

Glass formation in silicates: Insights from composition

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Abstract

The composition dependence of glass formation is examined in a variety of silicate systems that include alkali and alkaline earth alumin-, titano-, ferro- and ferrisilicates. Empirically, there is a clear correlation between wide extent of glass formation, possible crystallization from the melt of numerous compounds, and moderate liquidus temperatures. Vitrification with usual cooling rates is in contrast impossible when binary and ternary compounds are scarce and liquidus temperatures are high. These correlations imply that vitrification is favored by moderately negative enthalpies of mixing in the melt but made difficult by high configurational heat capacities. The close connection between glass formation and viscosity is reviewed in the light of these melt properties. That bulk viscosity is in general not directly relevant to the kinetics of crystal nucleation in particular indicates that vitrification theories cannot be considered as by-products of crystallization theories.

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1. Introduction

In any chemical system, glasses distinguish themselves from crystals by the extremely wide range of their solid solutions. Of course, this feature originates in the lack of long-range order that allows a variety of elements, having each their own bonding requirements, to be accommodated in various proportions within the glass structure. As a matter of fact, silicate glasses owe their long-standing practical importance to the ensuing possibility of varying almost at will their physical properties through changes in chemical composition.

Although silicate glasses can be prepared by other means, cooling of a molten phase remains by far the

most common vitrification process either in industry or in Nature. In addition to its practical importance, this process raises the still unsolved problem of the glass transition. From a fundamental standpoint, it indeed remains to understand how the disordered structure of the liquid is frozen in when the kinetics of configurational rearrangements become too slow with respect to the observation timescale (e.g., Donth, 2001).

On the other hand, it has long been known that glass-forming ability depends markedly on chemical composition. Following Zachariassen's (1932) work, various criteria have been proposed to account for these effects in geometrical or energetic terms (e.g., Vogel, 1994). Although these rules have been successful for "traditional" systems such as silicates or borates, they are not of general applicability. They can fail to describe how composition determines glass-forming ability in a given system and, more important, have proven inadequate for metallic or other newly discov-

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ered glass families. Alternatively, theories of glass formation could be considered as by-products of theories of crystal nucleation and growth since vitrification on cooling is obviously tantamount to bypassing crystallization (see Uhlmann, 1983; Scherer, 1991). As will be reviewed below, however, current nucleation theories have shortcomings that make them inappropriate for this purpose.

Regardless of their particular composition, glass-forming liquids share a common phenomenology which is exemplified by the viscosity of about 10^{12} Pa s that obtains at the glass transition under usual cooling rates of the order of 10 K/min. This feature suggests that some insights on the composition control of vitrification could be gained without having to delve into the details of crystal nucleation processes or into the specificity of bonding within a given system. In this paper, therefore, our goal will be to point out the importance of a few macroscopic features of importance to vitrification from the composition dependence of glass formation in silicate systems. To deal with large composition ranges while keeping simple melt compositions, we will consider ternary alkali and alkaline earth aluminosilicates, titanosilicates, ferro- and ferrisilicates.

The starting point will be the empirical correlations we describe between a wide extent of glass formation and a high number of crystalline compounds that can form from the melt. We will then examine the reasons for such correlations between equilibrium phase diagrams and kinetically determined areas of glass formation. In brief, vitrification is primarily related to viscosity which depends on bond strength and configurational entropy, i.e., on the same factors that determine thermodynamic mixing properties. In the last part of the paper, particular attention will be paid to configurational entropy whose direct relevance to theories of the glass transition and viscosity is embodied in the paradox of the Kauzmann's (1948) catastrophe and in the Adam and Gibbs (1965) theory of relaxation processes, according to which the temperature dependence of structural relaxation times is determined by that of configurational entropy.

2. Phase diagrams and glass formation

2.1. General remarks

In this section we will review the mutual relationships between glass formation and liquidus surfaces in ternary systems. The phase diagrams of simple silicates are generally well known (Levin et al., 1964). There are, however, exceptions for some of the systems of

interest to this study such as alkali ferrisilicates and potassium titanosilicates. In these instances, melting relations are, at best, known incompletely with the consequence that yet unreported ternary compounds could exist.

As phase diagrams depict only equilibrium relationships, they do not provide any information on crystallization to metastable phases near the glass transition which would be especially relevant to our study. In fact, this feature is probably very common for silicates. In Ca aluminosilicate melts, for example, Roskosz et al. (2005) observed widespread crystallization of yoshio-kaite, a metastable mineral whose composition can markedly depart from an average $\text{CaAl}_2\text{SiO}_6$ formula. Likewise, in molten Mg aluminosilicates Lejeune and Richet (1995) noted crystallization of aluminous enstatite ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), another metastable phase which is isochemical with pyrope.

As a kinetic phenomenon, glass formation depends on many factors so that the boundaries of glass-forming domains refer to specific conditions. These include the cooling rate of the sample as well as the nature of the container or that of the melting atmosphere because crystal nucleation is generally heterogeneous. Cooling rate is the most important since, as originally pointed out by Tammann (1898), any liquid could vitrify if cooled rapidly enough. Under well-defined conditions of homogenous nucleation, a more precise approach consists of determining the critical (minimum) cooling rate needed to restrict the crystal volume fraction to a given value, generally taken as 10^{-6} which is considered to be the resolution limit of the optical microscope. Such data are scarce, however, and are not always in mutual agreement as shown by available data for alkali silicates (Dietzel and Wickert, 1956; Havermans et al., 1970; Fang et al., 1983).

Another difficulty is that the cooling rate is precisely known only when it is slow or the sample very small. When large samples are quenched, cooling is necessarily faster near the surface than at the core of the sample as demonstrated by the existence of internal stresses (to be released on annealing). To remain close to usual laboratory conditions and make use of as much information as possible, we will consider in the following vitrification of gram-size samples under cooling rates of at most a few tens of degrees per second through the glass transition. In other words, we will deal with experiments that do not necessitate any special quenching procedure more complicated than dipping the bottom of a platinum crucible into water. With this criterion, vitrification domains for example include the Na_2SiO_3 and K_2SiO_3 compositions in binary alkali

silicates, which would have to be excluded for bigger samples or slower cooling rates.

Even for such common conditions, a consistent compilation of vitrification domains seems to be available for only part of the basic ternary systems of geochemical interest (Imaoka and Yamazaki, 1963). The domains represented below have thus been based on information reported in various publications and complemented by results gathered over the years in the authors' laboratory. For iron-bearing systems, use has in particular been made of available isofracts. Given the qualitative nature of the conclusions drawn in this study, any inconsistency resulting from this procedure would be inconsequential. Finally, note that only homogeneous glasses are dealt with. Hence, we will not consider glasses formed within the stable or metastable miscibility gaps that are prevalent in the SiO_2 -rich parts

of silicate systems. To facilitate comparisons between analogous systems, all ternary diagrams have been converted from the original weight percent to a mole percent basis in view of the large differences between the molar masses of the oxides considered. For clarity, part of the isotherms reported in the original diagrams will not be shown.

2.2. Aluminosilicates

As a network-forming cation, aluminum generally improves glass formation (Fig. 1). When Al_2O_3 is added to a binary metal oxide-silica melt, the viscosity increase caused by polymerization of the anionic framework ensures slower crystallization kinetics. The effect is particularly clear along the joins MSiO_3 – Al_2SiO_5 ($M = \text{Mg}, \text{Ca}$) where, contrary to MSiO_3 metasilicates,

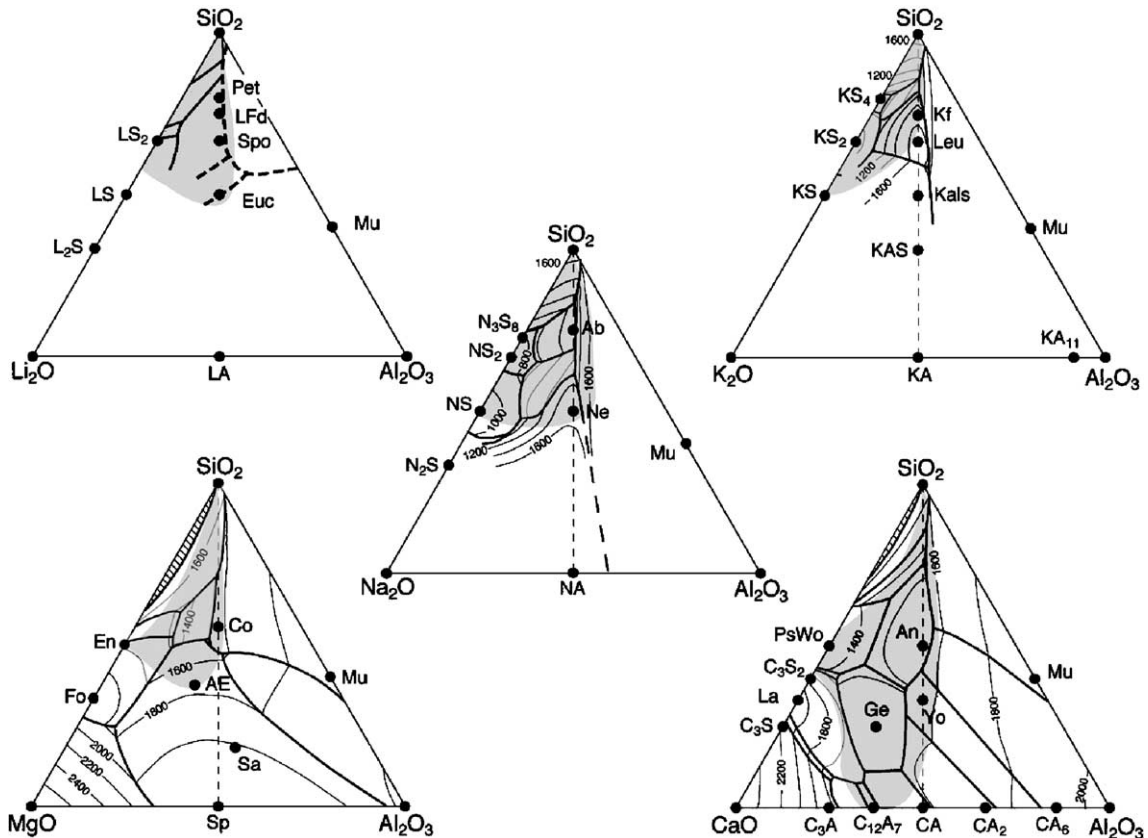


Fig. 1. Melting relations and glass formation in aluminosilicate systems. Data from Schairer and Bowen (1955, 1956) for alkali and from Levin et al. (1964) for alkaline earth systems. The stable miscibility gaps and ranges of vitrification are shown as shaded and grey areas, respectively, the meta-aluminous join as a dashed line. Abbreviations: A: Al_2O_3 ; K: K_2O ; M: MgO ; N: Na_2O ; S: SiO_2 ; Ab: albite ($\text{NaAlSi}_3\text{O}_8$); An: anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$); AE: aluminous enstatite ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$); C: CaO ; Co: cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{20}$); En: enstatite (MgSiO_3); Fo: forsterite (Mg_2SiO_4); Geh: gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$); KF: K feldspar (KAlSi_3O_8); Kals: kalsilite (KAlSiO_4); Leu: leucite (KAlSi_2O_6); Mu: mullite ($\text{Si}_2\text{Al}_6\text{O}_{13}$); Ne: nepheline (NaAlSiO_4); PsWo: pseudowollastonite (CaSiO_3); Sa: sapphirine ($\text{Mg}_4\text{Al}_{10}\text{Si}_2\text{O}_{23}$); Yo: yoshiokaite (shown here as $\text{CaAl}_2\text{SiO}_6$ although it covers a rather wide stoichiometry range). As drawn from observations made in the authors' laboratory, the range of glass formation in the Li system is much wider than reported by Moore and McMillan (1956).

compositions close to the meta-aluminous joins vitrify readily. On the other hand, as will be discussed below, high liquidus temperatures account for the poor vitrification ability beyond the meta-aluminous join regardless of the structural role of Al in peraluminous compositions.

Specifically, vitrification domains of aluminosilicates depend on metal cation. Consistent with the trends in the Al-free binary melts, glass formation occurs over a wider compositional range in alkali than in Mg aluminosilicates. The Ca system does not fit with this trend, however, since its glass-forming region is anomalously large and even extends to Si-free melts along the join CaO–Al₂O₃. Compared to the other systems of Fig. 1, Ca aluminosilicates have the important peculiarity that, as a result of a specially good match between the ionic radii of Ca²⁺ and other ions, a unusually great number of compounds are stable on the liquidus of the two limiting CaO–SiO₂ and CaO–Al₂O₃ binary systems. Barring the composition regions where liquidus temperatures are highest, one observes that the area of glass formation encompasses the compositions of existing binary and ternary compounds crystallizing from the melt. The correlation between the extent of glass formation and the existence of crystalline compounds also holds for the three other ternary systems of Fig. 1; the very wide range of glass formation of Ca aluminosilicates represents strong evidence for its actual significance.

2.3. Titanosilicates

Marked contrasts in liquidus temperatures, ternary compounds, and extent of glass formation between alkali and alkaline earth systems are evident in the ternary phase diagrams of Fig. 2. If one assumes that Ti⁴⁺ is a network-former cation, its substitution for Si⁴⁺ differs from (Al,Si) exchange because Ti⁴⁺ does not need to associate with a charge compensating cation. Hence, no analogies are to be drawn between the properties of alkali or alkaline earth titanosilicate melts and their aluminosilicate counterparts, save for regular variations induced by differences in the field strength of the alkali or alkaline earth cation. Like in aluminosilicates, however, one does observe that Ti⁴⁺ has greater affinity for alkali than for alkaline earth cations.

For alkaline earth titanosilicates, liquidus temperatures are higher in the Mg than in the Ca system, but their slight variations point to a dearth of specific association between the oxide components throughout the diagrams. There is a single ternary compound in the Ca system (titanite, CaTiSiO₅) and none in the Mg

system. Only along the binaries do we find two Ca titanates (CaTiO₃ and Ca₃Ti₂O₇) and three Mg titanates (MgTi₂O₇, MgTiO₃, and Mg₂TiO₄) whose melting temperatures range from 1550 to 1970 °C. On the other hand, glass formation requires rapid quenching, particularly for the Mg system. It is restricted to the eutectic valleys that runs from the metal oxide-silica systems toward the center of the diagrams, a feature that is also observed for barium titanosilicates (Cleek and Hamilton, 1956). Under similar quenching conditions, the compositional extent of vitrification increases in the order Mg, Ca, Ba.

Less information is available for alkali titanosilicates. The important difference with alkaline earth systems lies in a large number of binary and ternary compounds in alkali titanosilicate systems. There are four sodium titanates (Na₂TiO₃, Na₈Ti₅O₁₄, Na₂Ti₃O₇, and Na₂Ti₆O₁₃) with known melting points between 1030 and 1300 °C. There are also four ternary compounds (Na₂TiSiO₅, Na₂TiSi₂O₇, Na₂Ti₂Si₂O₉, and Na₂TiSi₄O₁₁), which begin to melt, incongruently for three of them, at temperatures lower than 965 °C. Correlatively, vitrification is easy for Na titanosilicates (Glasser and Marr, 1979). It is achieved throughout most of the composition range where melts can be prepared and even extends to compositions close to the binary compound 4Na₂O•TiO₂.

Liquidus data seem to be lacking for potassium-bearing titanosilicates. Glasses can nonetheless be quenched from 1100 °C in a still wider composition range than for the Na system (Rao, 1963). This suggests that liquidus temperatures should not be higher than those determined by Glasser and Marr (1979) for the sodium system outside of the miscibility gap where liquidus temperatures do not vary much with Ti content. Glass formation in particular extends to the binary K₂O–TiO₂ join near the 1:1 oxide ratio. From the correlation repeatedly observed between extent of vitrification and number of compounds, one may guess that there exist other crystalline potassium titanosilicates than the single compound currently known.

The last diagram of Fig. 2 deals with the Al₂O₃–TiO₂–SiO₂ system. Liquidus temperatures are consistently high. There are very few binary and no ternary compounds. Vitrification is almost nonexistent, except in a tiny domain near the SiO₂-rich part of the SiO₂–TiO₂ join (Kajiwara, 1988).

2.4. Ferrosilicates

Ternary phase diagrams determined under sufficiently reducing conditions for iron to be predominantly

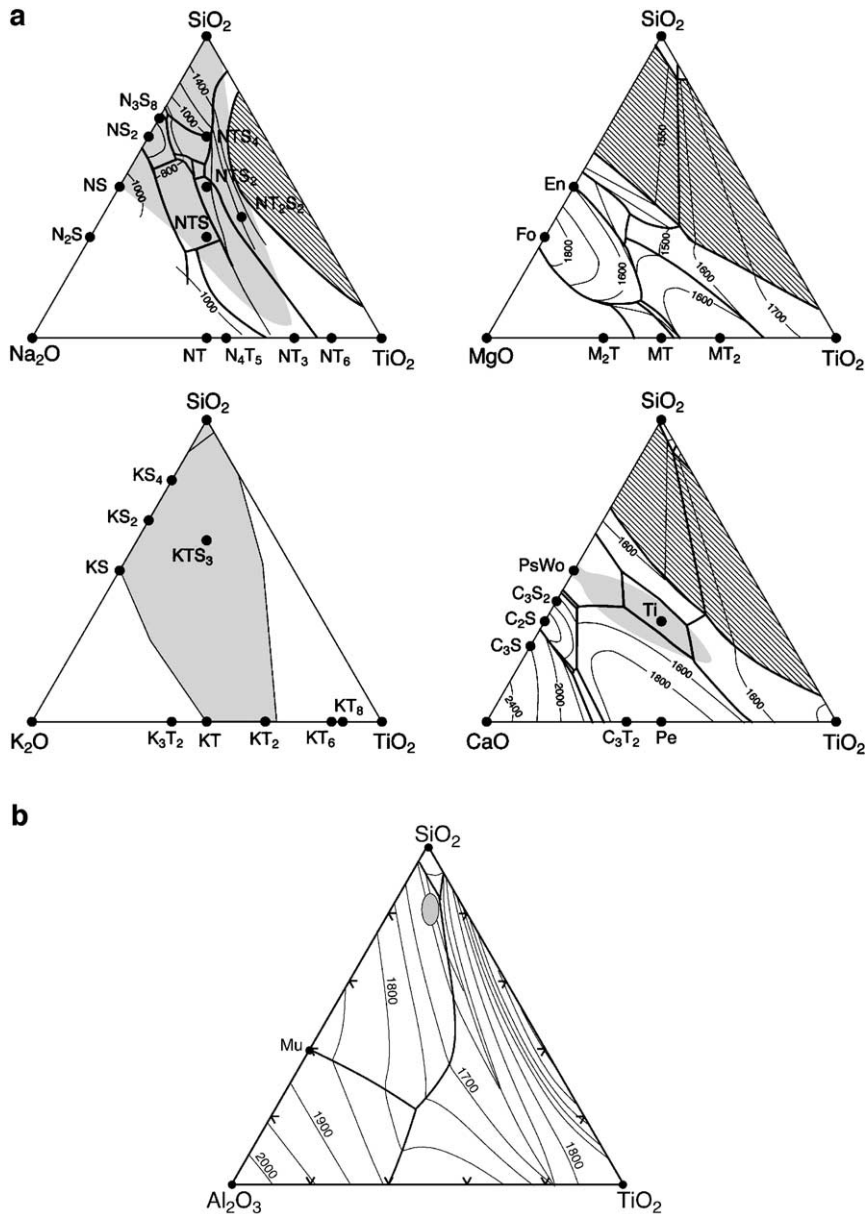


Fig. 2. Melting relations and glass formation in titanosilicate systems. (a) Alkali and alkaline earth systems. Data from Glasser and Marr (1979), Hamilton and Cleek (1958), Rao (1963), Massazza and Sirchia (1958), and De Vries et al. (1955) for Na, K, Mg and Ca-titanosilicates, respectively. (b) Alumino-titanosilicates (Kirschen et al., 1999; Kajiwara, 1988). Stable miscibility gaps and ranges of vitrification shown as shaded and grey areas, respectively. Abbreviations: K: K₂O; N: Na₂O; S: SiO₂; T: TiO₂; En: enstatite (MgSiO₃); Fo: forsterite (Mg₂SiO₄); Pe: perovskite (CaTiO₃).

ferrous are represented in Fig. 3. For the Mg and Ca systems, the glass-forming ability is either poor or nonexistent. In both cases, ternary compounds are lacking. Vitrification can be achieved in the low liquidus temperature valley at the center of the Ca diagram, but under more stringent conditions that involve smaller samples and higher quenching rates than for the other ternary systems considered in this paper (Kress and Carmichael, 1989).

Liquidus temperatures are markedly lower for alkali than for alkaline earth ferrosilicates (Fig. 3). Phase relations are well known for the “FeO”–K₂O–SiO₂ system (Roedder, 1952) where two ternary compounds exist and vitrification takes place over a wide composition range. Phase relations are less well known for the “FeO”–Na₂O–SiO₂ system. Schairer et al. (1954) identified at least one ternary compound, but they could not determine its nature. In addition, the stability field of

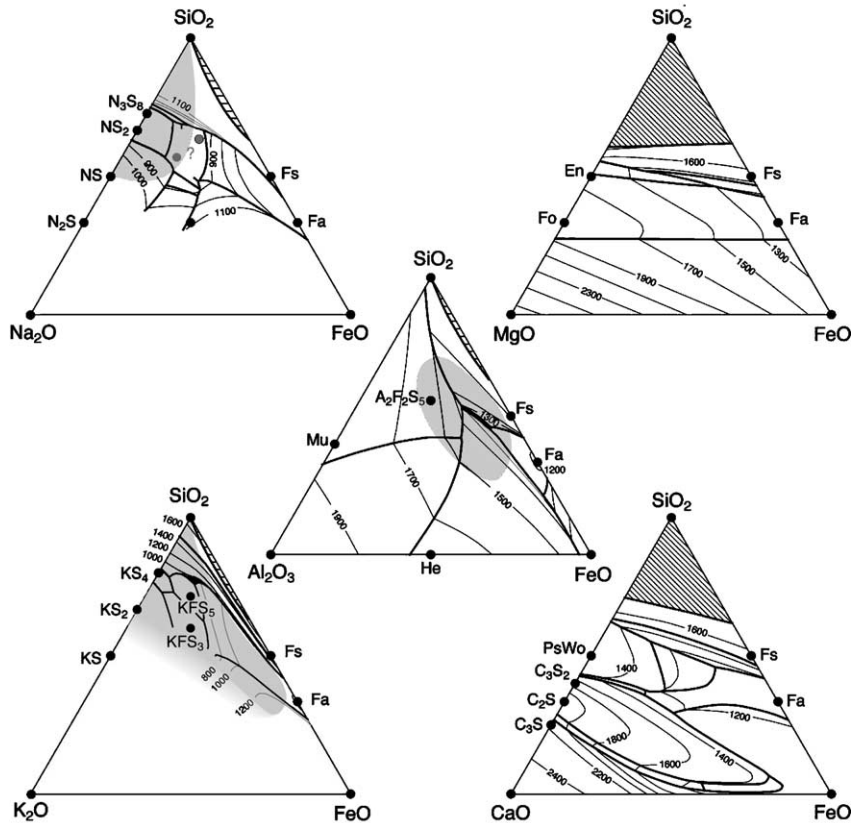


Fig. 3. Melting relations and glass formation in ferrosilicate systems. Data from Bowen et al. (1930) for Na, Roedder (1952) for K, Levin et al. (1964) for Mg and Ca-, and Schairer and Yagi (1952) for Al ferrosilicates. Stable miscibility gaps and ranges of vitrification shown as shaded and grey areas, respectively. Compound compositions not shown for the Na system (see text). Abbreviations: F: FeO; K: K₂O; N: Na₂O; S: SiO₂; En: enstatite (MgSiO₃); Fa: fayalite (Fe₂SiO₄); Fs: ferrosilite (FeSiO₃); Fo: forsterite (Mg₂SiO₄); Mu: mullite (Si₂Al₆O₁₃); Pe: perovskite (CaTiO₃); PsWo: pseudowollastonite (CaSiO₃).

this compound does not seem to match the Na₂FeSiO₄ stoichiometry reported for the crystal observed by Carter and Ibrahim (1952). These uncertainties notwithstanding, for both Na and K systems the area of glass formation encompasses the composition of ternary compounds. As judged by the rather wide composition ranges where the index of refraction of glasses could be measured, vitrification is easy in alkali ferrosilicates.

As a complement, we have included in Fig. 3 a diagram for the Al₂O₃–FeO–SiO₂ system for which a single ternary compound has been described. Consistent with the trends observed for other systems, it is hardly fortuitous that vitrification is restricted to a small region that runs from this compound to the vicinity of fayalite and ferrosilite, the two binary iron silicates.

2.5. Ferrisilicates

Available melting relations are still less abundant for oxidizing conditions where iron is primarily ferric and

could affect melt properties in a way similar to that of Al³⁺. Data are in fact lacking for Mg ferrisilicates. For the calcium system (Fig. 4), a difference with respect to aluminosilicates is a lower number of mixed compounds. There are three along the join CaO–Fe₂O₃, compared to five along the CaO–Al₂O₃ join, and no ternary compound against the two calcium aluminosilicates anorthite and gehlenite. Correlatively, glass formation is not readily achieved under conditions similar to those described above for ferrosilicates (Kress and Carmichael, 1989).

For sodium and potassium ferrisilicates, in contrast, glasses can form over large composition ranges which again encompass several ternary compounds. For sodium ferrisilicates, four such compounds have been described by Bowen et al. (1930), but only two, acmite (NaFeSi₂O₆) and (Na₂O)₅•Fe₂O₃•(SiO₂)₈, have been adequately identified. Although the available information is incomplete for potassium ferrisilicates, the important feature of the “Fe₂O₃–K₂O–SiO₂ system is the

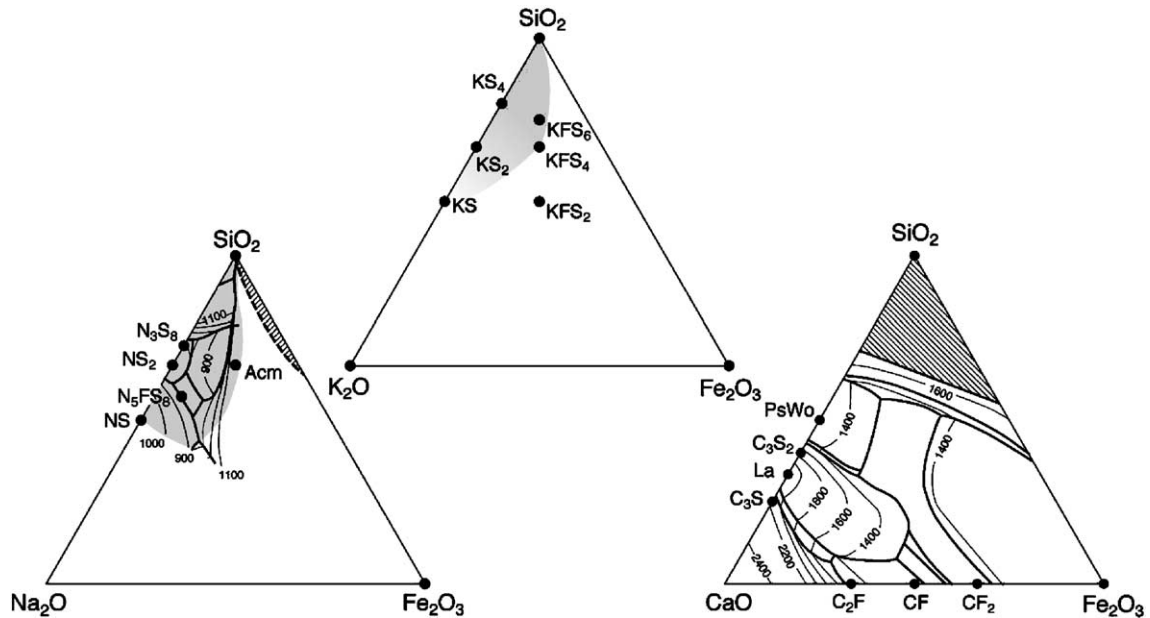


Fig. 4. Melting relations and glass formation in ferrisilicate systems. Data from Schairer et al. (1954) for Na, Faust (1936) and Faust and Peck (1938) for K, and Levin et al. (1964) for Ca ferrisilicates. Stable miscibility gaps and ranges of vitrification shown as shaded and grey areas, respectively. Abbreviations: Ac: acmite ($\text{NaFeSi}_2\text{O}_6$); F: Fe_2O_3 ; K: K_2O ; N: Na_2O ; S: SiO_2 ; La: larnite (Ca_2SiO_4); PsWo: pseudowollastonite (CaSiO_3).

existence of three compounds which have the same stoichiometry as K-feldspar, leucite, and kalsilite (Faust, 1936; Lange et al., 1986). As observed along the analogous meta-aluminous join, vitrification does not extend to the less SiO_2 -rich compositions.

3. Discussion

3.1. Crystal nucleation: limitations of current theories

Glass-forming ability in a system could be taken as the reciprocal of the maximum crystallization rate (Dietzel and Wickert, 1956), but this simple measure is inadequate as it would incorrectly neglect the considerable variations observed for the nucleation rate. On the other hand, Turnbull (1969) asserted that the condition for glass formation should be the absence of nucleation. But this approach also fails because homogeneous nucleation and growth rates are significant in temperature ranges that generally do not overlap. The consequence is that a nucleating crystallite may not be able to reach a detectable size and, thus, that nucleation does not necessarily prevent vitrification.

The goal of the time-temperature-transformation approach developed by Uhlmann (1972) is, therefore, to account for the interplay of nucleation and growth rates through determination of the time needed to achieve a given volume fraction of crystals as a function of

temperature. If both rates can be estimated, the crystal fraction achieved for a given cooling rate can be calculated and the results be compared to experimentally observed critical cooling rates. Good agreement has been reported in this way for simple silicate systems (Fang et al., 1983). Unfortunately, the derived nucleation and growth rates actually represented more fitting parameters than values calculated independently from basic theory.

In the classical nucleation theory (Turnbull and Fisher, 1949), the nucleation rate is determined by thermodynamic and kinetic barriers. The former depends on the bulk free energy and interfacial energy differences between the supercooled liquid and the nucleus, whereas the latter barrier is the molar activation free energy for a particle of the system to cross the liquid/nucleus interface. This parameter is usually described in terms of an effective Arrhenian diffusion coefficient determined from the shear viscosity of the melt through the Stokes–Einstein relationship. The problem is that nucleation rates calculated in this way may differ by 30 orders of magnitude from the observed values (e.g., Rowlands and James, 1979; James, 1985; Weinberg and Zanotto, 1989).

The classical nucleation theory has been modified in several ways, first of all through the use of temperature-dependent values for the interfacial energy (Rowlands and James, 1979) or for the enthalpy con-

tribution to the bulk free energy difference between the molten and crystalline phases (González Oliver et al., 2004). Alternatively, it has been assumed that the interfacial energy also depends on the size of the nucleus (Weinberg et al., 1992; Fokin and Zanutto, 2000), that the nucleus–liquid interface is diffuse (e.g. Gránásy and Herlach, 1995; Gránásy and James, 2000), or that the surface of the nuclei can be treated as a self-similar fractal (Sen and Mukerji, 1999). Better agreement with the experimental data has been achieved under these assumptions, but the problem remains that none of these parameters is prone to independent experimental determination with the consequence that nucleation rates are not really predicted.

On the other hand, the assumptions made for the kinetic barrier have been little questioned. Yet the basic assumption that shear viscosity data can be used to estimate particle diffusion is not warranted in view of the marked decoupling between bulk and local relaxation near the glass transition (George and Stebbins, 1998; Gruener et al., 2001). Another feature that is now being recognized is that nucleation in strongly supercooled liquids generally produces highly disordered, nonstoichiometric crystals that are often metastable and have a composition differing from that of the stable liquidus phases. Such phases have been observed in simple model melts like lithium disilicate (Deubener et al., 1993; Soares et al., 2003) as well as in more complex systems (Fokin et al., 2003; Longhi and Hays, 1979; Roskosz et al., 2005).

That kinetics can take over thermodynamics in nucleation is well exemplified by supercooled $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ liquid. Near the glass transition, congruent crystallization to aluminous enstatite is observed instead of formation of the equilibrium assemblage forsterite + sapphirine + cordierite (Lejeune and Richet, 1995). Since crystallization is accompanied by a 20% density increase, the factor limiting nucleation is element diffusion to form three different phases and not the large structural rearrangements required for congruent crystallization of aluminous enstatite. But the difficulty of incorporating kinetics in theories of glass formation is compounded by the fact that, owing to the decoupling between local and bulk relaxation, the diffusivity of network-modifying cations does not scale with viscosity. An important consequence is that crystals are nonstoichiometric and enriched in the most mobile network-modifying cation (Roskosz et al., 2005).

These purely kinetic and crystal chemical complications should of course be taken into account, but their bearing on the various assumptions made in nucleation

theory have still to be worked out. Given these difficulties, it is surprising that the variation of glass-forming ability with chemical composition, which has been determined for a great variety of oxide systems, has not really been subjected to detailed analyses. As extensively used when dealing with physical properties, composition can, in fact, be a sensitive probe (see Mysen and Richet, 2005). In the rest of this discussion, we will thus review a few general conclusions drawn from the phase diagrams shown in the previous section and, in particular, from the paradoxical correlation between the easiness of vitrification and the existence of numerous crystalline compounds.

3.2. Viscosity and glass formation

The close connection between viscosity and vitrification is embodied in the operational definition of the glass transition where melt viscosity is 10^{12} Pa s under experimental timescales of the order of 100 s. In this respect, the emphasis put on lack of nucleation to account for vitrification could be misleading. The reason is that, as noted above, bulk viscosity is the right scaling parameter for vitrification but not for crystal nucleation. In this process, decoupling of mobility between network-former and network-modifier cations plays an essential role as has been shown for a variety of alkali silicate and calcium aluminosilicate melts (Roskosz et al., 2005). In other words, the relevance of viscosity is more direct to vitrification than to nucleation.

Everything else being equal, any factor causing an increase of melt viscosity thus favors vitrification. As has long been recognized, glass formation is therefore easier near eutectics because freezing-point depressions enable lower temperatures and higher viscosities to be reached (Cohen and Turnbull, 1961). The effect will be illustrated for sodium and potassium silicate systems which show extremely large freezing-point depressions between pure SiO_2 and about 25 mol.% alkali oxide (Fig. 5).

In both systems, a sharp minimum is observed in the critical cooling rates for vitrification near the position of the deepest eutectic (Fig. 6). Now, viscosity is a strong function of temperature and composition. Both parameters can have markedly opposite effects along liquidus branches, however, because liquidus temperatures are not monotonous functions of composition. Addition of alkali oxide to pure SiO_2 first causes the viscosity to decrease tremendously. From 0 to a few mole percent Na_2O , the decrease is about 9 orders of magnitude at 1200 °C (Fig. 7a). These variations are so strong as to

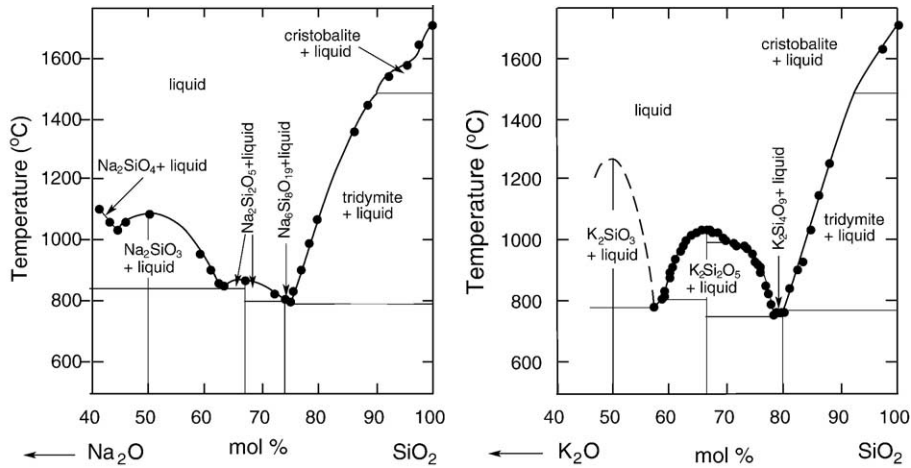


Fig. 5. Liquidus relations in the $\text{Na}_2\text{O-SiO}_2$ and $\text{K}_2\text{O-SiO}_2$ systems (Kracek, 1930; Kracek et al., 1937).

overwhelm any temperature effect, resulting in an initially rapid viscosity decrease along the liquidus (Fig. 7b). The composition dependence of viscosity is much smaller at higher alkali content where the effects of further temperature decreases of more than 500 K predominate. As a result, the viscosity increases up to a point that precedes the eutectic for the $\text{K}_2\text{O-SiO}_2$ system and nearly coincides with the eutectic for the $\text{Na}_2\text{O-SiO}_2$ system. Liquidus temperatures vary less at still higher alkali contents. When they increase, their effect add up with those of composition changes. The net effect is the continuous viscosity decrease shown in Fig. 7b.

Inspection of Fig. 7b suggests that vitrification is easy when the viscosity at the liquidus is at least of the order of 1000 Pa s. In view of the complex variations of viscosity along liquidus branches, the rather close match between the extrema of viscosity and critical

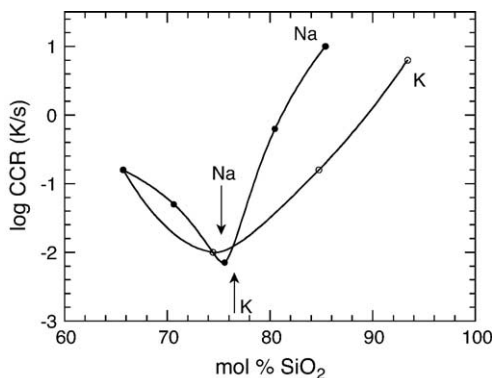


Fig. 6. Critical cooling rates for glass formation in sodium and potassium silicates. Data from Fang et al. (1983) for a crystal fraction of less than 10^{-6} . The arrows indicate the position of the deepest eutectics of the binary systems shown in Fig. 5.

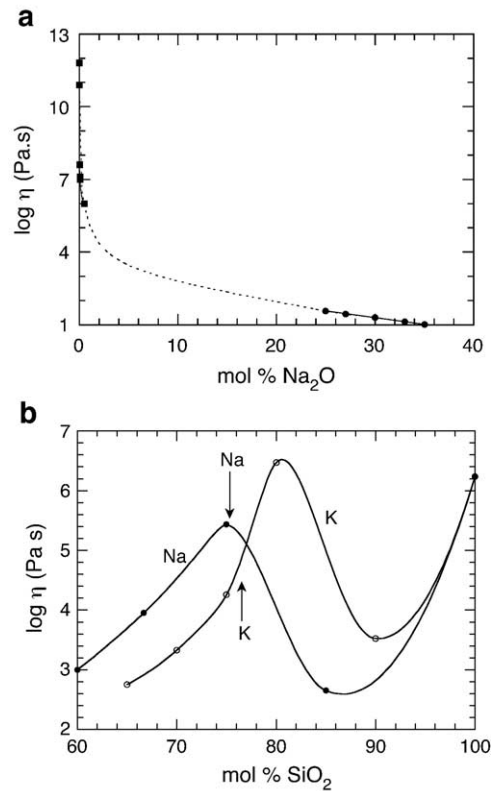


Fig. 7. The combined effects of composition and temperature on viscosity along liquidus branches in alkali silicate systems. (a) Viscosity of sodium silicate melts at 1200 °C (Bockris et al., 1955; Leko et al., 1977). (b) Viscosity of alkali silicate melts along the liquidus branches of Fig. 5. Data from Poole (1948) and Bockris et al. (1955). The arrows indicate the positions of the deepest eutectics of the binary systems.

cooling rates indicates that viscosity is indeed the major factor that controls vitrification in alkali systems. The same conclusion seems to apply to binary alkaline earth silicates which, as a result of stronger bonding, have much higher liquidus temperatures. With eutectic temperatures higher than 1400 °C, viscosity is much lower on the liquidus and glass formation more difficult even on the SiO₂-rich part of the systems where stable liquid unmixing occurs. Accordingly, vitrification is problematic below the 1900 °C melting point of forsterite where the viscosity of liquid Mg₂SiO₄ is 0.03 Pa s (Urbain et al., 1982).

Other examples, however, point to a more complicated picture. At the 1436 °C of the eutectic point of the CaO–SiO₂ system, vitrification is easy in spite of a rather low viscosity of 2 Pa s (Bockris and Lowe, 1954). Along the CaO–Al₂O₃ system, viscosities are still lower at the liquidus temperatures of the SiO₂-free melts that vitrify readily. For 61 mol.% CaO, viscosity is 0.5 Pa s at the liquidus temperature of 1510 °C (Urbain, 1983). Hence, viscosity at the liquidus is not a single scaling parameter for assessing glass-forming ability. The obvious reason is that vitrification does not take place at the liquidus, but at a much lower temperature. As will be made below, the temperature dependence of viscosity below the liquidus also has to be considered. In addition, other factors must be dealt with to account for the correlation between vitrification and crystalline compounds noted in the previous section. Enthalpy of mixing and configurational entropy are two such factors that will be considered in the rest of the discussion.

3.3. Enthalpy of mixing and compound formation

The fact that silicate melts are generally not ideal solutions is of direct interest because compound formation results from predominantly attractive interactions between the melt components. As such interactions give rise to negative enthalpies of mixing, they enhance freezing-point depressions and favor high viscosities near eutectic points.

Within a given system, however, the correspondence between the extent of glass formation and the existence of numerous compounds requires enthalpies of mixing to be of a moderate magnitude. Otherwise, too strong association gives rise to compounds with high melting temperatures and the kinetics of crystal growth would become too rapid even slightly below the liquidus. The contrast between sodium and potassium aluminosilicates clearly illustrates this effect. Association of Al³⁺ with its charge-compensating cation is stronger for K⁺

than for Na⁺ (see Mysen and Richet, 2005), with the result that liquidus temperatures increases more rapidly along meta-aluminous joins in potassium than in sodium aluminosilicates (Fig. 1). Starting from pure SiO₂, vitrification ends correlatively before the KAlSi₂O₆ composition is reached on the one hand, whereas it extends readily to NaAlSiO₄ on the other.

Available calorimetric data support this interpretation and indicate more precisely what should be meant by “moderate” enthalpies of mixing (Fig. 8). The decreasing extent of vitrification along meta-aluminosilicate joins from Na to K (Fig. 1) and Cs (Bollin, 1972) is borne out by the increasing magnitude of negative enthalpies of mixing. Then, one conversely concludes that glass formation is more extensive in Na than in Li aluminosilicates, as indeed shown in Fig. 1, because of the insufficient strength of the association between Al³⁺ and Li⁺ (Fig. 8), which is also apparent in the much lower viscosities of Li aluminosilicate melts compared to those of their Na counterparts (Boiret and Urbain, 1987; Urbain et al., 1982). Analogous correlations with enthalpies of mixing exist for alkaline earth systems where vitrification is much more restricted for Mg than for Ca aluminosilicates.

Data are not as extensive for other systems. The smaller domain of glass formation of K compared to Na ferrisilicates (Fig. 4) nonetheless correlates with the stronger association of K⁺ with Fe³⁺ as a charge-compensating cation, an effect similar to that just described

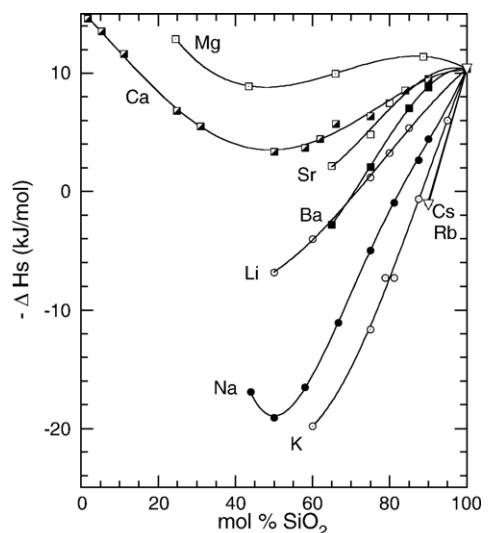


Fig. 8. Negative of enthalpies of solution in lead borate measured at 700 °C along the meta-aluminous join of alkali and alkaline earth systems (Roy and Navrotsky, 1984). In this representation, the enthalpies of mixing between the SiO₂ and aluminate components are simply given by the depth of the individual enthalpy wells.

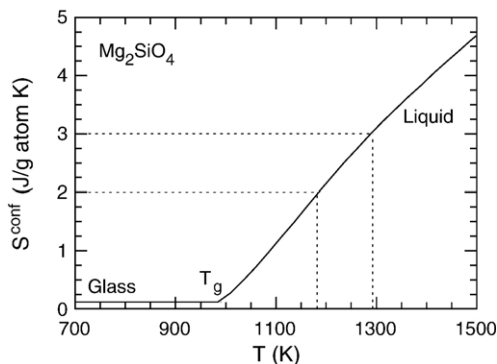


Fig. 9. Configurational entropy of liquid Mg_2SiO_4 against temperature (data from Richet et al., 1993). The dashed lines delineate the range of fictive temperatures for which the glass would have a configurational entropy in the typical 2–3 J/g atom K range of silicates.

for aluminosilicates. For titanosilicates, it is the marked contrast between compound formation in alkali and alkaline earth systems that testifies to the different nature of interactions of these cations with Ti^{4+} . In fact, alkaline earth titanosilicates and other systems where ternary compounds are scarce or lacking tend to show large fields of stable liquid unmixing (Figs. 2 and 3). These two features are indicative of predominantly positive enthalpies of mixing, which have also the consequence of limiting freezing point depressions and, thus, of lowering the viscosity.

3.4. Configurational entropy

As disordered solids, glasses differ from crystals by the existence of configurational entropy (S^{conf}). According to Kauzmann (1948), it is indeed the temperature at which S^{conf} would vanish that represents the lower bound to the interval in which a melt can supercool. That configurational entropy is an essential factor in vitrification is also indicated by the quantitative relationship between viscosity and configurational entropy found for silicate melts from the Adam and Gibbs (1965) theory of relaxation process (Richet, 1984).

The temperature dependence of configurational entropy is also important as reviewed by Deubener (2004) for alkali silicate melts. Another interesting example discussed by Richet et al. (1993) is that of glasses with the orthosilicate stoichiometry which are extremely difficult to quench. For Mg_2SiO_4 , the standard glass transition should be about 1000 K, as determined from extrapolations of data for joins in the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system (Richet et al., 1993) or from a comparison with a molten peridotite (Dingwell et al., 2004). At this

temperature, however, configurational entropy has already become negligibly small (Fig. 9). Vitrification thus requires extremely high cooling rates to quench a glass with a fictive temperature higher than the temperature of the Kauzmann (1948) paradox. As configurational heat capacity scales as the field strength of the cation (Stebbins et al., 1984), alkaline earth silicates lose configurational entropy more rapidly than alkali silicates (Fig. 10). This contributes to their less good glass-forming ability.

The configurational entropy can be conveniently split into chemical and topological contributions, the former resulting from mixing of structurally similar elements, the latter accounting for the disordered topology of the glass configuration (Richet and Neuville, 1992). On a gram atom basis, the configurational entropy of glasses quenched without special devices ranges from 2 to 3 J/g atom K, the higher values being generally due to high chemical entropy. Another evidence for the importance of entropy in vitrification is provided by the existence of the so-called “invert” glasses (Hänlein, 1933; Trap and Stevels, 1960), which are SiO_2 -poor but bear a number of other cations whose mixing gives rise to a specially high chemical contribution to configurational entropy.

For silicates, these materials illustrate what is informally termed the “principle of confusion” in the

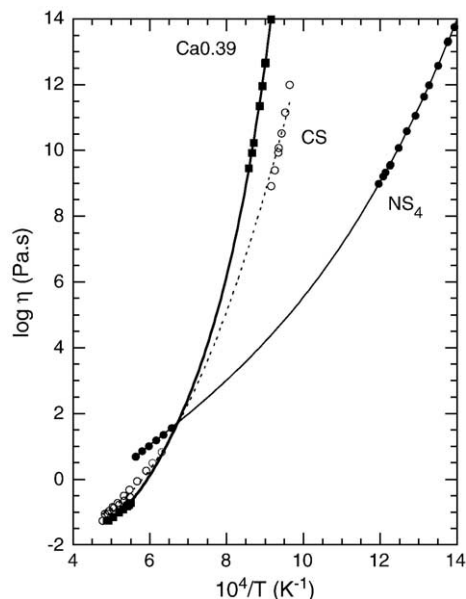


Fig. 10. Viscosity of molten sodium tetrasilicate (NS_4), calcium metasilicate (CS) and a calcium aluminate with 39 mol.% CaO (Ca0.39). Data from Bockris and Lowe (1954), Bockris et al. (1955), Urbain (1983), Neuville and Richet (1991) and Sipp and Richet (2002).

literature on chalcogenide and other exotic glasses (e.g., Lucas, 1999). According to this rule, a more complicated chemical composition translates into a greater number of compounds that could nucleate and, thus, in mutual competition such that crystal nucleation and growth is frustrated and does not take place on sufficiently rapid cooling. In other words, the probability of forming viable nuclei through composition fluctuations of the melt is lower when several compounds can form than if a single crystal structure is available. As noted above in the case of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ liquid, this effect is related to the difficulty of achieving the interdiffusion process required to form a given crystal in a melt of complex composition. Since crystal structures represent part of the configurational space explored by the liquid, the multiplicity of the possible crystal structures that can form should reflect the complexity of the potential energy landscape which governs relaxation in the liquid (Goldstein, 1969; Angell, 1988).

In conclusion, the lack of nucleation as a criterion for glass formation is probably not as relevant as it might seem because the kinetics of crystal nucleation are not controlled by bulk viscosity but, rather, by diffusivity of the most mobile elements attaching to the nuclei (see Roskosz et al., 2005). In contrast, the features reviewed in this paper indicate that the intrinsic properties of melts are of central importance for dealing with vitrification. The interplay of thermodynamic mixing properties is relevant, especially with regard to their configurational contributions which affect viscosity either directly, through their influence on relaxation times (Adam and Gibbs, 1965), or indirectly, through liquidus temperatures.

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