Characterisation of suspensions of nanosized glass powders

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Using nanosized powders, silica and multi-component glasses can be manufactured at significantly reduced temperatures. Starting point for the powdertechnological production route in most cases is a colloidal (particulate) gel derived from a suspension of nanosized particles. Therefore a great interest is as well the primary investigative inspection of the suspension under consideration as well as – in later production process – the process control when having to produce a suspension with identical poroperties repeatedly. Attenuated total reflectance infrared spectroscopy (ATR) is one of the appropriate tools for solving such problems in many regards. Complementary to ATR, Cryo-SEM micrographs of comparable suspensions are introduced.

Introduction

Apart from traditional melting, glasses can be prepared via sintering of nanosized powders at significantly reduced processing temperatures. For this purpose, these nanosized powders have to be dispersed and a homogeneous compact with high green density has to be formed[1]. Shaping of the greenbodies is performed with great advantage at room temperature from the suspensions with ceramic techniques. After drying and calcination to remove residual organic impurities, the porous greenbodies can be sintered to dense, transparent glassbodies. Process performance and reliability depends to a very large extend on the suspension properties. Particle size and agglomeration, spatial distribution of the nanosized particles in each batch and suspension viscosity are stronly correlated and have to be controlled therefore continuously.

The following text gives examples of such control by using the infrared spectroscopical technique of attanuated total reflectance (ATR). This method is favoured for many chemical applications since sample preparation is as easy a possible: liquids or gels, sometimes even elastic samples are brought into contact with the surface of an ATR-crystal, typically used are germanium or zinc selenide. The infrared light is guided into the crystall and – without an absorbing medium – reflected totally inside at the outer surfaces (see Fig.1). So – ideally and without a sample – the full intensity of the incident light is guided to the detector. Samples on the surface of the crystal cause light absorption in certain spectral regions. This happens by damping of the "evanescent" electric field of the light wave penetrating through the crystal surface into the (typically) first microns of the sample. The shape and intensity of the absorption bands recorded is characteristical for the material (the chemical compounds) and even the particle size of the nano-powders in the suspensions.

Experimental set-up

Aqueous suspensions of both nanosized and coarser silica powders were prepared. The nanosized fumed silica powders used were Degussa Aerosil OX 50 and A380 with a mean particle size of 40 and 8 nm respectively. The average size of coarser silica particles from several origin was some microns. For infrared spectroscopy, a Bruker IFS66v was used, the

sample chamber was purged with dry nitrogen permanently to remove water bands from ambient air. The ATR equipment used here is a standard one, it consists of a germanium crystal in a small mould, the angle of incident light is 45°.

Results and Discussion

Suspensions with different amounts of a nanosized fumed silica powders were prepared and ATR-measurement was carried out like described. Typically, spectra show many details of greater or minor interest, which have to be identified.

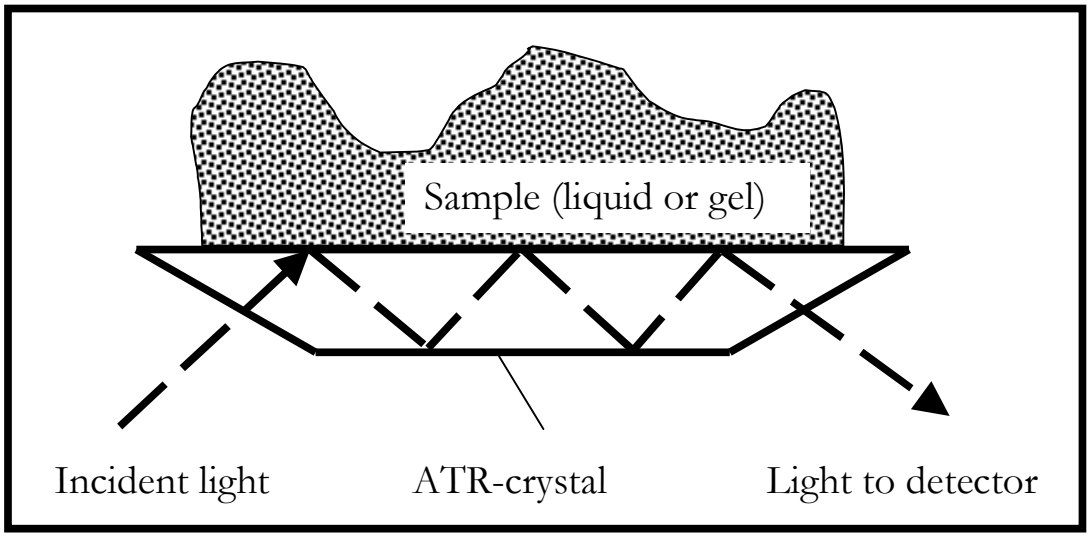

Figure 1: Typical arrangement for attenuated total reflectance measurement. The assembly is mounted within the sample chamber of an infrared spectrometer.

The spectra shown in Fig. 2 are already reduced in spectral region to show the absorption band typical for the silica particles in the suspension. Transmittance one (full transmittance) would mean no absorption of the sample. The reduction in transmittance results from the combination of water bands and the absorption due to silica particles.

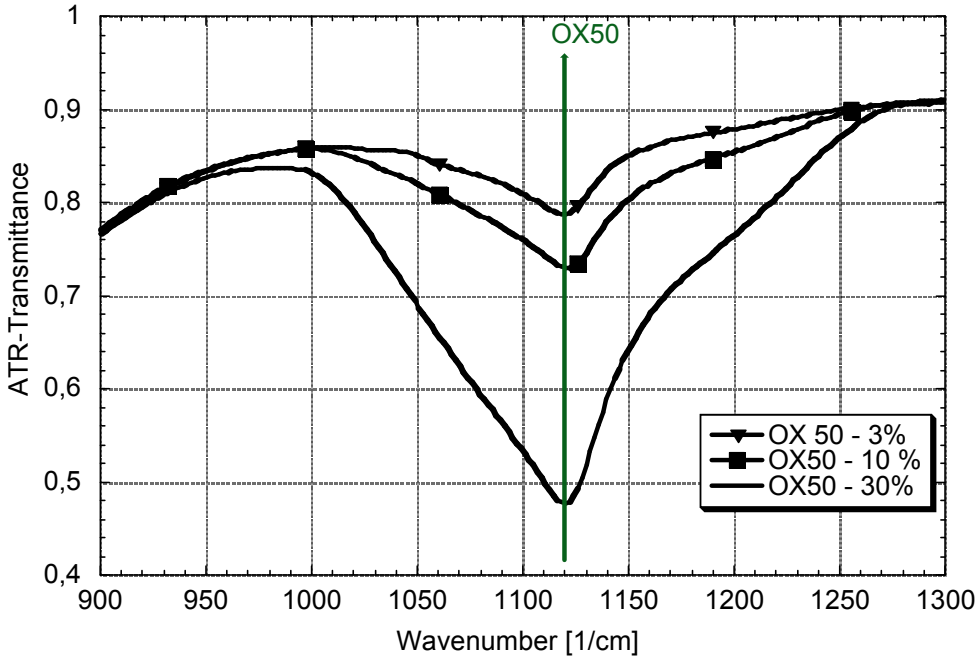

Figure 2: ATR-infrared spectrum of aqueous suspensions with different fused silica particle concentration. The spectral position of the absorption band can be correlated with bulk fused silica.

The spectral position of the absorption bands in the fig. 2 can be correlated to network vibrations of bulk silica. Clearly to be seen is the correlation between concentration of silica particles in the suspension and the intensity absorbed. This enables the method to be used for concentration measurement within a well-known set of suspensions.

When preparing colloidal or particulate gels, for some applications highly filled suspensions with larger particles are of interest. Fig. 3 shows spectra of such larger particles in suspensions. Clearly to be noted is the different shape of the absorption bands. With appropriate numerical methods, even this shape of the absorption bands can be deduced from bulk silica dielectrical properties[2]. Numerical analysis following the "effective media model" will be reported elsewhere. Having only molecular ATR-spectra of everyday´s chemical analysis in mind, the changes in shape might easily mislead to the assumption of different "chemical" composition. In fact, all the spectra in fig. 3 result from fused silica particles suspended in water.

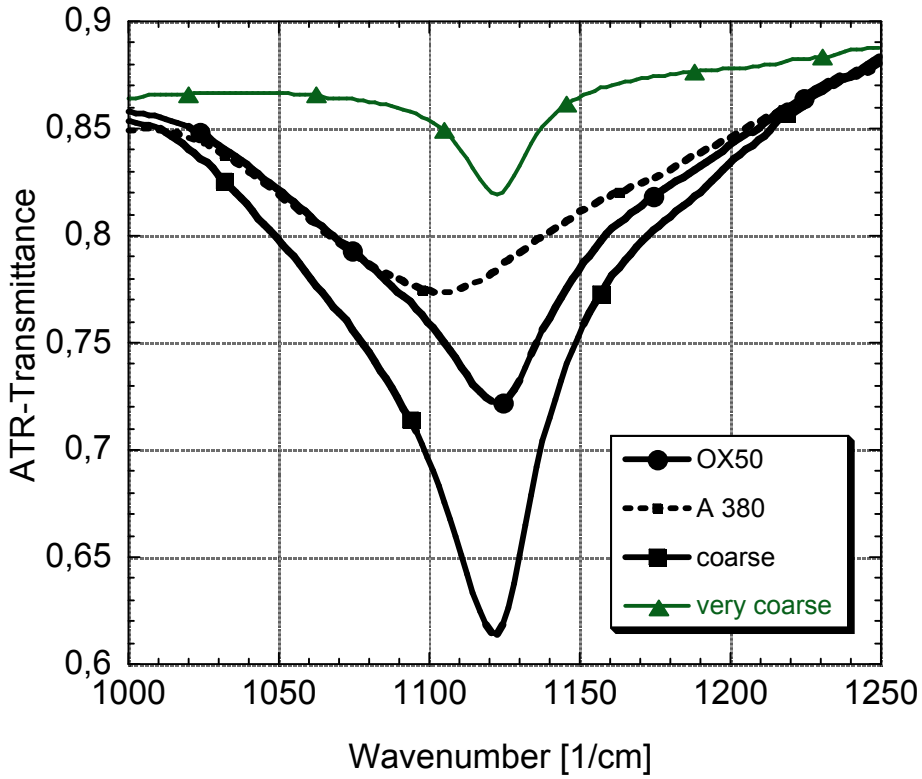

Figure 3: Different particles sizes in suspensions lead to diffent shapes of the absorption bands around 1100 1/cm.

One of the few suspension properties ATR-spectroscopy proves to be quite insensitive to is the degree of stabilisation within the suspension. This is certainly due to the fact that the wavelength of infrared light is much longer to typical particle dimensions. Therefore, ATR "averages" over suspensions water and particle content. So ATR-spectra of well-stabilized OX50-suspensions at pH=8 do not differ from spectra taken at pH=4, where particles show strong agglomeration. Both spectra are very similar to those in fig. 2. In this case, freeze-drying the suspensions and investigating microstructure by cryo-SEM is the appropriate method, see fig. 4

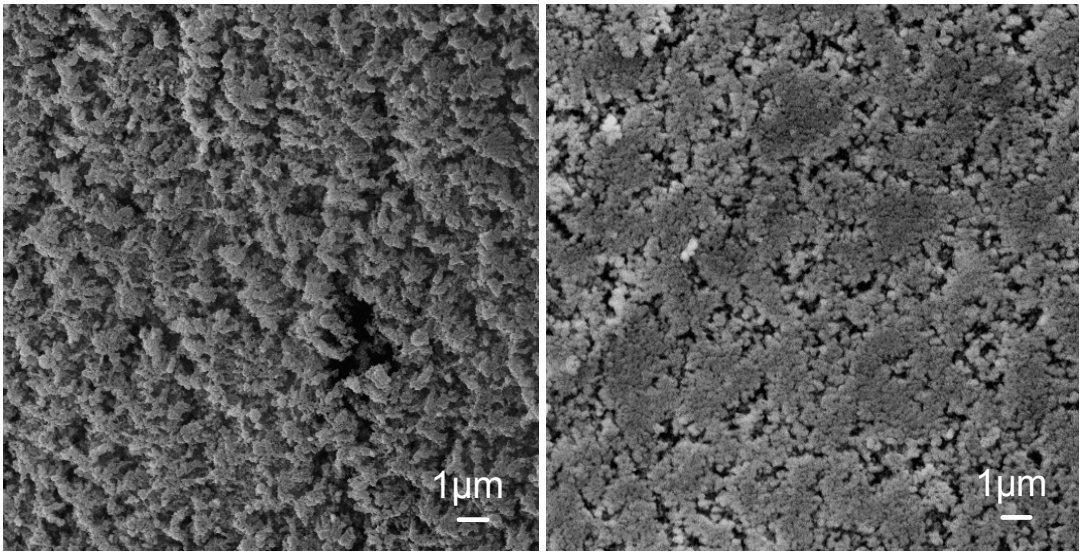

Figure 4: Cryo-SEM micrographs of aqueous suspensions with and without stabilisation. OX50, 30 wt%, at pH 4 slightly agglomerated (left) and stabilised (right) at pH 8.

As the cryo-SEM micrographs show, stabilised suspension (right) appear to be smoother compared to the unstabilised (left). The agglomerated particles on the left side have much more free space available for shear movement – so viscosity is much lower here.

Conclusions

Suspensions for colloidal gel processing of nanoscaled powders can be characterized with advantage by ATR infrared-spectroscopy. As known from broad application, ATR is sensitive to absorption bands identifying chemical compounds. In addition, the technique proves to be sensitive to concentration of the particles in the suspension and to some extend also to the particle size. This manifests in different shapes of the spectra and will be investigated further. To observe the degree of stabilisation, different techniques like cryo-SEM can be applied with advantage.

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[1] R. Clasen, J. Non-Cryst. Solids **89**, pp. 335-344 (1987).

[2] D.J. Bergman, Phys. Rep. C **43**, p. 377-407 (1978).