Defence Science Journal, Vol 46, No 2, April 1996, pp 105-107

Lead Sulphide-Doped Silica Xerogel by Sol-gel Technique

T.K. Singh and S.K. Sharma*
Defence Science Centre, Delhi-110 054

and

C.L. Jain
M.M.H. College, Ghaziabad-201 001

ABSTRACT

In this paper, a chemical process based on using sol-gel technique for the preparation of microcrystalline *PbS*-doped silica xerogel is described. Compared with the absorption spectra of bulk *PbS* crystals, the absorption edges of microcrystalline *PbS*-containing material exhibit large blue shift, due to confinement of microfine *PbS* particles in silica matrix. Because of the non-linear properties, this xerogel finds use in photonics as a cut-off filter.

1. INTRODUCTION

The materials with high third-order nonlinearity are of great interest for photonic application due to intensity-dependent refractive index of these materials. Such a material has been reported by incorporating microcrystalline dots of semiconductor, such as *CuCl, CdS, CdSSe*, etc. in glasses, e.g., silica glass and sodium borosilicate glass[1-3]. Sol-gel technique in its variation offers a process for preparing such materials[4].

In this paper, a process based on sol-gel technique for the preparation of microcrystalline *PbS*-doped silica xerogel is described.

2. EXPERIMENTAL DETAILS

Several materials were used in the preparation, which include tetraethylorthosilicate (TEOS) as a source of silica, methanol (A.R. grade) as a solvent, nitric acid (A.R., grade) as a catalyst, lead acetate and saturated H_2S water solution as a source of *PbS*, and double distilled water.

For the preparation of microcrystalline *PbS*-doped silica gel, first 10.4 g TEOS was hydrolysed by mixing with equal volume of methanol and 1.8 ml of 0.15 N HNO_3 solution for 1 h. To this solution, 15 ml methanolic solution of lead acetate was added. The mixture was stirred for 3 h. Finally, a mixture of 4 ml methanol + 1.5 ml of 0.15 N NH_4OH was added to adjust *p*H of sol to ~ 5. Uniform colourless sol was obtained at this stage. No reflexing of sol is required. The gels were cast in polythene petri dish. Gelation took place in 3 to 4 h. Colourless transparent gels were obtained. Two-stage hydrolysis—first acidic then alkaline —helped in obtaining colourless transparent gels rapidly. In the first stage during acid treatment, the condition was favourable for quick hydrolysis of alkoxy groups. In the second stage during alkaline treatment, the condition favoured fast condensation reaction. The high condensation rate in second stage also helped in drying the gel without fracture.

The gels were allowed to dry at room temperature for 24 h. Next day, the gels were immersed in saturated H_2S water solution for 24 h. After this, the gels were washed with distilled water and dried at 110 °C. Quantity of *PbS* in the xerogel was varied by adding calculated volume of lead acetate solution of known strength.

Received 24 February 1995, revised 29 August 1995
*Present Address : Director of Raj-bhasha, DRDO HQrs, Sena Bhavan, New Delhi-110 011

The xerogel obtained was investigated for its structure by X-ray diffraction measurements with Philips X-ray diffractometer, using monochromatic $CuK\alpha$ radiation. Optical absorption spectra were measured on 0.5 mm thick xerogel with Cary 17 D spectrophotometer.

3. RESULTS & DISCUSSION

Results of the X-ray diffraction patterns of xerogel are presented in Fig. 1 and absorption spectra are shown in Fig. 2.

Lead sulphide content in xerogels varies from 0.1 to 2.4 wt %.

The extent of colouration of the xerogels depends on the quantity of *PbS* in it, the colour being darker at higher content of *PbS*.

3.1 Effect of Treatment with Saturated H_2S Water on the Gel

Before treatment with H_2S water solution, the gels were transparent, but they shrank to some extent due to the loss of solvent and water in 24 h. At this stage, two kinds of groups exist on the surface of gel-alkoxy and hydroxyl groups. The treatment with H_2S appears to meet the following objectives:

(a) The H_2S water diffuses into pores and reacts with the *Pb* ions to form *PbS* precipitate in it.

$$Pb^{++} + H_2S \rightarrow PbS + 2H^+ \qquad (1)$$

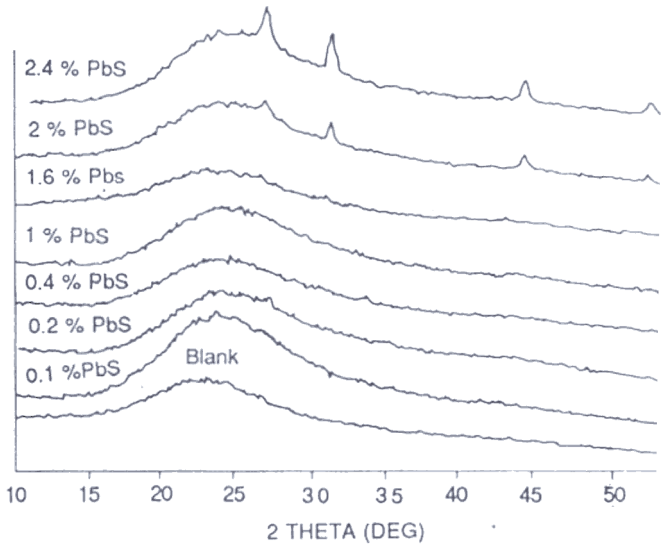

Figure 1. X-ray diffraction patterns of silica gel containing *PbS* and dried.

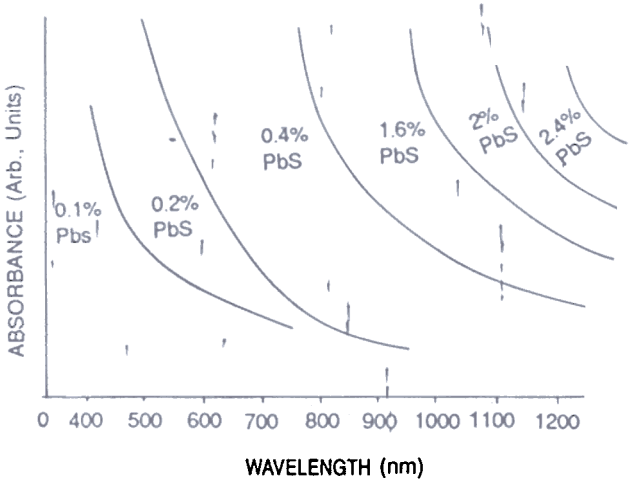

Figure 2. Optical absorption spectra of dried silica-gel containing *PbS* (The absorption edge for bulk *PbS* crystal is approximately 3020 nm and is not shown in the figure).

The quantity of *PbS* in the gel depends on the amount of lead acetate added at the initial stage in the sol.

(b) Water, on diffusion into pores, reacts with the residual alkoxy groups present in the gel and converts them into hydroxyl groups, thus increasing the number of hydroxyl groups on the surface of the particles by removing alkoxy groups from the gel, according to Eqn (2)

$$-Si\text{--}OC_2H_5 + H_2O \rightarrow -Si\text{--}OH + C_2H_5OH \qquad (2)$$

By applying this treatment, the gel could be dried very quickly while maintaining the shape [5].

Since alkoxy groups were also removed by this treatment, no heat treatment was required for removing these groups from the gel.

From the results of X-ray diffraction (Fig. 1), it was observed that the peaks at 2θ = 26 °, 36 °, 43 °, 51 °, and 53°, closely resemble those of cubic *PbS* crystals. The intensity of peaks varies with the content of *PbS* in the gels. When *PbS* content is very low, i.e. <1.6 % in the gel, the peaks could not be seen in X-ray curve due to limitation of the instrument.

From the results of absorption spectra (Fig. 2), it was observed that, when compared with the absorption spectra of bulk *PbS* crystals, the absorption edges on *PbS*-containing materials exhibit large blue shift because of confinement of fine *PbS* particles in silica matrix. The particles behave as quantum dots. As the quantity of *PbS* increases in silica xerogel, the

absorption edge shifts towards bulk *PbS* crystal which is approximately 3020 nm.

ACKNOWLEDGEMENTS

The authors are thankful to Shri V.K. Arora, Director, Defence Science Centre, Delhi, for his permission to carry out this work. Thanks are also due to Dr Surendra Pratap and Dr S.K. Shukla for useful technical discussions on the subject.

REFERENCES

1. Schmitt-Rink, S.; Miller, D.A. & Chemla, D.S. Theory of the linear and non-linear properties of semiconductor microcrystallites. *Phys. Rev. B.*, 1987, 35, 8113-25.
2. Jain, R.K. & Lind, R.C. Degenerate four-wave mixing in semiconductor - doped glasses. *J. Opt. Soc Am.*, 1983, 73, 647-57.
3. Butcher, P.N. & Cotter, D, The optical properties artificial materials. *In* The elements of non-linear optics. Cambridge University Press, Cambridge, 1990, pp. 275-94.
4. Nogami, M.; Walabe, M. & Nagasaka, K. Preparation of semiconducting sulphides microcrystalline - doped silica glasses by the sol gel process. SPIE, sol-gel optics, 1990, 1328, 119-24.
5 Minsume, T.; Nagata, H. & Manaba, S. Attempts to avoid cracks during drying. *J. Non-Cryst. Solids*, 1988, **100**, 239-40.