

SOL-GEL DERIVED CERAMICS

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Introduction

The synthesis of ceramic raw materials has become an important factor in ceramic technologies. The increasing demands to the performance of ceramic compounds has caused increased activities for the preparation of tailor-made raw materials. Amongst a variety of new syntheses like flame pyrolysis, reactive spray drying, plasma or laser assisted techniques, the sol-gel process plays an important and increasing role. The process describes the building up of an inorganic (in general an oxide) network by a chemical condensation reaction. There is numerous literature concerning sol-gel techniques for the synthesis of ceramics (1-12). Summarizing, one can say that despite of the tremendous effort in science there are still remarkable deficiencies in the knowledge of reaction mechanisms in systems beside SiO_2 and for multicomponent systems (including additives like sinter aids or dopants).

The sol-gel process

The sol-gel process provides an interesting potential: Multi-component systems can be prepared by homogeneous distribution of the single components in the starting liquid phase. Molecular precursors can be purified for ultrapure materials. The polycondensation process can be controlled by chemistry, and coating and fiber drawing processes can be established. In order to exploit this potential, however, it is necessary to take into consideration the above mentioned demands to advanced ceramics. This leads to two technology oriented processing routes: the synthesis of powders to be used in already established powder technologies and the synthesis of suspensions or slips to be processed in powderless processes.

The sol-gel process describes the formation of an inorganic network from small units. The units can be monomers, oligomers or colloids. The oligomeric or colloidal phase is called the sol. After the three-dimensional crosslinking of the units the gel is formed (Fig. 1). The reaction takes place in solution which can be aqueous or non-aqueous. In this sense, minerals like agate or chalcedony were formed by precipitation of $\text{SiO}_2 \cdot \text{H}_2\text{O}$ from solutions (13). Precipitation processes of hydroxides are also well-known in ceramic technologies but never really considered as sol-gel reactions.

The sol-gel process in the most common definition describes the controlled formation of inorganic materials from solutions. Reaction control can be achieved by rate control of the different steps, e. g. hydrolysis of organometallic compounds or control of the surface charge (zeta potential) of colloids. The control of this parameters permits the control of structure or microstructure and to tailor properties of gels. The process has gained importance for material synthesis during the last three decades

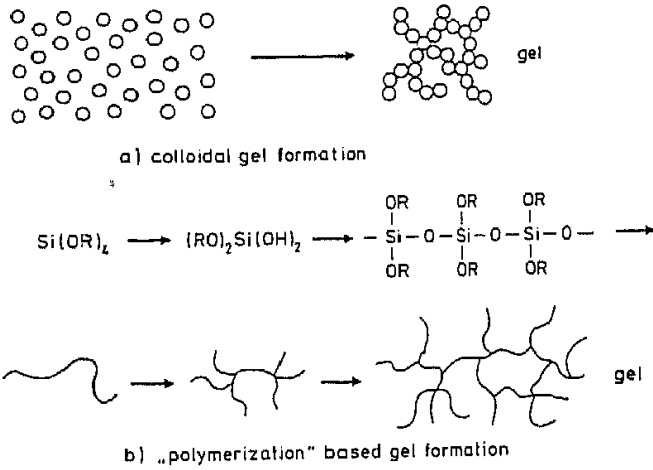


Fig. 1: Different types of gel formation.

by the work of Roy (14) and Dislich (15). A wide variety of techniques is available and so far, most of them are not sufficiently exploited. A general reaction scheme showing the variability is given in Fig. 2.

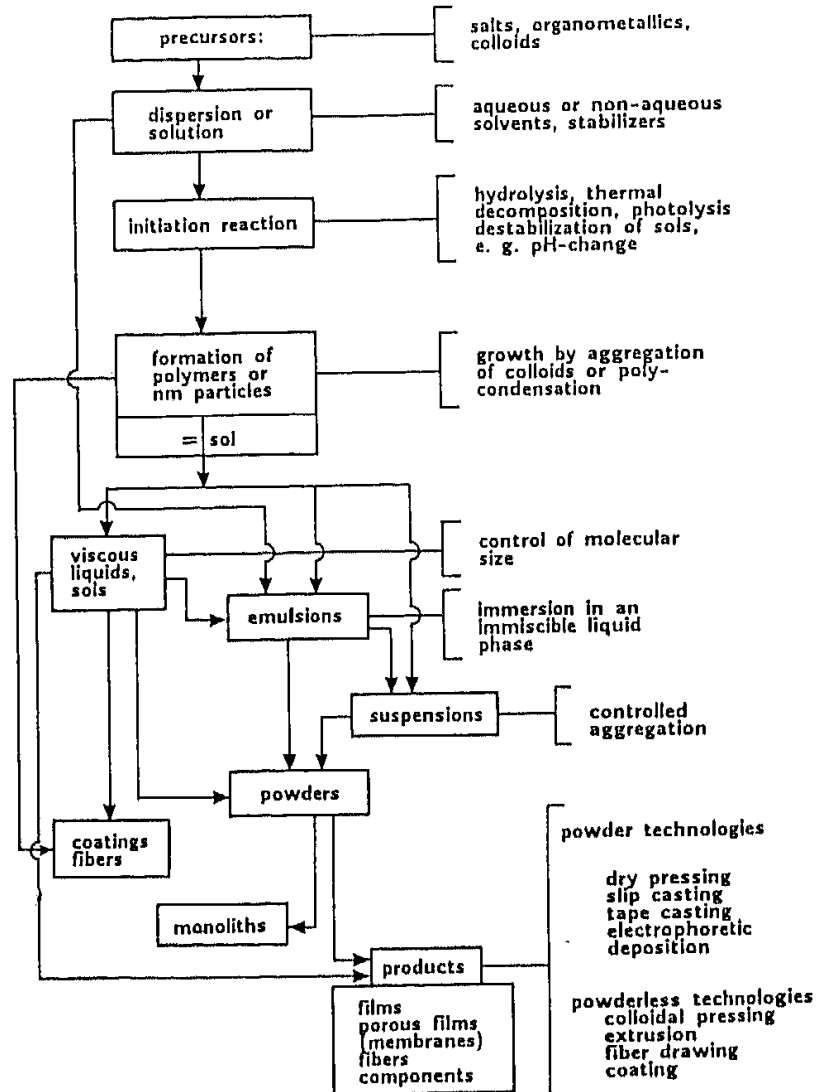


Fig. 2: Sol-gel technologies.

It has been shown (16) that monosized particles can be formed by the sol-gel route. The question whether monosized powders can help to improve properties of ceramics (e. g. defect size, processing, packing density) is old and not easy to be answered since it is difficult to separate the size distribution effect from other processing faults. Theoretically, a defectfree packing with monosized powders requires a perfect particulate crystal which is almost impossible to be achieved in practice. Powders with deviations from monosized distributions lead to packing defects shown in Fig. 3. Narrow distribution leads to a more homogeneous distribution of smaller defects. Both powders are sol-gel derived silicas. Due to the viscous flow sintering mechanism, in the case of silica the defects can be eliminated during sintering. In other systems the packing defects only become relevant, if they represent the critical defect size and are maintained in the sintered body. Experiments on monosized ZrO_2 prepared by a growth controlled sol-gel process (17) did not lead to defectfree green bodies by dry pressing (18). Fig. 4 shows an example of the almost monosized sol-gel ZrO_2 powder.

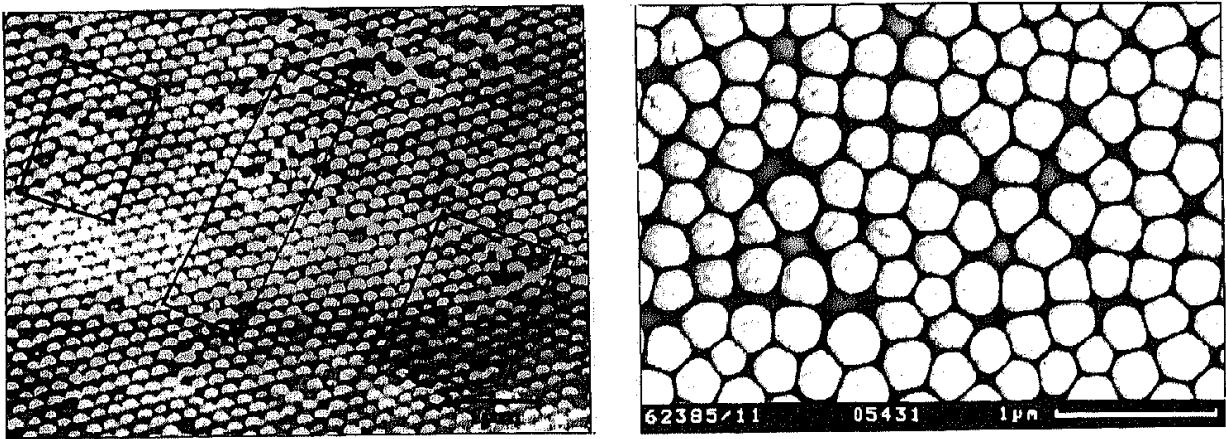


Fig. 3: Mono and narrow sized distribution based packing; \square : "large defect" areas.

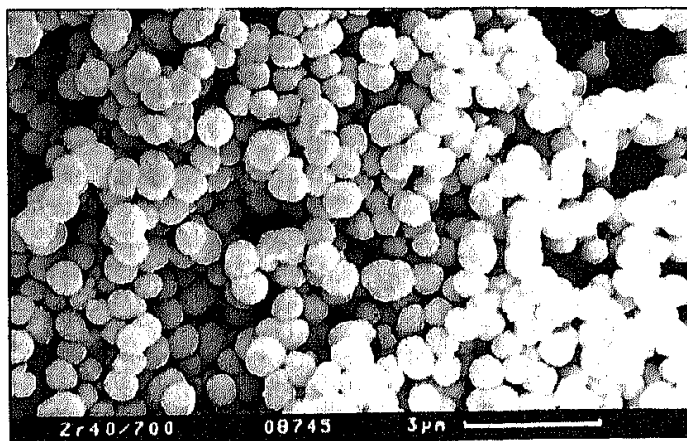


Fig. 4: ZrO_2 powder by a growth controlled sol-gel process.

According to (17) the size of the particles could be controlled by complexation of the precursor ($\text{Zr}(\text{i-prop})_4$) by acetyl acetone (acac). Another benefit of acac is the drastic increase of solubility in EtOH as solvent, thus leading to a high yield per reaction volume unit (100 - 300 g calcined powder per l reaction volume). The existence of a monosized formation region is in accordance with La Mer's theory for the appearance of monodispersed systems (the super saturation and nucleation regime is shifted to higher concentrations) (19 - 20). But La Mer's theory does not explain the fact, that the ZrO_2 spheres are aggregates of very small primary particles (Fig. 5). This can be explained by the aggregation model which postulates that the stroke frequency decreases with increasing particle size thus leading to a monosized dispersion by starting from very small particles with a narrow size distribution.

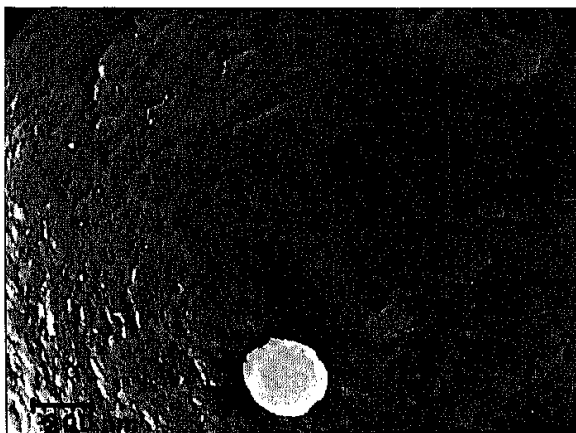


Fig. 5: ZrO_2 sphere, built up from nanosized primary particles.

As a consequence, one can say that there is probably no real need for monosized or very narrow distributions for ceramic powders.

One important advantage of these methods is that powders can be prepared ready to be used for processing without extensive milling, thus reducing the danger of contamination by abrasion of materials of the milling device. Another one is the high purity to be achieved by using pure precursors. Sol-gel powders, in general, show high specific surface areas after drying (up to some $100 \text{ m}^2/\text{g}$) mainly due to small pores. They cannot successfully be used for common ceramic processing as they are (e. g. high consumption of organic additives, low green densities, high shrinkage). A typical disadvantage of microporous sol-gel powders is the resulting bimodal pore size distribution in green bodies. Fig. 6 shows a typical example.

As a result it is very difficult to obtain full density during sintering. It seems to be difficult to transfer the benefits of the described intrinsic properties of sol-gel derived raw materials into "normal" ceramic processing. Up to now, only a few examples of sol-gel powder technologies exist which clearly

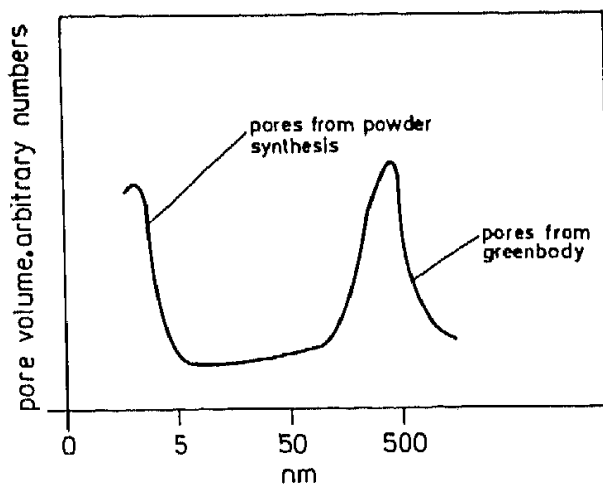


Fig. 6: Bimodal pore size distribution in green bodies from gel powders.

demonstrate sol-gel advantages. These are mainly observed with multicomponent systems, where diffusion limit occurs by interfaces, e.g. BaTiO₃ from BaCO₃ and TiO₂ or PZT from PbO/ZrO₂/TiO₂. PZT for example can be sintered to dense ceramics at temperatures between 850 and 900 °C (21-22) compared to the conventional powder technology which requires temperatures of more than 1200 °C. The "processing gap" exists here too: The perovskite structure of PZT forms already starting with 500 °C.

Another route of size control of particles is to form emulsions by immersing one liquid into another. Emulsion techniques for the preparation of ceramic powders have already been described (23 - 24). The general advantage of this route is the fact that the particle size distribution is determined by the emulsion formation and not by the sensitive thermodynamics of a growth reaction. Aqueous salt solutions can be used and dispersed in organic liquids and the pH is changed by amines or ammonia: A precipitation process takes place within the droplets of the emulsion, restricting separation effects of the droplet dimensions. The disadvantages of the method described in (23-24) are agglomeration, still taking place during drying of the precipitates, and salt anions, still being present and leading to serious disturbances in further processing. The use of ion exchange for introducing pH changes can help to avoid these problems completely (25). Fig. 7 shows a scheme of the process. The use of the ion exchanger requires a "transport molecule" (phase transfer catalyst = PTC) which is able to transport OH⁻ groups from the exchange resin to the aqueous droplets through the organic phase. Therefore, quarternary ammonium bases are appropriate (e. g. CH₃CH₂CH₂NR₃⁺Br⁻).

Another advantage of molecules of this type is their ability to adsorb on hydrophilic surfaces and to form micelles as demonstrated in Fig. 8.

These powders are characterized by low specific surface areas, high density, low water content and can be further densified

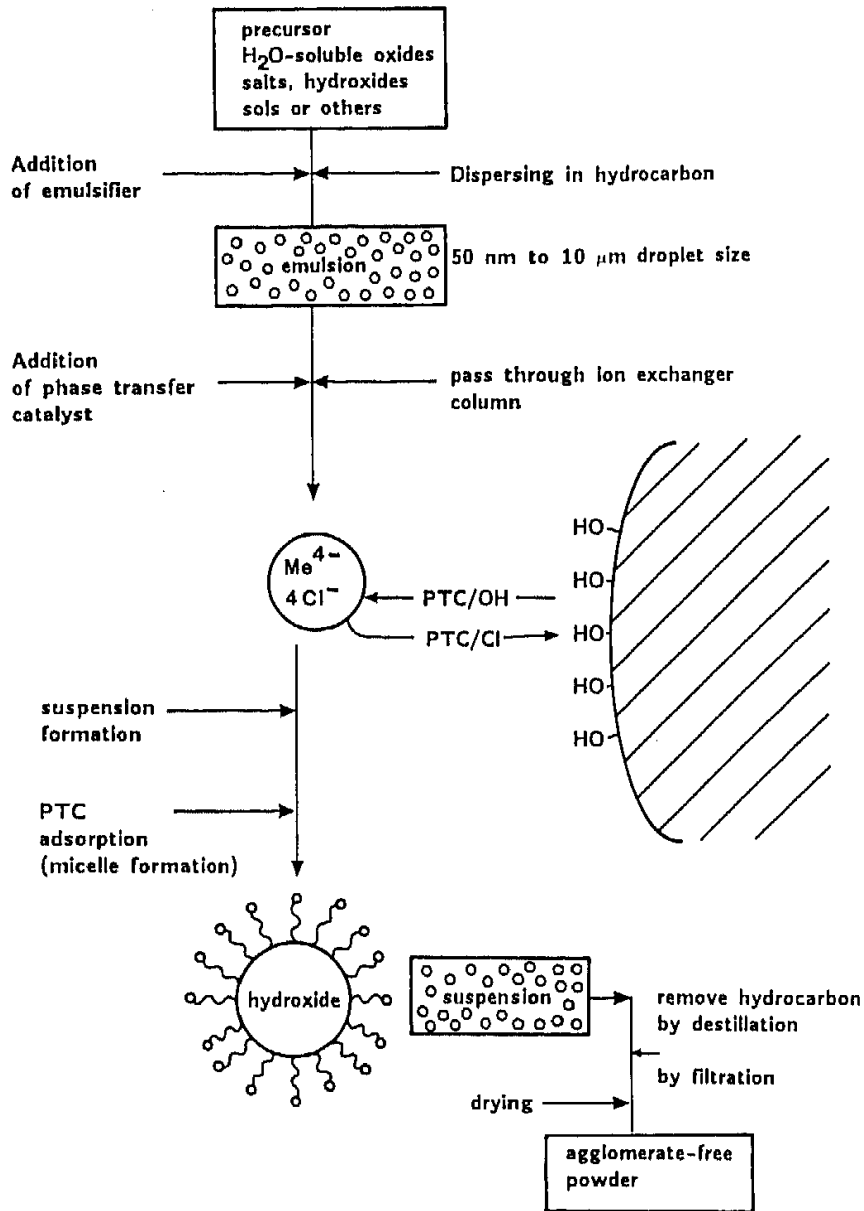


Fig. 7: Scheme of an emulsion process.

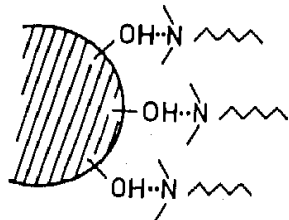


Fig. 8: Micelle formation of quaternary ammonium bases on hydrophilic surfaces.

without agglomeration and processed without milling directly to ceramics. The sol-gel process takes place within the droplets.

Rate control can be easily achieved by type and concentration of PTC and by the ion exchanger.

Powderless processing

It becomes obvious that major advantages of the sol-gel technique can be lost if one has to go through the powder processing step. Therefore, it becomes interesting to think about a way to avoid the "powder" step. In order to draw the right conclusions, one has to go a little deeper into some typical sol-gel characteristics. If one starts with monomers and ends up with a sol, the sol particle are in the nanometer range. In Fig. 9 a particle size distribution is shown for a PZT sol, which is manipulated by complex formers (22).

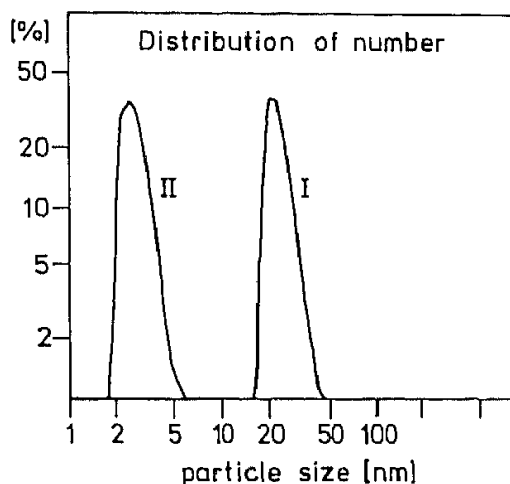


Fig. 9: Particle size distribution of two PZT sols according to (22); II = higher, I = lower complex former concentration.

Gelation takes place by formation of interconnections between these primary particles. Direct processing of these particles to ceramic bodies should lead to almost defectfree ceramics. One main obstacle of processing ultrafine suspensions (= sols) is their low solid content. As pointed out by Aksay (26), it is necessary to stabilize these suspensions. In general, this can be achieved by putting electrical charges onto the particle surfaces (zeta potential) but the decrease of the solid content is the major disadvantage. In Fig. 10, the package density D in a slip is plotted against the particle radius, assuming a 2 nm electric layer around the particle. One can see, that with decreasing particle size, the package density decreases rapidly.

This shows clearly the limits of zeta potential based sol stabilization with respect to solid contents of sols with decreasing particle radius. The solid contents of sols, e. g. from $\text{Al}(\text{i-prop})_3$, range around 5 to 10 % (27). Higher contents, in general, lead to gel formation. But it is possible to increase the solid content by reeptizing dried gel powders in sols by using HNO_3 as peptizing agent. An important measure for the

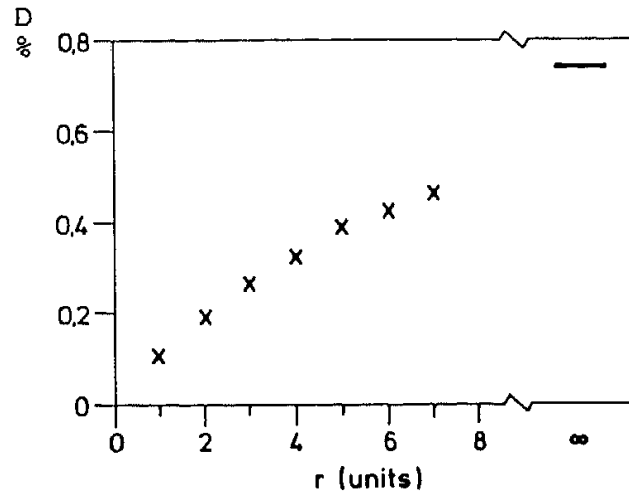


Fig. 10: Theoretical package density depending on particle size; r in nm units.

processing property of a sol is its viscosity. Low viscosities are necessary for casting or infiltration processes. Higher viscosities are required for extrusion. In Fig. 11 the viscosity of powder stuffed sols are shown. After redispersion, the average particle size is in the range of 20 nm.

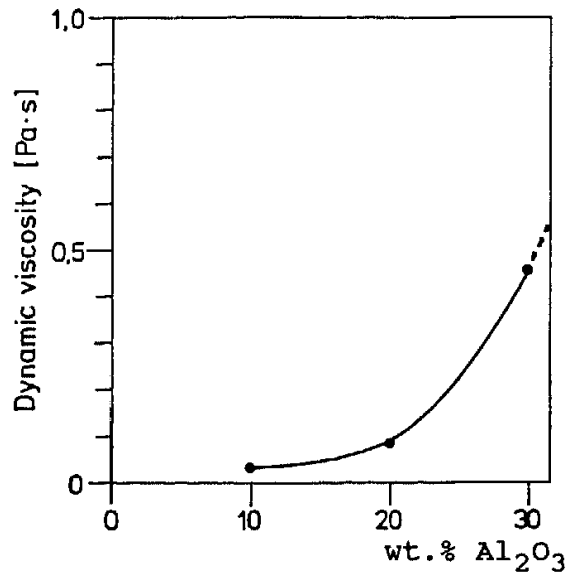


Fig. 11: Dependence of viscosity on solid content of sols.

Up to 30 wt.% of Al₂O₃ the viscosity is rather low, but even up to 50 wt.% the suspension can be processed, e. g. for extrusion or infiltration techniques. Thus, Al₂O₃ fiber mats were impregnated and can be used as insulation materials (28). Another way of powderless processing is shown in (29-30). By complexation of

Al-alkoxides, linear structures can be obtained which can be used for fiber drawing. Fig. 12 shows a sol having a viscosity suitable for fiber drawing.

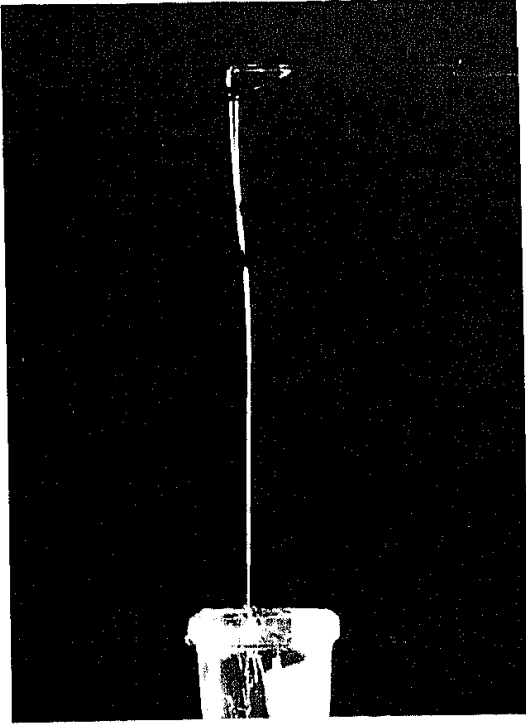


Fig. 12: Fiber drawable Al_2O_3 sol.

Conclusions

Sol-gel techniques offer an interesting route to novel ceramic processing techniques. Limiting barriers are still the costs of raw materials and problems in processing fine and ultrafine powders or sols to high level ceramics. The field of functional ceramics, where the costs of precursors might not play the limiting role, can be of high importance in the future.

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