



CONGRESO INTERNACIONAL DEL VIDRIO  
INTERNATIONAL CONGRESS ON GLASS  
INTERNATIONALER GLASKONGRESS  
CONGRÈS INTERNATIONAL DU VERRE

## **VOL. 1**

**Invited lectures  
Conferences invitées  
Gastvorträge**

# SYNTHESIS OF ORGANICALLY MODIFIED CLASSES BY SOL-GEL TECHNIQUES

H. SCHMIDT

Institut für Neue Materialien, Saarbrücken, Germany

## ABSTRACT

Sol-gel derived inorganic-organic composites can be prepared in homogeneities sufficient for optical applications. Therefore, it is necessary to control structure formation, especially with respect to the distribution or aggregation of inorganic network forming units and organics. Inorganic components can be kept on a nano level by growth control using stabilizers interacting with the surface of colloidal particles formed by sol-gel or precipitation reactions. Thus, colloidal particles  $< 10$  nm can be prepared and incorporated into inorganic-organic matrices to form transparent films on glass surfaces and having interesting optical properties. Semiconductor quantum dots as CdS, CdS/PbS or metals have been used.  $ZrO_2$  was used for refractive index adaption and organic ligands to photopolymerize the films. Photopolymerization was also used for patterning by laser writing, maskaligner techniques or embossing. Other organics like fluorine containing groupings have been used to create low surface free energy layers to reduce dust adsorption on the surface.  $\chi^3$  values have been determined to be in the range of  $10^{-9}$  esu and optical losses in planar waveguides are less than  $1$  dB/cm.

## INTRODUCTION

ORMOCERS (organically modified ceramics) are composite materials based on sol-gel derived inorganic units and organic groupings or organic polymeric chains. Due to the large number of parameters it is possible to synthesize numerous variations of different materials. The inorganic units of ORMOCERS can be synthesized by conventional sol-gel techniques. Starting with alkoxides undergoing a hydrolysis and condensation reaction, inorganic particulate polymeric sols can be obtained in the case of  $SiO_2$  (1). In the case of  $TiO_2$ ,  $ZrO_2$ ,  $Al_2O_3$  and numerous other oxides, however, as a rule, particulate sols are obtained. For optical applications light scattering has to be kept as low as possible. Therefore, the particle size should not exceed the lower nano range and the particle growth has to be controlled very thoroughly.

Organics can be introduced by various means, as described in detail elsewhere (2,3). The use of organosilanes of the type  $R'_nSi(OR)_{4-n}$  with  $n = 1,2$  allows to build in organic groups through a stable Si-C bond. For direct connection of organics to oxides of other elements as Ti, Zr, Al, Cu or Ag other links have to be provided, e.g.  $\beta$ -diketonates, carboxylates or ammine complexes (4). As organic ligands, a variety of groupings can be used, like aliphatic groupings, aromatic groupings, functional groupings or polymerizable groupings. Thus, a large variety of possibilities exists to synthesize materials. In this paper various examples are given which demonstrate the exploitation of these possibilities to develop materials useful for applications in connection with glass or optics.

#### CONTROL OF HOMOGENEITY

Glasses synthesized by sol-gel techniques do not necessarily have to be of high transparency in the gel state. During a temperature step at  $T \geq T_g$ , lacking homogeneity can be reestablished by diffusion or viscous flow processes in cases where the sol-gel synthesis has led to phase separation (e.g. pore formation). If organics are included, the temperature level of an after gelation treatment has to be below the decomposition temperature of the organic components and varies between 120 °C for very temperature sensitive materials like amines and 500 °C for high temperature resistant polymers or some aromatic groupings. This means, that homogeneity, in general, cannot be reestablished by temperature treatments, but has to be produced by synthesis control, and the final structure of the composite is already designed by the synthesis step, as schematically shown in Figure 1.

As a consequence of different reaction rates between the different units during the sol-gel synthesis step (hydrolysis and condensation of alkoxides), it is necessary to develop methods to avoid phase separation or to keep it at least on a nano range. Methods therefore, have been described by Yoldas (5) and Schmidt (6). Both authors suggest to create active species to react with counterparts either with high or low reactivities to form links on a molecular level and avoid phase separation (e.g. (1)).

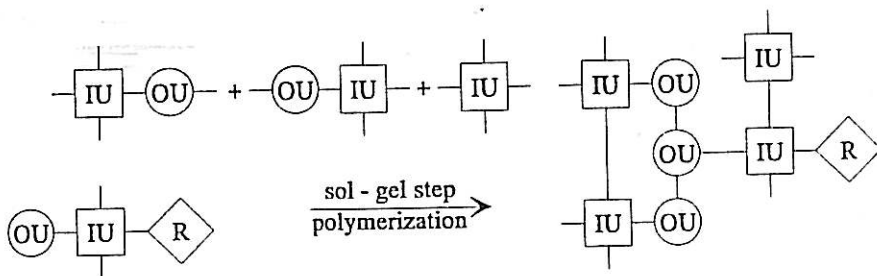
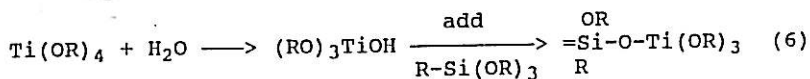
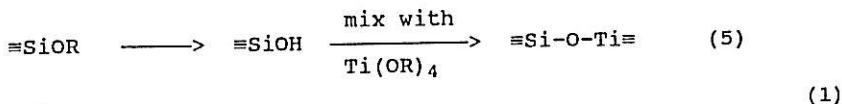


Figure 1. Schematics of structure formation of inorganic-organic composites: IU = inorganic unit e.g. alkoxide; OU = organic polymerizable unit; R = organofunctional unit.

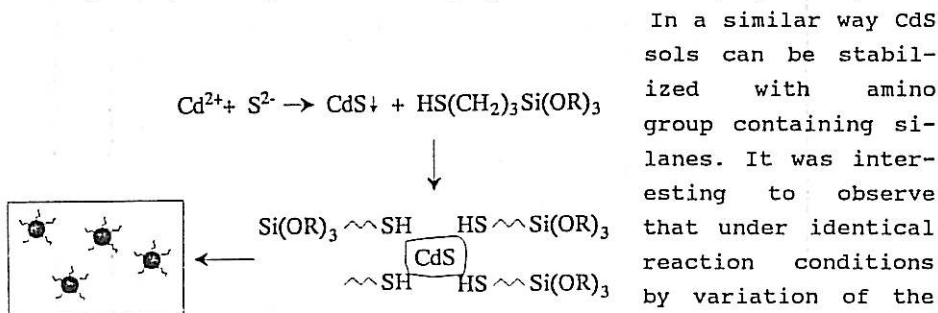


In both cases, homogeneous products are obtained. In the case of (5) the proposed mechanism is doubtful, since no Ti-O-Si bond could be found. In (6), no precipitation of  $\text{TiO}_2$  is observed after the reaction, indicating the incorporation of Ti into the network to be formed by chemical bonds.

Another means of controlling particle size is the control of the particle to environment interface by use of surface active ligands. In (7) it was shown, that only by variation of a complexing ligand the  $\text{ZrO}_2$  particle size could be changed from 100 nm to 3  $\mu\text{m}$ . Similar results could be obtained by Sanchez (4). In (8) it was shown, that complexing of Zr alkoxides with methacrylic acids (MAS) can be used to keep particle sizes of the hydrolyzed product below 5 nm which is sufficient for optical applications. In this case, the  $\text{ZrO}_2$  content can be used for adapting the refractive index of a system consisting of  $\text{ZrO}_2$  linked to MAS and  $\gamma$ -methacryloxypropyl triethoxysilane (MPTS) as a system to be

polymerized with MAS. It could be shown, that below a ratio of MAS to  $Zr(OR)_4 \leq 0.8$  the particle size increases rapidly and below 0.75 precipitation takes place. But, independent on  $H_2O$  addition, the Zr to MAS bond remains unaffected.

In similar ways, particle size tailoring can be carried out with other systems like semiconducting quantum dots, based on semiconducting oxides or sulfides (ZnO, CdS, PbS) or metals, becoming semiconducting, too, if particle sizes become small enough (9,10). It could be shown, that by proper choice of ligands CdS can be stabilized in form of 2 nm sized colloids and subsequently incorporated into polymeric matrices (Figure 2.).

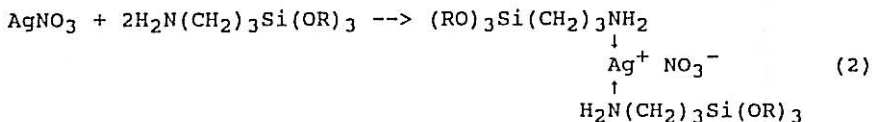


In a similar way CdS sols can be stabilized with amino group containing silanes. It was interesting to observe that under identical reaction conditions by variation of the ligand type linked to the silane the optical spectra defined by the band gap energy can be varied

Figure 2. Scheme of the formation of a CdS quantum dot composite

As ligands  $NH_2CH_2CH_2NH(CH_2)_3Si(OR)_3$ ,  $NH_2(CH_2)_3Si(OR)_3$  and  $HS(CH_2)_3Si(OR)_3$  were used. The results are shown in Figure 3.

$\chi^3$  effects have been measured on PbS coated CdS quantum dots. These materials show  $\chi^3$  effects of about  $10^{-9}$  esu. Due to the small particle the materials are highly transparent. Quantum dot formation can be obtained by use of amino grouping containing ligands from Ag or Au salts, too. In this case the formation of ammine complexes can be postulated according to eq. (2).



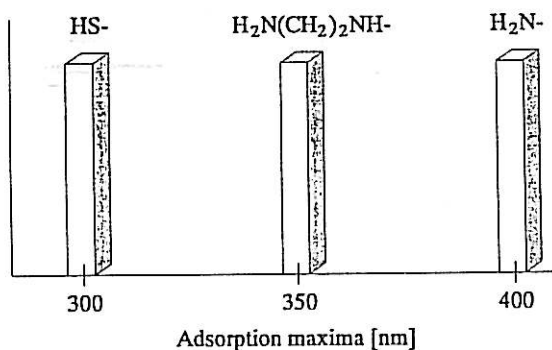


Figure 3. Absorption maxima of CdS quantum dot systems depending on ligand type; particle size around 2 nm (after 10)

into nano scaled Ag halides, showing a reversible photochromic behavior.

Another type of problem for homogeneity or phase separation control arises when the different components strongly differ in their polarity, so that phase separation occurs thermodynamically driven by surface free energy. An example is the synthesis of glass coatings with fluorinated groups showing a low surface free energy, generating the effect of a dust repelling surface behavior. In order to avoid phase separation during the synthesis reactions, the precursors must not be mixed in the initial step but have to be added in an optimized sequence, as shown in (11, 12). The system is synthesized from MTPS, Zr propoxide, MAS and a fluorine containing alkylalkoxysilane (1H,1H,2H,2H-perfluorooctyl triethoxy silane = FTS). Mixing of the precursors and addition of water leads to a cloudy system, separated into a fluorine rich and a fluorine-free phase. In Figure 4, the "homogeneous" and the "heterogeneous" route are compared in a flow diagramme.

The interpretation of the differences probably may be very complex.  $^{29}\text{Si}$  NMR investigations, however, show that Zr/MAS acts as a condensation catalyst on MTPS as well as on FTS. But a homogeneous incorporation of FTS into MTPS/Zr/MAS only takes place if sufficient monomeric ( $T_1$ ) silanols are present after hydrolysis period of sufficient length. The experimental proof for this

As shown in (10), it is possible to form Ag colloids in the nano range by photo-initiated nucleation. The optical spectra of these colloids indicate a relatively narrow particle size distribution as colloidal solutions. The system can be used to be incorporated into sol-gel materials and transformed

hypothesis is given in (8) by determination of hydrolysis and condensation kinetics.

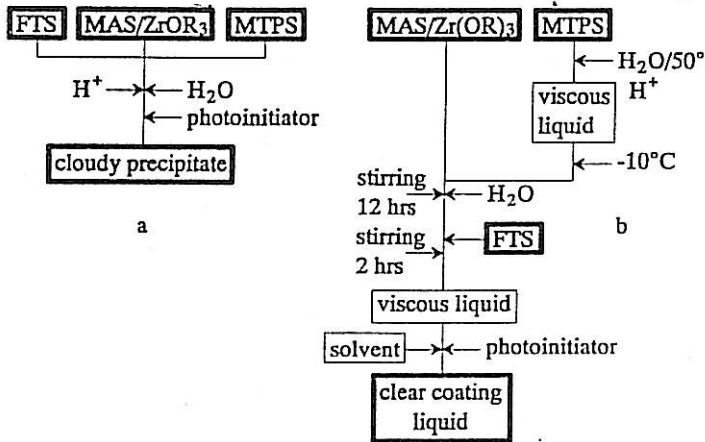


Figure 4. Comparison of two synthesis routes for fluorine modified ORMOCERS; a: one step (heterogeneous); b: multi step (homogeneous)

The methacryloxy group can be polymerized together with the MAS to build up additional polymeric chains (13). The polymerization yield is surprisingly high despite the rigidity of the system ( $\geq 80\%$  estimated by IR analysis). This curing step can be used for large area film coatings by continuous methods, but also for micropatterning techniques as described later. During the photocuring process, the "synthesized" homogeneity, as a rule, does not change due to the rigid inorganic network.

The described methods show that even in complex systems the chemistry provides means for synthesizing inorganic-organic composites with sufficient homogeneity to be used for optical applications.

#### MATERIAL DEVELOPMENTS

The described chemical principles can be used for the synthesis of materials. Two main groups of materials have been developed: passive and active optical materials. Passive materials can be used as coatings on glass surfaces with special properties or passive wave guides. Active materials comprise materials with nonlinear optical properties.

The synthesis principle described in the previous chapter for transparent fluorine containing coating systems has led to several systems to be used as glass coatings with low surface

energy (11). The surface free energy has been determined to be in the range of polytetrafluoroethylene, but the scratch resistance of the system is in the range of well-known ORMOCER scratch protecting systems for eye glass coatings (6). A very interesting property of the system is the fact, that a selfalignment during the coating and curing step takes place leading to a good adhesion to the glass surface and an enrichment of the energy lowering fluorine component in the surface. A model, therefore is shown in Figure 5.

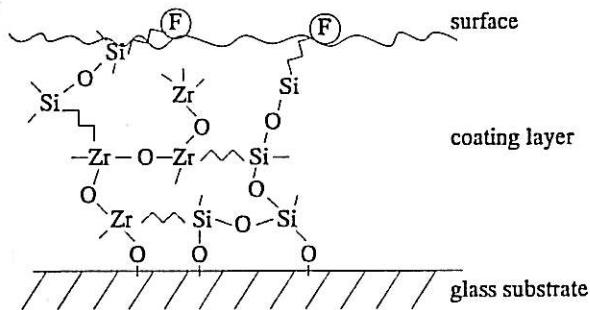


Figure 5. Model for the alignment of a fluorine containing highly transparent ORMOCER coating;  
 : organic chains; F: fluoroethyl grouping

The fluorine enrichment could be proved by ESCA, the condensation of the fluorine group carrying silane into the network by  $^{29}\text{Si}$  NMR. This alignment is the prerequisite for the perfect adhesion to glass surfaces and for the possibility to reduce the fluorine compound to about 1.7 mole-%.

The  $\text{ZrO}_2$  nanoparticles formed by hydrolysis and condensation of the Zr/MAS complex and detected by photon correlation spectroscopy (particle size of about 3 - 8 nm) are considered to be responsible for the hardness of the coating.

The  $\text{ZrO}_2$  content also influences the refractive index of such systems. This can be used if waveguide applications are envisaged. As shown in (13, 14) the optical loss of planar films is less than 1 dB/cm. The variation of  $n$  can be used to choose the proper range compared to a substrate or a cladding. Figure 6 shows the change of  $n$  depending on the Zr content in a system Zr/MAS/MTPS.  $n$  was measured for bulk materials only. But it can be seen from remarkable density differences between films and bulk, that the  $n$  of the films should be lower, too. As already



mentioned, the polymerizable methacryloxy groups can be used for micropatterning.

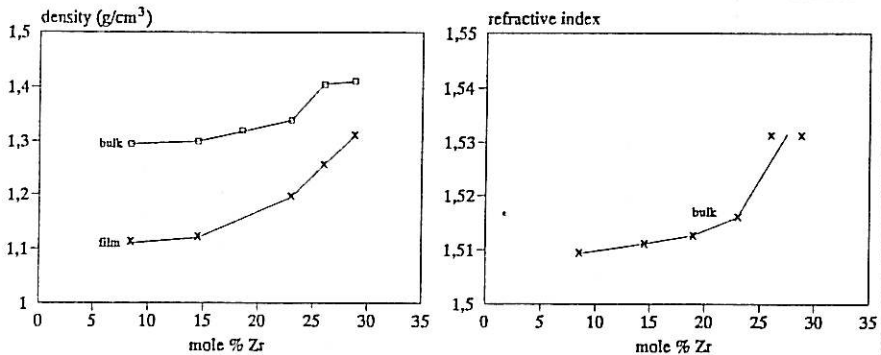
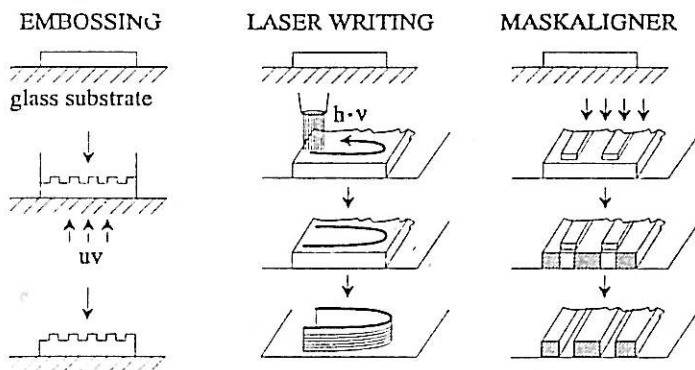


Figure 6. Refractive index  $n$  and densities of ORMO CER film and bulk materials (15)

In Figure 7, the methods used for ORMO CER micropatterning are summarized. All three methods, direct laser writing, photocuring assisted embossing as well as the maskaligner technique are based on the photocuring reaction of polymerizable groups.

ORMO CER FILMS  
(precoated)



Patterns produced by the three methods are compared in Figure 8. Maskaligner technique and laser writing require a development step. Not irradiated areas can be dissolved by a short treatment with acetone.

Figure 7. Scheme of three ORMO CER micropatterning techniques

Another technique recently developed is holography (16). In Figure 9, the holographic patterns generated by wavemixing on an ORMOCER surface are shown.

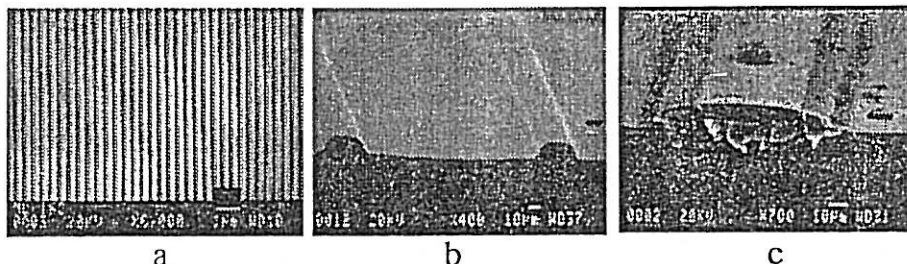


Figure 8. Patterns produced by embossing (a; bar = 1  $\mu\text{m}$ ); maskaligner technique (b; bar = 10  $\mu\text{m}$ ); direct laser writing (c; bar = 10  $\mu\text{m}$ ).

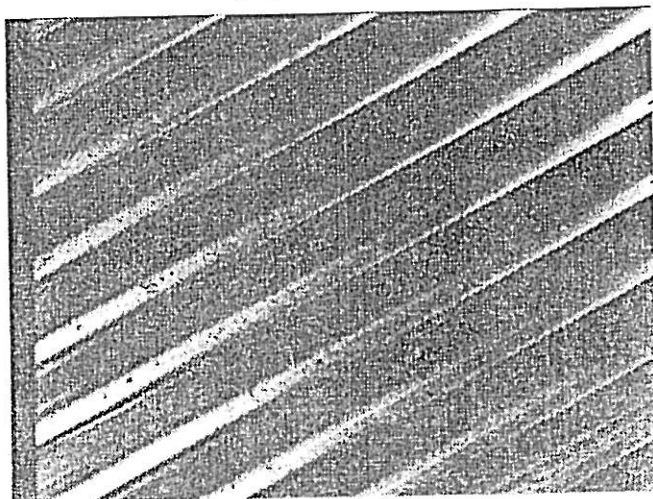


Figure 9. Holographic pattern produced by two wave mixing interferences as light source for polymerization

The aspect ratio is surprisingly high and the diffraction effectiveness of fabricated grids are three orders of magnitude higher compared to conventional grids.

The materials described so far can be considered as passive materials. The incorporation of active components can be carried out in various ways. Push pull molecules (dyes) already have been incorporated and films have been cured during poling (17). First

results show a significant  $\chi^2$  effect.  $\chi^3$  effects have been measured through incorporation of CdS quantum dots synthesized by the methods described in chapter 2 and in detail in (9, 10). In Figure 10, the spectra of CdS colloids are shown and it can be seen, that the type of ligand strongly influences the absorption

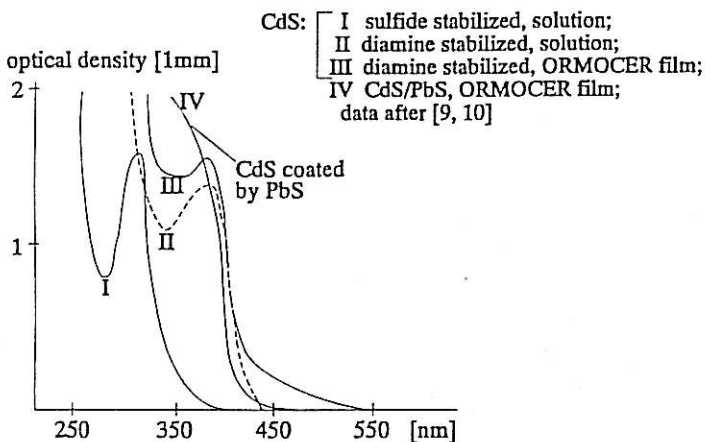


Figure 10. Adsorption spectra of quantum dot containing colloidal solutions and quantum dot containing ORMOCER films

spectrum of the quantum dots.

But it also shows, by comparing curve II and III, that the incorporation of the ligand stabilized quantum dots into ORMOCER films by sol-gel reactions and by subsequent photo polymerization of added MTPS does not change the spectrum significantly. This can be interpreted by the effect of the ligand,

which shields the influence of the changing matrix on the band gap energy. In a similar way, metal colloids can be generated from proper precursors. In (18) it is shown, that transparent gold colloid containing ORMOCER films can be prepared from gold ammine complexes by photoinitiated nucleation during the photocuring of the film. Metal quantum dots are interesting candidates for  $\chi^3$  effects, too.

#### OUTLOOK

Nanocomposite systems of the ORMOCER type prepared by the sol-gel process can provide an interesting base for passive and active optical materials. This is based on some important

properties of the system. First, they can be fabricated in a variety of compositions and the heterogeneity can be kept on a nano level. Second, due to the incorporation of polymerizable groupings and viscosity control, patterning techniques can be applied similar to polymers which opens the possibility of low cost processing. Third, a wide variety of active components can be integrated, creating special properties like low surface free energies or nonlinear optical effects. In order to exploit the described potential, it is necessary to put emphasis on the relation between synthesis, structures and physical properties. This is especially true for the quantum dot composites, which seem to be a hopeful new material for a variety of optical application.

#### ACKNOWLEDGEMENT

The author wants to thank Dr. H. Krug and Dr. L. Spanhel for their helpful discussion and the Minister of Research and Culture of the State of Saarland for his financial support.

#### REFERENCES

- (1) SCHERER, G. W., BRINKER, C. J.: The Physics and Chemistry of Sol-Gel Processing. Academic Press, New York - Boston, 1990
- (2) SCHMIDT, H.: In: Proceedings of the International Symposium on Molecular Level Designing of Ceramics; Eds.: Team of the NEDO International Joint Research Program, Nagoya, 1991, 59.
- (3) SCHMIDT, H.: In: MACKENZIE J. D. et al (Eds.) Chemical Processing of Advanced Materials. John Wiley & Sons, in print.
- (4) SANCHEZ, C., LIVAGE, J.: In: Proc. Eurogel '91, June 1991, Saarbrücken, North - Holland Publishers, in print.
- (5) YOLDAS, B. E., J. Mater. Sci. 12 (1977) 1203.
- (6) SCHMIDT, H., SEIFERLING, B.: Mat. Res. Soc. Symp. Proc. 73 (1986) 739.
- (7) RINN, G., SCHMIDT, H.: In: Ceramic Powder Processing Science, Eds.: Hausner, H., Messing, G. L., Hirano, S., Deutsche Keramische Gesellschaft e.V., Köln, 1989, 69.
- (8) SCHMIDT, H., KRUG, H., KASEMANN, R., MERL, N., GERHARD, V., TIEFENSEE, F., BRÜCK, S.: In: Proc. Int. Conf. "From Galileo's "occhialino" to optoelectronics: frontiers of optical systems and materials, Padova, June 1992, in print.
- (9) SPANHEL, L., ARPAC, E., SCHMIDT, H.: In: Proc. VI. Int. Workshop on Glasses and Ceramics from Gels, October 1991, Sevilla/Spain, J. Non-Cryst. Solids, in print.
- (10) SPANHEL, L., SCHMIDT, H., UHRIG, A., KLINGSHIRN, C.: In: Proc. MRS Spring Meeting, San Francisco, April 1992, Mat. Res. Soc. Sym. Proc., in print.
- (11) KASEMANN, R., BRÜCK, S., SCHMIDT, H.: In: Proc. Eurogel '91; Eds.: S. Vilminot, H. Schmidt, R. Naß. North-Holland Publishers, Amsterdam, in print.