Inorganic-Organic Sol-Gel Processing

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1. Introduction

The sol-gel process can be considered as a method using synthesis principles of inorganic chemistry to prepare ceramics and composites. The focus of the method is directed to materials. Due to the lack of broad large-scale applications (e.g. compared to metals and polymers), the synthesis route never has gained a comparable significance in chemical industry like polymers synthesis, for example. A few exceptions in the medium-scale range are abrasive materials like alumina, some inorganic fibers (Nextel, SiO_2) or barium titanate. Some larger-scale applications are coatings on TiO_2 pigments or wash coats on cordierite catalyst carriers. But in these applications, the use of the sol-gel route is already system-oriented. As a consequence of the low market expectations for not system-integrated materials (as "material market"), there never has been much effort made by material-producing industries like chemical industries for larger-scale materials developments as well as for basic material developments, and as a further consequence, the main activities for material developments take place in research institutes and universities. However, in numerous cases, this leads to the develoment of materials with very interesting properties, but low resonance in industry due to the lack of "system orientation", a focus of extremely high importance for materials user (not materials producer).

For this reason, it is necessary to create well-operating links (interfaces) between the scientific part of the sol-gel field and the user community. These interfaces would help to evaluate fundamental results in a very early state for their applicability and to direct them towards a system-oriented materials development. Furthermore, this would help to canalize the large variety of possibilities offered by the sol-gel route into directions to enable an easy transfer into industry.

Especially the fact that a great deal of the elements of the periodic system of elements can be used, the reaction can be influenced by numerous parameters (precursors, solvents, temperature, catalysts), and the possibility of incorporating organic components makes it very difficult to decide in an early state what is useful for practical application. To decide which results are useful for further development, needs a permanent dialogue with materials' users since materials can play the role of an enabling technology with key function for many fields.

In the following, it will be shown that strategical approaches combined with industrial dialogue can lead to a very wide material development gaining high interest for materials users. Of course, it is necessary to start with fundamental investigations to guarantee high-level innovation.

2. Strategical Approach

Sol-gel reactions, in general, are characterized by starting from molecular precursors. By a growth reaction colloidal or macromolecular type of system are formed which by gelation generate a three-dimensional network (gel). Stabilized colloidal sols can be used as an already oligomeric type of precursor, too. Stabilization, in general, is carried out by electric charges generated on the colloidal surface by absorption of ions or dissociation processes of reactive groupings, which, in general, is pH-dependent. Particle size in sols typically are in the range between several and 50 nm. Taking into account the range of electric charge repulsion (nm range), the solid content of sols, as a rule, is rather low. In fig. 1, it is shown how the interparticular distance effects the solid content as a function of the particle size.

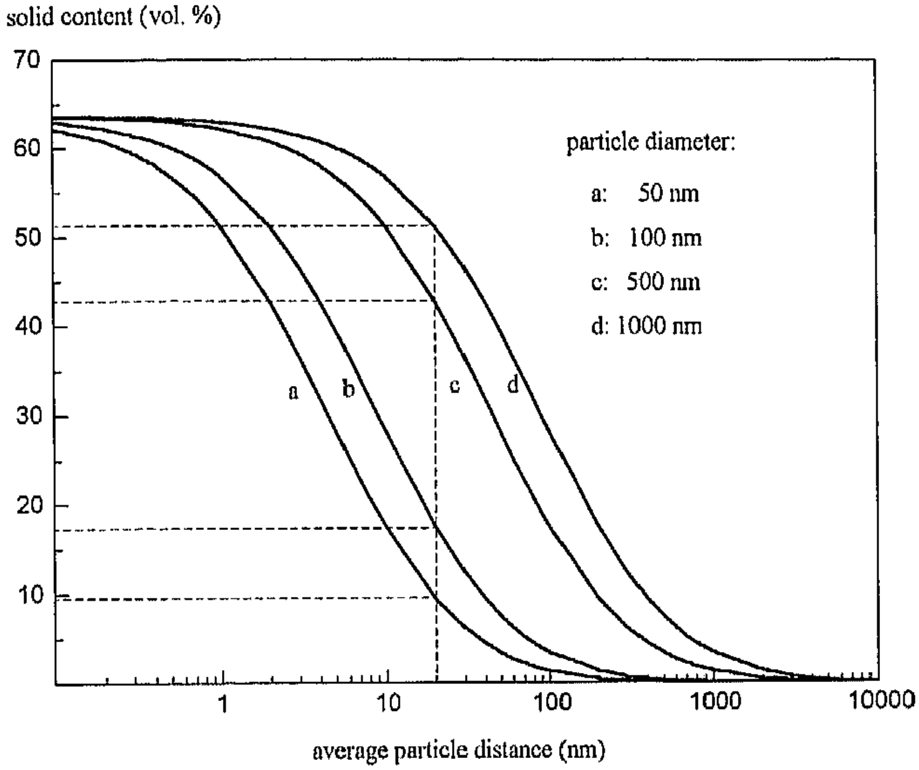


Fig. 1: Relationship between particle size, particle distance and solid content with spherical particles as model.

As one can see, in a system with small colloid diameters (the repulsion distance is in the range of nanometers) the solid content is extremely low.

Destabilization of sols leads to gelation, but due to the strong particle-to-particle interaction in oxidic colloidal systems, the OH groups dominating the particle surface, the gel network does not arrange in dense packing and the solid content of gels in most cases is below 20 vol.-%. This effect makes monolithic or thick-film processing extremely difficult since large shrinkage with stress formation takes place, leading to cracks within films above 1 μm thickness [1], and for monolithic processing, high sophisticated routes have to be used for large part fabrication [2, 3]. This is one of the reasons why sol-gel processing is not considered to be a good route for bulk processing.

This consideration leads to the conclusion that the control of the particle-to-particle interaction is a key issue for obtaining higher green densities through sol-gel processing. From the particle surface chemistry control, it can be expected that the relaxation behavior in gels can be increased, thus enabling in combination with higher packing densities monolithic processing in a way similar to conventional ceramic processes. Furthermore, if the surface modification is carried out with chemically reactive groupings, additional processing properties should be able to be obtained, such as polymerizability, (for example, to provide tailored incorporation of the small particles into polymer-type of matrices), to obtain resist behavior for photocuring or photolithography techniques.

Another interesting aspect of small particles are special properties related to their small dimension, for example metals or semiconductor quantum dots (variable band gap energies or plasmon resonance). So it is interesting for several reasons to develop methods to handle small sol-gel-derived particles since the gel process provides an easy means to synthesize them. Another very interesting point is the fact that Rayleigh scattering can almost be neglected completely if the particle size is kept below of 1/20 of the wave length of the used light for a variety of optical applications (if long-distance transmittance is not considered). This allows to develop optical systems where metal, ceramic or semiconductor particles are used for their solid state functions.

3. Surface Modification and Particle Growth

As a simple model for the growth reaction, the ΔG value of the surface-free energy versus the ΔG of the formation of the solid systems can be used. As long as there is no sink of the surface-free energy established, the particles grow as long as precursor molecules are present (fig. 2).

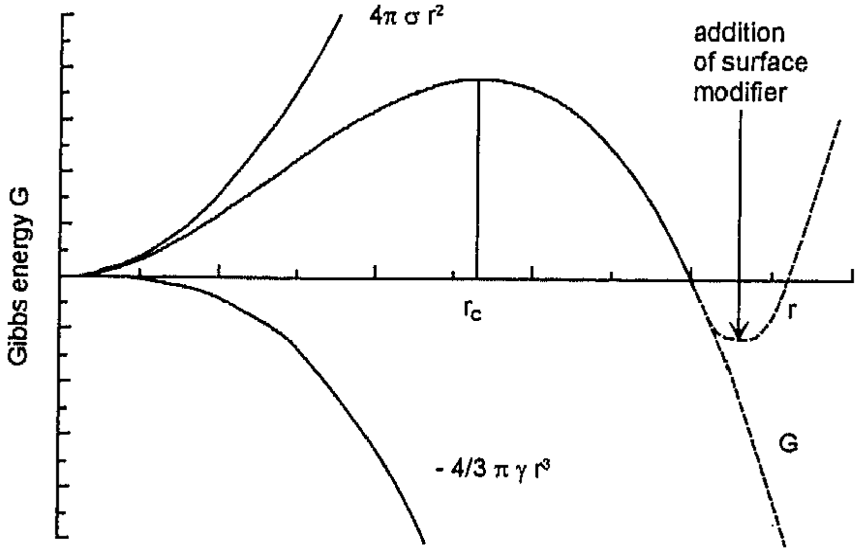


Fig. 2: Gibbs free energy as function of the particle radius.

The addition of molecules interacting with a growing surface is able to stop the growth process if the ΔG value for this reaction results in a lower G (total) than that for the growth reaction. Depending on this chemical nature, these interfacial active components can prevent the particles from growing together and thus avoid agglomeration. This could be demonstrated for nano-titanium nitride with 40 nm of particle size prepared by the CVR process from H. C. Starck company. The powder can be deagglomerated to its primary particle size of 40 nm using guanidino propionate as a surface modifier. Guanidino propionate forms a surface chelate compound to the Ti^{4+}, leading to a rather stable surface compound. Using this method, stable sols of titanium nitride can be prepared and processed to bulk parts (gels!) with a green density of nearly 60 % by volume, which is quite unusual for sol-gel processing. This process shows that by use of proper surface modification, packing density even with nano-particles (typical for sols) can be increased to a level at which conventional ceramic processing is possible. The firing of a green body up to 1350 °C leads to almost complete densification without grain growth, which is shown in fig. 3.

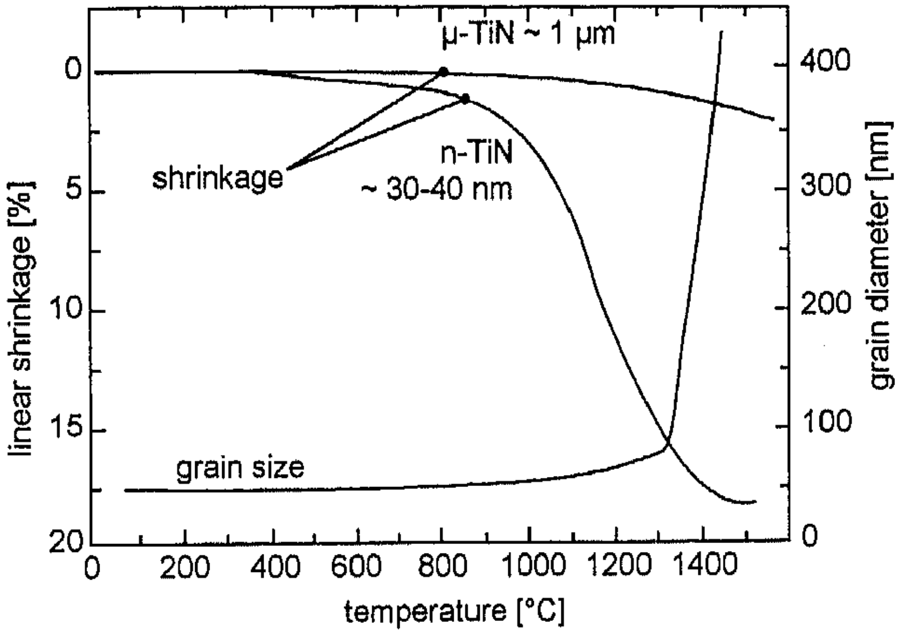


Fig. 3: Densification and grain growth in nano titanium nitride.

The sols can be used for coating of ceramic and steel, and the coatings up to 10 μm thickness can be densified between 1150 and 1300 °C. The reduction and sintering temperature is substantial since micro- or submicrometer titanium nitride only can be densified to full density under very special conditions at temperatures between 2200 and 2400 °C.

The message to be drawn from this example is that, taking care of the particle interaction, it is possible to end up with high green density gels, allowing conventional techniques for part fabrication sintering temperatures cut down to about 50 % of what is known from conventional ceramic processing. Moreover, the grain growth can be prevented, leading to a nano-sized crystalline structure with defects in the nano range. Microstructure tailoring then can be achieved by further heat treatment in a desired way. Control of particle-to-particle interaction allow to exploit the potential of sol-gel processing for monolithic ceramics, a dream which has been in the literature for more than 20 years, but never has become true. So, much effort should be put into the handling of small particles since this route seems to have a great potential for a new type of ceramic processing. Separating densification from grain growth in ceramic processing allows to tailor ceramic microstructure in a unique way compared to conventional processing. The principle of using interfacial active compounds can also be used for synthesizing agglomerate-free ceramic nano powders as shown for ZrO_2 and Y_2O_3/ZrO_2 [4]

4. Nanocomposites

As already mentioned in the introduction, small particles incorporated into transparent matrices allows to develop interesting optical properties. For example, as shown elsewhere [5], zirconia nano-particles can be synthesized from alkoxides using carboxylic acid as alkoxide modifiers. By using appropriate hydrolysis and condensation conditions, nano-particles can be obtained in a crystalline form, as shown by electron diffraction (fig. 4) with methacrylic acid as growth-controlling agent and methacryloxy silanes as an additional inorganic-organic matrix former [5].

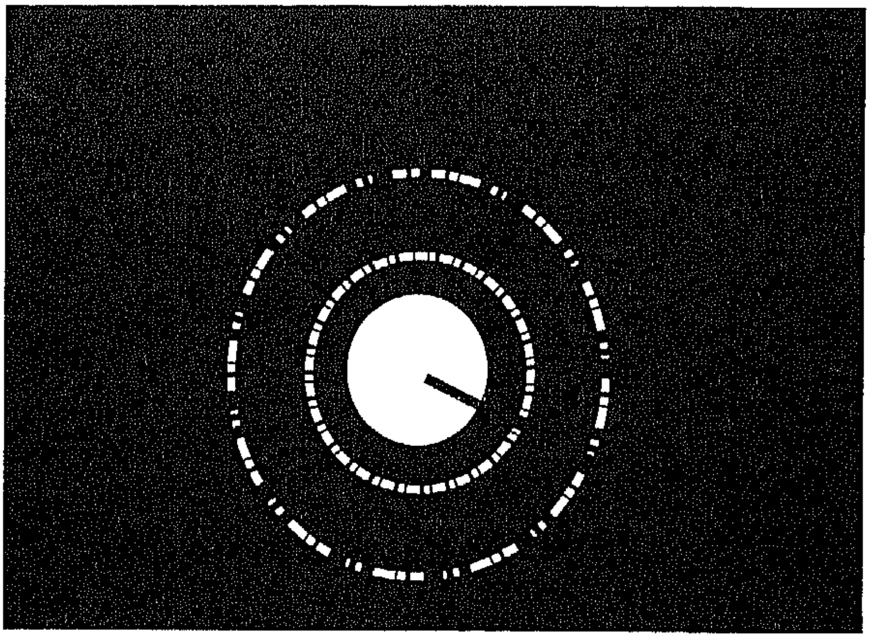


Fig. 4: Scheme of Electron diffraction pattern of zirconia particle containing nano-composite in an ormocer matrix consisting of methacryloxy silane and methacrylic acid as precursors after [6].

The crystalline phase with < 2 nm in diameter is obtained at temperatures below 120 °C. Electron diffraction patterns indicate that the crystalline phase is mainly monoclinic zirconia. Methacrylic acid is stably bond to the surface, as proved by ^{13}C NMR and IR, and the double bond of the methacrylic acid can be used to polymerize the colloids into organic matrices. One interesting aspect of this system is the matching of refractive indices for optical waveguides and claddings including photolithography. Optical losses in the 800, 1400 and 1500 nm range are detected to be below 0.3 dB/cm (resolution of the used method). The surface hardness of these systems is much higher than that of polymers, which is attributed to the nano-particles distributed in this system. The chemical durability, especially against organic sovents, is remarkably higher than that of polymers. These systems have been used for the fabrication of optical waveguides and microoptical components, as shown in fig. 5.

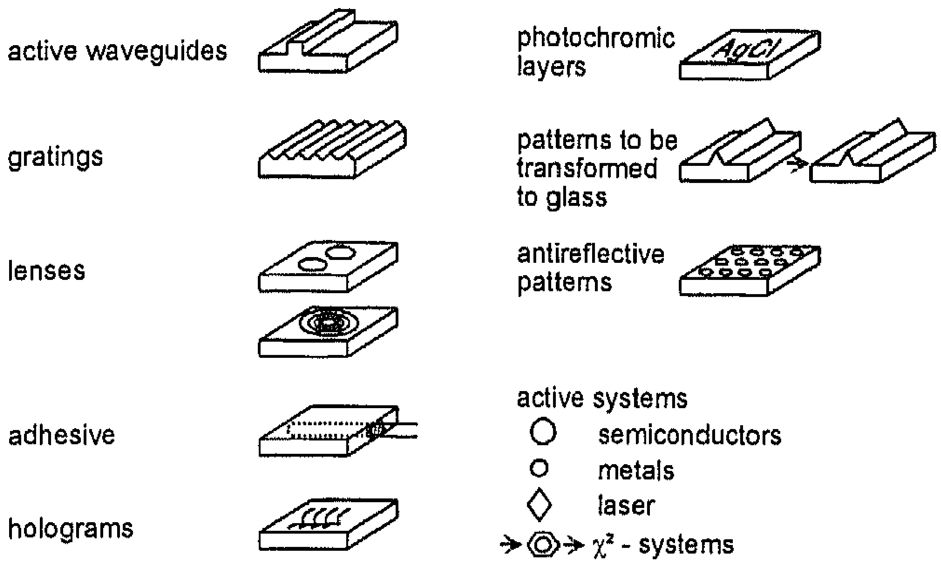


Fig. 5: Optical applications of nanocomposite systems.

As shaping techniques, laser writing, holographic techniques and embossing techniques have been used. Zirconia has been used as a model system so far. It is supposed that similar reactions can be carried out with a variety of other systems opening an interesting field of new optical composites.

In this connection, the question of the interfaces between small particles and the surrounding matrix arises. Due to the fact that the "interfacial volume" increases rapidly with decreasing particle size and can reach a volume fraction up to 50 %, as shown by Gleiter [7]. The question is how far interfacial phases can determine material properties and how far the structure of the interface will play a role. A composite has been synthesized [8] where nano-scale boehmite or γ-alumina particles with about 15 nm in diameter have been used as catalysts for epoxy groups linked to hydrolyseable and condensable silanes. By NMR measurements, it could be demonstrated that epoxy polymerization preferably takes place around the nano-particles and, in addtion to this, ≡Si-O-Al= bonds are formed from the silanes to the alumina surface. From this findings the model has been developed that the nano-particles are flexibly suspended in an inorganic-organic network, as shown in fig. 5. These systems can be prepared as transparent coatings and cured at comparingly low temperatures (90 - 120 °C) to scratch-resistant coatings. Comparing the mechanical properties with other systems, the scratch resistance is extremely high (fig. 6) and cannot be explained simply by the volume fraction of the nano-particles, which is only in the range of about 5 %. In fig. 6, a so-called drum test where coated surfaces are treated with abrasives in a turning drum shows the differences between different scratch-resistant coatings on plastics. The high performance of these coatings is interpreted by the interfcial structure since, for example, filling a polymer with 5 vol.-% of SiO_2 does not show this effect.

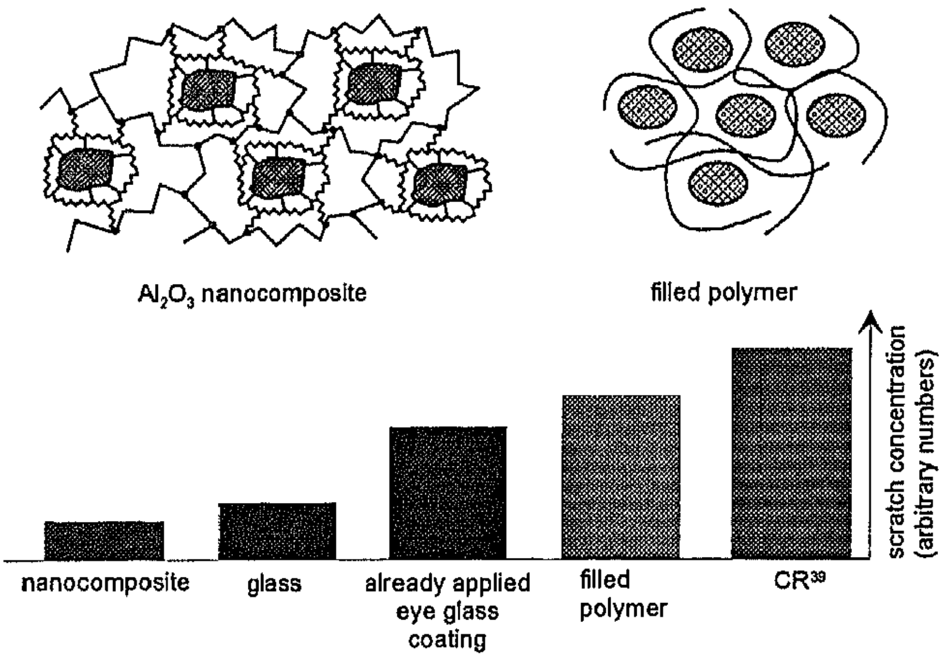


Fig. 6: Structural model of an Al_2O_3/epoxysilane nano-composite compared to filled polymers, an abrasion resistance of various hardcoatings after drum testing.

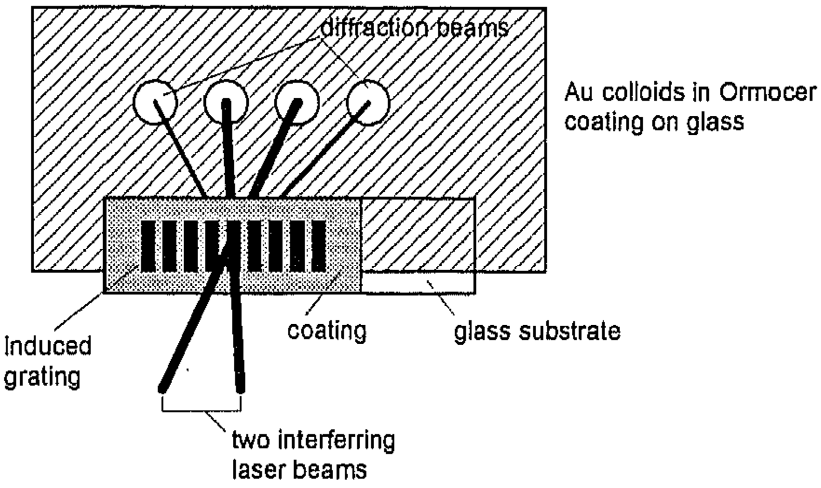
This system can be used as a basis for incorporating additional functions like low surface-free energy coatings [9], hydrophilic coatings with permanent wettability [10].

The coating systems is used in industry for protecting plastig eye glass lenses from mechanical damage. This type of materials can be considered as "interfacial phase-determined materials".

The sol-gel process opens the possibility for another new class of materials. Especially the coatings with low surface-free energy, which have an oleophobic and hydrophobic character at the same time, in addition to this show a very interesting structural effect [10]. During the coating a self-alignment takes place meaning that the groupings responsable for the low surface-free energy turn to the surface whereas polar groups turn to the substrate to form good adhesion. Primary driving force is the reduction of surface-free energy. This is another opportunity for sol-gel processing, using multicomponent sols with self-aligning properties based on the chemical properties of the single components to tailor gradient functional coatings. Summarizing, one can say that there is a great field of opportunities for intelligent materials development, based on this type of nano-composites, especially with respect to interfacial property-determined new materials.

Another type of nano-composite has been synthesized by using semiconductor or metal colloids. For the synthesis the same approach as described above has been used with the proper choice of interfacial active molecules as key. For example, in cadmium sulfide, precipitated under control of compunds with complex forming properties (sulfides or amines) and incorporated into inoganic-organic ormocer type of matrices, fluorescence emissivity can be changed by the electron donator or acceptor behavior of the growth-controlling or -stabilizing ligands. If amino group-containing ligands are used, a strong blueshift compared to sulfidic groupings is observed. This shows that the ligands interfere with positions occupied by the electron after the formation of the electron-hole pair as an intermediate location [11]. It is interesting how far the energy of these electron positions can be related to the lifetime. This question is under investigation at present. But one can say that it should be possible to tailor fluorescence wavelength as well as lifetime of semiconductor quantum dots by proper choice of surrounding ligands. In the described case of amino and sulfido ligands, silanes carrying these groupings are used in order to be able to incorporate the particles into sol-gel processing.

Similar synthesis reactions can be carried out with a series of different metals like lead, silver, palladium, palatinum and gold. In the case of gold it could be shown that extraordinarily high χ^3 coefficients can be detected by self-induced refractive grading measurements, as shown in fig. 7 [10].



$$\chi^{(3)}_m = 2.6 \cdot 10^{-6} \text{ esu}$$

Fig. 7: χ^3 values of gold-ormocer nanocomposites measured by the self-diffraction grating experiment.

Since, as electron microscopy shown, the particles are not spherical, the high χ^3 values are attributed to the non-spherical shapes, which is in accordance with theoretical considerations.

5. Conclusions

As one can see, there is a great possiblilty of using sol-gel processing for tailoring interesting new materials based on small particles. This is of interest for a variety of different topics which are

- nano-processing of ceramics to obtain high packing densities and low sintering temperatures and to separate densification from microstructure formation, especially grain growth. This can lead to a new type of ceramic processing, especially for achieving monolithic components from sol-gel processing with low defect rates or tailored microstructure;

- synthesis of particulate systems in the nano range from glasses, ceramics, metals and semiconductors for composites either using special properties related to the small dimensions (quantum effects) or interfacial properties resulting from the large interfacial area (interfacial phase-determined materials).

Summarizing, there is to say that the potential of sol-gel techniques is by far not at its end. New aspects are arising with excellent perspectives for fundamental research as well as for applications. A small selection with systems under development is given by the "sol-gel tree" in fig. 8.

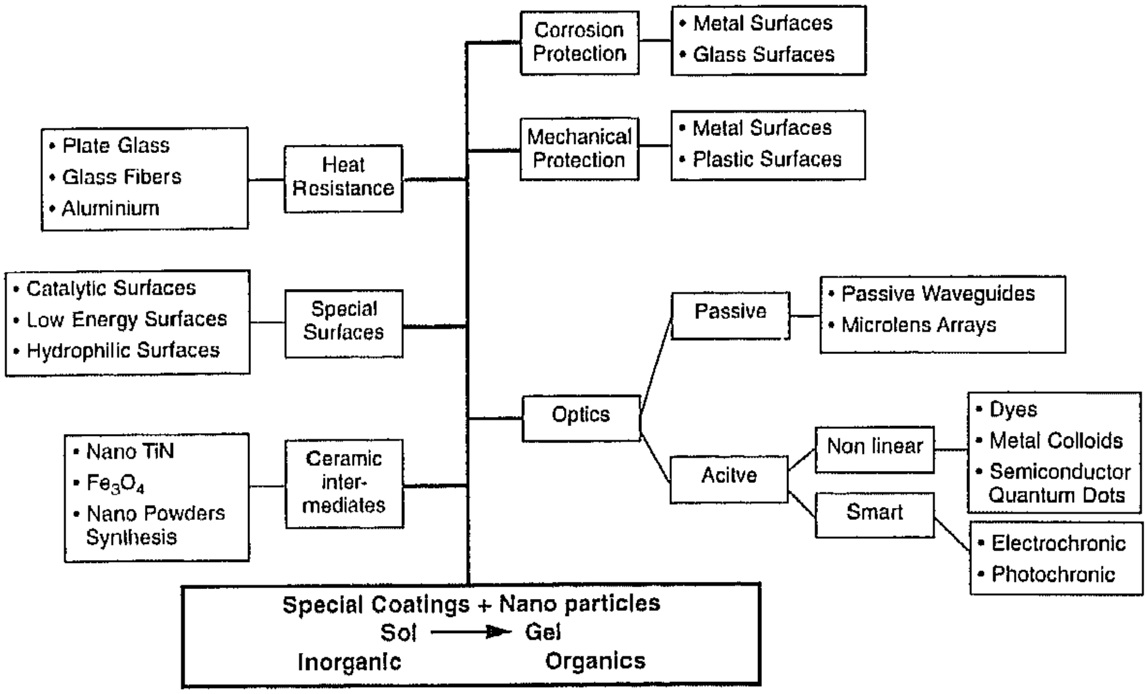


Fig. 8: Scheme of sol-gel tree for nano-processing techniques.

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