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# Chemical Synthesis of Optical Grade Ceramic Precursors: A Spectrophotometric Approach for Analysis

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**Abstract:** Extremely controlled hydrolysis of a rapidly water-absorbing alkoxide was performed so as to achieve a gel of high optical transmittance. An aluminium sec-butoxide precursor was structurally modified using ethyl acetoacetate in varying stoichiometric ratios. The sol–gel synthesis of the chelated alkoxide was conducted under closely monitored conditions of humidity, temperature and ultrasonic power and the hydrolysing water was added at extremely slow rates using callibrated micropipettes. Molecular level homogeneity was ensured by adopting an intense, contact mode probe type ultrasonication of the chelated alkoxide in presence of excess alcohol, until the alumina sol sonogelled on the addition of a stoichiometric amount of water. The sonogels were seen to possess an extremely high optical transmittance as a result of the novel processing and synthesis technique proposed and developed by us. Uv-visible spectrophotometric analysis of the sonogelling sol at every water addition was performed and a gel of over 95% transmittance could be obtained at a chelate ratio of 1:2, with 15 ml isopropyl alcohol, at a water addition rate of 0.4 ml $h^{-1}$ $g^{-1}$ of alkoxide, under an ultrasonic power of 90 watts. 

## 1 INTRODUCTION

Aluminium alkoxides are salts of alcohols known for their high affinity for water. Uncontrolled hydrolysis of these precursors results in a gelatinous precipitate of aluminium hydroxide having an opaque,[1] porous,[1,2] irregular[3] microstructure and a broad particle size distribution.[2] These gels may be either amorphous or crystalline depending on the processing temperature and conditions. Since these variables directly affect the microstructure of the ceramic, a microstructural control over the sol to gel transformation essentially involves a control over the rate of hydrolysis of the alkoxide. To get a phase of narrow particle size distribution, or a monolith of high isotropicity, the freshly precipitated species is peptized using inorganic or organic acids.[1] However, the anions-typically chlorides, nitrates and sulphates present in these peptizing agents act as trace impurities and cause conductivity fluctuations or lattice imbalances when used for semi-conductors or fiber optics applications.

From a purity and chemical integrity viewpoint, a more attractive way of processing these gels is by controlling the rate of alkoxide hydrolysis. This is best achieved by using chelating agents. Some of these agents can be removed at will at a later stage in the processing without leaving any trace impurities behind. Beta-diketones fall in such a family of chelating agents and this area has been of current interest for some time now. As an added advantage, merely by adjusting certain parameters including the rate of water addition, the amount of alkoxide in the batch, the volume of alcohol in the system and the chelating agent to alkoxide mole

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ratio, a transparent gel may be obtained.[1,3] Stable, transparent gels find tremendous applications in the processing of optical, ophthalmic, and infra-red glasses for defence applications and in the manufacture of disposable contact lenses. Chemical additives such as ethyl acetoacetate and acetylacetone[4–9] which chemically modify the alkoxide precursor have been successfully used to produce nano-alumina, but optical transmittance studies on intimate, contact mode ultrasonically produced alkoxide gels has not been done so far, and this has formed the thrust of our experimental efforts.

The rapid rate of hydrolysis of the alkoxide precursor is due to the presence of an electronegative alkoxy group which makes the metal atom highly prone to a nucleophilic attack. A replacement of the reactive alkoxy group with a less hydrolysable entity is the key step in the chelation process. Chelating agents occupy the sites of probable water attack, chemically modify the entire precursor and reduce the rate of hydrolysis. Previous studies have focused on the structures, as well as the retarded rate of hydrolysis of alkoxides using a varying chelate ratio from 0.25 to 3.0 moles of ethyl acetoacetate to aluminium sec-butoxide,[4,9,10] but optical transmittance effects have not been quantified so far.

## 2 EXPERIMENTAL

### 2.1 Materials

The aluminium sec-butoxide (ASB) used in the experiments was of 97% assay (Fluka) and was used as is. The iso propyl alcohol (IPA) (Fluka) with a 96% assay was dried by a 4 h storage in a desiccator containing calcium oxide previously heated to 800°C. The ethyl acetoacetate (EAA) (Spectrochem) with a 96% assay was used as received. Milli-Q water (18 MΩ-cm) was used to hydrolyse the chelated alumina sols.

### 2.2 Methods

#### 2.2.1 Preparation

About 3.0 g of ASB was weighed out in a teflon coated, screw-capped sample bottle in a glove box, under inert gas flow, so as to minimise atmospheric hydrolysis. About 15 ml of previously dried IPA was added to it and the mix ultrasonically agitated at 18.750 kHz at 90 watts output for approximately 600 s on a Branson-450 probe type sonicator, using a 12 mm diameter probe disruptor horn tip. The immersion of the probe tip was adjusted to about 2 mm below the liquid level in order to achieve maximum turbulence[11] and ultrasonication efficiency. To counteract the effects of heating, and to eliminate the generation of the presently undesirable high temperature phases of aluminium hydroxide,[1] the alcoholic alkoxide was enclosed in a cooling jacket to maintain a temperature of 28°C throughout the sonication period.

For a stoichiometric 1:1 chelating ratio, about 1.5 ml of EAA was added to the sonicated, alcoholic alkoxide using a previously dried pipette. Continuous sonication under 28°C conditions for about 1200 s was performed to complete the room temperature alkoxide chelation process as reported in literature.[4,8,9] For a 1:2 chelate ratio, about 3.0 ml of ethyl acetoacetate had to be added under similar sonication and temperature conditions.

#### 2.2.2 Reaction

For an unchelated alkoxide sonicated with 15 ml IPA, it was seen from previously conducted pilot experiments that such a system sonogels at the addition of 0.6 ml of added water. From similar experiments, it was ascertained that 1:1 weighed batches of chelated alkoxides sonogel under the ultrasonic probe after the addition of 1.0 ml water when it is added at the rate of 0.1 ml every 300 s under continuous sonication conditions. Similarly, 1:2 chelated systems room temperature sonogel under the ultrasonic probe at 1.8 ml water at the same water addition rate. Water addition was done using previously dried, calibrated micropipettes (Top Syringe Mfg. Co. Ltd.,). Experimentally, it was seen that isopropyl alcohol: (i) served as a good mutual solvent for the ASB-EAA system (ii) retarded the gelation time sufficiently so as to reach the water to alkoxide molar ratio of 3.3:1 or 7:1 at the desired rate of water addition and (iii) ensured a transparent sol by providing an increased dispersing volume.

Water addition was stopped at the gel point which occurred at 0.6 ml for an unchelated alkoxide, 1.0 ml for a 1:1 chelate and 1.8 ml for a 1:2 chelate as was indicated from previously conducted pilot tests. Batches of EAA chelated ASB with 20 ml IPA, at 0.1 ml water increments, were then taken up for spectrophotometric characterization during the sol to gel transition.

#### 2.2.3 Characterization

For characterization of the entire sol to gel synthesis at differing chelate ratios, the uv-visible spectrophotometric analysis technique was chosen on the basis of its direct or indirect ability to reveal the microstructure. The percentage optical transmission studies were done using the UV Spectophotometric analyzer (Shimadzu 160) at a 10.0 mm path length, at a source wavelength of 520 nm, using matched pair quartz couvettes. About 5.0 ml of the

alcoholic, chelated alkoxide was extracted from the reaction vessel situated under the sonicator, after every water addition. Sols in varying stages of sonogelation were transferred to one couvette with the other couvette containing a sample of unhydrolysed, alcoholic alkoxide which served as a spectrophotometric baseline for all transmittance observations. Transmittance data for unchelated, 1:1 chelated and 1:2 chelated alkoxide sols in varying states of sonogelation was recorded; each at 0.1 ml intervals of water added. The emergent data for the three distinct ratio chelated alkoxide systems is as shown in Table 1. A plot of optical transmittance vs amount of water added obtained from experimental data is shown in Fig. 1. Transmittance curves have also been established for 1:3 chelated sonogels but have not been discussed in depth in this paper, given their large volume shrinkage, and a tendency to develop surface and bulk imperfections which severely restrict their engineering applications. It is interesting to note however that samples prepared in a chelate ratio in a large excess of 1:3, did not sonogel under the action of the sonicator probe and gelation was seen to initiate only after about 75 days of exposure to the atmosphere indicating an extremely slow humidity induced hydrolysis leading to transparent gels. Since gelation did not feature the use of contact-mode ultrasonication in the rheopectic evolution in the microstructure of high ratio chelated alkoxides, an investigation into the optical transmittance values for these systems has not formed the current focus of our research.

## 3 RESULTS AND DISCUSSIONS

In the optical transmittance measurements of chelated and unchelated alkoxide sonogels, with data points at each water addition, the following features were observed.

1. An unchelated alkoxide dropped in its transmittance from 100% before the start of hydrolysis to 17% at the addition of 0.1 ml water at a constant, slow rate of hydrolysis. At the next water addition, the transmittance reduced still further to about 14% and by the time about 0.6 ml of water had gone into the system, the sol had completely sonogelled under the sonicator probe tip giving an optical transmittance of about 8%. This indicates that microstructural control over the unchelated sonogel is extremely poor essentially because the hydrolysis cannot be regulated so as to ensure a transparent state throughout the sol to gel transition.
2. A 1:1 chelated system was found to decrease more gradually in optical transmittance, with each water addition, as compared to an

**Table 1. A comparison of the optical transmittances obtained from unchelated, as well as 1:1 and 1:2 ASB/EAA chelated alkoxide systems, at controlled water addition rates of 0.4 ml water $h^{-1} g^{-1}$ of ASB. An unchelated ASB sonogells at a transmittance of 8% at the addition of 0.6 ml water. A 1:1 EAA chelated ASB sonogells at the addition of 1.0 ml of water and has an optical transmittance of 26.8% at its gel point. The 1:2 chelated system sonogels at 1.8 ml of added water, at an optical transmittance of 96.3%**

| S.No. | Amount of water (ml) | Optical transmittance at 520 nm (%) | | |
|---|---|---|---|---|
| | | Unchelated ASB | ASB/EAA=1:1 | ASB/EAA=1:2 |
| 1 | 0.0 | 100.00 | 100.00 | 100.00 |
| 2 | 0.1 | 17.00 | 91.50 | 99.90 |
| 3 | 0.2 | 14.00 | 83.50 | 99.70 |
| 4 | 0.3 | 13.00 | 64.60 | 99.50 |
| 5 | 0.4 | 10.00 | 41.60 | 99.10 |
| 6 | 0.5 | 8.00 | 40.10 | 98.80 |
| 7 | 0.6 | 8.00* | 38.90 | 98.50 |
| 8 | 0.7 | No further measurement | 34.50 | 98.30 |
| 9 | 0.8 | | 33.40 | 97.90 |
| 10 | 0.9 | | 27.60 | 97.70 |
| 11 | 1.0 | | 26.80* | 97.50 |
| 12 | 1.1 | | No further measurement | 97.20 |
| 13 | 1.2 | | | 97.00 |
| 14 | 1.3 | | | 96.60 |
| 15 | 1.4 | | | 96.40 |
| 16 | 1.5 | | | 96.40 |
| 17 | 1.6 | | | 96.30 |
| 18 | 1.7 | | | 96.30 |
| 19 | 1.8 | | | 96.30* |
| 20 | 1.9 | | | no further measurement |

* Signifies the point of sonogelation of the alkoxide sol.

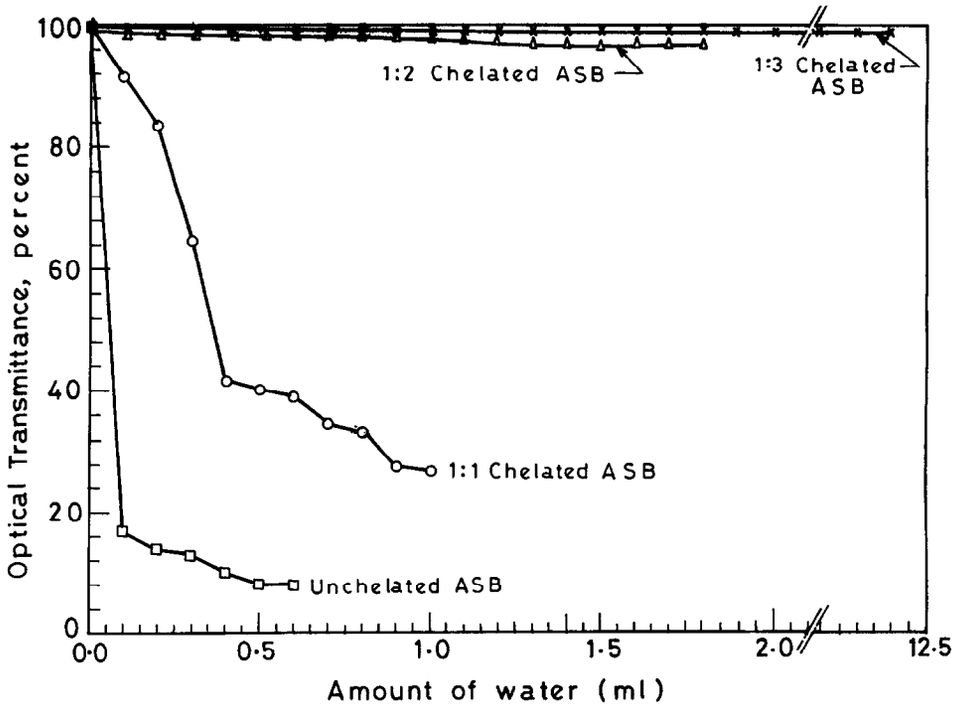


**Fig. 1.** Graph showing the change in optical transmittance in alkoxide sols, with the amount of hydrolysis water added to the system. The variation plotted is at a water addition rate of 0.4 ml $h^{-1}$ $g^{-1}$ of ASB at an ultrasonic power of 90 watts. It may be observed that the minimum optical transmittance at 520 nm is over 95% corresponding to a 1:2 chelated sonogel and over 99% for a 1:3 chelated sonogel.

unchelated alkoxide. At the first water addition, the optical transmittance was seen to decrease to about 92%. Optical transmittance values however, continued to fall with each water addition, reaching a minimum of about 27% at the sonogelling point suggesting thereby, an improved hydrolysis control as compared to an unchelated alkoxide, but still not acceptable for influencing or engineering the fluid, labile and dynamic microstructure.

3. A 1:2 chelated system was observed to decrease extremely slowly in optical transmittance, at each water addition. It could be seen that the same amount of water that brought about an 83% transmittance drop in unchelated systems and a 10% drop in a 1:1 chelated system could bring about only a 0.1% decrease in the optical transmittance in a 1:2 chelated alkoxide. As a result, when a 1:2 chelated system sonogelled at a water addition of 1.8 ml, it was found to possess a minimum optical transmittance of over 96% suggestive of an excellent microstructural and hydrolysis control.

Figure 1 which is a plot of optical transmittance vs amount of water added during hydrolysis is shown for unchelated, 1:1 chelated 1:2 chelated and 1:3 chelated alkoxides. Before the addition of any water into each of these systems, the optical transmittance values at a characterizing wavelength of 520 nm (10 mm path length, using a Shimadzu-160 uv-spectrophotometer with matched pair quartz couvettes) was 100%. In each of these systems, when 0.1 ml water was added, the optical transmittance in an unchelated system dropped to about 17%, that in a 1:1 chelated system to 92% and that in 1:2 and 1:3 systems dropped negligibly by 0.1% or even less. This drop continued right upto the gel point. An unchelated system on sonogelling, at the addition of 0.6 ml water, was seen to have a transmittance of about 8%. A 1:1 system gelled at 1.0 ml and had an optical transmittance of about 27% at its sonogel point. A 1:2 system however, gelled at 1.8 ml and had a minimum optical transmittance of about 96.3% at the sonogelling point. A 1:3 system sonogelled at 12.4 ml and had a minimum optical transmittance of over 99.9%. It may be noted that the time taken to add 12.4 ml of water at the rate of 0.4 ml $h^{-1}$ $g^{-1}$ of alkoxide, was extremely large. It might be possible however, to increase the rate of water addition and still achieve a transparent sonogel, but this would almost certainly require a higher ultrasonic power at the sonicator probe tip so as to prevent localized etching of the chelated species which causes opacity. The ultrasonic power generated at the sonicator probe tip for this set of experiments was 90 watts, which was kept constant for all chelate ratios.

Optical transmittance measurements were performed on 1:1, 1:2 and 1:3 chelated alkoxides in an effort to compare their respective optical properties

from an engineering applications viewpoint. At the sonogelling point, a 1:3 chelated alkoxide was seen to possess a transmittance of over 99% which is the highest recorded value so far. However, these gels were found to possess a high shrinkage with time and developed surface and bulk cracks on a 48-h exposure to the atmosphere. In contrast, a 1:2 chelated sonogel was found to be chemically and integrally stable for at least 200 days. Details on the synthesis of 1:3 chelated sonogels are reported elsewhere[12] and within the specific experimental limits it has been established that chelated sonogels offer a new access to the development of high transmittance optical grade alumina gels which is not feasible using currently employed conventional processing techniques.

A comparison between conventionally produced alumina gels and those produced on contact mode ultrasonication of a chelated alkoxide precursor is shown in Fig. 2. The schematic is an evaluation of the optical transmittances achieved on controlled hydrolysis, processing and ultrasonication of chelated alkoxide sonogels. All the samples (A through E) were measured for optical transmittance values at their gel point. Sample A which is an unchelated ASB processed aluminium hydroxide sonogel had a gel transmittance of about 8%. Sample B, prepared in accordance with previously established experimental procedures[1] was found to have a transmittance of about 87% at its gel point as against the reported value of about 90%. Sample C is a 1:1 chelated sonogel which was seen to have an optical transmittance of above 93% at a water addition rate of $0.1\,ml\,h^{-1}\,g^{-1}$ of ASB and a transmittance of about 27% at the water addition rate of $0.4\,ml\,h^{-1}\,g^{-1}$ of ASB. It may be observed that merely by reducing the rate of water addition from $0.4\,ml\,h^{-1}\,g^{-1}$ to $0.1\,ml\,h^{-1}\,g^{-1}$, it is possible to increase the optical transmittance from about 27% to about 93% without increasing the ultrasonic power or by adding excess alcohol. Sample D is a 1:2 chelated alumina sonogel shown to have a transmittance of 95% at its gel point. Sample E is a 1:3 chelated alumina sonogel which was found to have a gel transmittance of over 99%.

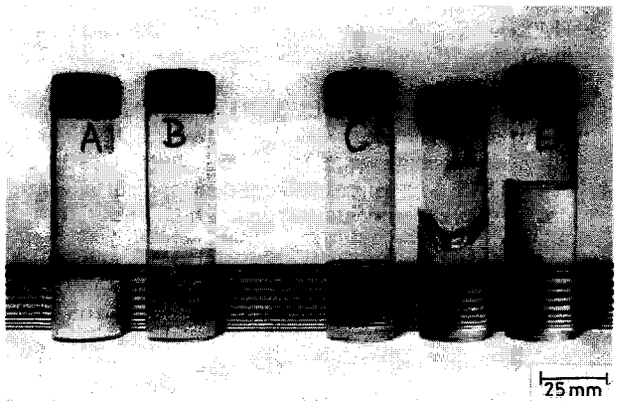


**Fig. 2.** A comparative evaluation of the optical transmittances achieved as a result of processing aluminium hydroxide gels through different synthesis routes. Samples A and B are the result of current art while samples C, D and E are the result of proposed technique. Sample A is a sonogelled, unchelated ASB which gave a gel transmittance of about 8%. Sample B, processed according to the experimental procedure outlined in Ref. 1, was found to show a gel transmittance of about 87%. A 1:1 EAA chelated ASB (sample C) which would, under a water addition rate of $0.4\,ml\,h^{-1}\,g^{-1}$ of ASB, give a transmittance of about 27%, was found to show a transmittance of about 93% at a water addition rate of $0.1\,ml\,h^{-1}\,g^{-1}$. Sample D is a 1:2 chelated alumina sonogel which gave an optical transmittance of 95% at its gel point. Sample E is a 1:3 chelated alumina sonogel which was found to have a gel transmittance of over 99%.

Water addition is stopped at the gel point which occurs at 1.0 ml for a 1:1 chelate, 1.8 ml for a 1:2 chelate and 12.4 ml for a 1:3 chelate, as indicated from previously conducted pilot tests. It can be observed that as the chelate ratio is increased, the amount of water required to unchelate, hydrolyse and subsequently sonogel a chelated alkoxide increases sharply. For chelate ratios above 1:3 it was seen that even after very large amounts of water were added to the system, the chelated alkoxide did not sonogel *in-situ*. A 1:4 chelated system for example, did not sonogel even after 35.5 ml of water was added. A pseudogel characterized by a localized increase in viscosity at the sample surface was seen in such a case. The sample was found to convert to a true gel only on leaving it undisturbed for about seven days inside the glove box. Additionally, a 1:10 ratio chelated alkoxide took up about 600 ml of water without insitu sonogelling and though the sol transmittance was appreciably above 99.8% at all stages, an onset of time-assisted gelation was seen only after about 75 days after sample preparation.

Hence, from an engineering viewpoint, chelate ratios above 1:3 need very large amounts of water to dechelate and it is expected that about 1.0 g of $Al_2O_3$ resulting from over 635 g (in 1:10 systems) of alumina gel necessitates high shrinkage and crack development in the optical material. Besides, these systems do not gel as a result of ultrasonication and hence do not fall within the scope of this paper which is limited to 1:1 and 1:2 chelated alkoxides, and as a limiting case example to 1:3 chelate ratios also.

It may hence be concluded that a 1:2 and a 1:3 chelated alkoxide with 15 ml alcohol when hydrolysed at 0.4 ml water per hour per gram of ASB, under contact mode, intense ultrasonic mixing gives a sonogel having an extremely high optical transmittance, i.e. above 95%. A 1:3 chelated alkoxide gives a sonogel with more than 99.9% optical transmittance and it is expected that in any attempt

to achieve a transparent fired product from a transparent gel, as has been proved possible,[1] such a sonogel would yield a monolith with a high shrinkage and possess surface as well as bulk defects as a result of uncontrolled drying. Hence from an engineering viewpoint, a 1:2 sonogel is expected to command a wider range of applications as compared to a 1:3 chelated sonogel.

## 4 CONCLUSIONS

On the basis of the spectrophotometric evidences provided, it may be concluded that an alumina gel having an optical transmittance of at least 95% can be prepared by ultrasonically agitating an aluminium sec-butoxide, ethyl acetoacetate mix in a 1:2 molar ratio. The presence of alcohol is an aid to achieving high transmittances in which the most crucial microstructural control is provided by an extremely slow water addition rate of about $0.4\,ml\,h^{-1}\,g^{-1}$ of alkoxide or lower and an intense molecular level ultrasonic agitation achieved by subjecting about 35 ml of reactants to an ultrasonic dispersing power of 90 watts.

Feasibility studies currently underway[12–14] indicate that still higher transmittances may be obtained on using higher chelate ratios, higher amounts of alcohol, slower water addition rates, vigorous, prolonged ultrasonication, a control over the temperature, periodic ultracentrifugation and incorporating drying control chemical additives into the chelated alkoxide batch.

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## REFERENCES

1. YOLDAS, B. E., A transparent porous alumina. *Ceram. Bull.*, **54** (1975) 286–288.
2. PIERRE, A. C. & UHLMANN, R., Gelation of aluminum hydroxide sols. *J. Am. Ceram. Soc.*, **70** (1987) 28–32.
3. OGIHARA, T., NAKAJIMA, H., YANAGAWA, T., OGATA, N. & YOSHIDA, K., Preparation of monodisperse, spherical alumina powders from alkoxides. *J. Am. Ceram. Soc.*, **74** (1991) 2263–2268.
4. NASS, R. & SCHMIDT, H. J., Synthesis of an alumina coating from chelated aluminium alkoxide. *J. Non-Cryst. Solids*, **121** (1990) 329–333.
5. MEHROTRA, R. K. & MEHROTRA, R. C., Reactions of aluminium alkoxides with acetylacetone, benzoylacetone and ethylacetoacetate. *Can. J. Chem.*, **39** (1961) 795–801.
6. WENGROVIUS, J. H., GARBAUSKAS, M. F., WILLIAMS, E. A., GOING, R. C., DONAHUE, P. E. & SMITH, J. F., Aluminium alkoxide chemistry revisited: synthesis, structures and characterization of several aluminium alkoxide and siloxide complexes. *J. Am. Chem. Soc.*, **108** (1986) 982–987.
7. SANCHEZ, C., LIVAGE, L., HENRY, M. & BABONNEAU, F., Chemical modification of alkoxide precursors. *J. Non-Cryst. Solids*, **100** (1988) 65–71.
8. SCHMIDT, H., Chemistry of material preparation by the sol-gel process. *J. Non-Cryst. Solids*, **100** (1988) 51–57.
9. NASS, R. & SCHMIDT, H. J., Synthesis of an alumina coating from chelated aluminium alkoxide. *J. Non-Cryst. Solids*, **121** (1990) 329–333.
10. HEINRICH, T., RAETHER, F. & MARSMANN, H., Growth and structure of single phase mullite gels from chelated aluminium alkoxides and alkoxysilanes. *J. Non-Cryst. Solids*, **168** (1994) 14–22.
11. BARENHOLZ, R., GIBBES, D., LITMAN, B. J., GOLL, J., THOMPSON, T. E. & CARLSON, F. D., A simple method for the preparation of homogeneous phospholipid vesicles. *Biochemistry*, **16** (1977) 2806–2808.
12. HARIDAS, M. M. & BELLARE, J. R., Synthesis of highly transparent sonogels from chelated alkoxides, Indian Patent application 95/BOM/487.
13. HARIDAS, M. M. & BELLARE, J. R., Microstructure evolution in chelated partially hydrolysed alumina sols during sonogelling. *Bull. Mater. Sci.*, **20** (1997) 49–66.
14. HARIDAS, M., Microstructure development in ceramic precursors: experimental studies. Ph.D. thesis, I. I. T. Bombay, India, 1997.