Optica Applicata, Vol. XXXI, No. 1, 2001

Influence of the temperature of preparation process on refractive index of sol-gel matrices

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The preparation of sol-gel materials in the form of bulks and thin films at different temperatures is described. The procedure involves running the reaction at 50 °C and 90 °C in an open vessel. Such an approach enables acceleration of hydrolysis and condensation reactions. This procedure yelds crack-free sol-gel glasses. The changes in refractive index of sol-gel materials were studied by using Pulfrich refractometer. The experimental data indicates significant differences in the optical properties of sol-gel glasses, depending on the temperature during the preparation. The samples show normal dispersion, whereas a higher refractive index was stated for films prepared at a higher temperature.

1. Introduction

Sol-gel glass-like materials are prepared by the acid or base hydrolysis of silicate precursors (*e.g.*, tetraethylortosilicate TEOS) mixed with water and catalyst and stirred for a few hours. This process usually performed at room temperature leads to hydrolysis of the Si–O–R bonds. The longer the hydrolysis, the larger the amount of Si–OR groups that undergoes hydrolysis to the Si–OH form. The chemistry of the sol-gel process comprises several steps that are well described in the literature [1].

After the hydrolysis the pH of the obtained homogenous hydrolysate in gradually brought up to ca. 6 by means of a diluted ammonia solution. This results in quick (several minutes) gelation and formation of the "wet" gel. Subsequently, the obtained gel can be aged for a few days in water or ammonia solution. This process reduces the mechanical stress during the drying of the gel and prevents, to some extent, the risk of the sample cracking. However, the cracking of sol-gel materials produced by means of alkoxides hydrolysis, due to large shrinkage during the drying step, is a serious problem. The shrinkage-fracture syndrome is particularly significant in films. The drying control chemical additives (DCCA) such as surfactants or formamide are employed to prevent fracturing during the drying step [2]. HARUVY and WEBBER [3] described the preparation of sol-gel films at higher temperatures. The key element in the method proposed above is direct reaction of alkoxysilane monomers with alcohol (or water) at 50–90 °C.

The samples investigated were prepared at 50 °C and 90 °C in an open vessel. This procedure accelerates hydrolysis and condensation. Influence of temperature on the sol-gel characteristic can appear in refractive index changes. In order to improve the optical parameters of sol-gel glasses it is desirable to obtain the higher value of refractove index *n*. It is generally known that the typical glasses used in ophthalmology have the refractive index about $n = 1.5$. It is proposed in this paper that hydrolysis should be performed at an elevated temperature in order to obtain a higher refractive index of the matrices being prepared.

2. Sol-gel materials

Two different types of the sol-gel matrices: bulk and thin film, were examined. The bulks were prepared from precursors in the following proportions: 24 ml H_2O : 19 ml TEOS : 1 drop of 36% HCl (TEOS – Tetraethoxysilan 98% from Aldrich). The thin films were obtained from 85 ml of ethyl alcohol, 10 ml of TEOS, 3.2 ml of Triton X-100 (Aldrich), 2 drops of 36% HCl. All samples were dried for two weeks. The synthesis of the sol-gel was performed using the apparatus presented in Fig. 1.

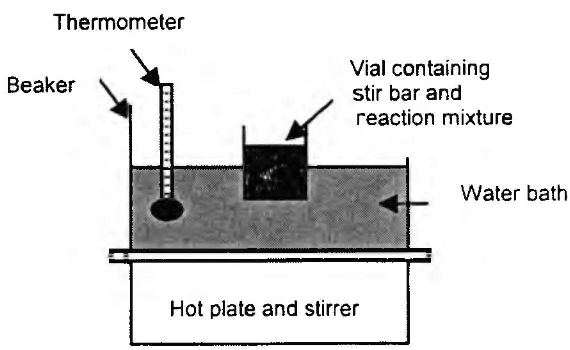

Fig. 1. Experimental apparatus used for the sol-gel production at different temperatures

A clean vial with magnetic stir bar was filled with the following substrates: TEOS, ethyl alcohol, triton and 2 drops of HCl. A water bath stirrer-hot plate assembly retained the preset temperatures of 50 °C or 90 °C. The reaction mixture was stirred at a speed of 200/min, thus to avoid splashing during the vigorous hydrolysis. For acid-catalysed gels, 5 ml of alcohol was added after 20 min and then after 50 minutes 10 ml of alcohol was added to regain initial volume. When the stir bar movement slowed down, the syrupy liquid was quickly removed from the bath and poured into the mould. After that the samples were dried at room temperature for two weeks. The final products were obtained in the form of 5 mm thick xerogel cylinders with a diameter of 20 mm. The same shape was ensured for both types of matrices – prepared both as films and bulks.

3. Refractive index measurements

The measurements of refractive indices were performed by means of computer aided Pulfrich refractometer. The samples were correspondingly prepared, so that the sol-gel matrices were rectangular in shape with the dimensions $10 \times 10 \times 5$ mm. Both sides of the rectangle were polished prior to goniometric measurements. The angle between these two polished sides should be equal to $90° \pm 10'$. The samples were placed on the refractometer prism with known refractive index (Fig. 2).

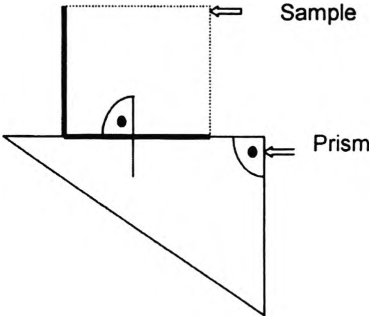

Fig. 2. Measuring method used in the Pulfrich refractometer

A visual inspection of the samples revealed the fact that the bulk type matrix was less transparent than the film type one. The films produced at 90 °C were more transparent than those hydrolysed at 50 °C. The same behaviour was observed for bulks. However, in this case, we are not able to polish the samples, which are produced at 50 °C and 90 °C, since they broke easily during polishing. This can be the result of the chemical content, as bulks are prepared by using water, whereas for films water is substituted with alcohol. The films produced at room temperature broke during polishing, as well.

Table compares the refractive indices of sol-gel materials hydrolysed at different temperatures. It was not possible to measure the refractive index for all the lines in the case of a film hydrolysed at 50 °C, due to the scattering of light. For the same reason only one measurement was possible for bulks produced at room temperature. The results demonstrate that in the case of films the refractive index increases with increased preparation temperature. Comparing the sol-gel bulk and film, one can notice that the refractive index significantly differs in those two types of

T a b l e Refraction index for three sol-gel materials produced at different temperatures: 90 °C, 50 °C and 22 °C.

		Refractive index n		
Line	λ [nm]	Film 90 °C	Film 50 °C	Bulk 22 °C
c	656.28	1.48057	not available	not available
C	643.8	1.48104	not available	not available
d	587.56	1.48339	1.47353	not available
e	546.07	1.48561	1.47507	1.49251
f	486.13	1.48997	not available	not available
F	479	1.49049	not available	not available

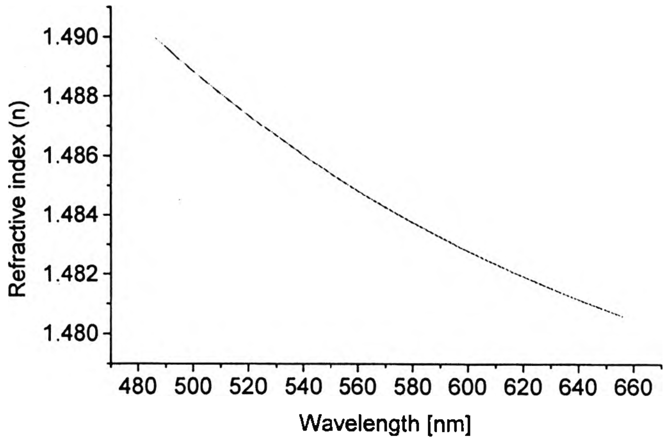

Fig. 3. Dispersion curves for sol-gel glass hydrolysed at 90 °C.

materials. For the spectral line 546.07 nm the highest refractive index was measured for the bulk, the lowest one for film produced at 50 °C. The normal dispersion is observed.

Figure 3 shows the dispersion curve of the sol-gel material hydrolysed at a temperature of 90 °C. The refractive index decreases with increasing wavelength and is higher than the refraction index of the sol-gel matrix prepared at 50 °C.

4. Transmittance measurement

In order to compare the sol-gel matrix with an ordinary glass, the transmittance measurement were performed. The transmittance was examined in the spectral range 300–800 nm. Figure 4 demonstrates the UV-VIS transmission spectra of film

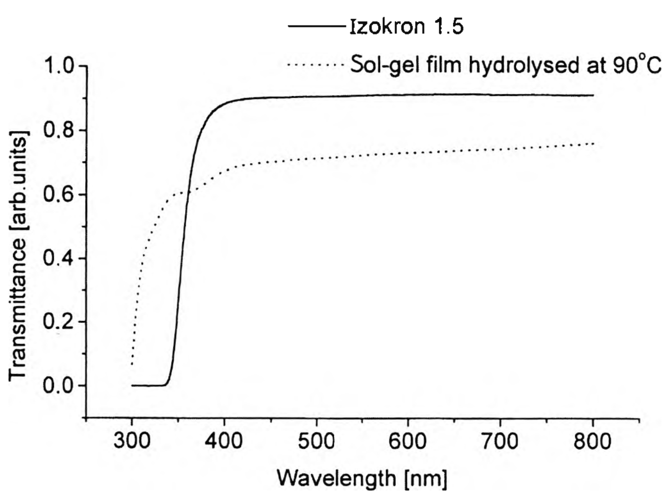

Fig. 4. UV-VIS transmission spectra of film hydrolysed at 90°C ($n_e = 1.485$) – dotted line, and mineral glass "Izokron 1.5" ($n_e = 1.525$) – solid line.

hydrolysed at 90 °C ($n_e = 1.485$) and mineral glass "Izokron 1.5" ($n_e = 1.525$) produced by Jelenia Góra Optical Glass Co. (Poland). The higher transmission in visible light is observed for mineral glass. In visible range the transmission is constant (not wavelength dependent). In UV the mineral glass shows a significant decrease of transmission, which is required for optical glasses. The transmittance of sol-gel is slightly lower than that of mineral glass. No cut-off in UV is observed. The transmission increases with wavelength.

5. Closing remarks

We have reported on the refractive index and transmittance measurements of sol-gel derived materials. It has been observed that the processing temperature influences the refractive index values. In the case of films the refractive index increases with increased preparation temperature. The normal dispersion is observed. Applying elevated temperatures of hydrolysis results in mechanically more stable matrices and higher refractive index of the samples.

Acknowledgment – The support of the State Committee for Scientific Research (KBN), Poland, Grant No. 8T11E 02915 is gratefully acknowledged.

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Received July 17, 2000