SAXS studies of phase separation in borate glasses and structural transformations in precursors of silica glass

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Abstract. — Applications of SAXS to structural studies of oxide glasses are reviewed. The evolution in the basic understanding of the mechanisms involved in microphase separation in borate glasses is presented. Experimental SAXS results and their comparison with classical theories of spinodal decomposition and more recent statistical theories are discussed. Other applications of SAXS, such as the structural characterization of the « sol-gel route » to obtain silica glasses is outlined.

1. Introduction.

Transparent glasses have been considered as essentially homogeneous materials. SAXS and electron microscopy studies performed in the fifties demonstrated that many of these macroscopically homogeneous glasses are in fact heterogeneous at a submicroscopic scale. It was established that a number of silica and borate-based binary and more complex glasses exhibit a fine structure associated with a microphase separation process.

The microstructure of a number of phase separated glasses consists of segregation zones with sizes ranging from about ten Angstroms to several hundred Angstroms. The submicroscopic size of the heterogeneities and the existence of an electronic density contrast between the phases makes SAXS an adequate experimental technique for the study of these materials.

Phase separation in multioxide glasses is associated with the existence of a miscibility gap in their phase diagram. The gaps correspond to a condition of quasi-equilibrium of these materials. When the glass system has many oxide components, basic studies of the process of phase separation become complex. For this reason, theoretical and experimental investigations of phase separation are usually performed on binary or quasi-binary glasses. These studies generally deal with an initially homogeneous sample outside the miscibility gap, which is brought by fast quenching into the gap and is maintained in it at a constant temperature. The structural characteristics of the phase separating glasses are then studied at increasing heat-treatment times. The question is to establish the features of the unmixing process starting with the initially quasi-homogeneous glass and leading to the final equilibrium two-phase material.

The conventional method to produce glasses involves the melting of the raw materials and the subsequent more or less fast cooling of the melt. In order to produce common silica-based glasses, the use of high temperature (1 500 to 2 000 °C) furnaces is required. The « sol-gel route » to obtain oxide glasses is an alternative procedure which starts from a liquid solution of alkoxides, containing the oxide of the resulting glass, water and alcohol. After several processes at rather low temperatures, from room temperature up to about 1 000 °C, monolithic and extremely pure glasses can be produced. By an appropriate control of the preparation and heating conditions, a variety of porous glasses can also be obtained. These materials exhibit interesting structural, thermal and optical properties which make them useful for many applications, such as transparent and opaque insulators, gas filters, Cerenkov detectors, catalytic substrates, etc.

The method to produce monolithic and homogeneous glasses by the sol-gel route involves aggregation of monomers in a liquid phase, gelation, aging, drying and sintering. Through all the partial steps, the evolving system is heterogeneous at a submicroscopic scale. In a number of glass precursors, the heterogeneity size covers the range from some Angstroms to several hundred Angstroms along all the process. By an adequate choice of the components and the control of the various preparation steps, it is possible to obtain monolithic and porous glasses with designed properties.

This paper reviews the main experimental results and conclusions of the SAXS studies done by the author and his collaborators concerning phase separation in borate glasses and the sol-gel procedure to obtain silica glasses.

A standard X-ray source and a SAXS goniometer were used for the experiments done until 1980. The experiments carried out since 1981 were performed at the LURE synchrotron radiation facility, in Orsay. Most of the experiments referenced in this review correspond to kinetic studies performed *in situ* using temperature-controlled cells for the samples. Two experimental workstations which provide intense, pin-hole collimated and monochromatic X-ray beams were used for the reported studies. The recording of the scattered X-ray photons was performed by means of gas position-sensitive detectors.

2. Phase separation.

Phase separation in multioxide glasses is related to the existence of a miscibility gap in the phase diagrams. Most of the basic experimental investigations of phase separation deal with simple binary or quasi-binary systems. Silica-based and borate glasses are the most thoroughly studied systems. A schematic miscibility gap corresponding to a binary or quasi-binary system is presented in figure 1. The two-phase region is divided into two subdomains by a so-called spinodal line. This line is a boundary enclosing the composition-temperature domain for which the continuous variation in composition in an initially homogeneous matrix does not require overcoming any free energy barrier. The thermodynamic theories which were used to describe phase separation suggested the existence of two different and well-defined mechanisms for phase separation : spinodal decomposition, within the central part of the miscibility gap, and nucleation and growth between the spinodal line and the gap boundary.

The thermodynamic linear Cahn's theory for spinodal decomposition [1] was widely applied to the study of metastable aggregation in metallic solid solutions. The main prediction of this theory concerns the time evolution of the q-component of SAXS intensity, $I(q)$, produced by phase separating binary systems. This evolution is expressed by

$$I(q, t) = I(q, 0) e^{2R(q)t} \tag{1}$$

$R(q)$ being an amplification factor which is positive for $q < q_c$ and negative for $q > q_c$. For $q = q_c$ (the crossover), the SAXS intensity remains constant during the phase separation
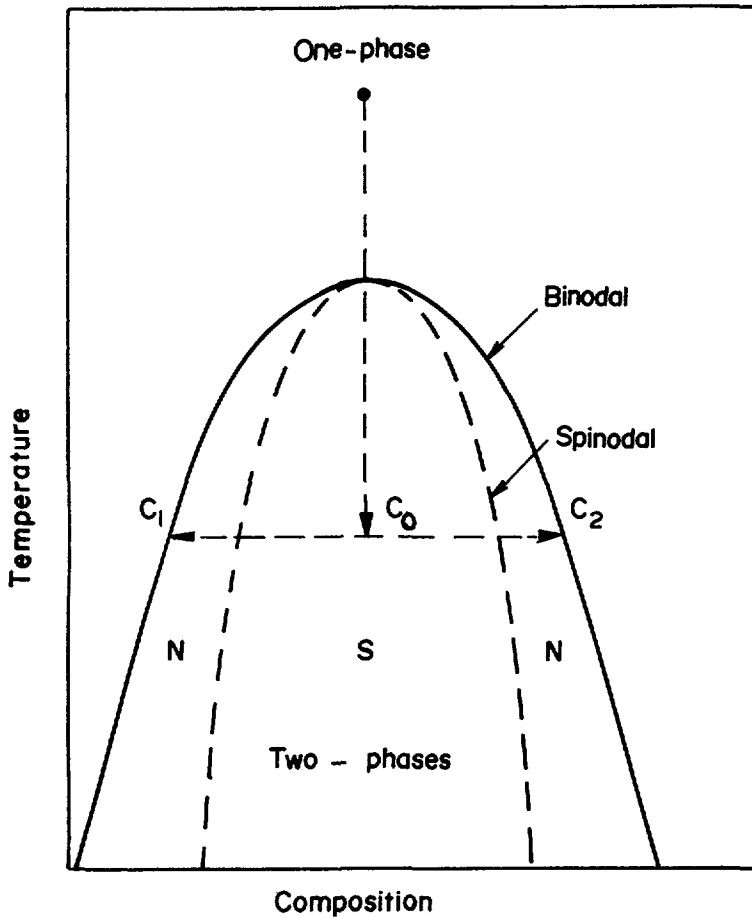
Fig. 1. — Schematic phase diagram of a binary solution with a miscibility gap. A typical temperature-composition path in phase separation studies is indicated (c_0 is the composition of the initial homogeneous phase and c_1 and c_2 are the compositions of the final phases). The « spinodal » and « nucleation and growth » domains are indicated by S and N, respectively.

process. This theory applies to the first stages of phase separation. At more advanced stages, non-linear contributions should be added and, consequently, a more complex evolution of SAXS intensity curves is expected.

The solid solutions between the spinodal and the binodal lines are expected to separate in two phases through the formation of nuclei of one of the stable or metastable equilibrium phases and its subsequent growth. The classical diffusion theory for the growth of spherical nuclei immersed in a isotropic matrix predicts the average size of the zones R at a time t :

$$R \propto t^{1/2} \qquad (2)$$

At advanced stages of phase separation, when the matrix approaches its equilibrium composition, a coarsening process becomes dominant. In this process, the smaller particles dissolve and the larger grow at their expense. The expected time evolution of the average

radius of the spherical zones in this coarsening stage is given by the Lifschitz and Slyozov equation [2] :

$$R^3 - R(0)^3 = Kt \qquad (3)$$

K being a constant.

The theoretical time evolution described by equations (2) and (3) can be experimentally verified by SAXS, using the Guinier law to determine the average radius of gyration of the segregation zones. The assumption of a spherical shape for the zones can be safely applied to glasses, since electron microscope studies put in evidence the presence of isolated spherical droplets in many vitreous systems near the binodal boundary. The direct application of Guinier's law to these systems may be subject to errors because they cannot be considered as diluted solutions of isolated particles. In practice, the droplets exhibit a size distribution which make Guinier's law applicable even to moderately diluted particle systems.

The first SAXS investigation of phase separation which tried to test the Cahn linear theory for spinodal decomposition [1] in glasses was published by Zarzycki and Naudin [3]. The experimental results of these authors concern the B_2O_3-PbO-(Al_2O_3) quasi-binary system. This study is in qualitative accordance with Cahn's theory. The agreement cannot be considered as a quantitative verification of the theory for spinodal decomposition because the experimental $R(q)$ functions exhibited clear deviations from the predicted q-dependence. In addition, a clear crossover of the experimental SAXS curves was not observed.

Another study of the B_2O_3-PbO-(Al_2O_3) glass system at two temperatures, within the spinodal domain, was performed [4]. This study showed clear deviations of the experimental SAXS results from those predicted by the linear theory for spinodal decomposition. The time evolution of $I(q, t)$ indicated a pronounced deviation from equation (1) during the earliest stage of the process. The same study [4] verified the applicability of equation (3) for a glass system within the spinodal region of the miscibility gap.

An explanation for the deviation of the experimental SAXS results [4] for glasses from those predicted by the theory for spinodal decomposition was tried [5]. It was argued that the probable existence of a structural relaxation after the thermal quenching of the homogeneous glass may affect the first stages of phase separation. The transient variation in the atomic mobility was assumed to be a simple exponential function with a characteristic relaxation time [5]. This model of a relaxing structure explained the deviation of the experimental $I(q, t)$ function from the behavior stated by equation (1). Nevertheless, the model does not describe the absence of the crossover of the experimental curves nor the deviation of the experimental $R(q)$ function from the theoretically expected one in a simple way.

Parallel to these experimental studies of phase separation in glass systems, many investigations dealt with the formation of Guinier-Preston zones in metallic binary solid solutions (Al-Zn, Al-Ag, etc.). The linear theory for spinodal decomposition applied to alloys showed an agreement with the experimental results which was in general better than in the case of glasses. The reasons for this different behavior were unclear at the time.

One strong difference between the studied borate glasses and metallic alloys concerns their speed of cooling during the quenching process. Metallic homogeneous solid solutions can be more easily retained by fast cooling than oxide glasses. Even using fast splat-cooling techniques, the low thermal diffusivity coefficient of glasses puts serious limitations on the maximum attainable cooling rate. It was considered that the reason for the failure of the linear theory for spinodal composition to explain the experimental SAXS results for glasses quantitatively was the eventual practical impossibility of attaining the « first stages » of phase separation in the isothermal studies of glasses. As a matter of fact, the linear theory applies for systems with small variation in the initial composition.

A new attempt to describe the unmixing process in glasses started with the assumption that an appreciable amount of phase separation occurs during the quenching. Several samples of

the same B_2O_3-PbO-(Al_2O_3) glass were cooled down to room temperature at different rates and studied by SAXS [6] before any subsequent heat treatment. A good agreement between experimental results and a linear theory of spinodal decomposition during continuous cooling [7] was established. This result seemed to confirm the first ideas about the glass samples which were investigated under isothermal conditions. The conclusion was that the « early stages » of phase separation mostly occur for these samples during the cooling process and, consequently, all the previously performed experimental isothermal studies correspond to « advanced stages » for which the linear Cahn theory does not apply.

A new statistical theory was developed in the seventies to describe the unmixing process in solid solutions [8]. This theory involves the numerical solution of a kinetic equation [9] for binary systems and describes the initial clustering of the atoms and the advanced coarsening stage as well. The calculation of the structure function, which is proportional to the SAXS intensity function $I(q, t)$ was carried out by Monte Carlo simulations [10].

The time evolution of the scattering intensity $I(q, t)$ predicted by the statistical theory, exhibits a remarkably simple behavior for advanced times of phase separation. The experimental test of this theory for the advanced stages can be done through the analysis of the variation with time, under isothermal conditions, of several functions related to SAXS intensity integrals. As an example, the function

$$q_1(t) = \int I(q, t)\, q\, dq \bigg/ \int I(q, t)\, dq \qquad (4)$$

should theoretically have the simple t-dependence :

$$q_1(t) \propto t^a \qquad (5)$$

where a is a negative constant which depends on the mechanism of clustering.

Monte Carlo simulations also demonstrated the dynamical scaling of the SAXS intensity functions $I(q, t)$. It was deduced that the SAXS intensity functions for different times at constant temperature, plotted as $I(q/q_1)\, q_1^3$ versus q/q_1, should scale as a single time-independent and characteristic function $S(x) = I(x) \cdot q_1^3$, x being equal to q/q_1.

Another feature of the statistical theory is that it holds for any composition within the miscibility gap. It does not predict any sharp boundary between spinodal and nucleation and growth domains. Since this theory becomes very simple for advanced stages of unmixing, its use for a better understanding of the phase separation mechanism in glasses appeared to be worthwhile.

The first application of the statistical theory to investigate phase separation in glasses by SAXS was done on a borate system inside the spinodal domain of the phase diagram [11]. An additional SAXS investigation of borate glasses at two temperatures and of two compositions (in the central part and near the boundary of the miscibility gap) were carried out later [12].

The statistical theory explains the main characteristics of the SAXS results related to phase separation in borate glasses [11]. The good agreement between theory and experiment verified the correctness of the assumptions involved in the statistical theory for advanced stages of phase separation. The good agreement was found for compositions inside the « spinodal » and in the « nucleation and growth » region as well. This suggests that the statistical theory does describe phase separation in the whole miscibility gap.

An experimental result which remains unclear concerns the composition dependence of the scaled SAXS function $S(x)$. Theoretical evaluations of the scaled SAXS function indicate that they are peaked curves with a half-maximum width which depends on the composition. This scaled structure function was calculated by several authors for simple models [13]. Its half-

maximum width turns out to be lower for compositions in the central part of the miscibility gap than for compositions near the binodal boundary. Experimental SAXS studies of quasi-binary borate glasses lead to an opposite conclusion [12]. A half-maximum width 15 % lower for a composition close to the binodal than that corresponding to the central part of the gap was experimentally observed.

The inconsistency mentioned in the precedent paragraph may be due to the fact that SAXS experiments were not done on rigorously binary systems. To verify that, similar SAXS studies should be carried out in two-oxide glasses. It must be pointed out that borate glasses (as for example B_2O_3-PbO) are not adequate for this purpose because in this binary system most of phase separation occurs during cooling. Al_2O_3 is added to the binary borate glasses in order to increase their viscosity and, consequently, to reduce phase separation during cooling. Silica glasses (SiO_2-Na_2O, SiO_2-Li_2O, SiO_2-BaO) are more suitable for the suggested investigation. An alternative reason for the lack of agreement between the theoretical and experimental composition dependence of the scaled structure function may be the eventual impossibility for the simple theoretical models to describe the real structure of the studied quasi-binary glasses.

3. The « sol-gel route » to glass.

The « sol-gel route » is an alternative method for obtaining monolithic homogeneous and porous glasses. It does not require the melting of raw materials and involves several stages, starting from liquid solutions of alkoxides, water and alcohols at room temperature. The different stages of this procedure are : monomer aggregation, gelation, aging, drying and sintering. A schematic picture of the method is given in figure 2.

Aggregation, or clustering, proceeds by the hydrolysis of the alkoxide monomers and further polycondensation in liquid phase. The clusters increase in size by different mechanisms of growth depending on the chemical conditions. Several mechanisms may be responsible for cluster growth such as particle-cluster or cluster-cluster aggregation [14]. The kinetics of clustering is controlled by diffusion or chemical reaction, depending on the efficiency of the « sticking » effect when two particles come into contact after diffusion through the liquid phase. Different types of clustering mechanisms in real solutions, which are used as glass precursors, are responsible for the formation of aggregates with fractal structure [14]. Real fractal structures are characterized by three parameters. One of them, r_0, corresponds to the size of the primary particle which builds up the fractal aggregates. Another parameter is the overall size, R_0, of the clusters. The third parameter is the dimensionality D of the fractal objects, which depends on the mechanism of cluster growth. These three parameters can in principle be easily determined in ideal systems by SAXS : the crossovers of the SAXS curves in log-log scales permit the evaluation of r_0 and R_0 and the slope of the central part yields the fractal dimensionality D, as shown in figure 3. The experimental SAXS plots associated with a fractal structure exhibit the above mentioned features provided $R_0 \gg r_0$. The simple equation

$$I(q) \propto q^{-D} \qquad (6)$$

holds for $1/R_0 \ll q \ll 1/r_0$.

After some time, which depends on composition and temperature, the gelation of the solutions containing the growing clusters eventually occurs. Microscopically, gelation corresponds to the percolation of the individual clusters. The isolated clusters build up a continuous structural network at the gel point.

The resulting structure is not stable after gelation. Monomers still can diffuse through the liquid matrix leading to additional structural modifications. This process is so-called gel aging.

Liquid
solution

Aggregation

Gelation

Aging

Drying
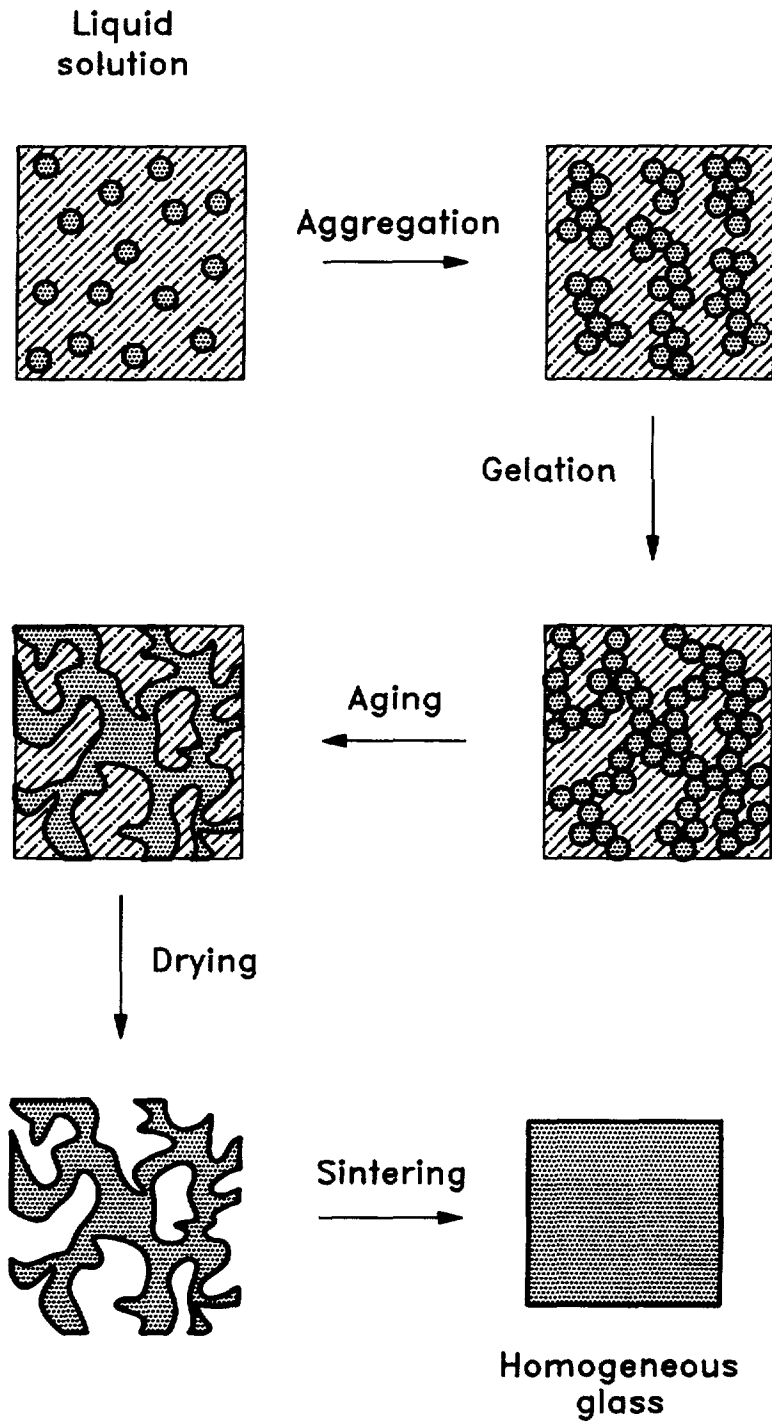
Sintering

Homogeneous
glass

Fig. 2. — Structural transformations in the sol-gel procedure to obtain homogeneous glasses (schematic).
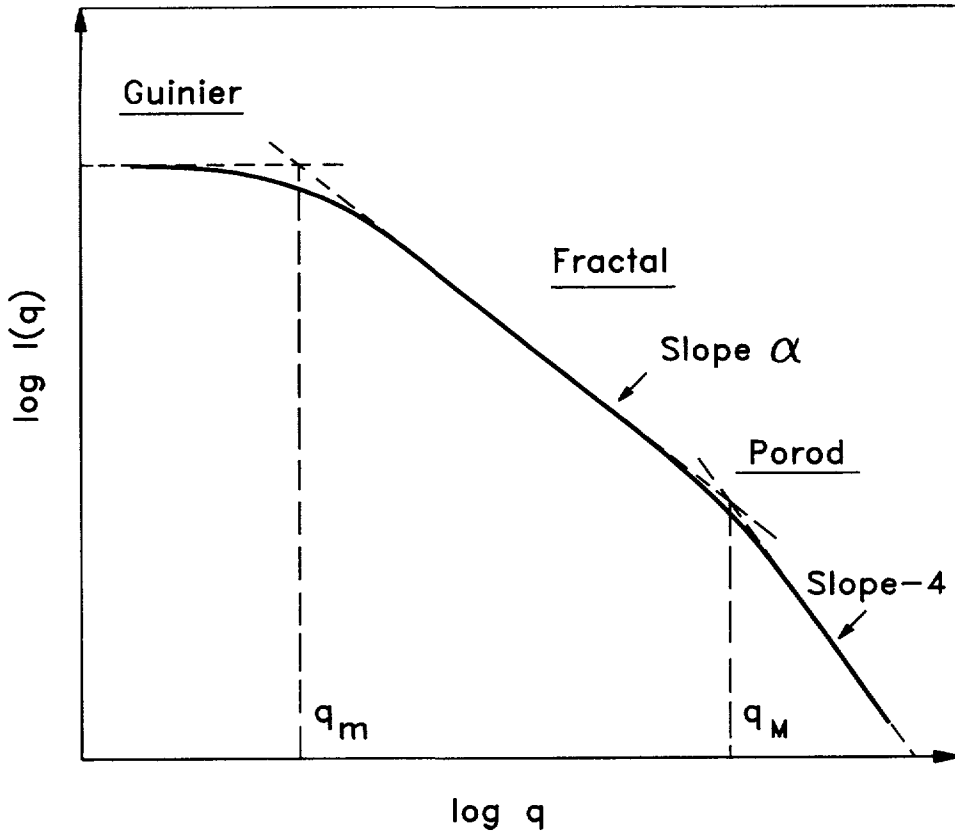
Fig. 3. — Ideal SAXS plot from a fractal structure in a log-log scale. The parameters r_0, R_0 and D are given by $1/q_M$, $1/q_m$ and $|\alpha|$, respectively. The presence of both crossovers in actual experimental plots depends on the sizes of the primary particles and fractal aggregates.

After aging, the wet gel is dried. The drying is often performed under hypercritical conditions of pressure and temperature in order to suppress the strong capillary effect of the interfaces liquid-gas within the micropores. Using this technique monolithic porous aerogels (dry gels) are obtained. The aerogels may be more or less compact depending on the dilution of the precursor solutions. In extreme conditions, the density may be very low. In the case of aerogels of silica, very light aerogels having about 1 % of the density of homogeneous silica glass were obtained.

The last stage of the procedure to obtain monolithic homogeneous glasses is the heating of the aerogels at increasing temperatures in order to evaporate the organic components and, at higher temperatures, to eliminate the porosity. This last sintering process should be carried out at temperatures as low as possible in order to avoid crystallization.

The structural properties of the final monolithic homogeneous or porous glasses depend on the composition of the precursor solution and on the conditions under which each one of the preparation stages is carried out. This makes the characterization of every stage of the process useful. Many silica and other glass precursor materials exhibit a very fine submicroscopic structure from the initial monomer solution to the gel and aerogel states. Therefore, the SAXS technique can be used to study all structural evolution occurring along the sol-gel process.

The most common silica glass precursor solutions are liquid mixtures of TEOS-water-ethanol and TMOS-water-methanol. They were experimentally studied by SAXS under acidic and basic conditions using different alkoxide/water and alkoxide/alcohol ratios.

An experimental SAXS study of the clustering process in solutions of TMOS-water-methanol suggested different mechanisms of aggregation for different TMOS/water ratios [15]. The ratio R controls the degree of monomer hydrolyzation and is defined as $R = $ (mol TMOS/mol water). Guinier plots of SAXS results were applied to characterize the growth of the clusters. The $\log I$ versus $\log q$ plots of the SAXS curves, for increasing aggregation times, approached a straight line for both acid and base catalyzed solutions. The fractal dimensionality values corresponding to the solutions under acidic conditions, were $D = 2.00$ for $R = 1$ and 2 and $D = 2.14$ for $R = 4$. In the case of a base-catalyzed solution with $R = 1$, a higher value of the fractal dimensionality was obtained ($D = 2.60$). An analysis of these experimental SAXS results, based on a model which assumes a polydispersivity in cluster size, was tried. For a polydisperse system having a number distribution in cluster mass given by $N(m) \propto m^{-\tau}$, the SAXS intensity exhibits the same potential dependence on the scattering wavevector as equation (6), but in this case the exponent depends on D and τ [16] :

$$I(q) \propto q^{-\alpha} \quad \text{with} \quad \alpha = D(3 - \tau). \tag{7}$$

For three dimensional clusters, the percolation theory predicts $D = 2.5$ and $\tau = 2.2$ [16] and then equations (7) yield $\alpha = 2.0$. The experimental values of α for the acid-catalysed sols studied in reference [15] are close to 2, in good agreement with the model of percolation clusters. It should be pointed out that equations (7) holds strictly for dilute cluster solutions. Since the experimental results reported in reference [15] concern undiluted solutions, the conclusion concerning the mechanism of gel formation may be biased by concentration effects.

The SAXS plots in log-log scale of the wet silica gels prepared from the precursor solutions mentioned in the precedent paragraph show more complex features [17]. Two linear regions were observed for most of the compositions. This was attributed to the existence of a two-level fractal structure : the primary particles having a size of about 2 A generate fractal clusters with an average size of 20 A and these clusters grow up to larger dimensions building up secondary fractal objects. In the case of gels, the parameter R_0 obtained from SAXS plots corresponds to a correlation distance, instead of representing a radius of gyration, because after gelling clusters are no longer isolated zones. The experimental results of reference [17] indicated that the aging process decreases the correlation length. This suggests that aging modifies the structure and destroys its fractal features.

The drying produces some minor variations in the resulting aerogel structure as compared with that of the precursor wet gel [18]. The asymptotic behavior of the experimental SAXS curves corresponding to aerogels satisfy Porod's law :

$$I(q) \propto q^{-4} \tag{8}$$

This suggests a smoothing effect of the hypercritical drying on the finer structure of the wet gels. The second upper level of the fractal structure of the wet gels is not modified by drying [18].

The sintering process in aerogels was also studied at increasing temperatures by SAXS. The experimental variations in SAXS curves demonstrate the progressive loss of the fractal characteristics of the structure. SAXS results on aerogels are consistent with a two-phase model composed of mesopores and a « light » matrix [19]. These results suggest the existence of micropores immersed in the matrix which are responsible for its low density.

A simple geometrical model of a hierarchical structure composed of spheres which contains 13 equal spherical particles, this structure being repeated at several levels, was proposed for dense aerogels [20]. This model was demonstrated to be consistent with SAXS experiments and BET measurements [21].

The reported SAXS studies of the structural transformations related to the sol-gel procedure have recently been extended to other systems such as mixed titania-silica [22], silica with formamide additions [23], zirconia [24], tin oxide gels [25] and silica gels which contain small semiconducting CdS particles [26].

4. Final remarks.

A number of SAXS studies of glasses was reported. It was shown that this technique provided useful information on phase separation processes in borate glasses and other more complex structural transformations concerning silica glass precursor materials.

The use of synchrotron radiation was helpful for the reported SAXS investigations. It allowed extensive studies of samples under many preparation conditions within a reasonable time. The SAXS workstations at LURE permitted the study of different kinetic processes which require good quality measurements in short time (typically a few minutes) intervals.

SAXS results could be directly and easily connected and compared with the related theories dealing with the mechanisms of structural transformation. This feature of the SAXS technique has an evident importance for basic research.

The structural characterization of the studied glasses may also have technological relevance. As a matter of fact, the knowledge of the effects of the physico-chemical conditions, along all the transformation process, on the structure of the resulting glasses is a necessary condition for correct material designs.

Acknowledgements.

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