

CHEMISTRY OF PREPARATION OF CERAMIC POWDERS BY SOL-GEL TECHNIQUES

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INTRODUCTION

The synthesis of ceramic powders is of increasing importance due to the increasing requirements for ceramic materials. Modern structural ceramics like SiC, Si₃N₄ or Al₂O₃ depend on appropriate synthesis technologies due to the lack or the insufficient quality of natural raw materials. Amongst the various preparation techniques the precipitation or crystallization has gained the highest importance, e.g. the Bayer process for alumina. Smaller scale techniques (lab scale or test scale) for special requirements are under investigation: decomposition of salts (e.g. oxalates) or of alkoxides, reactive spray drying, gas phase reactions like plasma decomposition or electron beam evaporation (especially for nanosized powders). The sol-gel process for the synthesis of ceramics has been a matter of investigation for several decades now. The following main advantages were the driving force for this work: to receive higher purities due to purer precursors, to obtain raw materials with better sinter activities, to get more homogeneous powders in multicomponent systems and to tailor grain size and distribution. A survey over the state of art is given in [1-10]. One can conclude, that these papers show the high potential of the sol-gel process. The number of commercial sol-gel derived products is increasing but a major breakthrough for industrial production has still not taken place. Main obstacles, therefore, are the raw material costs which very often are not able to compete with common powders. The cost optimization by chemical engineering may help in some cases. Moreover, the large scale production of agglomerate-free grain size controlled powders is still difficult.

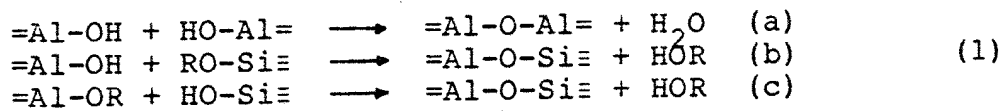
The chemistry of powder synthesis is very complex and characterized by a high number of influencing parameters. The polycondensation process of reactive monomers to "particles" involves several steps very difficult to be monitored by instrumental analysis. The polymeric structures to be formed depend on the starting system, thermodynamics and surface and colloid chemistry. Since ageing processes (e.g. densification or syneresis of gels,

crystallisation from gels) are normally kinetically controlled and very slow, amorphous gels are produced in the first step. As a summary of [1-10], one can say, that chemistry is still a black box for most ceramic systems with respect to mechanisms, kinetics and thermodynamics to gel property relations. In this paper, no attempt can be made to clear up this situation but it will illustrate how chemistry can be used to solve special problems in connection with ceramic powder production.

2. GENERAL CONSIDERATIONS

2.1. HOMOGENEITY

The synthesis of ceramic powders is mainly controlled by the structure defining condensation process of reactive groupings (1).



In this case, Al and Si are two components with extremely different reaction rates. To investigate the influence of reaction conditions on processing properties, a mullite was prepared by two different ways: In the first case, the tetraethoxysilane (TEOS) was prereacted with water before addition of Al-sec-butylate (ABS). In the second case, aqueous concentrated HCl was added to a mixture of TEOS/ABS. Addition of water to a mixture of TEOS and ABS in presence of HCl leads to a clear sol after 0.5 hrs of refluxing, but calcination up to 900 °C leads to still amorphous materials as shown by the X-ray diffractogram (figure 1, curve a). If TEOS is prehydrolysed with water before ABS addition, a clear sol can be obtained too, which can be transformed into mullite at 900 °C completely (figure 1, curve b).

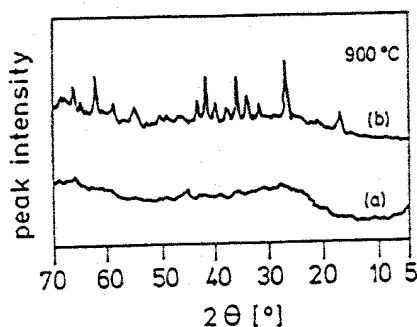


Figure 1. X-ray diffractograms of a 900 °C heat treated mullite gel without (a) and with (b) prehydrolysis of the silane.

The observation is attributed to the fact that in the prehydrolyzed case the alumina is much more homogeneously linked (see equation 1c) to the partially hydrolysed or condensed silica oligomers than in the non-prehydrolyzed case. The resulting inhomogeneity causes longer diffusion paths and leads to a decrease of the crystallization rate.

The three component system $\text{PbO}-\text{TiO}_2-\text{ZrO}_2$ is important for the synthesis of PZT piezoceramics. Starting with an oxide mixture,

sintering temperatures of $> 1\ 200\ ^\circ\text{C}$ are required for PZT formation. The sol-gel route should enable to reduce the perovskite formation temperature and, as a consequence, the sintering temperature substantially due to the possibility of getting more homogeneous and more reactive powders. Therefore, three different sol-gel routes were compared by preparation of a sol from Ti and Zr alkoxides and $\text{Pb}(\text{CH}_3\text{COO})_2$ or $\text{Pb}(\text{NO}_3)_2$. Two alcoholic gels with acetic acid (one precipitated by acetone addition and one by H_2O addition) and one aqueous sol with HNO_3 were prepared. The aqueous sol was transformed into a powder by an emulsion technique in petrol ether [11]. All gels showed extremely high crystallisation activity (figure 2) and sinter activity (figure 3). The aqueous

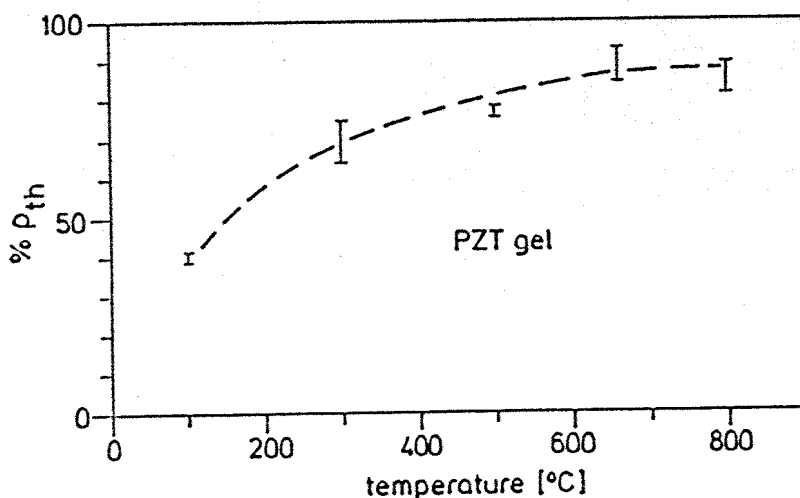
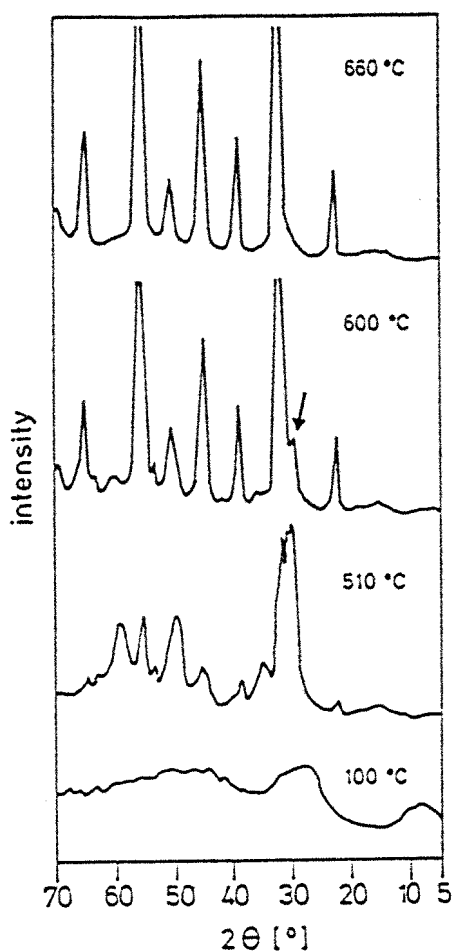


Figure 2. Perovskite formation of PZT sol-gel powders; arrow indicates intermediate PbO formation (only with alcogels).

Figure 3. Sintering behavior of alcogels of compacted powders, atmospheric conditions.

gel did not show any PbO formation. The homogeneity is better than indicated by the high resolution EDAX scan (figure 4) with a resolution of $> 7.5\ \text{nm}$. Whereas in alcoholic sols a phase separation between $\text{TiO}_2/\text{ZrO}_2$ and PbO seems to occur, leading to X-ray detectible PbO_2 at $600\ ^\circ\text{C}$, in the aqueous gel, a more homogeneous incorporation of the lead takes place. EDAX analysis in the dry gel, however, does not show lead clusters. The formation of crystalline PbO (crystallite size $> 0.1\ \mu\text{m}$) must be due (at least partially) to a higher degree of mobility of the PbO in alcogels. Addition of β -diketones (e.g. acetylacetonone = acacH) as

complex formers influence the primary particle size, as determined by dynamic laser light scattering. As a function of the addition of acacH to the reaction mixture of the alcosols, different size distributions can be obtained (figure 5).



Figure 4. Zr distribution in a PZT gel (acetone precipitation).

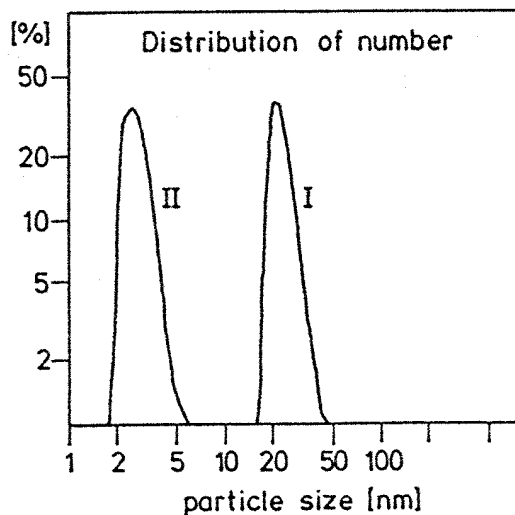


Figure 5. Primary particle size distribution in alcoholic PZT sols: (a) with and (b) without complex former, Zr:acacH = 1:1 after [11].

This is an extremely important finding with respect to particle size tailoring and the preparation of nanosized powders and points out the high potential of "organic assisted processing" (OAP) techniques for ceramic material preparation. As already established by Hench [12] for sol-gel synthesis of glasses, organics as intermediates can help to overcome serious problems of sol-gel preparations.

2.2. OAP TECHNIQUES

One interesting aspect of organic processing was already described above: The influence of complex formers on particle size and distribution can be attributed to the change of solubility of oligomers and the stability of colloids. The stability of sphere shaped particles mainly depend on their size, surface energy, surface tension, and solubility. Surface tension and surface energy can be influenced by weak ligands or adsorbed molecules. As shown by Strehlow [13], a relative energy minimum for different particle sizes can be calculated as a function of the solvent causing a variation of solubility. Based on this, a process was developed to synthesize agglomerate-free ZrO_2 powders with size controlled spherical particles and with a volume yield up to 100 g/l [14]. Agglomerate-free dry powders can be obtained by spray drying of the suspension. Figure 6 shows the different particle sizes and the microstructure of the spheres. Figures 7 and 8 show the "monosized particle formation area" in the $HNO_3/H_2O/acacH$ diagram and the dependence of particle size on acacH concentration. The

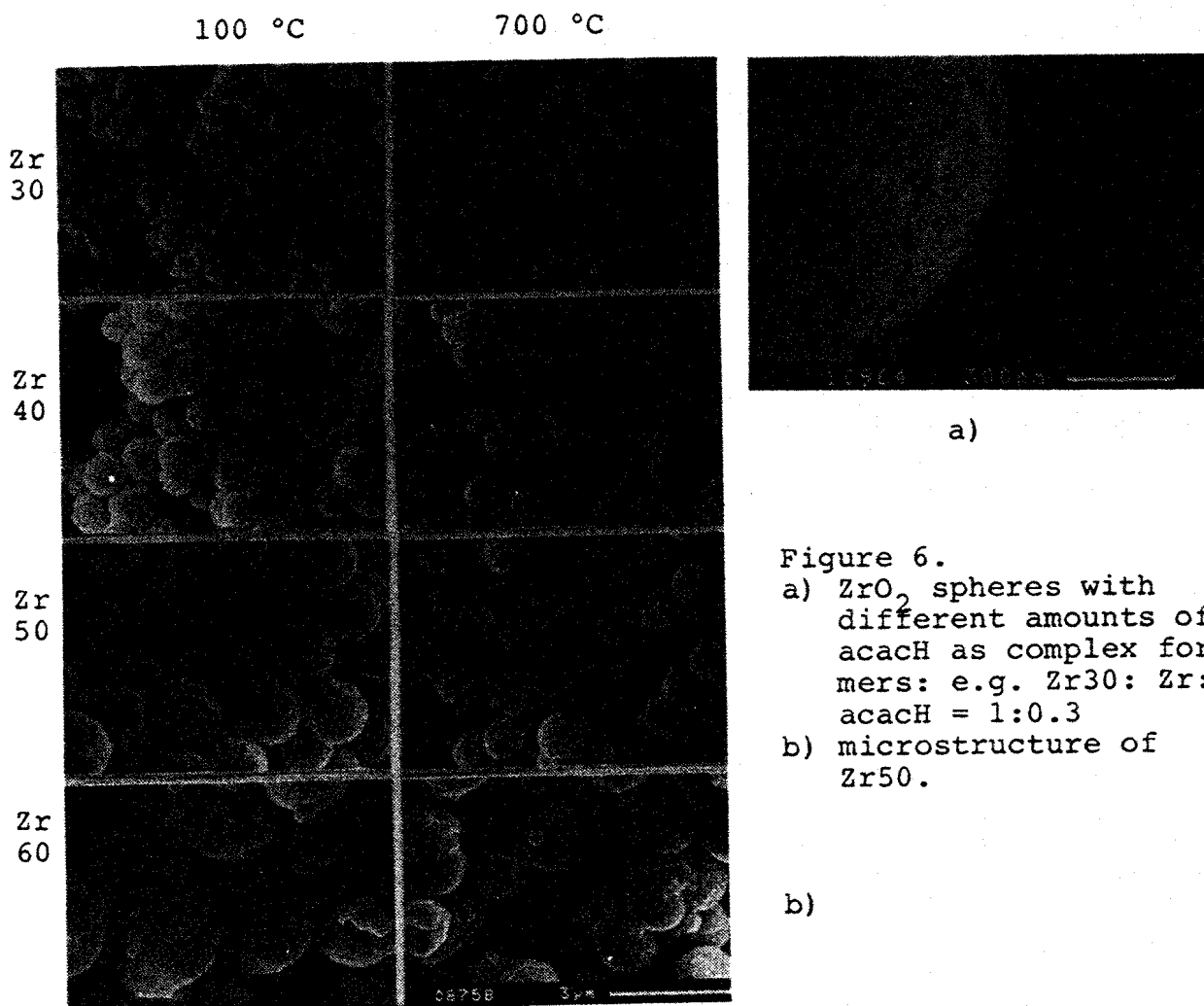


Figure 6.
 a) ZrO_2 spheres with different amounts of acach as complex formers: e.g. Zr30: Zr: acach = 1:0.3
 b) microstructure of Zr50.

b)

sphere size can be easily controlled between 0.2 to 3 μm . Smaller particle sizes would require different separation techniques but seem to be possible.

Similar behavior can be observed with $Al(n-but)_3$ by complexing it with acach and hydrolysing it subsequently: Primary particle size determined by light scattering varies from 1.5 to 3 nm and the BET surface from 25 to 300 m^2/g if the acach:Al ratio is changed from 1 to 2.

Complex formation is a useful tool for $BaTiO_3$ sol-gel preparation, too. $BaTiO_3$ has been prepared from $Ba(CH_3COO)_2$ and $Ti(OR)_4$ with acetic acid as complex former in ethanol. Water addition to the mixture results in a clear gel and LAXS analysis of the amorphous material shows the existence of hexanuclear Ti-acetate and tetranuclear Ba-acetate complexes [15]. Heating up results in X-ray amorphous $BaCO_3$ and TiO_2 , a complete transformation of the $BaCO_3/TiO_2$ mixture into the perovskite structure takes place at 650 $^\circ C$. The low transition temperature can be attributed to the fine dispersion resulting from the stabilization effect of the organic ligand which prevents phase separation and cluster formation.

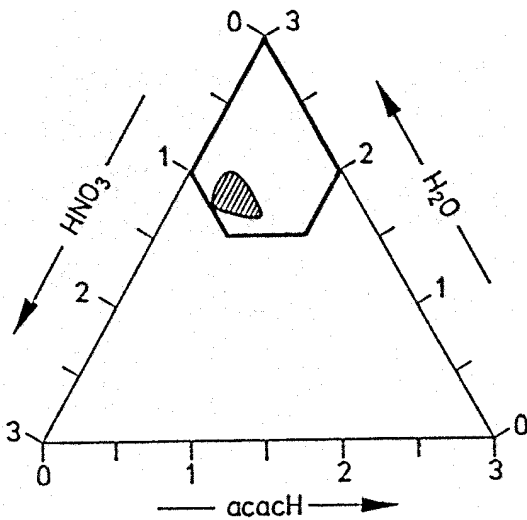


Figure 7. Area of stable, agglomerate free particles (hatched area).

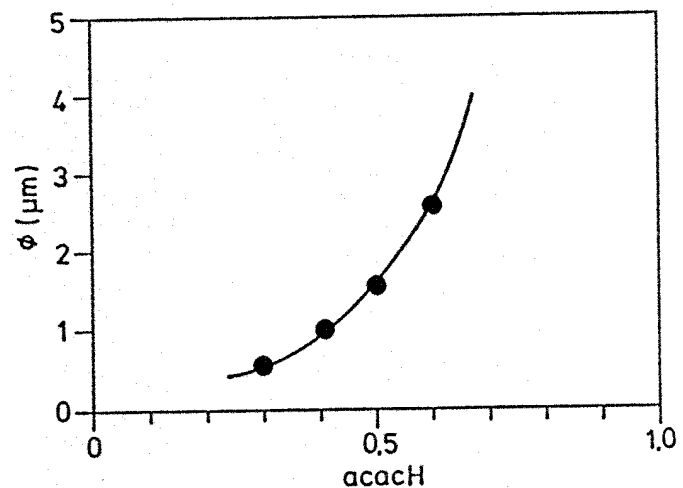


Figure 8. Particle diameter versus complex former (Zr:acach).

2.3. SHRINKAGE

The shrinkage problem is one of the main obstacles for drying sol-gel derived green bodies. In order not to lose reactivity the powders normally are not calcined at higher temperatures and pressed bodies shrink remarkably due to low grain densities. In order to overcome these difficulties, ceramic bodies were formed using a mixed process. A sol binder was mixed with Al_2O_3 sol-gel powders calcined at different temperatures, ceramic bodies were formed, and drying and sintering shrinkage were determined (figure 9).

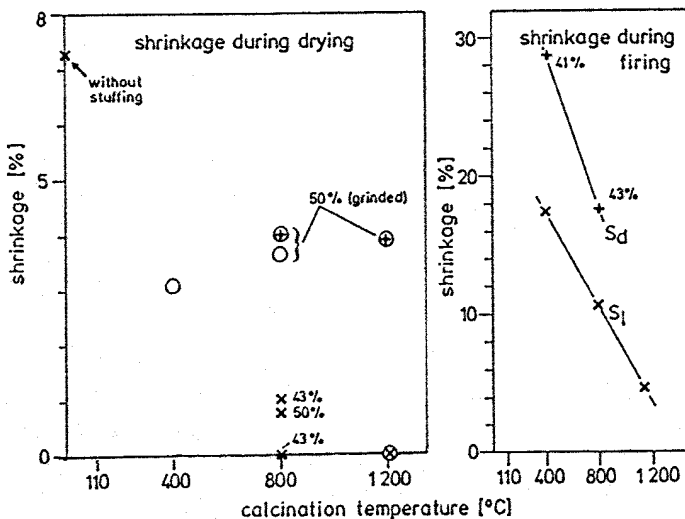


Figure 9.

- a) Drying shrinkage of gels stuffed with sol-gel powders and calcined at different temperatures; numbers indicate the total Al_2O_3 content of the dried (110 °C) body. o: after one day; +: one week later; x: two weeks later.
- b) Firing shrinkage: S_d = thickness; S_l = length.

The main results show, that due to the mixed processing the drying shrinkage as well as the firing shrinkage can be controlled and kept within moderate ranges. Due to the sol as binder, the systems show high sinter activity.

3. CONCLUSION

The sol-gel process appears as a useful method for the preparation of special ceramic powders. Chemistry is a powerful tool for tailoring the powder properties like agglomeration, particle size, powder reactivity, or shrinkage but is not applied yet with the full range of possibilities. Further developments are necessary including chemical engineering for economic production techniques.

4. ACKNOWLEDGEMENT

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