The structure of lithium silicon sulphide glass systems

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Abstract. We present in this paper a statistical model of the growth of amorphous and crystalline structures which is applied here for the investigation of binary $(1 - x)\text{SiS}_2\text{–}x\text{Li}_2\text{S}$ glasses. Having defined local configurations (referred to as *singlets* in what follows), and the ways in which they can assemble together, we establish the statistics of *doublets* and *triplets* produced by agglomeration. We obtain fairly good predictions for the glass transition temperature T_g, the composition of mixtures of glass and crystalline phases at $x = 0.5$, and the Li_2SiS_3 and $\text{Li}_6\text{Si}_2\text{S}_7$ phases for greater values of x. The model predicts also the ratios of typical microstructures and other interesting data, among which are the cooling rates that are necessary to form the glass.

1. Introduction

The aim of this article is to apply a statistical and dynamical model to binary $\text{SiS}_2\text{–}\text{Li}_2\text{S}$ systems. The model, which is based on the study of statistical growth of crystalline and amorphous structures, seems to be akin to other recent theoretical models that have been used in attempts to analyse the glass formation [1–4]. A detailed description of the physical insight and the construction of the model have been given already in [5] and numerous applications have been performed with some success [6–9]. We shall compare the predictions of the model with the experimental data concerning thiosilicate-based glasses. Their usefulness as solid electrolytes [10, 11] and the advantage of the very high conductivities (10^{-3} Ω^{-1} cm^{-1} in the doped glasses) inspired considerable developments in the experiments and glass production during the past decade [12–15]. Most of the results that we present here are obtained by numerical methods, although we shall develop the adapted differential equations describing the formation of glass through an analytical scheme.

For the reader's convenience, it is worth recalling the main ideas of the model and its most important properties.

Although growth processes of disordered materials are quite complex phenomena, it seems possible to describe glass formation by using elementary basic configurations and processes which may take place in the liquid or the supercooled state, and to express their assembly rules in a simple fashion. It is necessary to choose for that a few stable local configurations which will become the building blocks in the growth process. As in previous models based on local structures [16, 17], we shall directly derive these local configurations from the study of the glass structure or the corresponding liquid. This leads to the definition of local configurations (*singlets*) best adapted to describe substantially short- and intermediate-range order, for which some evidence exists in thiosilicate glasses (SiS_4 tetrahedra always exist, whatever the degree of range order [18]). We shall suppose that the

entire process is carried out in the supercooled liquid so that the system can still be imagined in the vicinity of a thermodynamical equilibrium and so that Boltzmann factors can be used for the evaluation of relative probabilities of the configuration. An adequate number of steps should be realized in order to give a realistic description of the agglomerates appearing in the supercooled liquid, and to apply the model in a thermodynamical limit. One of the simplest ways of describing the structural evolution during the process is to combine the structure with a probabilistic description.

Let us denote by $P_i^{(0)}$ the probability of finding a given '*singlet*' i among N local configurations. After joining them together into doublets, we can evaluate new relative probabilities defined by

$$P_i^{(1)} = \frac{1}{2}\left[2P_{ii}^{(1)} + \sum_{j \neq i} P_{ij}^{(1)} \right] \tag{1}$$

where

$$P_{ij(m)}^{(1)} = \frac{W_{ij(m)}}{Q_1}(2 - \delta_{ij})P_i^{(0)}P_j^{(0)}e^{-E_{ij(m)}/kT}. \tag{2}$$

We have defined in equation (2) a statistical factor $W_{ij(m)}$ which is equal to the number of ways in which a given doublet can be obtained. The subscript m refers to the bonding type of the *doublet*. We have also denoted by $E_{ij(m)}$ the energy cost of the assembling of two singlets i and j. It mainly corresponds to a bond energy which depends on the geometry of the matching types. Q_1 is the normalizing factor that keeps the sum of probabilities equal to 1:

$$Q_1 = \sum_{i,j}^{N} \sum_m W_{ij(m)} P_i^{(0)} P_j^{(0)} e^{-E_{ij(m)}/kT}. \tag{3}$$

These constructions are repeated at each step of the process [5].

In order to obtain a time-dependent equation for the probabilities, we shall define a function $s(t)$ chosen between two well-defined limits [19]. $s(t)$ is supposed to be smooth, with $ds/dt \geqslant 0$, and corresponds roughly to the number of steps realized ($0 \leqslant s(t) \leqslant 1$ for the first step, $1 \leqslant s(t) \leqslant 2$ for the second one, etc). At each step, $s(t)$ gives an approximate measure of the density of multiplets already formed versus the multiplets produced during the former step.

$$s(t) = \left\langle \sum_j jN_j \Big/ \sum_j N_j \right\rangle - 1 \tag{4}$$

where N_j represents the total number of multiplets with j atoms in the sample and the average symbol $\langle\ \rangle$ refers to a sample which is sufficiently representative that the local fluctuations do not matter any more. Therefore, we can evaluate the approximate probability of finding the ith elementary configuration as follows, for each step of agglomeration (i.e. each value of k):
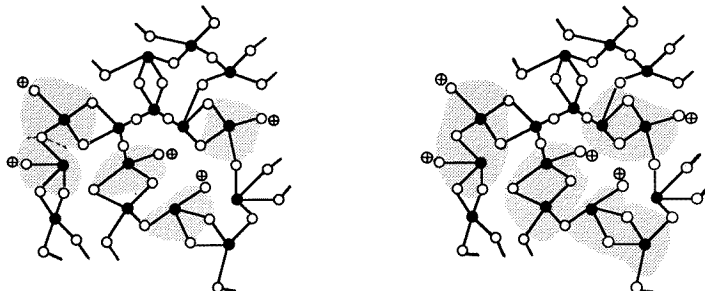
$$P_i(t, T) = (k - 1)\left[\frac{s(t)}{k - 1} - 1\right]P_i^{(k)} + k\left[1 - \frac{s(t)}{k}\right]P_i^{(k-1)}. \tag{5}$$

For $0 \leqslant s(t) \leqslant 1$, it is simply

$$P_i(t) = (1 - s(t))P_i^{(0)} + s(t)P_i^{(1)} \tag{6}$$

where $P_i^{(1)}$ is obtained from (1). The constraint

$$\sum_{i=1}^{N} P_i^{(k)} = 1 \tag{7}$$

Figure 1. A schematic representation of a glass network. For $k = 1$, we assume that it is equivalent to tile the network with singlets $[P_3^{(0)}]$ or with doublets $[P_{j3(m)}^{(1)}]$, giving a graphical illustration for one of the equations (8) (the one with $i = 4$). The same happens for the other configurations involved.

remains satisfied at each step k.

The derivative with respect to t yields [5]

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = \frac{\mathrm{d}s}{\mathrm{d}t}[P_i^{(k)} - P_i^{(k-1)}] = 0 \tag{8}$$

which is a system of $N-1$ non-linear equations with $N-1$ independent variables $P_i^{(0)}$. The study of the singular points of the system leads directly to the values of $P_i^{(0)}$ corresponding to the local glass structure. It can also be interpreted as the configuration that will globally dominate at the end of the process. The nature of the singular points depends on the roots appearing after linearization of system (8) [20]. If the characteristic equation of the linearized system has all of its roots with a positive real part, it is an unstable point; if all real parts are negative, we have a stable point. The solutions thus show the preferential composition of the multiplets characteristic for the short-range structure. If the roots are of both kinds, we get a saddle point. We assume that the saddle point corresponds to a metastable solution since it is neither an attractor, nor a repulsive point. It will be interpreted as a non-crystalline glassy state which can quite faithfully represent the average local glass structure. The hypothesis of such a physical interpretation has been introduced previously [5] and typical applications are currently under consideration [21]. Secondly, the relative probability of an elementary configuration should not vary from one step to another because we can also say that the construction of the whole vitreous matrix structure with elementary *singlets* or with *doublets* (already sharing more information about MRO than the *singlets*) should be equivalent; hence

$$P_i^{(0)} \sim P_i^{(1)}. \tag{9}$$

In other words, this means that the structure can be tiled with multiplets of similar sizes, yielding at each step of growth a better approximation of the structure (figure 1).

Nevertheless, it is necessary to introduce a cooling term in order to give a more realistic description of the process. It has been observed indeed that Li_2S–SiS_2 glasses are very difficult to obtain by ordinary quenching because they have a strong tendency towards crystallization due to their edge-sharing character (double Si–S–Si bonding) [13]. The experiments that have been carried out on glasses with different values of Li_2S concentration used the twin-roller quenching technique which involves very rapid cooling, of the order of 10^6 K s^{-1} [22]. $SiSe_2$–Li_2Se glasses are also obtained by this technique [23]. We must introduce therefore the cooling term which has been used previously in order to explain

the stabilization of amorphous structures [24]. The new term that has to be added to the right-hand side of the system (8) in order to take into account the effects of rapid cooling contains explicitly the derivatives of the probabilities with respect to the temperature T, so the equation takes on the following form:

$$\frac{dP_i}{dt} = \frac{ds}{dt}[P_i^{(k)} - P_i^{(k-1)}] + \frac{dT}{dt}\frac{\partial P_i}{\partial T} = 0. \tag{10}$$

2. Application to $x\mathrm{Li_2S}$–$(1-x)\mathrm{SiS_2}$ glasses

Experimental observations suggest a natural definition of the required local configurations. Structural as well as electrical data on lithium silicon sulphide glasses obtained mainly through NMR and Raman spectroscopy lead to the definition of stable local configurations [25, 15]. Silicon sulphide glasses are composed of polymeric chains of edge- and corner-sharing tetrahedra ($\mathrm{SiS_4}$ units). The elementary building block which appears in the liquid and in the glass state is a tetrahedron formed by a silicon atom with four sulphur atoms at its corners. With adjunction of the modifier $\mathrm{Li_2S}$, the sulphur atoms at the corners are saturated progressively by lithium atoms (creating instead ionic $\mathrm{Li^{\oplus}S^{\ominus}}$ bonds), so they do not bridge any more silicon atoms, and they break the edge-sharing chains of tetrahedra. These sulphur atoms are currently called '*non-bridging sulphur*' (NBS) atoms and their frequency varies with the concentration x. Increasing the concentration leads to the occurrence of $\mathrm{SiS_4^{\ominus}}$, $\mathrm{SiS_4^{2\ominus}}$ and $\mathrm{SiS_4^{3\ominus}}$ tetrahedra. At the limits of the glass-forming domain (e.g. for $x > 0.66$), all Si–S–Si bonds are destroyed, and only isolated $\mathrm{SiS_4^{4\ominus}}$ units are expected.
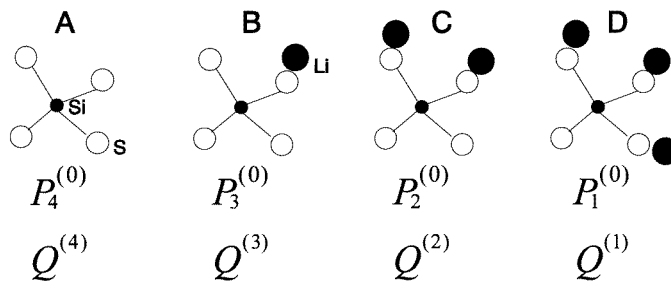
Figure 2. The four elementary configurations (*singlets*) with their corresponding probabilities $P_i^{(0)}$ and their corresponding NMR notation $Q^{(i)}$.

We define the respective probabilities of four elementary configurations A, B, C and D, denoted $P_4^{(0)}$, $P_3^{(0)}$, $P_2^{(0)}$ and $P_1^{(0)}$ (figure 2). The fact that there are only few elementary configurations favours the establishment of very simple assembling rules, and limits the number and the complexity of the resulting probabilities. The binding energies, which depend on the nature of the sulphur bonds, will be considered as free parameters to be determined. The joining of two local configurations can be realized in two different ways. Two tetrahedra can be joined together by corners or by edges ($m = 1$ or 2). This yields two different binding energies depending on the type of junction. These particular energies will be denoted, according to the situation, by a_1 and a_2. With the initial probabilities of four *singlets* and two binding energies, we can establish the probabilities of occurrence of doublets and triplets in three dimensions appearing during the first two steps. We use in the construction the Boltzmann factors $e_m = \exp[-a_m/kT]$ with $m = 1, 2$, and the statistical weights which are given by the number of ways leading to the multiplet under

$$P_{32(1)}^{(1)} = \frac{12}{Q_1} P_3^{(0)} P_2^{(0)} e^{-a_1/kT}$$

$$P_{22(2)}^{(1)} = \frac{2}{Q_1} P_2^{(0)2} e^{-a_2/kT}$$
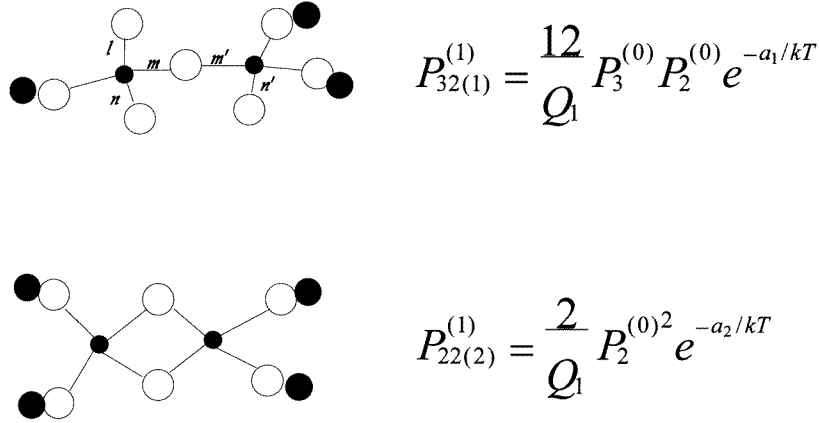
Figure 3. Two doublets: a corner-sharing B–C and an edge-sharing C–C doublet with their corresponding probabilities. With labelled Si–S bridges, there are 12 different ways to obtain the same doublet 32(1) (*m–m'*, *m–n'*, etc) which gives the statistical weight $W_{32(1)} = 12$.

consideration. The energies a_m correspond to the previously defined energies $E_{ij(m)}$ and, obviously, they depend only on the bonding type (corner-sharing tetrahedra involve energy a_1 and edge-sharing tetrahedra involve energy a_2). Indeed, given a bonding type, the energy remains constant whatever multiplet is considered (A–A, A–B, etc) because it corresponds in all situations to a Si–S–Si bond. Some typical probabilities obtained using equation (1) are given in figure 3.

The first step yields 16 doublets; the second one leads to the formation of 60 triplets (figure 4), most of which are obtained in two or three different ways. As there are four elementary configurations, the system (10) corresponds to a set of three equations with three variables $P_i^{(0)}$ ($k = 1$ for the first step and $k = 2$ for the second one):

$$P_4^{(k)} - P_4^{(k-1)} - \frac{|\mathrm{d}T/\mathrm{d}t|}{\mathrm{d}s/\mathrm{d}t} \frac{\partial P_4^{(k)}}{\partial T} = 0$$

$$P_3^{(k)} - P_3^{(k-1)} - \frac{|\mathrm{d}T/\mathrm{d}t|}{\mathrm{d}s/\mathrm{d}t} \frac{\partial P_3^{(k)}}{\partial T} = 0 \tag{11}$$

$$P_2^{(k)} - P_2^{(k-1)} - \frac{|\mathrm{d}T/\mathrm{d}t|}{\mathrm{d}s/\mathrm{d}t} \frac{\partial P_2^{(k)}}{\partial T} = 0.$$

The last variable is given by the normalization equation:

$$P_1^{(0)} = 1 - P_2^{(0)} - P_3^{(0)} - P_4^{(0)}. \tag{12}$$

We can still reduce the number of independent equations. Indeed, the modifier concentration x can be expressed in terms of the initial probabilities $P_i^{(0)}$ leading to another reduction of the system (11). The concentration x can indeed be evaluated as

$$\frac{N_{\text{Li}_2\text{S}}}{N_{\text{SiS}_2}} = \frac{x}{1-x} = \frac{1}{2}[P_3^{(0)} + 2P_2^{(0)} + 3P_1^{(0)}] = \frac{1}{2}[3 - 3P_4^{(0)} - 2P_3^{(0)} - P_2^{(0)}]. \tag{13}$$

The above relation can be interpreted as the equation for local charge conservation [26], i.e. the sum of all positive charges $\text{Li}^\oplus$ must be equal to the sum of the negative ones which exist in the local configurations [5]. This will reduce the system (11) to a set of two
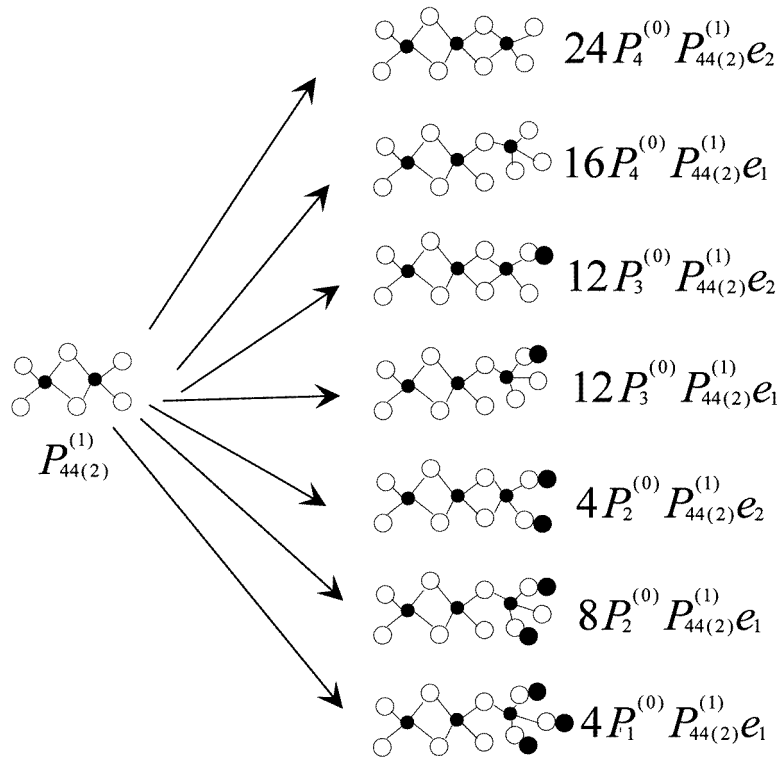
$$24 P_4^{(0)} P_{44(2)}^{(1)} e_2$$

$$16 P_4^{(0)} P_{44(2)}^{(1)} e_1$$

$$12 P_3^{(0)} P_{44(2)}^{(1)} e_2$$

$$12 P_3^{(0)} P_{44(2)}^{(1)} e_1$$

$$4 P_2^{(0)} P_{44(2)}^{(1)} e_2$$

$$8 P_2^{(0)} P_{44(2)}^{(1)} e_1$$

$$4 P_1^{(0)} P_{44(2)}^{(1)} e_1$$

Figure 4. From doublets to triplets; expressions for the unrenormalized probabilities.

independent equations with two variables $P_i^{(0)}$, and the domain of physical solutions will be contained within the symplex defined by

$$0 \leqslant P_4^{(0)} \leqslant 1 \qquad 0 \leqslant P_3^{(0)} \leqslant 1 \qquad 0 \leqslant P_2^{(0)} \leqslant 1$$
$$0 \leqslant 1 - P_4^{(0)} - P_3^{(0)} - P_2^{(0)} \leqslant 1 \tag{14}$$

and lying on the plane defined by equation (13). This amounts to limiting the investigation over the concentration range $x = [0, 0.5]$, since we have chosen only the four aforementioned configurations (figure 5).

3. Results and discussion

The complexity of the system (11) prevents one from obtaining an analytical resolution. We have therefore used, as before [6], a computer program based on the generalized Newton method. We chose to express the coupling energies a_1 and a_2 in electron volts as we suppose that their value must be of the order of a fraction of 1 eV, comparable to similar values obtained for this type of glass [27]. The solutions which appear at the borders of the domain will be identified with the usual stoichiometric crystalline compounds such as the metathiosilicates (for $P_2^{(0)} = 1$) or the pyrothiosilicates (for $P_1^{(0)} = 1$). These solutions should be obtained only for particular small concentration ranges, satisfying equation (13).

The solutions lying inside the symplex will represent the glassy state because of their metastable character and because of the fact that they represent a mixture of all possible
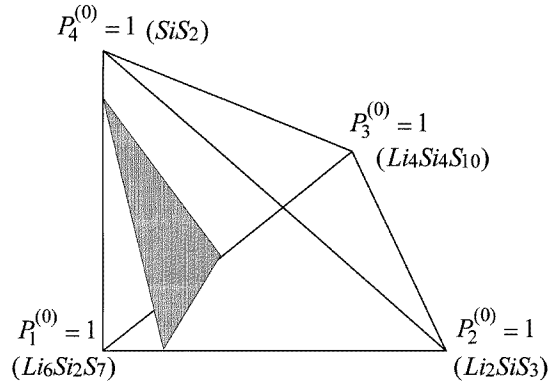
Figure 5. The three-dimensional symplex in which all of the solutions of the system have to be found. The summits correspond to a probability equal to unity identified with the corresponding crystalline compound (dithiosilicate, metathiosilicate and pyrothiosilicate).

configurations corresponding to the maximum of the configurational entropy. Then we can start the resolution of (13) by systematically scanning a reasonable domain of variation of the parameters a_1, a_2 and of T. The most explicit experimental constraint that we have to satisfy is that of matching the glass transition temperature T_g obtained experimentally by Eckert and co-workers [28, 29] (table 1). As before, we identify the lower limit of the temperature range in which we find solutions for the system (11) with the glass transition temperature. The probabilities of finding each of the four configurations can in fact vary with respect to the temperature during the quenching of the liquid, but their variation should be stopped when the liquid, is frozen (at T_g), even on a very small scale.

Table 1. The glass transition temperature of the system Li_2S–SiS_2 as a function of x, the concentration of Li_2S.

x	0	0.3	0.38	0.4	0.42	0.5	0.6
T_g (°C)	453	341	330	341	330	338	334

We fit also the dimensionless factor Λ, defined by

$$\Lambda = \frac{|dT/dt|}{T \, ds/dt} \tag{15}$$

which appears in equation (11). Testing this experimental constraint by an iterative method, we obtain the best fits for

$$a_1 = 0.29 \text{ eV}$$
$$a_2 = 0.31 \text{ eV.} \tag{16}$$

The values obtained are quite similar and can eventually show that the edge-sharing tendency of the SiS_2 glass is much more stronger than in the selenide analogue glass, as proposed on the basis of experiment [28] (in a previous application, we found $a_1 = 0.20$ eV and $a_2 = 0.32$ eV for the $SiSe_2$-based glass [6]). The best fits of the factor Λ are displayed in figure 6. The glass transition temperature agrees quite well with the experimental data for both steps and depends slightly on the cooling factor Λ, as in the experimental preparation of the glass (tables 2 and 3).
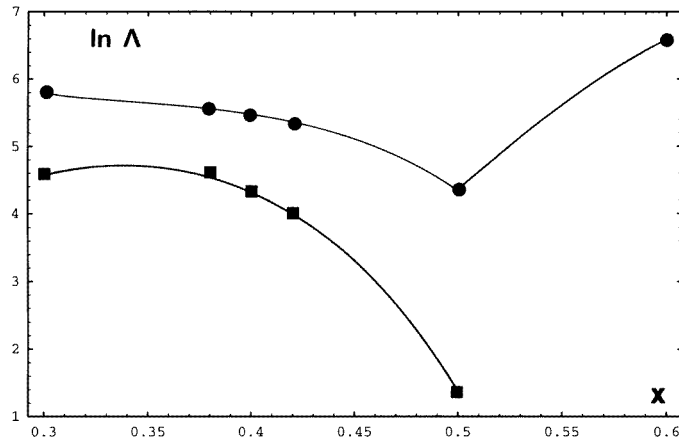
Figure 6. A log plot of the dimensionless cooling factor Λ obtained for the first (circles) and second step (squares).

Table 2. An example of the influence of the cooling factor Λ on the value of the glass transition temperature obtained, at $x = 0.5$.

Λ	T_g (°C)
79	338
80	333
83	331

Table 3. The predicted glass transition temperature (in °C) and the corresponding solutions of the reduced system for the first (I) and second step (II) of agglomeration.

x	T_g	$P_4^{(0)}$	$P_3^{(0)}$	$P_2^{(0)}$	$P_1^{(0)}$
0.3	156(I)	0.572	0.007	0.414	0.008
	341(II)	0.571	0.000	0.428	0.000
0.38	166(I)	0.389	0.011	0.587	0.014
	330(II)	0.454	0.089	0.236	0.222
0.4	300(I)	0.3346	0.011	0.640	0.014
	341(II)	0.423	0.095	0.208	0.171
0.42	330(I)	0.280	0.019	0.675	0.026
	330(II)	0.392	0.097	0.181	0.330
0.5	338(I)	0.003	0.004	0.984	0.009
	338(II)	0.086	0.192	0.352	0.368
0.6	334(I)	0.003	0.001	0.001	0.995

One should note that the T_g-values obtained with the first step of agglomeration are somewhat spurious for $x < 0.4$. We suggest that the second step is best adapted for this concentration range, i.e. the network structure is more accurately described by a
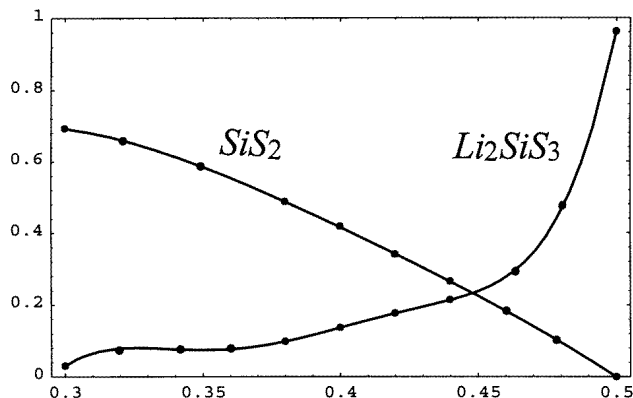
Figure 7. Probabilities of finding the SiS_2 and the Li_2SiS_3 phase for the first step of agglomeration.

larger size effect produced by *triplets* rather than *doublets*. Nevertheless, the first step of agglomeration yields a solution with high A- and C-probabilities, identified with a mixture of the progressively vanishing SiS_2 network (a large $P_4^{(0)}$-value) and the growing Li_2SiS_3 phase with large amounts of C-configuration (figure 7). This is consistent with the experimental proposal made on the basis of ^{29}Si NMR spectroscopy data. Indeed, the most important structural change induced by the modifier Li_2S is the breakdown of the network former SiS_2 produced by depolymerization (through the creation of $Li^{\oplus}S^{\ominus}$ bonds). In contrast to the case of the oxygen glass system (i.e. SiO_2–Li_2O), there are no $Q^{(3)}$-units created but rather $Q^{(2)}$-units, sharing two non-bridging sulphur atoms [28, 29]. This corresponds to a high value of the $P_2^{(0)}$-solution obtained with the first step and second step (table 2), and the behaviour seems to be quite similar to that of the selenide analogue [6]. The difference from the latter system is the prediction of *two types* of metathiosilicate phase, namely the high- and low-temperature crystalline forms of Li_2SiS_3, corresponding either to an edge-sharing dimer (called $E^{(1)}Q^{(2)}$), or to a corner-sharing polymer (called $E^{(0)}Q^{(2)}$). In the silicon selenide glass, there seems only to be the corner-sharing phase, and solutions were obtained in this sense [6], and the general breakdown of the network occurs in this system more rapidly than in the sulphide glass, in agreement with observation (figure 8(a)).

At $x = 0.5$, one has a pure Li_2SiS_3 phase, identified with the high $P_C^{(0)}$ reaching unity. Inserting the solutions obtained and the energies allows the computation of the probabilities of *doublets* and *triplets*, and shows that the glass is indeed a mixture of the $Q^{(2)}$-dimer and polymer, in the proportion of 1:3 (figure 8(b)). The NMR investigation yielded a proposal of 23:77 [29]. The cooling factor Λ decreases from $x = 0.3$ to $x = 0.5$ and reaches its minimum value at this concentration, and then it grows rapidly for greater concentrations (figure 6). The behaviour of $\Lambda(x)$ is in close correspondence with the experimental quenching rate which is necessary to form the glass [30], and shows that the glass-forming tendency attains its maximum at around $x = 0.5$, because Λ is very low (glass can be formed by simple water quenching for close concentrations [31]).

As mentioned in table 3, we obtain at $x = 0.6$ a pure $Li_6Si_2S_7$ phase ($P_1^{(0)} \sim 1$) which is also in close agreement with the proposal of Eckert and co-workers [28]. The glass is then composed of corner-sharing $Q^{(1)}$-tetrahedra, but the production of the alloy is very difficult, since the factor Λ attains its maximum value, which seems to correspond with
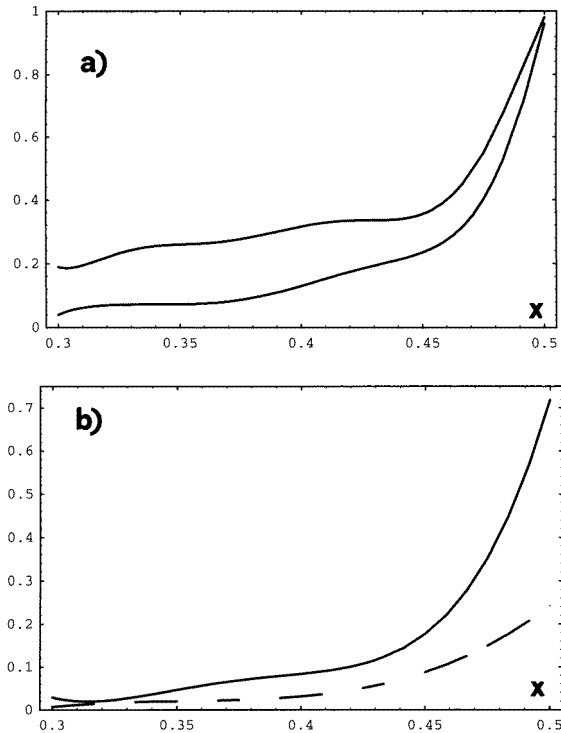
Figure 8. (a) The growth of the metaphase in the sulphide (Li_2SiS_3) (lower line) and in the selenide (Li_2SiSe_3) (upper line) glass systems. (b) The composition of the metathiosilicate phase as a function of x: the high-temperature crystalline form (the edge-sharing $Q^{(2)}$-dimer; dashed line) and the low-temperature form (the corner-sharing $Q^{(2)}$-polymer; solid line).

what is experimentally observed (for lower values of Λ, the system (11) yields only the crystalline solutions, i.e. the corner solution of the symplex $P_1^{(0)} = 1$).

The second step gives further insight into the structural change in the network, in particular for low values of x. In addition to the main behaviour, characterized by the decrease of the SiS_2 phase and the growth of the metathiosilicate phase, we can see that bigger clusters can also share substantial rates of $Q^{(3)}$- and $Q^{(1)}$-configurations. The solution disappears at $x = 0.6$; the triplet approximation is no longer significant here, because the glass is composed of $Q^{(1)}$-*doublets* only.

4. Summary and conclusion

The application of the statistical model to SiS_2-based glasses which has been presented in this paper shows quite consistent results with what is generally observed experimentally, and it allows a quantitative description of the structure to be obtained. It gives a precise behaviour of the variation of the configurations $Q^{(k)}$ with respect to the concentration of the modifier x, by using only two independent parameters ($a_2 - a_1$ and Λ) which can nevertheless also be compared to experimental data. With these two parameters, we have been able to demonstrate the following features.

(1) The first step describes the main structural change of the network which is the

vanishing of the network former and the growth of the Li_2SiS_3 phase composed of the crystalline high- and low-temperature metathiosilicate forms, reaching the proportion of 1:3 at $x = 0.5$.

(2) The destruction of the network former seems more pronounced than in the selenide analogue glass.

(3) The second step gives more precise insight into the structural change by predicting the possibility of the existence of $Q^{(3)}$-species in greater clusters.

(4) We have obtained a fair dependence of the glass transition temperature on x for both steps of agglomeration. Both steps show that the variation of the cooling factor Λ with x is very close to the one necessary to obtain the glass.

We believe that other typical properties of these glasses can be obtained in the future, such as the density and conductivity, or usual thermodynamical functions.

Acknowledgments

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[19] An obvious reason for the introduction of the function $s(t)$ is that the agglomeration process is carried out during the temperature decrease and with growing time, following the so-called '*T–T–T*' curves (time–temperature–transition):
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These curves could be completely constructed if we had at our disposal the parametrized functions $T(s)$ and $t(s)$, giving a satisfactory meaning and a reliable physical interpretation of our function $s(t)$.
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