and methoxy group of GLYMO and excess water were removed in vacuum. The product was a viscous liquid. This product was diluted with *n*-propyl alcohol (10%, w/w) and hereafter referred to as G1. Dissolved in *n*-propyl alcohol (10 mL) was 1×10^{-3} mol of $\text{Zr}(\text{OPr}^n)_4$. After stirring for 10

min, 0.1 and 0.5 mol of 2-MEAA were added dropwise to the solution, for each mol of $\text{Zr}(\text{OPr}^n)_4$, respectively. The mixture was allowed to react for 2 h at ambient temperature. The solvent and the liberated alcohol were removed in vacuum, and a primrose yellow liquid designated as Z1 was obtained. Then, 0.1 and 0.5 mol of Z1 complex was slowly added to G1, for each mol of GLYMO, and the mixture was stirred for 1 h. $\text{Pb}(\text{NO}_3)_2$ solution (5 mL) was added to the G1-Z1 mixture ($\text{Pb}^{2+}/\text{GLYMO}$: 0.1 and 0.01 mol). The final mixture was stirred for 1, 15, and 24 h. Thus, four coating systems were obtained where $\text{GLYMO}/\text{Zr}(\text{OR})(2\text{-MEAA})/\text{Pb}^{2+}$ ratio (mol/mol) is 1/0.1/0.1 in system I, 1/0.1/0.01 in system II, 1/0.5/0.01 in system III, and 1/0.5/0.1 in system IV. It should be noted that because gelation occurred for system I when $\text{Pb}(\text{NO}_3)_2$ solution was added into the G1-Z1 mixture, while systems II, III, and IV stayed homogeneous and transparent during the stirring, only UV-light absorption properties of systems II, III, and IV were investigated. After the stirring procedure for each system, the glass surface was coated with the systems by dip-coating method.

RESULTS AND DISCUSSION

In the $^1\text{H-NMR}$ spectrum of the product formed by the reaction between $\text{Zr}(\text{OPr}^n)_4$ and 2-MEAA, new peaks appeared at 5 and 2.2 ppm. The chemical shifts of these peaks were similar to that of the enol tautomer of 2-MEAA. The acidic proton of 2-MEAA was observed at 3.1 ppm and it disappeared when 2-MEAA was coordinated to Zr atom. In the $^{13}\text{C-NMR}$ spectra of uncoordinated (UC) and coordinated (C) 2-MEAA, the chemical shifts of carbonyl carbons are observed as 166.9 (UC, keto form), 200.1 (UC, keto form), 172.9 (C, enol form), and 186.6 (C, enol form) ppm, respectively. According to these results, the enol form of 2-MEAA is bonded to zirconium. In the FTIR spectrum of the complex, because no bands were seen in the carbonyl region 1740–1715 cm^{-1} , two carbonyl groups of 2-MEAA must be in a chelating coordination mode.

UV measurements show that change in agitation time, temperature, Zr complex, and Pb^{2+} concentrations have an important effect on the UV-light absorption of the coating systems. Figure 1(a–c) shows the UV transmission of coating system II after 1, 15, and 24 h agitation.

According to Figure 1(a), temperature has no significant effect on UV-light transmission property of this coating system. Except for 300°C, UV transmission was high at all temperatures. Only, 8.5% (λ : 325 nm), 6.25% (λ : 350 nm), and 4% (λ : 375 nm) decrease in the UV transmission at 300°C. However, this coating system obtained by 1 h agitation is not suitable for UV-light absorption. The surface was colorless from the beginning of heating and up to 300°C; it takes a light

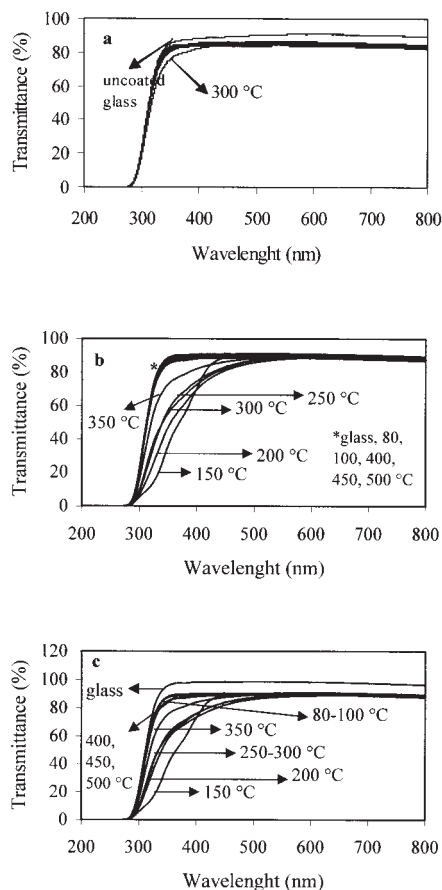


Figure 1 UV transmission of system II coated glass after 1 (a), 15 (b), and 24 h (c) agitation.

yellow color at 300°C and became colorless after 300°C. Condensation reaction takes place between alkoxides after hydrolysis. Condensation reaction can be completed very fast, but sometimes it takes a long time to complete this reaction^{32,33} because condensation cannot occur between GLYMO and Zr complex after 1 h agitation and Pb^{2+} ion is not coordinated with the condensation product. It was believed that the decrease in transmittance of the coated surface is probably due to higher porosity of the surface. Figure 1(b) shows that the agitation (15 h) and temperature have an important effect on UV-light transmission of coating. At 80, 100, 400, 450, and 500°C, the UV-light absorption property of the coated glass is similar to uncoated glass. It was observed that the transmittance was [λ (nm): 300/325/350; T%] 21.41/73.16/88.66 at 80°C, 21.0/71.19/86.23 at 100°C, 13.98/35.67/52.99 at 150°C, 25.34/46.92/59.67 at 200°C, 20.02/69.23/85.02 at 400°C, 21.81/73.19/88.09 at 450°C, and 21.67/73.03/87.06 at 500°C, respectively. When 400, 450, and 500 nm wavelengths were considered for the same temperature, optical transmittance of the coated glass was [λ (nm): 400/450/500; T%] 90.89/91.06/91.17 at 80°C, 88.37/88.77/88.67 at 100°C, 70.34/88.93/90.04 at

150°C, 69.85/81.18/85.79 at 200°C, 88.71/89.70/90.25 at 400°C, 90.10/90.37/90.49 at 450°C, and 89.33/89.82/89.65 at 500°C, respectively. Important changes on UV-light transmission were observed between 150 and 400°C. It was clearly seen that the film obtained by system II agitated for 15 h is very suitable for UV absorption after treatment at 150°C relative to system II agitated for 1 h. While the surfaces were colorless up to 150°C, primrose yellow at 150°C, yellow at 200°C, primrose yellow at 250°C, and became colorless again after 300°C, it should be noted that the coated surfaces were homogeneous and transparent after thermal treatment. It can be due to the epoxide ring-opening and then epoxide polymerization occurred on the surface as the temperature increased, whereas the condensation occurs between GLYMO and Zr complex. Observed yellow color and high UV-light absorption can be caused from a change in oxidation state of Pb ion from 2+ to 4+ and $\pi \rightarrow \pi^*$ transition of olefinic group on 2-MEAA. Transmission reaches maximum in all wavelengths after 300°C. This arises in the form of an inorganic network that contains $-O-Si-Zr-O-Pb-O-$ bonds by removal of organics. Because the oxidation state of Pb changes from 4+ to 2+, the yellow color of the coating becomes colorless and transparent again. Figure 1(c) shows that the agitation time (24 h) and temperature also have an important effect on the UV-light transmission of the glass coated with system II after 15 h agitation [see Fig. 1(b)]. At 80, 100, 400, 450, and 500°C, UV-light transmission of the glass-coated glass was similar to uncoated glass. The coated surface obtained after 24 h agitation and heat treated at 150°C is suitable for UV-light absorption. However, UV-light transmission of the film obtained after 15 h agitation was better than 24 h agitation. It was observed that the transmittances at 300, 350, 400, 450, 500, and 550 nm [15 h/24 h, T%, 150°C] are 5.11/5.57, 35.67/38.73, 70.34/72.74, 88.93/89.0, 90.04/89.97, and 90.21/90.0, respectively. It is clearly seen that the coated surface obtained after 15 h agitation has minimum transmission at the UV region and maximum transmission at the Vis region than obtained after 24 h agitation. When agitation time and temperature are considered, the optimum conditions for this coating system are 150°C and 15 h agitation.

Figure 2(a–c) shows UV–Vis-light transmission of coating system III after 1, 15, and 24 h agitation time. This coating system was prepared by keeping GLYMO and Pb^{2+} concentrations constant and by changing Zr complex concentration from 0.1 to 0.5 mol/mol of GLYMO.

According to Figure 2(a) [contrary to Fig. 1(a)], at 80, 100, 150, 200, 250, and 450°C, UV–Vis absorption of the coated glass was similar to uncoated glass. Significant changes on UV–Vis light absorption were observed at 300, 350, and 400°C. The sample thermally treated at 300°C has considerably low transmission at the UV

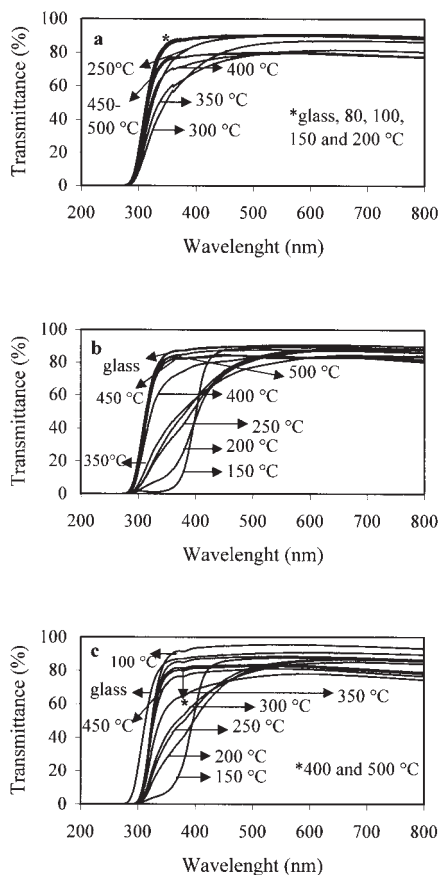


Figure 2 UV transmission of system III coated glass after 1 (a), 15 (b), and 24 h (c) agitation.

region and showed maximum transmission at the Vis region. For example, the transmittances were [λ (nm): 300/350/400/450/500, T%] 8.29/51.55/70.35/80.27/84.45 at 300°C, 10.77/57.03/68.36/75.04/78.43 at 350°C, and 15.17/68.38/74.06/77.04/78.61 at 400°C. Although the surfaces are colorless up to 250°C and after 450°C for 1 h agitation, they take a light yellow color at 250°C. The color changes to dark yellow between 300 and 400°C. We think that the observed dark yellow color may be caused by the oxidation of Pb^{2+} to Pb^{4+} and by the removal of organics process, as carbon oxidation. Because the concentration of Zr complex was increased in system III and the amount of organic groups removed by carbon oxidation is high, this type of color change seems possible. The surface becomes colorless again after 450°C. After 400°C, the surface was unhomogeneous, porous, and cracked.

Figure 2(b, c) shows that the coated surfaces that have maximum UV-light absorption and minimum VIS-light absorption was obtained at 150°C. It is seen that agitation time has no significant effect on UV-Vis light transmission of these coating systems. The coated surface obtained after 15 h agitation has very suitable UV-Vis light transmission than obtained after 24 h agitation, as shown in Table I.

TABLE I
Transmissions of System III Coated Glass after 15 and 24 h Agitation at 150°C

λ (nm)	T% (15 h)	T% (24 h)
300	1.56	0.30
325	1.13	3.55
350	2.06	7.09
375	10.14	20.08
400	47.84	56.51
425	81.92	81.63
450	87.39	85.41
475	88.24	86.52
500	89.01	97.08
525	89.04	97.39

According to Table I, the coated surface obtained after 15 h agitation has very suitable UV-light absorption and Vis-light transmittance for this coating system. The coated surfaces obtained after 15 h agitation were transparent and homogeneous at 80, 100, 450, and 500°C and they took primrose yellow at 150°C, yellow at 200 and 250°C, mousy at 300°C, primrose yellow at 350 and 400°C, and the coating becomes colorless after 400°C.

Figure 3(a, b) shows transmissions of system IV coated glass after 15 and 24 h agitations. This coating system was prepared by keeping Zr complex concentration (Zr-complex/GLYMO: 0.5) constant and by changing Pb^{2+} concentration from 0.01 to 0.1 mol/mol of GLYMO. Gelation occurred as soon as Pb^{2+} solution was added into the G1-Z1 mixture and gelled solution turned to transparent and homogeneous solution after 7–8 h agitation. Therefore, only 15 and 24 h agitation were studied during the experi-

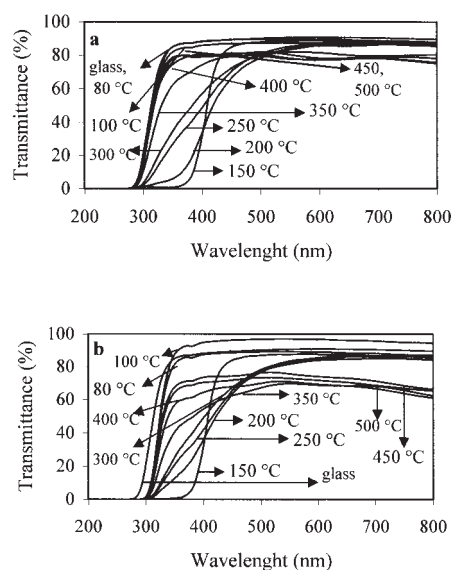


Figure 3 UV transmission of system IV coated glass after 15 (a) and 24 h (b) agitation.

ments. Results indicated that significant changes were observed by using different agitation times (15 and 24 h) and high Pb^{2+} concentration depending on temperature. At 80 and 100°C, UV absorption of the coated glass was almost similar to uncoated glass at 15 h agitation [Fig. 3(a)]. UV-Vis light transmission starts to decrease significantly as the temperature was increased from 350 to 500°C [Fig. 3(b)]. However, in both agitation times, it was observed that the absorption of coated surfaces heat-treated between 350 and 500°C was different to uncoated glass. It was not possible to obtain a completely transparent coating after 350°C. UV-Vis light absorption of system IV coated surfaces were nonuniform, because some portions of the surfaces are rough and/or smooth. However, in both agitation times, it was observed that the coated surfaces heated at 150°C are seen suitable for optical application.

CONCLUSIONS

New coating materials were prepared via condensation and polymerization reactions of alkoxides by sol-gel process. Various concentrations of Zr complex and Pb^{2+} ion, agitation times, and temperatures were studied. According to the overall results, UV-Vis light absorption properties of coating systems obtained after 15 h agitation at 150°C are very suitable for optical applications.

Coating system III obtained at 300°C for 15 h agitation is very suitable system for absorbing UV-light when Pb ion and Zr complex concentrations are low (system II), when absorption property of the coatings is good, and, when agitation time and treatment temperature is considered, system II is also the best coating system for UV absorption. When the 475- to 550-nm range is considered to be the most sensitive wavelengths for the human eye, 150° treatment temperature and 15 h agitation time are the most appropriate reaction conditions for UV-light absorption application.

References

- Ulrich, D. R. *J Non-Cryst Solids* 1988, 100, 174.
- Sorek, Y.; Reisfeld, R.; Weiss, A. M. *Chem Phys Lett* 1995, 244, 371.
- Reisfeld, R. *Opt Mater* 2001, 16, 1.
- E. Brinker, C. J.; Clark, D. E.; Ulrich, D. R. *Better Ceramics Through Chemistry*; Elsevier: New York, 1984.
- Klein, L. C., Ed. *Sol-Gel Technology for Thin Films, Fibers, Performs, Electronics, and Specialty Shapes*; Noyes Publications: Park Ridge, NJ, 1988.
- Arpaç, E. *Chemistry-89, Chemistry and Chemical Engineering Symposium*; Kuşadası, İzmir, 1989.
- Arpaç, E.; Avşar, E. *Turk J Chem* 1997, 21, 420.
- Novak, B. M. *Adv Mater* 1993, 5, 422.
- Schmidt, H.; Rinw, G.; Nab, R.; Spor, D. *Mater Res Soc Symp Proc* 1988, 121, 743.
- Uhlmann, D. R.; Teowee, G.; Boulton, J. J. *Sol-Gel Sci Technol* 1997, 8, 17.
- Que, W.; Hu, X. *J Sol-Gel Sci Technol* 2003, 28, 319.
- Yang, L.; Saavedra, S. S.; Armstrong, N. R. *Anal Chem* 1994, 66, 1254.
- Yoshida, M.; Prasad, P. N. *Chem Mater* 1996, 8, 353.
- Schmidt, H.; Krug, H.; Kasemann, R.; Tiefensee, P. *Proc SPIE* 1991, 1590, 36.
- Sorek, Y.; Reisfeld, R.; Finkelstein, I.; Ruschin, S. *App Phys Lett* 1993, 63, 3256.
- Riberios, J. L.; Messaddeq, Y.; Goncalves, R.; Ferrari, M.; Montagna, M.; Aegerter, M. A. *Appl Phys Lett* 2000, 77, 3502.
- Cruzz, P. D.; Bergstresser, P. R. in *Photomedicine for Clinical Dermatologists*; Lim, H. W.; Soter, N. A., Eds.; Marcel Dekker: New York, 1992.
- Urbach, F. in *Biological Response to Ultraviolet-A Radiation*; Urbach, F., Ed.; Valdenmar Publishing: Overland Park, KS, 1992.
- Donatti, D. A.; Ruiz, A. I.; Moraes, F. G.; Vollet, D. R. *J. Sol-Gel Sci Technol* 2003, 28, 28.
- Ramanam, S. R.; Ganguli, D. *J Non-Cryst Solids* 1997, 212, 299.
- Jia, W.; Wang, Y.; Figueroa, I. R.; Liu, H. *Colloids Surf A* 2001, 179, 185.
- Fujita, K.; Tanaka, K.; Hirao, K.; Soga, N. *J Appl Phys* 1997, 81, 924.
- Kundu, D.; Mukherjee, R. *J Mater Sci Lett* 2003, 22, 1647.
- Schmidt, H. *J Non-Cryst Solids* 1994, 178, 302.
- Kasemann, R.; Schmidt, H.; Wintrich, E. *Mater Res Soc Symp Proc* 1994, 346, 915.
- Schmidt, H. K. *J Sol-Gel Technol* 1997, 8, 557.
- Phillip, G.; Schmidt, H. *J Non-Cryst Solids* 1984, 63, 283.
- Judeinstein, P.; Oliveira, P. W.; Krug, H.; Schmidt, H.; *Adv Mater Optics Electron* 1997, 7, 123.
- Kasemann, R.; Schmidt, H.; Arpac, E.; Gerhard, V.; *Ger. Pat. DE* 4338361 (1995).
- Menning, M.; Endres, K.; Schmitt, M.; Schmidt, H. *J Non-Cryst Solids* 1997, 218, 373.
15. Chu, L.; Daniels, M. W.; Francis, L. F. *Chem Mater* 1997, 9, 2577.
- Nass, R.; Arpac, E.; Glaubitt, W.; Schmidt, H. *J Non-Cryst Solids* 1999, 121, 370.
- Hoebbel, D.; Nacken, M.; Schmidt, H. *J. Sol-Gel Sci Technol* 2001, 21, 177.