Optica Applicata, Vol. XXIV, No. 3, 1994

Mesoporous silica glass – a substrate material for non-linear optics *

CH. KAPS

Fachhochschule Jena, Germany.

R. SCHUBERT

Friedrich-Schiller-Universität Jena, Germany.

The aim of the paper consists in the finding of a technology for generation of non-linear optical materials, composed of (vycor-) silica glass, semiconductor particles, precipitated inside the pores, and a polymer stuffing. As a result of investigation, solid composite samples characterized by an extensive relaxed order and a good chemical durability have been obtained. The evidence for sufficient optical transparency and selected non-linear optical properties is given.

1. Introduction

Integrated optical components of the communication equipment, accomplishing "active" operations like switching or controlling, must contain materials with non-linear optical properties. For instance, nanocrystalline semiconductor particles with a size-determined electronic band structure or organic dyes and polymers with conjugated π-bindings demonstrate such non-linear optical behaviour, expressed by an intensity-dependence of either the optical transparency or the refractive index ($\chi^{(3)}$-effect).

The development of an optical material of good mechanical and chemical stability, high performance and suitability for technical handling, as well as containing nanocrystals or dye molecules with the power of "active" operations, is a challenge to the materials science.

For generation of integrated optical active components, a considerable interest has been focused on the search for a material which unites the advantages of moderate charge for production of glass with the profitableness of these special optical properties of not very stable substances. Up to now, the glass companies offer the cut-off glass types, which are fabricated via an addition of small amounts of cadmium chalcogenides in the process of glass-melting at high temperatures (1300–1400 °C). However, the application of these glasses is strongly limited to the red-yellow spectral range, caused by the poor selection of the thermal stable crystals (CdS and CdSe, only).

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* This paper has been presented at the *Seminar on Alkali Silicate Glasses PGL'94*, held in Karpacz (Poland), June 6–10, 1994.

It is the aim of this paper to demonstrate some selected results from the preparation of optical composite materials by chemical deposition of related particles in porous vycor glasses under soft conditions near to room temperature, especially from the fabrication of convenient silica substrates with a network of mesopores (4–10 nm) for that purpose.

2. Generation on nanoporous silica glass – the vycor process

The so-called vycor technique for generation of high-silica glasses has been known since about 1944 [1]. The vycor process consists in the following procedure. First of all, a sodium boro-silicate glass is melted. In an annealing process, the prepared glass samples are separated in a sodium-borate phase and in a silica glass phase. Next, the net-like sodium borate phase will be extracted by mineral acids resulting in a porous, sponge-like silica glass. Finally, the highly dispersed silica glass can be collapsed to a bulk oxide glass at moderate temperatures near to 1000 °C.

Using such porous silica glasses for generation of a composite material, the sponge-like silica should meet all requirements of a substrate for controlled depositions of solid-state particles with tailored optical properties. Above all, a definite system of pores in the nanometer range, constancy of the sample mensuration and chemical stability are the important features for that application.

Corresponding to the aim of this paper, the generation of a highly transparent composite material for the non-linear optics requires the following three technological steps:

a) fabrication of a mesoporous silica glass,

b) deposition of suitable particles with definite non-linear optical properties in the mesopores of the silica substrate,

c) stuffing of the remaining volume of the pores by adapted organic polymers for a sufficient optical transparency and for chemical preservation.

3. Three-step fabrication technique for optical composite materials

3.1. Preparation of the mesoporous substrate glass

The data on the glass-forming region of the system $Na_2O-B_2O_3-SiO_2$, including the phase-separation range and a lot of technical applications of porous glasses, have been collected by JANOWSKY and HEYER [2]. Corresponding to the literature and our own experience, a glass composition with a molar B_2O_3/Na_2O ratio of about 3/1 permits a phase-separation and a sodium-borate elution process with a minimum mechanical stress in the porous glass samples. Regarding the intended "non-stop" two-phase morphology of the separated glass, the molar glass composition denoted $V6\{(Na_2O)_7(B_2O_3)_{23}(SiO_2)_{70}\}$ was chosen as starting material in all investigations.

In spite of the complex feedback of annealing, phase-extraction and of the drying procedure on the material properties, the systematic variation of annealing parameters (temperature 510–550 °C, duration 4–100 hours) and an additional modi-

fication of the basis glass by an admixture of Al_2O_3 up to 3 mol% allowed one to find out conditions for nearly stressless mesoporous glass samples.

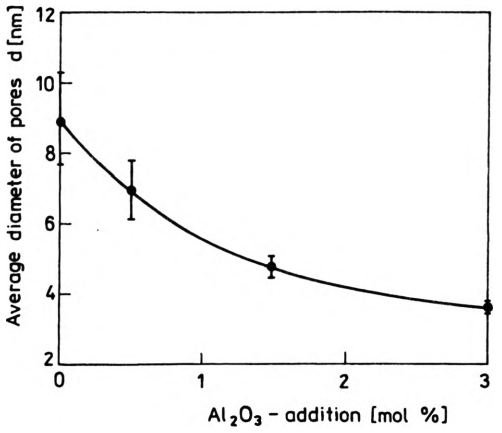

Fig. 1. Diameter of pores depending on Al_2O_3-additions in the basis glass, estimated in mesoporous silica substrate glasses

Figure 1 demonstrates average pore diameters, calculated from an N_2-desorption isotherm (BET measuring system: PMI sorptometer 4800), depending on Al_2O_3-addition in the basis glass (annealing: 530 °C, 16 h; extraction: 3 M HCl, 3MNH_4Cl, 90 °C, 16 h and 3 times distilled water 100 °C, 0.5 h). This result shows that it is possible to control the pore diameter by the Al_2O_3-addition down to values a little bit smaller than 4 nm. The decrease of the value of scattering, observed with diminution of the pore diameter, corresponds to a tendency towards phase separation in glasses, caused by a remarkable increase of the glass viscosity.

Moreover, we could find a correlation between the given Al_2O_3-addition and qualified annealing conditions for either stress-poor or well-relaxed mesoporous

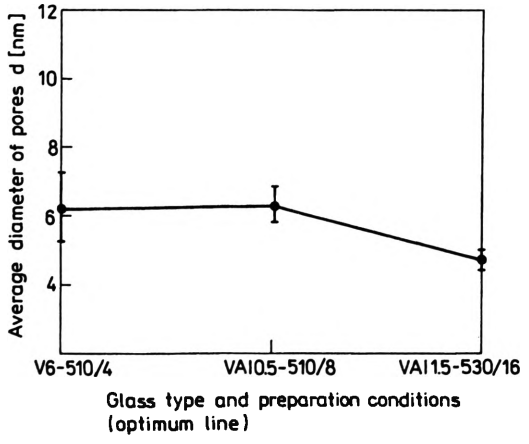

Fig. 2. Diameter of pores in different mesoporous silica substrate glasses after optimum annealing

glass samples. For every Al_2O_3-content, there exists a corresponding optimum temperature-duration pair of annealing parameters. These pairs and the resulting change of pore diameter, estimated in the so-called optimum line of preparation conditions, are represented in Fig. 2. The numbers provide the following information: glass V6 with Al_2O_3-addition – annealing temperature/annealing time.

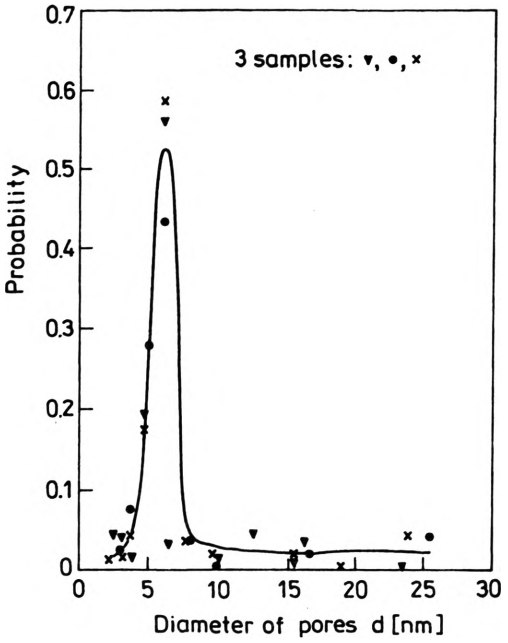

Fig. 3. Distribution of diameters of pores in a mesoporous silica glass, prepared from the basis glass V6, annealing conditions 510 °C, 4 h; extraction (3 M HCl, 3 M NH_4Cl)-solution, 90 °C, 16 h; distilled H_2O, 100 °C, 3 × 0.5 h. Average diameter of pores: 6.0 ± 1.0 nm

Figure 3 shows a small distribution of the diameters of pores, estimated on the basis of N_2-desorption measurements performed on the three glass examples (V6 – 510/4). The mean value of 6.0 ± 1.0 nm corresponds to a BET surface of about 95 m^2/g and a volume of pores of about 0.15 cm^3/g.

Figures **4a, b** and **c** permit a representative insight into the network-like morphology of pores in the glass substrates. The micrographs are taken from thin films of the mesoporous glass by high-resolution electron microscopy (HREM, JEM 100C). The films were prepared through a grinding process (down to 50 μm) and a thinning procedure by ion bombardment (down to some 10 nm) for a direct transmission. Figure **4a** verifies a quasi-homogeneous, but porous material over an extention of more than 1.5 μm. In Figure **4b**, the connectivity of the pore system is evident. A mean diameter of a little bit less than 10 nm can be estimated from Fig. **4c**. However, branching points with larger extensions are observable, too. A small modification during the preparation of the films (ion impingement) could not be excluded.

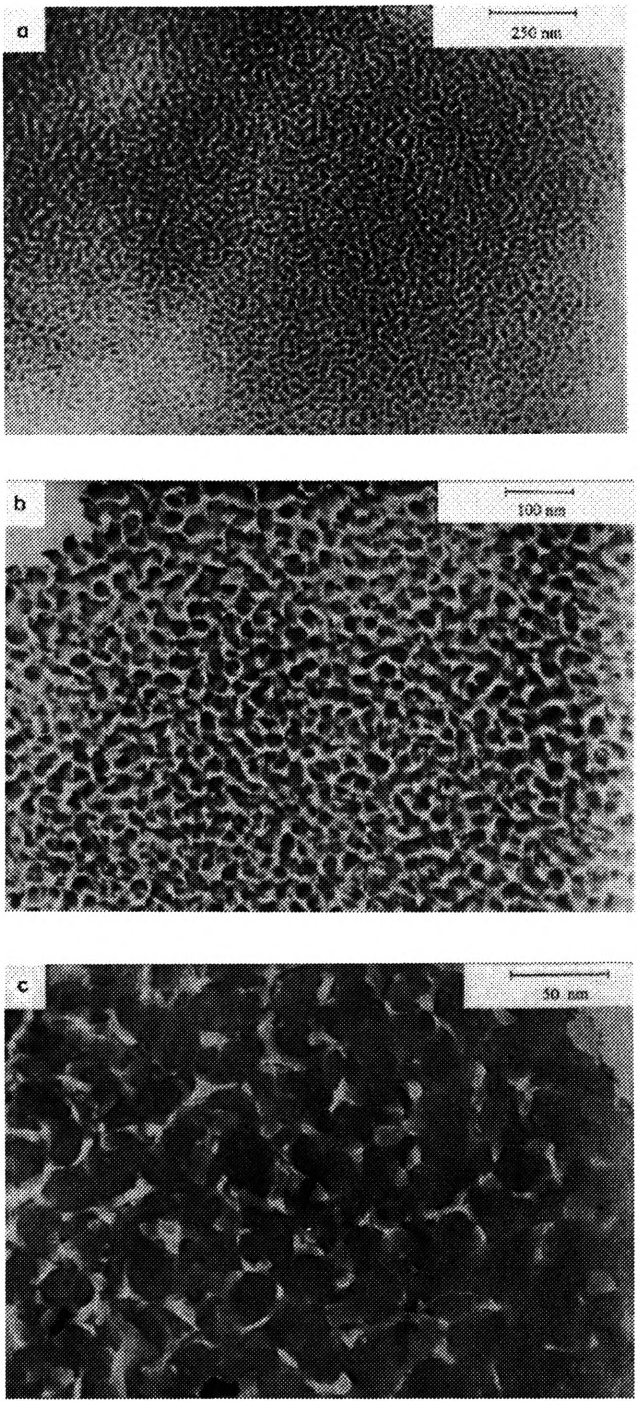

Fig. 4 (a, b, c). HREM electron micrographs of thin films of mesoporous silica prepared from the basis glass V6 (direct transmission); HREM conditions: $U_b = 100$ kV, $\lambda_{corr} = 3.7$ nm

3.2. Chemical deposition of different nanocrystals in the mesopores

The porous glass substrates enable precipitation of a lot of semiconductor crystals by penetration with several solutions and gases for intended reactions under "soft chemistry" conditions near to room temperature. For instance, there is a simple preparation procedure for introduction of chalcogenides. Three examples are expressed by Eqs. (1)–(3). The reactions take place in the presence of traces of water from the aqueous salt solutions (chlorides), introduced, first of all, after a trial process at 80 °C (2 h):

$$CdCl_2(\text{solid}) + H_2S(\text{gaseous}) \rightarrow CdS(\text{solid}) + 2HCl, \quad (1)$$

$$2SbCl_3(\text{solid}) + 3H_2Se(\text{gaseous}) \rightarrow Sb_2Se_3(\text{solid}) + 6HCl, \quad (2)$$

$$HgCl_2(\text{solid}) + H_2S(\text{gaseous}) \rightarrow HgS(\text{solid}) + 2HCl. \quad (3)$$

In every case, the HCl is a volatile by-product. Further on, thermal decomposition of special chalcogeno-complexes (for instance, thio-urea complexes) can also be used for deposition of nano-crystals [3]. LONG and BOLELLI [4], [5] carried out photo-decompositions of acid–base complexes for such a purpose.

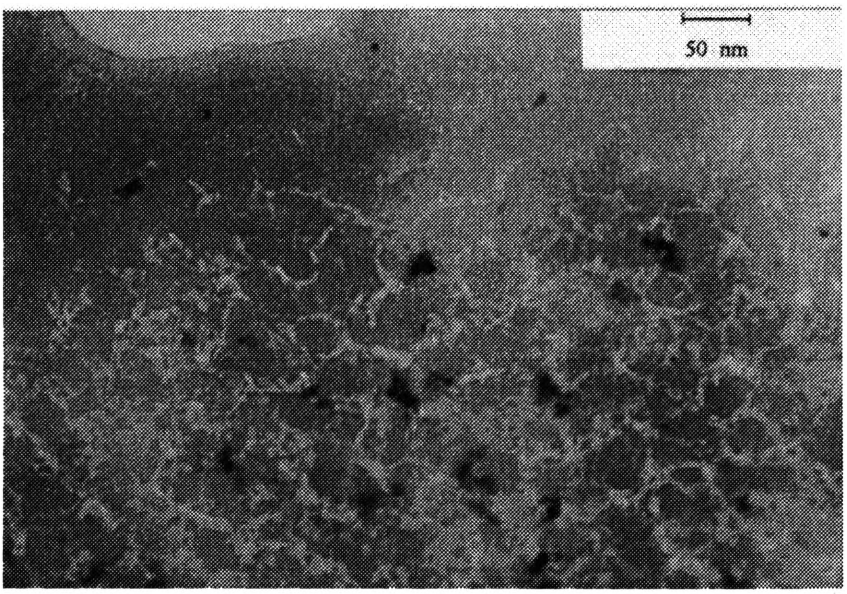

Fig. 5. HREM electron micrograph of a thin film of mesoporous silica glass with precipitated CdS particles (black areas)

In Figure 5, the electron-micrograph shows the CdS particles precipitated in a mesoporous silica glass in reaction corresponding to Eq. (1). The large contrast is due to electron density being four times as high under conditions of direct transmission. It is obvious that the particles are dominantly precipitated in branching positions of the pores.

3.3. Optical refinement

In the third technological step, the pores with the deposited semiconductor particles are filled due to polymerization process of special monomers (MAOPTS or TEGMA, for instance). This procedure is necessary for sufficient optical transparency, which is slightly reduced in the mesoporous glasses by light scattering effects on the interphases between the glass material and the air-filled pores. It could be found that previous hydrophobation of the pore inside by hexamethyl-disilacane vapour is a useful tool for an efficient joint between the glass and the in-situ forming polymer material.

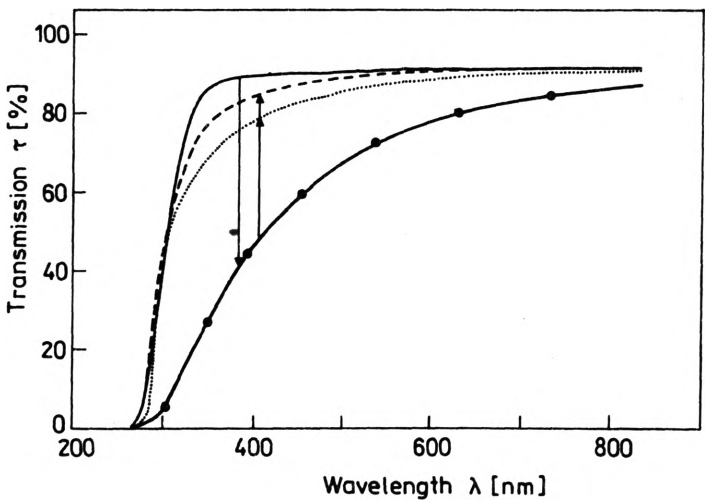

Fig. 6. Transmission spectra of substrate glasses in different stages of their generation (thickness of sample 2 mm). —— phase-separated basis glass, —●— mesoporous silica glass, open pores, ... mesoporous silica glass, filled with MAOPTS, – – – mesoporous silica glass, filled with TEGMA

Figure 6 demonstrates the effect of stuffing the remaining volume of the pores by means of changes in the UV-VIS transmission spectra at different preparation states of glass samples. In the visible range, the optical transmittance of MAOPTS-filled mesoporous silica glass reaches approximately the values of the unleached starting material.

4. Selected optical properties of the composite materials

Figure 7 gives an insight into diversity of positions of the optiacl absorption edges over the visible range of the spectrum, realized by introduction of different heavy metal sulfides as semiconductor particles. Only in a few cases, the position of the observed optical absorption edges corresponds to electronic band gap of the bulk semiconductor. It cannot be excluded that elementary mercury or lead is also formed in a small extent.

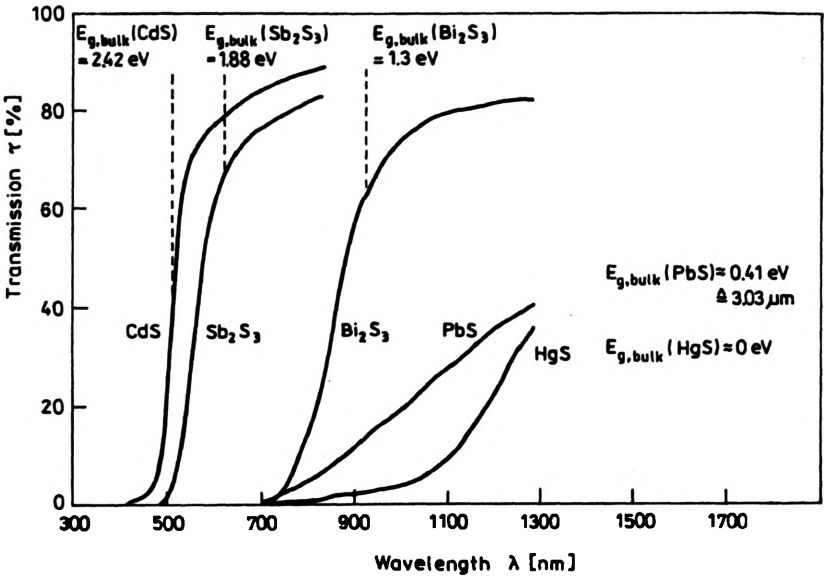

Fig. 7. Transmission spectra of mesoporous silica substrate glasses with different chalcogenide particles (precipitation). Sulphides (0.1 M $CdCl_2$; 0.1 M $SbCl_3$ in 3M HCl; 0.1 M $BiONO_3$ in 3 M HCl; 0.1 M $HgCl_2$; 0.1 M $Pb(CH_3COO)_2$ and wet H_2S-gas). Thickness of the samples 2 mm

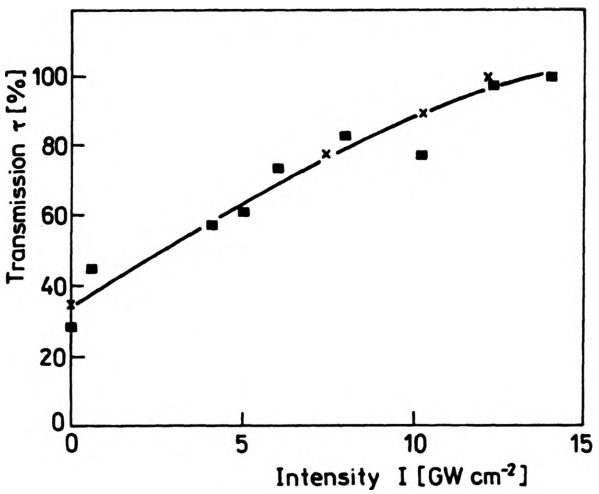

Fig. 8. Dependence between transmission and intensity. Thickness of sample 0. 3 mm. ■ — composite material with CdSe particles. corresponding to Eqs. (1) and (2), × — commercial cut-off glass OR 3. Wavelength $\lambda = 165$ nm

ALTSCHULER *et al.* [6] observed a systematic change of the refractive index of $\Delta n > 2 \times 10^{-2}$ over a depth of 2.5 mm in mesoporous glasses, characterized by a maximum at the middle of the glass plates. This fact was interpreted as a result of

the systematic change in the local elution conditions during the simultaneous extraction of the sodium-borate phase from both sides. We measured the refractive index profile on polished cuts of mesoporous (6 nm pores) glass plates, filled by polymers of TEGMA, by refracted-near-filed method [7]. For both usual two-side as well as one-side leached samples, the measured refractive index n of the composite material amounts to 1.455 ± 0.0025. A systematic change with an index maximum in the middle was not detectable. Though we could see sometimes an relict plane in the middle of mesoporous glass samples, if these resulted from a two-side elution.

Finally, Figure 8 verifies the increase of the optical transmittance of a representative composite material, prepared in the three-step fabrication, as described above. It is evident that transparency of the selected CdSe-containing composite glass plate can be enlarged by a factor of more than 2 under the given experimental conditions. The increase is comparable to the values of commercial cut-off glass OR3 (Schott Glass works).

5. Summary

Resuming, it can be stated that the prepared composite glasses, based on mesoporous silica via vycor-process, offer a useful material with nonlinear optical properties. Convenient fabrication parameters could be shown for nearly stressless samples with optical quality. The "soft chemistry" conditions of the precipitation of different semiconductor particles permit applications in the whole range of the visible spectrum.

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Received August 5, 1994